

Role of Fertilizer and Micronutrient Applications on Arsenic, Cadmium, and Lead Accumulation in California Cropland Soils

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SUMMARY AND CONCLUSIONS

Introduction Fertilizers and micronutrients are manufactured products containing certified amounts of plant nutrients to facilitate crop growth when applied on cultivated lands. In addition to the active ingredients, however, fertilizers and micronutrients may contain trace elements such as arsenic (As), cadmium (Cd), and lead (Pb) that are potentially harmful to consumers of the harvested products if the substances of concern are absorbed by plants during the course of growth. Trace elements may enter commercial fertilizers by being present in the raw materials used for manufacturing and blending. The California Department of Food and Agriculture analyzed the arsenic, cadmium, and lead contents of selected phosphorus fertilizers and micronutrients marketed in the state and found the following results:

Element	Phosphate Fertilizer (mg kg ⁻¹)		Zinc-Iron-Manganese Micronutrient (mg kg ⁻¹)	
	Range	Mean	Range	Mean
Arsenic	nil to 85	8.5	0.2 to 74	32
Cadmium	nil to 3,734	173	nil to 5,000	477
Lead	nil to 595	21	19 to 73,500	21,156

The results showed that majority of the fertilizers and ingredients for formulating fertilizers were free of the trace elements or low in the contaminant levels. However, there were isolated incidences where the arsenic, cadmium, and lead contents of the products far exceeded the typical concentrations of those in the cropland soils. If added as apart of the fertilizers and micronutrients, these elements may accumulate over time in the receiving soils, as they are relatively immobile in comparison to the plant nutrients. In this manner, their concentrations in the soil will rise, resulting in greater plant uptake.

Did applications of phosphorus fertilizers and micronutrients cause an increase in the concentrations of potentially hazardous trace elements such as arsenic, cadmium, and lead in California cropland soils? This report summarizes the findings from field surveys of vegetable production soils in seven production regions and presents conclusions drawn from the results.

Approach Phosphate fertilizers and micronutrients are routinely used in crop production. In each cropping or growing season, however, the quantities required per unit of cultivated area to support a successful harvest were moderate. Judging from the concentrations and distributions of arsenic, cadmium, and lead in the fertilizers and micronutrients, the trace element inputs to cropland soils, although frequent and long-term in nature, are inherently low in intensity. Even though their concentrations in the fertilizers and micronutrient supplements may be significantly elevated, the amounts of arsenic, cadmium and lead added to soils through each application are small in comparison to the mass of the receiving soils. This makes the changes difficult to detect by routine measurements due to errors incurred in field soil sampling and limitations in the sensitivity of analytical methods. The trace element content of the soils may also be changed through natural weathering processes, by atmospheric fallout, and due to plant absorption. In addition, there are other sources of inputs such as pesticides and irrigation water. Thus, it is essential to separate the contributions of the other causes and the fertilizer applications on the changes in trace element concentrations in the cropland soils. In practice, it is difficult if not impossible to apply the fertilizers and micronutrients uniformly across large production fields. The inherent spatial variability of the fields and the limitations on the mass of soils sampled would introduce experimental errors that could render the final results inconclusive. These factors must be taken into account in developing a study plan.

- 1. Analyze the arsenic, cadmium, and lead contents of the benchmark soils to determine the long term changes of the baselines in California.**

In 1950, Dr. R. J. Arkley of the University of California, Berkeley identified 50 locations across the state where the soil profiles were representative of the soil types found in California. At the time of selection, these soils were undisturbed and uncultivated. Since

then, conditions at some of the locations have changed. The soils were sampled in 1967 for analysis of their elemental compositions (Bradford et al., 1967). These soils were again sampled in 2001. The changes in the arsenic, cadmium, and lead contents of soils collected in 1967 and 2001 provide a snapshot of changes in the trace element baselines of soils across California over 35 years. These benchmarks serve as the reference point to judge the significance of changes detected on cropland soils. If changes are observed, the data will provide the information for accounting the shift in the baseline levels.

2. Take samples of soils used for long-term vegetable productions in major production regions across the state.

Accumulations of arsenic, cadmium and lead, if they indeed occur, would more likely be detected in the surface layers of cropland soils receiving long-term and high-intensity fertilizer and micronutrient applications. Vegetable productions require considerably higher levels of fertilizer inputs than other crops. The climate in California often permits year-round production and multiple crops are harvested annually. As a result, croplands dedicated for vegetable production in the state would receive more fertilizers and are more likely to accumulate trace elements. The soils receiving frequent and heavy fertilizer applications would represent the worst-case scenario, and any accumulations of arsenic, cadmium, and lead that occurred would be susceptible to detection in the field survey. In order to establish trends, however, large numbers of specimens were needed. It was also imperative that additional samples be obtained to establish the baseline levels from which comparisons could be made.

Samples were collected across the entire state on field trips spanning more than 12 months. Quality control and quality assurance protocols were established to insure

consistencies in the sample collection procedure and to authenticate the accuracy of the analysis, as well as to effectively pool the data for conclusions. Only in this manner could the outcomes be properly evaluated.

Findings – Benchmark Soils The comparisons of arsenic, cadmium, and lead concentrations of benchmark soils in 1967 and 2001 provided our snapshot on changes occurring over time in the baseline levels of non-cultivated soils:

a. Arsenic

Year	Range (mg kg ⁻¹)	Median (mg kg ⁻¹)	Mean (mg kg ⁻¹)
1967	1.8 – 20.5	8.5	8.8 ± 4.3
2001	1.8 – 16.6	6.5	7.6 ± 3.7

b. Cadmium

Year	Range (mg kg ⁻¹)	Median (mg kg ⁻¹)	Mean (mg kg ⁻¹)
1967	0.03 – 0.44	0.17	0.18 ± 0.10
2001	0.07 – 0.53	0.19	0.22 ± 0.11

c. Lead

Year	Range (mg kg ⁻¹)	Median (mg kg ⁻¹)	Mean (mg kg ⁻¹)
1967	3.6 – 25.0	11.4	12.0 ± 5.3
2001	4.9 – 26.8	13.6	14.6 ± 5.5

Overall, the baseline levels represented by the concentrations of these elements in the benchmark soils did not change significantly over this 35-year time period. It appeared that the baseline levels of potentially hazardous trace elements such as arsenic, cadmium, and lead remained in the same order of magnitude if the soils were not affected by external factors. As a result, there was no need to correct for the baselines when the data from the cropland soils were analyzed.

Findings – Cropland Soils When the phosphorus fertilizers and micronutrients were applied, the amounts applied invariably exceed the amounts taken up by plants. In addition, parts

of plant biomass would be reincorporated into the soil after the crop harvests, thus recycling portions of the nutrients and contaminants. Therefore, active ingredients of phosphorus fertilizers, along with micronutrient ingredients namely phosphorus (P), zinc (Zn), iron (Fe), and manganese (Mn), are expected to accumulate in cropland soil receiving routine applications. The phosphorus contents of the cultivated soils would invariably increase in proportion with the amount of the fertilizers used. Iron and manganese are abundant in soils. Increases in their concentrations could not easily be distinguished from the already high background levels. However, zinc contents of the soil would be sensitive to the inputs and may be used as an indicator of micronutrient inputs. The longer the land has been cultivated, the greater the accumulation. Therefore, the total phosphorus and zinc contents of the soils in a production region are indicative of the amount of fertilizer and micronutrient additions to the soils. If arsenic, cadmium and lead were introduced into cropland soils by the fertilizer and micronutrients applications, their concentrations in the soil of a production region would increase in proportion to the corresponding soil phosphorus and zinc concentrations, respectively.

To assess the effects of the fertilizer and micronutrients applications, the arsenic, cadmium and lead contents of soils collected in a region were plotted as dependent variables against the corresponding phosphorus and zinc concentrations as the independent variables. If a sufficient number of samples was collected and analyzed to cover the ranges, trends would emerge. The trends are based on the attributes exhibited by the entire data population and not be effected by a small numbers of outliers as the number of data points on each graph were large. This way, the effects of the spatial variability of the fields and measurement errors on the outcomes may be minimized. The baseline concentrations of arsenic, cadmium and lead for that region were used as references.

Four possible scenarios might emerge from the comparisons of data for cropland soils and the baselines. They are described as follows:

Scenario	Description of Trend	Interpretation
1	Soil trace element concentrations of the region remained within the baseline range regardless of the phosphorus or zinc concentration of the soils.	Soils in the region were not affected by the fertilizer or micronutrient applications.
2	Soil trace element concentrations of the region exceeded or were exceeding the baseline but their concentrations did not rise in proportion to the phosphorus or zinc concentrations of soils.	The trace element contents of the soils were affected by diffuse sources other than phosphorus fertilizers or micronutrients.
3	Soil trace element concentrations of the region exceeded or were exceeding the baseline but their concentrations increased in proportion to the phosphorus or zinc concentrations of soils.	The phosphorus fertilizers or micronutrients applications increased the trace element contents of soils.
4	Soil trace element concentrations of the region exceeded the baseline for the entire range as indicated by phosphorus or zinc concentrations of the soils and showed a rising trend.	The trace element contents of soil in the region were affected by the combination of diffuse sources and fertilizers.

Based on the criteria, we evaluated the data. The arsenic, cadmium, and lead accumulations in the cropland soils in each surveyed production region were evaluated separately in terms of phosphorus fertilizer and micronutrient applications. In the following tabulations, the notation baseline denotes that the concentrations of the elements of concern remain within the baseline range; the notation diffuse sources denote that the elevated concentrations in the soils were caused by inputs other than phosphorus fertilizers and micronutrients; and the notation P fertilizer or micronutrients denotes that the applications of phosphorus fertilizer or micronutrients resulted in the elevated concentrations in soils.

Production Region	Arsenic	Cadmium	Lead
Oxnard and Ventura Area	Baseline	P Fertilizer	Diffuse Sources
Santa Maria and San Luis Obispo Valley	Diffuse Sources	Diffuse Sources	Diffuse Sources
Colusa/Glen County	Diffuse Sources	Baseline	Baseline
Fresno	Baseline ¹	Baseline	Baseline
Coachella Valley	Baseline	Diffuse Sources	Baseline
Imperial Valley	Baseline	Diffuse Sources	Baseline
Monterey/Salinas Valley	Baseline	Diffuse Sources	Diffuse Sources

¹While remaining in the baseline range, the arsenic contents of soils showed a rising trend.

Arsenic In five of the seven production regions surveyed in California, the arsenic contents of the cropland soils remained within the baseline ranges. In the remaining two production regions, the arsenic concentrations of the soils shifted upward across the board. Either the entire population, or at least the upper end of the concentration range, exceeded the baseline level. The accumulations in the soils, however, could not be attributed to the applications of phosphorus fertilizers or micronutrients and were from diffuse sources.

Cadmium The cadmium concentrations of cropland soils in one of the seven surveyed production regions had exceeded the baseline and showed clear signs of rising with respect to the phosphorus content of the soils. It was concluded that the phosphorus fertilizer applications had caused the cadmium concentrations of the soils to rise. Judging from how small the amount of contaminants found in the phosphorus fertilizers currently being marketed in California, the trend we observed undoubtedly reflected the legacy of high cadmium phosphorus fertilizer and heavy applications in the past. In four of the remaining six production regions, the cadmium concentrations in the cropland soils shifted upward across the board. Either the entire population, or at least the upper end of the concentration range, exceeded the baseline level. In these cases, the elevated lead concentrations in the soils were caused by diffuse sources other than phosphorus fertilizers and micronutrients. For the remaining two production regions, the

cadmium contents of the soils remained within the baseline. The applications of phosphorus fertilizers and micronutrients did not affect the cadmium contents of soils in these two regions.

Lead Applications of phosphorus fertilizers and micronutrients had no effect on the lead concentrations of the cropland soils in California. In four of the seven production regions, the lead concentrations remained within the baseline range. In remaining three production regions, the lead concentrations had shifted upward across the board. Either the entire population, or at least the upper end of the concentration range, exceeded the baseline level. In these cases, the elevated lead concentrations in the soils were caused by diffuse sources other than phosphorus fertilizers and micronutrients.

Findings – Trace Elements in Plant Tissue At the time of soil sampling, the leaf tissue of plants grown at the sampling locations were collected in two of the seven regions. At the other regions, the fields were not planted at the time of soil sampling. Based on limited data, we found that the arsenic contents of the leaf tissue were below the limit of detection using atomic absorption spectroscopy. The lead concentrations of plant tissue were within the baseline ranges of plants. At the region where cadmium contents of soils were affected by the phosphorus fertilizer applications, the cadmium concentrations of the plant tissue were linearly correlated to the phosphorus and cadmium concentrations of the soils. When the region where the cadmium contents of the soils were affected by diffuse sources, the cadmium concentration of the plant tissue did not appear to be affected by the soil cadmium contents.

Conclusions

We collected and analyzed a large number of soil samples from the vegetable production fields in seven regions across the state, examining the samples' arsenic, cadmium, lead, phosphorus, and zinc contents. Based on the analysis, we have concluded that long-term use of

phosphorus fertilizers and micronutrients could cause the arsenic, cadmium, and lead contents of the cropland soils to rise if the products used contained high levels of these elements. However, the applications of phosphorus fertilizers and micronutrients were not the primary sources of trace element accumulation in cropland soils in California. A total of 42 cases involving 7 production regions, 3 contaminant elements, and two fertilizer elements were examined. Of the 42 cases we evaluated, we came across one positive case in which the cadmium content of the cropland soils in one production region showed a trend to increase due to phosphorus fertilizer applications. Even in this region, the soil cadmium levels at significant number of the sampled sites remained within the baseline range. More often, the arsenic, cadmium, or lead contents of the cropland soils showed a trend of becoming elevated due to factors other than applications of phosphorus fertilizer and micronutrients (19 of the 42 cases). In the remaining 22 of the 42 cases, the arsenic, cadmium, and lead contents of the soils remained within the baseline ranges. Even in the cases where the arsenic, cadmium, and lead contents of cropland soils exhibited a trend to shift upwards, significant percentages of the soils sampled were still within the baseline concentration ranges. Vegetable production requires greater amounts of fertilizer and micronutrient inputs. The outcomes illustrated by this study represent the worst-case scenarios with respect the applications of fertilizer and micronutrients. In this regard, the integrity of the cropland soils in California has not been significantly affected by normal fertilizer and micronutrient application practices.

Cropland soil is a non-renewable natural resource of the state. To safeguard it from further introduction of trace elements, it is imperative that the contents of the potentially harmful elements in fertilizers and micronutrients be tracked and regulated, and that other sources of trace element inputs to cropland soils be identified and brought under control.

INTRODUCTION

Elements present in the lithosphere are routinely transferred to the biosphere and vice versa through biogeochemical processes. Humans acquire energy and essential nutrients largely from food grown in soils and from products of animals that forage on plants supported by soils. As a result, the elemental profiles of biota inherently resemble the geochemical composition of their habitats (Cannon, 1964; Shacklette, 1980). Trace elements are transferred in the same manner. Their concentrations in native plants have frequently been used as markers to track mineral deposits (Cannon, 1960; Brooks et al., 1978; Reeves and Brooks, 1983; Lee et al., 2004). Terrestrial-borne trace elements, in excess or deficiency, have caused many endemic diseases around the world. For example, symptoms of fluoride toxicity in sheep were observed in Iceland ~1,000 years ago (Roholm, 1937); long-term exposures to food grown in selenium-deficient soils have for centuries caused the Kashan and Kaschin-Beck diseases, crippling disorders of bones and heart, respectively throughout China (Anonymous, 1989); and millions of inhabitants of areas with iodine-deficient soils in eastern Africa are still susceptible to goiter (Jaffiol, et al., 1992).

In the scientific literature at the beginning of the 20th Century, evidence first emerged to show that deficiencies and excesses of trace elements in soils profoundly influence the vitality of plants supported by the soil, as well as the vitality of animals consuming those plants. Over time, the role of trace elements on the metabolisms of animals, plants, and microorganisms have been delineated and more elements have continuously been added to the original list. Today, the nomenclature “trace element” is employed loosely to categorize an ensemble of otherwise unrelated elements that, in small quantities, may beneficially or adversely affect the wellbeing of biota. Interpreted in the broadest sense, trace elements can encompass more than two-thirds of the 91

naturally occurring elements. It is imperative that this discussion be limited only to those that may impact the utilization and preservation of natural resources in California:

- Barium, copper, iron, manganese, molybdenum, and zinc are essential for higher plants, terrestrial mammals, and aquatic organisms.
- Fluoride, nickel, and selenium are essential for metabolism in mammals.
- Arsenic, cadmium, mercury, and lead have no known beneficial biological function and are always harmful even in small quantities.

On several occasions, cadmium, mercury, and selenium, while present in low concentrations, were found to bio-accumulate along the food chain and adversely affect organisms occupying the upper echelon of the food web. Even for elements that are beneficial to the metabolism of biota, detrimental effects may occur when their concentrations are only slightly higher than the optima.

By and large, trace elements occur naturally in soils, and the primary minerals and parent materials that make up the earth's crust are the original sources of these elements. In igneous rocks, trace elements are distributed among the minerals according to the general rules of association, their radii and ionic charges. Weathering processes and the cycles of formation of sedimentary rocks redistribute the trace elements among the hydrolyzates, oxidates, carbonates, and evaporates. While the mineral composition of soils defines their origin, trace elements of soils may be influenced by the prevailing processes of soil formation, which alter their chemical forms and redistribute the elements in the soil profile, resulting in a wide range of variations of concentrations and availability in soils.

Trace elements, such as arsenic, cadmium and lead are ubiquitous in soils. The amounts of these elements naturally present in a given soil is dependent on several factors, including parent material composition, biogeochemical processes, and external contributions. Various

natural and anthropogenic input sources may cause these elements to become more concentrated in the soil over time. Natural sources of trace element input include volcanic eruptions, atmospheric fallout and soil erosion. The more likely causes of soil enrichment, however, are anthropogenic. These manmade inputs can be from particulate emissions from stationary and mobile sources, and from irrigation water, pesticide, biosolids, animal manure and fertilizer applied directly to the soil. The airborne trace elements can be carried by the atmospheric currents, and thus may circulate globally and be deposited over a very wide area. Applications of arsenic, cadmium and lead-rich materials are a more localized form of contamination, resulting in a concentrated addition to a much smaller area of soil.

Fertilizers are regularly applied to agricultural fields to obtain optimum crop yields. For some crops, such as vegetables, it is necessary to fertilize the soil prior to each planting. In California, vegetables are produced year round. For some fields, two to three crops may be harvested in one year and large amount of fertilizers may be applied. In the Imperial Valley, for example, lettuce is grown for 90 to 120 days to maturity. The process requires 1.22 m (4 feet) of irrigation water and uses 560 kg ha⁻¹ (500 pounds acre⁻¹) of dihydrate ammonium phosphate (DAP) fertilizer (11-52-0) and 202 kg ha⁻¹ (180 pounds acre⁻¹) of water-run nitrogen fertilizer (Mayberry, 2003). Applications of phosphorus fertilizers and micronutrient supplements may contribute to increased trace element loads because some of their ingredients may be contaminated with arsenic, cadmium and lead (Williams and David, 1976; Mulla et al., 1980; McLaughlin et al., 1995; Raven and Loeppert, 1997).

Arsenic, cadmium and lead can enter commercial fertilizers by being present in the raw materials used for manufacturing and blending. For example, cadmium is a contaminant of the phosphate rock used to manufacture phosphate fertilizers. Its concentration can vary, depending

on fertilizer origins, from essentially nil to as high as 500 mg kg⁻¹ P (McLaughlin et al., 1996). Zinc-iron-manganese supplements can also be a major contributor of arsenic, cadmium and lead. In many cases, the raw material used to manufacture these supplements is industrial waste (Bowhay, 1997). A manufacturer can obtain industrial waste products that contain a high percentage of a desired element and convert it into a fertilizer which commonly is certified by its active nutrient ingredients. However, these waste products can also contain high levels of potentially toxic elements. In fact, some materials that would be considered hazardous wastes for disposal purposes contain a high enough percentage of an essential element that they can be classified as fertilizers and be land applied (Bowhay, 1997).

Once arsenic, cadmium and lead enter the soil, their mobility is limited. Arsenic in the natural environment behaves similarly to phosphorus, and is readily immobilized in the soil through surface adsorption and/or chemical precipitation. Cadmium and lead are also readily adsorbed by clays and organic matter, or they can form sparingly soluble precipitates in the soil. While the amount of contaminant being added with each application of fertilizer may be small compared to the total soil volume, repeated applications can lead to a gradual buildup of these elements in the root zone over time.

The concentration of an element in plant tissue is influenced by its concentration in soils. Loganathan et al. (1995) reported that if factors such as the soils' pH and organic matter content are equal, the amount of cadmium taken up by plants is in proportion to the amount accumulated in the topsoil. Once the trace elements are taken up into the plant tissues, they do not partition equally between the various parts of the plants. The partitioning is dependent on crop species. In general, the concentrations in the leaves or stalks of the plants are higher than those in the grain or fruit.

The accumulation of arsenic, cadmium, lead, and other potentially hazardous trace elements in agricultural soils is a concern because these soils serve as an entry point for elements into the human food chain. The primary pathways of human exposure, once the elements are in the soil, are either the soil-plant-human pathway or the soil-plant-animal-human pathway. Arsenic, cadmium and lead are of particular interest because they have no known beneficial metabolic function. Even for elements that are beneficial, there is usually a narrow margin of safety between meeting the biological needs and the threshold for adverse effects.

Adverse health effects have been linked to the ingestion of arsenic, cadmium and lead. Chronic exposure to arsenic can lead to liver injury, peripheral vascular disease and black foot disease. Arsenic can also interfere with enzyme function and cause several types of cancer (IARC, 1980). Chronic exposure to cadmium has been linked to pulmonary disease and renal tubular dysfunction (Kobayashi, 1978, Ryan et al., 1982). The long-term health effects resulting from lead exposure include decreased growth and development in children, impaired hearing and even brain damage (Nriagu, 1988; U. S. Environmental Protection Agency, 1986). The body can mistake these elements, particularly cadmium and lead, for essential elements. Individuals with a diet deficient in essential nutrients are at a greater risk. The World Health Organization (WHO) estimates that the adult human intake of arsenic, cadmium and lead from food on a global basis is 18, 25 to 70 and 60 $\mu\text{g day}^{-1}$, respectively (WHO, 1996). For arsenic and lead, the exposures are well below the recommended maximum daily intake limits of 130 and 230 $\mu\text{g day}^{-1}$. For cadmium, intake is already approaching the recommended upper threshold of 70 $\mu\text{g day}^{-1}$ (WHO, 1996).

Not only is plant uptake a concern for human health, but the health of the crop can also be endangered. Once trace element concentrations reach critical levels in plant tissues, they can

lead to a reduction in crop yield, or in severe cases, all-out crop failure. This type of loss can have significant economic ramifications. Agriculture is a major contributor to California's economy. Crop production per year is a \$20-billion-dollar industry, contributing significantly to the world's fifth largest economy (USDA, 1997). In fact, one in 10 jobs in the state is related to agriculture (Carle, 2000). With 39 per cent of California's land, approximately 11 million acres, committed to crop productions, arsenic, cadmium and lead contamination through fertilizer application could potentially be a widespread and long-term environmental issue.

There is no federal law in the United States that regulates contaminants in fertilizers. In March 1998, Washington became the first state to pass legislation regulating contaminants in fertilizer. It limited the annual loading of contaminants, restricting the total application of arsenic, cadmium and lead to 0.33, 0.089, and 2.22 kg ha⁻¹ yr⁻¹, respectively (WAC, 1998). The standards adopted by Washington were based on the Canadian standards established as part of the Fertilizer Act and Regulations of Agriculture and Agri-Food Canada in August 1996 (Bowhay, 1997). These standards in turn were based on regulations set in 1980 for sludge-treated soil, and they establish cumulative loading limits for each element based on its potential toxic effects. Limits for arsenic, cadmium and lead are 15, 4, and 100 kg ha⁻¹, respectively, and are based on 45 years of application (Bowhay, 1997). To meet these standards, manufacturers need to identify the most likely sources of these contaminants and either eliminate or minimize their presence in the fertilizer products. Similarly, the European Union established limits on arsenic, cadmium and lead contents in soils used to grow edible plants, setting annual loading limits for trace elements in agricultural soils. The European Union has proposed to follow up on the rules by refusing to import agricultural goods that are grown on soils exceeding these limits.

In January 2002, California's regulations to limit arsenic, cadmium and lead concentrations in fertilizer materials went into effect. The regulations require that for each per cent of available zinc, manganese, iron or phosphate in the fertilizing material, the arsenic, cadmium and lead concentrations do not exceed 4, 6, and 20 parts per million, respectively. The limits for arsenic and cadmium will incrementally decrease annually to reach a final threshold of 2 and 4 parts per million, respectively, in 2004. In addition to establishing a numeric limit of these elements in fertilizers, the regulations require that the fertilizers be adequately labeled to ensure proper usage of these materials.

Public concern has also been raised about possible crop damage, and potential threats to human health, that arise from increased arsenic, cadmium, and lead content in soils. In *Fateful Harvest*, the author Duff Wilson describes his investigations into adverse health effects and crop failures occurring in Quincy, Washington, USA (Wilson, 2001). He learned that growers in the region unknowingly used fertilizers that were locally produced from industrial wastes. These wastes contained high concentrations of several toxic metal elements and organic chemicals that could contaminate the receiving soils and the crops they supported.

This report summarizes results of the investigations on:

- Arsenic, cadmium and lead contents of in the benchmark soils of California
- Arsenic, cadmium and lead contents of selected agricultural soils in California
- Roles of fertilizer and micronutrient applications on arsenic, cadmium and lead accumulation in cropland soils.

LITERATURE REVIEW

Background Concentrations of Trace Elements

Background concentration refers to the natural elemental level in the soil without human interference (Kabata-Pendias, 2001). It is important to determine this concentration to ascertain whether a soil has been enriched with, or depleted in, an element by natural and/or manmade causes. The natural metal concentrations of soils can vary depending on the parent material composition as well as the formation processes that the soil undergoes. Summarizing data from several investigations, the background concentrations of arsenic, cadmium and lead of soils in California can range from essentially nil to 13, 1.7 and 97 mg kg⁻¹ soil, respectively (Bradford et al., 1996; Chen et al., 1999; Connor and Shacklette, 1975). Geographical variations require that many samples be taken to fully characterize the distributions in a region.

Arsenic occurs in more than 200 minerals, and is present mainly in the heavy mineral fraction of the soil (Kabata-Pendias, 2001). Its predominant chemical form in these minerals is arsenate. The lowest levels of arsenic can be found in sandy soils, particularly those derived from granite. Higher arsenic concentrations are associated with alluvial soils, soils rich in organic matter, and soils derived from shales (Woolson et al., 1971). The mean soil arsenic concentration ranges from 4.4 mg kg⁻¹ in podzols to 9.3 mg kg⁻¹ in histosols (Kabata-Pendias, 2001).

Cadmium is present in magmatic and sedimentary rocks and its concentrations do not usually exceed 0.3 mg kg⁻¹ (Holmgren et al., 1993). It is likely to be concentrated in argillaceous and shale deposits (Kabata-Pendias, 2001). Cadmium is strongly associated with zinc in its geochemistry and exhibits greater mobility than zinc in acid soils. The mean concentrations of

cadmium in soils range from 0.37 mg kg^{-1} in pedsols to 0.78 mg kg^{-1} in histosols (Kabata-Pendias, 2001).

The natural lead content of soils arises primarily from the weathering of parent materials, such as galena (PbS) (Kabata-Pendias, 2001). However, most soils are likely to be contaminated with this metal (Nriagu, 1996) because of widespread lead pollution, particularly from atmospheric emissions from vehicles burning leaded gasoline, which deposit lead on the soil. Studies of soils in remote regions suggest that baseline values for lead, without anthropogenic interference, should be about 20 mg kg^{-1} (Gough et al., 1988). The concentrations of lead in soils generally vary from 10 to 40 mg kg^{-1} (Kabata-Pendias, 2001).

Several investigations have attempted to characterize the background concentrations of trace elements, and in doing so, have also illustrated their variability of distribution within a region. Baseline concentrations of trace elements in soils have been reported for California (Bradford et al., 1996), Florida (Ma et al., 1997), the United States (Shacklette and Boerngen, 1984), China, and Europe (McGrath, 1986; Dudka, 1993). By comparison, the average soil concentrations of arsenic and cadmium in California are lower than the average concentration of these elements in soils in other parts of the world (Bradford et al., 1996; Berrow and Reaves, 1984; Ferguson, 1990). The lead concentration of California soils, however, is higher than the averages determined for the rest of the United States. This elevation could be attributed to the fact that California is a developed and populous state. Emissions from mobile sources, namely automobiles, have distributed lead widely throughout the state. Although leaded additives of gasoline have been banned for more than 30 years, the legacy of past uses has nonetheless persisted.

Trace Elements in Fertilizers

Fertilizer additions to agricultural soils are necessary to adequately supply nutrients essential to plant growth. However, fertilizers are not always unadulterated products. In addition to the desired ingredients, they may contain, most notably, trace element contaminants that will be inadvertently added to the soil. Once in the soils, the loss processes for these elements can be very slow, which can lead to their accumulation in the soil over time. The source of the fertilizer contaminant can be either manmade or natural. Under current practices, industrial waste, even materials classified as hazardous wastes, are sometimes recycled into fertilizers. These waste-derived ingredients may contain an essential element, such as zinc, which qualifies them to be marketed as a fertilizer, but they often contain other potentially toxic elements. Fertilizers derived from natural sources may also contain undesirable substances.

Phosphate rock is the primary stock material for commercial phosphorus fertilizers. It is mined in many locations globally, and thus has a wide range of trace element concentrations naturally occurring in the rock. These trace elements are transferred into the phosphorus fertilizer product through the manufacturing process and incorporated into agricultural soil when the products are applied. Kpombekou-A and Tabatabai (1994) compared the metal contents of 12 phosphate rock samples taken from various locations in the United States and Africa. They reported that the cadmium concentrations for their samples ranged from 5 to 47 mg Cd kg⁻¹ P, with a mean of 19 mg Cd kg⁻¹ P. In eastern United States, the rock phosphates from Florida had lower cadmium concentrations (10 – 11 mg kg⁻¹ P) than those found in North Carolina (42 mg kg⁻¹P). The rock phosphates mined in Africa were generally low in cadmium contamination, except for those from Togo and Tunisia that exceeded 40 mg Cd kg⁻¹ P. The lead concentrations ranged from 7 to 43 mg Pb kg⁻¹ P, with a mean of 18 mg Pb kg⁻¹ P. More than 50 per cent of the

rock phosphate specimens from Africa exceeded 20 mg Pb kg⁻¹ P, and only the sample from Niger was below 10 mg kg⁻¹ P. The lead contents of the rock phosphates from the United States varied from 9 to 11 mg Pb kg⁻¹ P. Raven and Loeppert (1997) conducted a study in which they compared the trace element composition of 24 types of fertilizers and soil amendments. They reported that, in general, concentrations of trace elements in fertilizers fall in this descending order: rock phosphate > sewage sludge > phosphorus fertilizer > organic amendments and liming materials > potassium fertilizers > nitrogen fertilizers. The arsenic concentrations of the samples they examined were stable, with the average concentration of 18.5 mg kg⁻¹P and 13.7 mg kg⁻¹P in rock phosphates and phosphate fertilizers, respectively (Raven and Loeppert, 1997). The concentrations of cadmium and lead in the assorted fertilizers and soil amendments were much more variable. For example, cadmium concentrations in the two rock phosphate samples were 0.8 and 48.8 mg kg⁻¹, illustrating the variability related to the source of the rock phosphates. The same trend was observed in the lead content of the two rock phosphate samples. The sample that was low in cadmium was also low in lead (4.6 mg kg⁻¹), and the sample that was high in cadmium was correspondingly higher in lead content (29.2 mg kg⁻¹). The processed fertilizers such as Monoammonium Phosphate (MAP), Diammonium Phosphate (DAP), and Triple Super Phosphate (TSP) had variable cadmium concentrations, but the lead concentration per unit of phosphorus increased in the order of: TSP > DAP > MAP.

Bowhay (1997) conducted a survey of trace element contaminants in fertilizers and micronutrient supplements marketed in Washington state. The zinc, iron, manganese supplements that were made from industrial by-products all had high levels of arsenic, cadmium or lead (Table 1). The arsenic content of these materials was relatively constant compared to the other two elements. Cadmium and lead concentrations varied widely among the different

materials. The manganese sulfate and the Micronutrient Mix #1 had the lowest concentrations of cadmium, and the Granular Zinc #1 had the highest content of cadmium, approaching 0.03 per cent of in the material. The Granular Zinc #1 material, which contained nearly 18 per cent zinc, also contained more than 1 per cent lead as a contaminant.

Table 1. Trace Element Contents of Selected Fertilizer Materials in Washington

Material	Arsenic (mg kg⁻¹)	Cadmium (mg kg⁻¹)	Lead (mg kg⁻¹)	Zinc (mg kg⁻¹)
Granular Zinc #1 **	34	275	11,300	178,000
Granular Zinc #2 **	35	52	1,400	203,000
Manganese Sulfate **	30	3	100	61
Micronutrient Mix #1 **	17	2	11	67,000
Micronutrient Mix #2 **	83	55	3,590	94,300
Monoammonium Phosphate (MAP)	7	0.3	2	54
Diammonium Phosphate (DAP)	18	7	3	82
Rock Phosphate	30	3	2	385
Ammonium Phosphate Sulfate	4	145	4	1,480
Ammonium Polyphosphate	5	25	2	315
Triple Superphosphate (TSP)	31	119	21	1,260

*Data from Screening Survey for Metals in Fertilizers and Industrial By-Product Fertilizers in Washington State (Bowhay, 1997)

**Material is of an industrial by-product origin

The fertilizers in the survey that were not of an industrial by-product origin also exhibited variable ranges of arsenic, cadmium and lead. For these materials, the findings of Bowhay (1997) were similar to those reported by Raven and Loeppert (1997). Cadmium had variable concentrations in the fertilizers, probably due to the source of the phosphate rock. The lead and arsenic contents followed the increasing trend that TSP > DAP > MAP.

California Department of Food and Agriculture (1997) surveyed the arsenic, cadmium and lead contents of selected commercial fertilizers and soil amendments marketed in the state and found that the concentrations of these elements in P fertilizers and Fe-Mn-Zn micronutrients varied widely (Table 2). While a few of the materials had high levels, the arsenic, cadmium, and lead concentrations in the overwhelming majority of the phosphate fertilizers were low or barely

detectable. The concentrations of arsenic, cadmium, and lead in the zinc-iron-manganese mineral micronutrients covered the entire range. Generally, granulate contained much higher amounts of contaminants than the solution for foliar spraying.

Table 2. Arsenic, Cadmium, and Lead Contents of Selected Commercial Phosphate Fertilizers and Mineral Micronutrients in California

Element	Phosphate Fertilizer (mg kg ⁻¹)		Zn-Fe-Mn Micronutrient (mg kg ⁻¹)	
	Range	Mean	Range	Mean
As	nil to 85	8.5	0.2 to 74	32
Cd	nil to 3,734	173	nil to 5,000	477
Pb	nil to 595	21	19 to 73,500	21,156

Derived from data in California Department of Food and Agriculture (1997)

The broad ranges of arsenic, cadmium and lead concentrations in the fertilizer materials illustrate the need to track the concentrations of contaminants in these materials and screen out those that are undesirable for uses on croplands. Judging from the available data, the outcome could be negligible impact if the fertilizers used contained minimal amounts of contaminants; or, the outcome could be significant accumulation of arsenic, cadmium, and lead in receiving soils if the fertilizers with high levels of arsenic, cadmium and lead were used for an extended period.

Effects of Fertilizer Application on Trace Element Contents of Soils and Crops

While arsenic, cadmium and lead occur naturally in soils, their concentrations may rise rapidly due to anthropogenic inputs (Grant and Bailey, 1997). One potential source is a contaminant in fertilizers. However, their concentrations in fertilizers are typically sufficiently low that one single application will not result in a measurable increase in their total contents in the receiving soils. As phosphorus frequently is a limiting nutrient element in crop production systems, phosphorus fertilizers are routinely applied. Several investigators have observed that over many years of continuous applications, a measurable increase in total concentrations of

arsenic, cadmium and lead in the soils was detected. The increases also contributed to the enhanced availability of these elements to plants.

Arsenic Arsenic accumulated in soils that had appreciable amounts of calcium, iron, and aluminum. Woolson et al. (1971) found elevated arsenic concentrations in the soil resulting from repeated fertilizer applications when the reactive iron content of the receiving soils was high. In soils with low reactive iron concentrations, arsenic can also accumulate by forming complexes with reactive aluminum or exchangeable calcium. If reactive iron and aluminum and exchangeable calcium are low in the soil, the arsenic species are mobile and may be leached from the soil (Woolson et al., 1971).

Arsenic in the soils may be phytotoxic to crop plants (Woolson et al., 1973) and crop tolerance to arsenic differs among species (Jacobs et al., 1970). Creger and Peryea (1994) observed that arsenic contents of plants grown on lead arsenate-contaminated soils were positively related to soil arsenic levels. Excessive accumulation of arsenic in plant tissues can lead to stunted plant growth and a reduction in yield (Kabata-Pendias, 2001). In examining the arsenic contamination of soils on plant growth, Woolson et al. (1971) observed that the average plant growth on the contaminated soil was about 64 per cent of plants grown on control soils. Phosphorus in the soil may counteract the arsenic toxicity to plants, through a competitive absorption of these two elements by plants. Hurd-Karrer (1939) observed that when ratios of phosphorus to arsenic were 4:1 or less, the growth of wheat plants (*Triticum spp.*) was stunted. At the phosphorus-to-arsenic ratio of 1:1, growth retardation occurred at soil arsenic concentrations of 10 mg kg⁻¹ or higher.

On the other hand, several studies have noted that phosphorus amendments increased the availability of arsenic to plants (Alam et al., 2001; Creger and Peryea, 1994; and Peryea, 1991

and 1998). The similarities of the chemistry of arsenic and phosphorus create a competition between the two elements for binding sites in soils. Starter fertilizers containing phosphorus, particularly MAP, can increase soil arsenic solubility and mobility (Peryea, 1991). Peryea (1991) found that arsenic released by phosphorus amendments tended to remain in a readily soluble form, thereby making it more plant-available. In fact, arsenic displacement by phosphorus is so effective that Alam et al. (2001) suggested phosphorus addition as an effective means of extracting arsenic from contaminated soils.

Jiang and Singh (1994) investigated the effect of chemical forms and sources of arsenic on crop yield and arsenic concentration in plant tissue. They conducted a three-year greenhouse experiment in which they applied arsenic as either sodium arsenite or disodium hydrogen arsenate at the rate of 0, 2, 10, 50, and 250 mg kg⁻¹ soil in year 1 and investigated the residual effects in years 2 and 3. They found that arsenite was quickly oxidized to arsenate in the soils and there was little difference between the two forms of arsenic, as far as their impacts on plant growth and absorption. The application of arsenic at a rate greater than 50 mg kg⁻¹ led to significant decreases in yields. This corresponded to marked increases in the crop concentration of arsenic. The arsenic concentration in plant tissue was directly correlated to the arsenic application rates. The arsenic availability of the treated soils appeared to decrease over time, as the concentrations in plant tissue successively decreased in years 2 and 3.

In a similar experiment, Jiang and Singh (1994) applied NPK fertilizer, containing 10, 100, and 3,000 mg As kg⁻¹ as sodium arsenite to ryegrass (*Lolium spp.*) and barley (*Hordeum vulgare L.*), respectively. The application of arsenic-containing fertilizer, even as high as 3,000 mg kg⁻¹, had little effect on crop yields. The arsenic concentration in both barley (*Hordeum vulgare L.*) and ryegrass (*Lolium spp.*) was not significantly affected by the fertilizers containing

10 and 100 mg As kg⁻¹. However, arsenic concentrations were eight and five times higher in the barley (*Hordeum vulgare L.*) and ryegrass (*Lolium spp.*) grown in soils treated with fertilizer containing 3,000 mg As kg⁻¹ compared to those respective crops receiving the fertilizer containing 10 mg As kg⁻¹. The arsenic in soils became less available to both crops over time. Additional doses of phosphorus were added in years 2 and 3 to examine the influence of phosphorus on arsenic availability to plants. In the loamy soil, the additional phosphorus did not affect the arsenic concentration of plant tissue. In the sandy soil, which had a relatively low arsenic or phosphorus retention capacity, the additional phosphorus increased the arsenic toxicity to plants.

Helgesen and Larsen (1998) examined carrots (*Daucus carota L.*) grown on arsenic contaminated soil. The carrots were grown in soils with seven levels of arsenic concentrations, ranging from 6.5 mg kg⁻¹ in the control plot to 917 mg kg⁻¹ in the most heavily contaminated soil. They observed progressive adverse effects in the carrots as the arsenic concentration of the soil increased. In the soil with arsenic concentrations of 93.3 and 338 mg kg⁻¹, they observed a decrease in the length of the harvested carrots as well as wilting and partial yellowing of the carrot tops. In the three most contaminated soils, containing 406, 679, and 917 mg kg⁻¹ of arsenic, the phytotoxic effects of arsenic resulted in complete crop failures. On average, in the four soils that produced harvestable crops, 0.47 per cent of the total arsenic in soil was absorbed by the above-ground plant parts. This was equivalent to as much as 1.5 mg kg⁻¹ of arsenic available to the carrots in the arsenic contaminated soils.

Cadmium Research results demonstrated that pH, organic matter content, and mineral components of the soils would influence the chemical activities and plant availability of cadmium (Tiller, 1989; Forbes et al., 1976). In acid soils, the organic matter and iron and

manganese oxides largely control the cadmium solubility. In alkaline soils, precipitation of cadmium compounds is the predominant factor in determining the solubility of cadmium (Kabata-Pendias, 2001). These reactions tend to inhibit cadmium movement in the soil, thereby contributing to its accumulation in the surface layer.

Several investigators have demonstrated increases of cadmium content in soils as a result of phosphate fertilizer applications (Williams and David, 1973; Mulla et al., 1980; He and Singh, 1993; McLaughlin et al., 1997). Williams and David (1973) reported that up to 80 per cent of the cadmium applied in phosphate fertilizers was retained in the upper 10 cm of the soil. They also noted that, if pH remained constant, increased soil cadmium concentration resulted in an increase in the plant uptake (Williams and David, 1976). Lime was added to some of the treatments to examine the effects of pH on cadmium availability to plants. In these trials, the cadmium content of the plants grown on the soils receiving lime and fertilizer was significantly less than those not receive the lime. They attributed this to the decreased availability of cadmium at the higher pH (Williams and David, 1976).

Mulla et al. (1980) examined the cadmium accumulation in soils that received 36 years of annual superphosphate fertilization as a result of a long-term fertility trial. Total cadmium concentrations of the 0 to 15 cm soil depth in the treated area were as much as 14 times higher than that of the control. The elevated cadmium levels of the treated soils decreased with depth such that the cadmium concentrations below 30 cm were no longer significantly different from that of the control. The DTPA-extractable cadmium in the treated soils was four to six times higher than that of the control. However, results of the field trials showed that the cadmium contents of barley (*Hordeum vulgare L.*) harvested from the treated areas were not significantly different from those in the control area.

Richards et al. (1998) examined cadmium accumulations in barley plants and soils that received annual phosphorus applications of 0, 22.5, 45, and 90 kg P₂O₅ ha⁻¹. They found no evidence that cadmium accumulated in soils or that cadmium uptake by barley plants was increased, after 29 years of cultivation. Assuming an average of 85 mg Cd kg⁻¹ P₂O₅ in the fertilizers used, the amount of cadmium added to the soil during the course of the experiment would be 0, 24, 48, and 96 g Cd ha⁻¹ for the four levels of phosphorus treatments. The cadmium concentrations, if evenly distributed throughout the surface 50 cm soil depth, should have increased by 0.007, 0.015, and 0.030 mg Cd kg⁻¹ and these changes should have been detectable, given the methods used for analysis. Richards et al. (1998) postulated that the cadmium might have been lost through leaching beyond the 50 cm soil depth or removed by plant uptake. Since the cadmium removals by the above ground biomass were not significantly different among the treatments, Richards et al. (1998) concluded that the added cadmium was leached beyond this layer of soil, which was low in organic matter, and freely drained. Given that there would be errors associated with the field trials, soil samplings, and laboratory analysis, the cumulative errors might have masked the small expected changes.

He and Singh (1994a) compared the cadmium uptake by oats (*Avena sativa L.*), ryegrass, carrot and spinach (*Spinacia oleracea L.*) grown on sandy and loamy soils that were amended with either a cadmium salt, low cadmium NPK fertilizer, high cadmium NPK fertilizer, and rock phosphate for comparable amounts of cadmium input. Their results showed that the plants grown with the high cadmium NPK fertilizer accumulated the most cadmium. In the sandy soil, the cadmium uptake by oats and ryegrass was two times more than those grown in control soil with no treatments. For the phosphate rock treatment, the cadmium contents in the plant tissue were not significantly different from those in plants grown on the control soil. They attributed this to

cadmium being strongly bound in the apatite structure of the phosphate rock, making it more recalcitrant and less available to plants. He and Singh (1994b) also examined how these plant tissue concentrations were related to the DTPA-extractable and NH_4NO_3 -extractable cadmium of the soils. They found that the cadmium uptake by plants was significantly correlated with the soil cadmium extracted by both of these methods. Application of the high cadmium NPK fertilizer increased the extractable soil cadmium, while the application of either the low cadmium NPK fertilizer or the phosphate rock did not result in significant increases of extractable cadmium. The results of He and Singh (1994b) found that depending on soil type, pH and plant species, the correlation between the plant uptake and the DTPA- or NH_4NO_3 -extractable cadmium varied. Under certain conditions one was better correlated with plant uptake than the other.

In a follow-up study, Singh and Myhr (1998) conducted a field experiment to examine cadmium uptake by barley grown on soils. They applied three separate types of cadmium, in the forms of the NPK fertilizer (at 0.03, 2.7 and 12 g Cd ha⁻¹ yr⁻¹), CdCl_2 (at 12 g Cd ha⁻¹ yr⁻¹), and phosphate rock (at 12 g Cd ha⁻¹ yr⁻¹). The cadmium contents of harvested plant tissue and the DTPA- and NH_4NO_3 -extractable cadmium of the soils were determined. The amounts of extractable cadmium in both cases increased in proportion with the cadmium application rates. Across the board, the NH_4NO_3 -extractable cadmium of the phosphate rock treatments, at the same treatment level, was lower than the extractable cadmium in the NPK fertilizer or the CdCl_2 treatment. Although the extractable cadmium of the soils increased in proportion with the amounts of cadmium applied, the plant uptake of cadmium did not exhibit any significant increase. The outcomes were contradictory to the earlier findings of the greenhouse experiments that He and Singh (1994a, 1994b) reported. Singh and Myhr (1998) attribute these discrepancies to the controlled conditions of the greenhouse as well as the confinement of root volume in

contaminated soils. In contrast, the roots of the field-grown plants were free to roam beyond the soil layer where the contaminants were concentrated. Roots in pot-grown plants remained in contact with the contaminated soils the entire time.

Lead As with cadmium, the solubility of lead in soil is pH- and organic-matter dependent. Lead tends to precipitate out and form lead-organic complexes at high soil pH. The end products are chemically rather stable (Kabata-Pendias, 2001). Lead also has a propensity to be adsorbed by clay minerals, organic matter, and iron-, manganese-, and aluminum-hydroxides. Together, these characteristics make lead a very immobile metal in soils (Kabata-Pendias, 2001). Hrsak et al. (2000) reported that soils remained persistently polluted by lead and cadmium because they had formed complexes that were poorly soluble in water.

Cabrera et al. (1994) found that farmlands in southern Spain had unusually high concentrations of lead ($116 \pm 68 \text{ mg kg}^{-1}$) compared to other regions. They attributed the elevation to the application of contaminating industrial wastes and lead-containing fertilizers (including municipal biosolids). They noted that the low-lying farmlands, which had fine texture and were rich in organic matter, retained higher levels of lead than the soils at higher grounds, which had coarse texture and were low in organic matter.

Gzyl (1990) examined the lead concentrations of parsley (*Petroselinum crispum L.*), carrots, celery (*Apium graveolens L.*) and beets (*Beta vulgaris L.*) grown in rural and urban soils in Poland. The lead concentrations were 50 times higher in the contaminated urban soils than in the uncontaminated rural soils. The outcomes showed that the lead contents in 586 of the 756 plant tissue samples exceeded the recommended maximum safe concentration for vegetables, 0.3 mg kg^{-1} fresh weight. Parsley and celery had the highest concentrations of lead.

Investigations showed that the bioavailability and mobility of lead in soils can be attenuated with the addition of phosphates (Rabinowitz, 1993; Laperche et al., 1996 and 1997). Laperche et al. (1997) demonstrated that apatite reacts with lead in soils to form pyromorphite. The lead content in the above-ground plant tissues were reduced while the lead and phosphorus content of plant roots increased due to the formation of pyromorphite on the root surface. The formation of pyromorphite decreased the availability of lead to plants and increased the “geochemical stability” of the lead in soil (Laperche et al., 1997).

Tu et al. (2000) found that phosphorus fertilizers altered the distribution of lead when soil and lead were separated into water soluble-exchangeable, specifically-adsorbed, oxide-bound, organic matter and residual fractions. The presence of phosphorus significantly lowered the amount of lead in the soluble-exchangeable fraction and elevated the amounts of lead in the specifically adsorbed and oxide-bound fractions.

Food Chain Transfer

Because arsenic, cadmium and lead have the potential to accumulate in cropland soils and be absorbed by plants, these potentially harmful elements may be inadvertently transferred through the food chain. Consequences of the chronic poisoning resulting from exposures to these elements are well documented (IARC, 1980; Ryan et al., 1982; Nriagu, 1988; U. S. EPA, 1986).

To determine if their concentrations in the harvested crops are rising, it is first necessary to establish the baseline concentrations in plant tissue. Wolnik et al. (1983a and 1983b) surveyed the cadmium and lead contents in major raw agricultural crops produced across the United States. This large-scale field-based study collected approximately 300 samples each of lettuce (*Lactuca sativa L.*), peanuts, potatoes (*Solanum tuberosum L.*), soybeans (*Glycine max L.*), sweet corn (*Zea mays L.*) and wheat from locations in 12 major production states (not all crops were

available in all states). The sampling locations were carefully selected to ensure they were not influenced by known contamination sources. The mean cadmium levels ranged from 0.078 mg kg⁻¹ (wet weight) in peanuts to 0.26 mg kg⁻¹ (wet weight) in lettuce. Because the results were reported on a wet-weight basis, it is difficult to make comparisons between crops and, for the same crops, between locations, since each sample had a different moisture percentage. Wolnik et al. (1983a) also noted that the same cultivar of a crop was not always grown in all of the locations.

The lead content in these samples was low also, with only a few samples exceeding 0.5 mg kg⁻¹ on a wet-weight basis. The average concentrations for the crops ranged from 0.009 mg kg⁻¹ (wet weight) in potatoes to 0.042 mg kg⁻¹ (wet weight) in soybeans. The lead contents of the crops were separated into two groups with lettuce, peanuts and potatoes containing 0.013, 0.010 and 0.009 mg Pb kg⁻¹, respectively. The remaining crops contained 0.042, 0.033, and 0.037 mg Pb kg⁻¹ for soybeans, sweet corn and wheat, respectively. These values illustrated the expected trace element levels of crops produced from soils that were not exposed to pollution, and represented the baseline levels from which crops produced in other areas could be judged.

Helgesen and Larsen (1998) grew carrots in Denmark on soils containing 30 mg kg⁻¹ arsenic and applied the plant uptake data in the context of a worst-case scenario for human health. They noted that per capita, Danes consume an average of 376 g of vegetables per day. Assuming that the entire daily vegetable consumption was represented by carrots (*Daucus carota L.*), and the arsenic in the carrots was present in inorganic form, the resulting estimated arsenic intake would not exceed the provisional tolerable weekly intake (PTWI) of 15 µg kg⁻¹ body weight) even when contributions from other food and water sources were included.

Dudka et al. (1996) grew crops on cadmium-contaminated soils and assessed the risk of dietary cadmium intake from foods grown on these soils. They assumed that the cadmium concentrations of the cereals and potato in the daily diet were represented by the cadmium concentrations of barley (*Hordeum vulgare L.*) and peeled potatoes from their experimental plots and that at least 50 per cent of the weekly consumption of cereals and potatoes came from the contaminated soils. Under this scenario, the dietary cadmium intake would increase from 200 to 435 $\mu\text{g week}^{-1}$ when cadmium concentrations in potatoes and barley grain were 1.0 and 0.6 mg kg^{-1} dry weight, respectively. The level of exposure however was still within the safe reference dose of 500 $\mu\text{g week}^{-1}$ (Dudka et al., 1996). Extrapolating from the cadmium concentrations in harvested plants, they estimated that the cadmium concentration of the soils could reach 30 to 35 mg kg^{-1} before the cadmium intake of the exposed individuals would exceed the threshold.

Gzyl (1990) grew carrots, celery, parsley, and beets on lead-and-cadmium contaminated soils in urban and rural areas in Poland. Based on the concentrations in the harvested crops, the lead intake could contribute between 2 to 22 per cent of its recommended PTWI of 3 mg week^{-1} and the cadmium intake could contribute between 4 to 81 per cent of its recommended PTWI of 0.4 to 0.5 mg week^{-1} . While the cadmium and lead concentrations in the parsley and celery were considerably higher, the beets and carrots were more significant sources of the cadmium and lead intakes as greater quantities of them were consumed.

Nwosu et al. (1995) observed that lead uptake by lettuce remained steady and the cadmium uptake continued to rise in proportion to the concentrations of the corresponding elements in the soils. They concluded that cadmium is transported relatively freely through the porous media and absorbed with little restriction, while lead is strongly adsorbed in the soils.

Methods of Sample Digestion

Arsenic, cadmium, and lead are customarily analyzed by atomic absorption spectroscopy for which the elements in soils must be extracted or dissolved into solution form. For determination of the total quantities of the soils, there are two approaches to digestion of soil samples, namely total recoverable digestion and total decomposition. A total recoverable digestion method leaches trace elements from the soil without fully decomposing the solid soil matrix. As a result, there is residual material that remains at the end of the process. This material theoretically could retain some of the elements of interest. The total decomposition method is able to bring the entire soil sample into solution. At the end of this digestion, no solid residue remains. By dissolving all of the substances in soil, the chemical matrix of the solution becomes complex and the concentrations of unrelated elements will be considerably higher than the elements of interest, thus increasing the potential for interference during the course of the determinations.

The U.S. EPA has recommended three methods to digest soils for elemental analysis. All of these methods require that the sample be first mixed thoroughly to achieve homogeneity and sieved, if necessary, to pass a USS #10 sieve. Method 3050B is a total recoverable hot plate digestion procedure designed to dissolve “almost all elements that could become environmentally available.” This method employs treatment of 1 to 2 g of soil with aliquots of HNO_3 and heating to $95^\circ\text{C} \pm 5^\circ\text{C}$ until no further oxidation is observed. The sample is then treated with aliquots of H_2O_2 and heated $95^\circ\text{C} \pm 5^\circ\text{C}$ until the effervescence subsides. Elements bounded in the silicate mineral structures are not normally dissolved by this procedure. Method 3051 is a microwave-assisted total-recoverable digestion procedure. This method employs 0.5 g of soil and 10 ml of HNO_3 in a fluorocarbon microwave digestion vessel. The mixture is

irradiated in the microwave oven for 10 minutes, reaching 175°C within 5.5 minutes and remaining between 170 and 180°C for the remainder of the time. For all of the microwave-assisted digestion methods, the vessels should be equipped with a pressure relief system that regulates the pressure in the system to 110 ± 10 pounds per square inch (psi). Method 3051A differs from Method 3051 only in that it allows for the addition of HCl to the digestion to improve the recovery of selected elements. Method 3052 is a microwave-assisted total decomposition procedure. This method employs 0.5 g of soil, 9 ml of HNO₃, and 3 ml of HF in a fluorocarbon microwave digestion vessel. The quantity of HF used may be adjusted from 0 to 5 ml depending on the matrix of the sample. The mixture is irradiated for 15 minutes, raising the temperature of the contents to $180^{\circ}\text{C} \pm 5^{\circ}\text{C}$ within 5.5 minutes and holding at that temperature for the remaining time.

Link et al. (1998) described the development and validation of the U.S. EPA Method 3051A, a microwave-assisted soil digestion method that includes HCl as a part of the reagent. During the course of the digestion, the Cl⁻ forms complexes with selected metals and thus stabilizes the analytes in the solution phase. The addition of the Cl⁻ did not have adverse effects on the analytes which otherwise exhibited good recoveries. Link et al. (1998) concluded that microwave digestion of soil samples had several advantages. Closed vessel microwave heating allowed the digestive contents to reach higher pressures and temperatures, reducing the time of reaction from several hours to minutes. It also minimized the potential losses of analytes due to volatilization. Finally, microwaves with temperature feedback control allow for a better transfer of standard methods between laboratories and analysts than the traditional hot plate methods.

Chen and Ma (1998) prepared 40 Florida surface soils for elemental analysis using the four official U.S. EPA digestion methods. A graphite furnace atomic absorption

spectrophotometer was used to determine the concentrations of arsenic, cadmium and lead in the digested solutions. An ICP-MS was used to determine the concentrations of barium (Ba), beryllium (Be), chromium (Cr), copper (Cu), manganese (Mn), molybdenum (Mo), nickel (Ni), antimony (Sb), selenium (Se) and zinc (Zn) in the digested solutions. They found that Method 3052 (a total decomposition method) consistently produced concentrations higher than or equal to the outcomes of Methods 3050, 3051, or 3051A (total recoverable digestion methods) for most of the elements analyzed. Chen and Ma (1998) also examined the elemental recovery efficiency of Method 3051A and Method 3052 employing a National Institute of Standard Testing reference soil (NIST SRM 2711). For both methods, the recoveries of cadmium, lead, zinc and phosphorus were all well within ± 20 per cent of the certified values. The recovery for arsenic (79 per cent) was slightly lower due to enhanced background noise during the analysis. They noted that background noise could reduce the analytical sensitivity for many elements including arsenic, cadmium, and lead, when they were determined by the ICP-OES method.

Wei et al. (1997) assessed the extraction efficiencies of the U. S. EPA Methods 3050 and 3051, a microwave-assisted digestion and a hot plate digestion procedure, respectively. The U. S. EPA Method 3051 was designed as an alternative procedure to Method 3050 for regulatory purposes where large number of samples might have to be processed in a timely manner. These two procedures are expected to yield comparable final results. The recovery for lead, zinc, nickel, copper, and cadmium for Method 3050 ranged from 94-101 per cent, with precision ranging from 1.8-13 per cent. For Method 3051, the recovery of the elements ranged from 89-97 per cent, with precision ranging from 1-3 per cent. While the recoveries yielded by both Method 3050 and Method 3051 were acceptable, the precisions of the determinations employing Method 3051 in some cases were less consistent than those of the Method 3050. The microwave-assisted

digestion procedure produced more reproducible outcomes than those obtained using the hot plate digestion procedure.

Lorentzen and Kingston (1996) also compared the outcomes of the hot plate digestion procedure with those of the microwave-assisted digestion procedures of the U. S. EPA Method 3050B. They concluded that the advantage of preparing many samples at one time using the hot plate digestion was offset by the difficulty of maintaining identical heating conditions for all of the samples. For example, the temperature of digestion flasks could vary by as much as 35°C, depending on their positions on the hot plate. They also reported that microwave systems employing power control did not regulate the temperature precisely. The temperature in the reaction cells of the power-controlled microwave system was usually 10 to 15°C higher than the required 95°C. In contrast, microwaves equipped with temperature feedback control were capable of maintaining the temperature with an accuracy of $\pm 2^\circ\text{C}$. Consistency in temperature control will improve repeatability of the analysis.

Nieuwenhuize et al. (1991) experimented with the aqua regia extraction of several trace elements in two certified reference materials employing microwave-assisted heating, and compared the results to those obtained from the same procedure employing the conventional reflux extraction method. They showed that, in round-robin comparisons, the microwave-assisted extraction produced consistent results. The concentrations of cadmium, chromium, copper, iron, manganese, lead, and zinc in the certified references determined by three separated laboratories were in close agreement. For cadmium, copper, manganese, lead, and zinc, the outcomes produced by the conventional reflux extraction were not significantly different from those of the microwave-assisted heating. For chromium and iron, however, the recoveries were significantly higher using the microwave-assisted heating rather than the conventional reflux. When the

concentrations of these seven elements in 30 soils, sediments, and biosolids samples were compared, no significant difference was found between these two methods.

MATERIALS AND METHODS

Sampling Strategy

Phosphate fertilizers and micronutrients are routinely used in crop production. However, in each cropping or growing season, the quantities required per unit surface area to support a successful harvest were moderate. Judging from the concentrations and distributions of arsenic, cadmium, and lead in the fertilizers, the trace element inputs to cropland soils, although frequent and long-term in nature, are inherently low in intensity. In the meantime, trace elements are also being removed from the root zone through plant uptake, leaching, and surface runoffs. Even though their concentrations in the fertilizers and micronutrient supplements are significantly elevated, the amounts of arsenic, cadmium and lead added to soils through each application are small in comparison to mass of the receiving soils, making the changes difficult to detect due to limitations in the sensitivity of analytical methods. The trace element content of the soils may also be changed through natural weather processes and by atmospheric fallout. Thus, it is essential to separate the contributions of the natural causes and the fertilizer applications on the changes of trace element concentrations in cropland soils.

In practice, it is difficult if not impossible to apply the fertilizers and micronutrients uniformly across large production fields. The inherent spatial variability of the fields and the limitations on the mass of soils sampled would introduce experimental errors that could render the final results inconclusive. In a cropland production system, there are other sources of trace element inputs (Chang and Page, 2000). Farmers seldom make routine applications of biosolids, animal manure, or reclaimed wastewater to their crops. However, in certain situations, the impacts from these applications – as well as from atmospheric fallout – may be comparable to or more significant than those from fertilizers. In the past, chemicals containing arsenic and lead

were used to formulate herbicides and insecticides, especially for uses in orchards and vineyards. Monosodium arsenate is still a registered herbicide for deep-rooted weeds. Legacies of past practices may have a profound effect on the outcome of a field survey on trace accumulations in cropland soils. However, records of past applications and cropping history of any given field are virtually non-existent. These factors must be accounted for in developing a study plan.

To resolve the above-described issues, we devised two approaches:

1. Analyze the arsenic, cadmium, and lead contents of the benchmark soils to determine the long term changes of the baselines in California.

In 1950, Dr. R. J. Arkley of the University of California, Berkeley (Bradford et al., 1967) identified 50 locations across the state where the soil profiles are representative of those in California. At the time of selection, these soils were undisturbed and uncultivated. Since then, conditions have changed. The soils at these locations were sampled in 1967 for analysis of their elemental compositions (Bradford et al., 1967 and 1996). These soils were sampled again in 2001. The changes in the arsenic, cadmium, and lead contents of soils collected in 1967 and 2001 will provide a snapshot on changes in the trace element baselines of soils across California over the past 35 years. These will serve as the reference point to judge the significance of changes detected on cropland soils.

2. Sample soils used for long-term vegetable productions in major production regions across the state.

Vegetable production requires considerably higher levels of fertilizer than other crops (Mayberry, 2003). California's climate permits year-round production, and multiple crops are harvested annually. As a result, croplands dedicated for vegetable production in the state would receive more fertilizer and are more susceptible to accumulating trace elements. The

soils receiving frequent and heavy fertilizer applications would represent the worst-case scenario, and the accumulations of arsenic, cadmium, and lead, if they occurred, would more likely be detected in such a field survey. For this purpose, seven production areas, namely the Oxnard and Ventura Area, Santa Maria and San Luis Obispo Valley, Colusa and Glen County, Fresno, Coachella Valley, Imperial Valley, and Monterey and Salinas Valley, were selected for soil sampling. We purposely excluded the fruit production orchards and vineyards where arsenic and lead-based pesticides were frequently used in the past. At the site, we chose locations that were away from roads where frequent vehicle traffic was expected and avoided field structures, power poles, and electrical installations. This way, the external interferences might be minimized.

The soils in the selected regions have been in cultivation since the beginning of the 20th Century. In the past 40 years, many of the fields have been intensely cultivated for vegetables. The crop planting and fertilization histories of the fields, however, were not traceable. Instead of seeking definitive cause-and-effect relationships between the amount of fertilizers and the increases of trace element contents in the corresponding soils as Williams and David (1976), we decided to establish trends. In this respect, the soil samples collected in each region would be pooled and treated as a homogeneous sampling population. The arsenic, cadmium, and lead concentrations of the soil may be plotted as dependent variables against the soils' phosphorus or zinc concentrations as independent variables, which are indicators for applications of phosphorus fertilizers and micronutrients. If the fertilizer and/or micronutrients applications have caused the trace elements to accumulate in the receiving soils, there should be trends for those trace elements to increase in step with the phosphorus and/or zinc content of the soils. It is essential to collect a large number of soil samples to

insure that the soil sampling covers a wide range of fertilizer inputs, thereby reflecting any trace element inputs. To insure that the background levels of the soils do not affect the outcomes, it is also essential that the areas sampled have similar soil properties.

Soil Sample Collection

Benchmark Soils The locations of the benchmark soils were identified by R. A. Arkley of University of California, Berkeley in 1950. The initial soil samples were no longer in existence. The soils at these locations were sampled by G. R. Bradford in 1967 (Bradford et al., 1967 and 1996). We revisited these locations according to the directions given in the original field notes. Most of the sites were located in sparsely-populated and remote areas, and the conditions had not changed since the last soil sampling. They were wild lands, rangelands, pastures, and low-input and low-intensity agricultural lands. Not all of the locations were available in 2001. The land use in several locations had been drastically altered since the soil sampling in 1967. For example, two locations were converted to subdivisions and access to two other locations was denied by the land owners. In at least three instances, residential or commercial structures were built on the locations. In these situations, alternative locations were established whenever possible. Otherwise, the sites were dropped from the 2001 field sampling.

Vegetable Fields In each vegetable production region, the sampling locations were identified and selected with the assistance of individuals familiar with fertilizer distribution and agricultural production in the local area. The locations were selected for the uniformity of soil properties and to cover a wide spectrum of fertilizer application history ranging from short- to long-term.

Field Soil Sampling Procedure

To ensure consistency in sample collection, the same detailed sampling protocol was followed at each location. Once a location was selected, its coordinates were recorded using a global positioning system (GPS). Samples were taken a minimum of 50 m from the edge of a field to avoid influences from the road. Efforts were made to avoid areas near utility poles, wood structures, and field pumping stations. A two-inch (5 cm) bucket auger was used to collect soil samples 20 cm deep at each location, thus excluding organic debris at the surface. At each site, five samples, approximately 10 m apart, were taken along a transect. Each of the five samples was a composite of four to five sub-samples that were taken along a two-meter line perpendicular to the transect. Between each sample, the sampling equipment was cleaned to prevent contamination. Approximately 500 g of soil were collected, field-screened to pass a 1 mm sieve opening, and stored in a plastic bag. Samples were transported from the field inside thermo-insulated storage chests.

We were unable to locate uncultivated and undisturbed sites at which the baselines for trace elements in the soils could be established. At selected locations within each region, samples were also taken at a depth two meters below the surface. The sampling equipment was cleaned between each sample to prevent contamination. Samples were then handled and processed in the same manner as the other soils. The soils in agricultural regions have deep and homogeneous profiles. It is reasonable to assume that the concentrations of arsenic, cadmium, lead, phosphorus, and zinc of soil at this depth represent the baselines for the region.

Sample Preparation The soil samples were air-dried in a greenhouse. A sub-sample was taken, ground with a porcelain mortar and pestle to pass the openings of a 200-mesh (75 μm)

sieve, and dried in an oven overnight at 105 °C prior to be used for dissolution and elemental analysis.

Soil Digestion Aliquots of the soil samples were digested in accordance with U.S. EPA Method 3052, which results in the total dissolution of all soil particles. According to this method, a 0.25 g soil sample was combined with 9.0 ml HNO₃, 4.0 ml HF and 1.0 ml of deionized water in a digestion vessel. The mixture was heated in a microwave oven for a total of 15 minutes. The program was set to deliver 100 per cent power (1200 W) to raise the temperature to 180 ± 5 °C within 5.5 minutes and hold that temperature for the remaining 9.5 minutes. The CEM Mars 5 microwave system with HP-500 Plus digestion vessels and PFA (perfluoro alkosy ethylene) liners was used for the procedure. It was capable of monitoring both the temperature and pressure of a representative sample during the digestion. Between each set of digestions, the liners were soaked for at least two hours in a 2 M nitric acid bath and rinsed thoroughly with deionized water.

After completing the microwave heating process, the vessels were placed in a freezer for 15 to 20 minutes to allow the temperature to cool. The resulting solutions were quantitatively transferred to 25 ml volumetric flasks. Deionized water was used to rinse any remaining droplets from the sides and cap of the liners and to dilute the volume. The solutions were then transferred to plastic scintillation vials to be stored for the elemental analyses.

Plant tissue Plant tissue samples were washed with dilute non-ionic detergent solution, rinsed with tap water and deionized water, dried in an oven at 65°C, ground to pass 0.1 mm open screen, and stored. Aliquots of grounded plant tissue samples were again dried at 65°C, microwave digested employing mixtures of concentrated nitric and hydrochloric acids, dilute to volume.

Elemental Determinations

The determinations of total arsenic, cadmium and lead concentrations in the solutions were made using a Perkin Elmer AAnalyst 800 atomic absorption spectrometer equipped with a graphite furnace atomizer (GFAAS). Standards were prepared to calibrate the instrument by diluting stock solutions of each element in 1 per cent optima nitric acid. A $50 \mu\text{g l}^{-1}$ standard was used for the analysis of arsenic and lead, and a $5 \mu\text{g l}^{-1}$ standard was used for the cadmium analysis. The auto-sampler used was capable of making the serial dilutions necessary to establish multiple points for a calibration curve. The 1 per cent optima nitric acid solution was analyzed to provide a calibration blank. The analysis of each element also required that matrix modifiers be added to each sample prior to analysis. For arsenic analysis, $5 \mu\text{l}$ 0.1 per cent Pd and $5 \mu\text{l}$ of 0.06 per cent $\text{Mg}(\text{NO}_3)_2$ were added to $20 \mu\text{l}$ aliquot of sample or standard. For lead and cadmium analyses, $5 \mu\text{l}$ 1 per cent $\text{NH}_4\text{H}_2\text{PO}_4$ and $5 \mu\text{l}$ of 0.06 per cent $\text{Mg}(\text{NO}_3)_2$ were added to $20 \mu\text{l}$ aliquot of sample or standard.

Total phosphorus and zinc concentrations in the solutions were determined using a Perkin Elmer Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). To calibrate the instrument, standards containing 0.1, 1, and 10 ppm phosphorus and zinc were prepared by diluting stock solutions with 1 per cent optima nitric acid. This diluent was also included in the analysis as a calibration blank.

Quality Control/Quality Assurance

To ensure the accuracy and precision of the analyses, quality control and quality assurance protocols were implemented to check the consistency of outcomes from batch to batch.

The accuracy of arsenic, cadmium and lead determination by the instruments was verified using the NIST Trace Elements in Water Standard (NIST 1640). After the arsenic, cadmium, and

lead calibration curves for GFAAS were established, this standard was analyzed and the outcomes checked against certified values. The NIST water standard was not certified for phosphorus, so a separate standard was used to check the accuracy of the calibration curves on the ICP-OES. A zinc and phosphorus standard was prepared by diluting commercially-available stock standard solutions of these elements with 1 per cent optima nitric acid. To eliminate a carry-over of error, the calculations of dilutions and the preparation of this check standard was performed by someone other than the person preparing the calibration standards. If the recoveries of the standards were not within ± 10 per cent of the certified value, the calibration curve would be rejected and a new one prepared.

The accuracy of the soil processing and analysis was determined by including standard reference material with every batch of 12 soil samples digested. The National Institute of Standards and Technology (NIST) standard reference material NIST 2709 (San Joaquin Soil) was employed. The concentrations determined by our analysis were compared to the certified values for the material. If the recovery was within ± 10 per cent of the certified value, the analyses were accepted. If the standard recovery was outside of this limit, the analysis for all of the samples in the set would be rejected and repeated.

To ensure the precision of the analysis, each sample was digested and analyzed in duplicate. The concentrations of analyte in the replicates were compared and the analysis was evaluated based on the relative percentage difference (RPD), which is calculated as the absolute difference between two replicated analyses divided by the mean of replicates expressed in percentage. The analysis of a sample would be rejected if RPD was greater than 10 per cent, and the analysis would be repeated.

Spiked samples were also used to establish if matrix interference was causing amplification or decrease in signal response. A known amount of standard was added during the digestion procedure, and the recovery of that standard was determined. If the recovery of the standard exceeded ± 10 per cent of the amount added, the analysis was rejected and repeated.

RESULTS AND DISCUSSION

Accuracy, Precision, and Background Interference

During the course of the investigation, more than 1,000 soil samples were collected at locations across the state. The collection of soil samples and the subsequent chemical analyses were all conducted in batches over two years. To ensure consistency in sampling and analysis, strict quality control and quality assurance protocols were followed. It was imperative to establish the consistency and reliability of the results.

Precision of Analysis - Duplicate Samples Approximately 85 per cent of the samples met the RPD < 10 per cent criterion on the first run. Ninety-six per cent of those rejected had RPD < 20 per cent. The rejected samples were typically soils with low concentrations of the element of interest, and the difference between the replicates that caused the determinations to fail was quite small. The RPD became exaggerated when the small differences were divided by an equally small mean. In the case of cadmium analysis, a difference of only 0.01 mg kg⁻¹ was sufficient to reject many of the analyses.

Several factors affected the precision of the chemical analysis and might have caused the relative percentage difference between the replicates to fall into the 10 to 20 per cent range. Purposely, replicate samples were always digested in separate batches, which also led to their analysis as separate batches. The GFAAS instrument was programmed to recalibrate after every 10 determinations and the ICP-OES instrument was programmed to recalibrate after every 20 determinations. Even if they were analyzed during the same run on the instrument, it is unlikely that they would be referenced against the same calibration curve. The conditions of the instrument could have changed between the calibrations, causing a slight shift in the instrument

readings. When the concentration of the element of interest was low, the shift might be sufficient for the relative percentage difference to exceed the 10th percentile range. Frequently, the discrepancies were resolved when the analyses were repeated and the replicates were paired and read under the same calibration curve. The discrepancies in 25 per cent of the remaining 4 per cent that failed to meet the RPD requirements were resolved through reanalysis of digested solutions. For the remaining approximately 3 per cent of the original analysis, the entire process had to start over. For those samples requiring re-digestion and analyses, the analytical errors of the original analyses could be attributed to either inadequate cleaning of the vessels between digestions or error in the sample handling and processing, such as in weighing and diluting.

Interferences of Background Matrices - Spiked Samples When samples were spiked with known amounts of the element of interest, the spike recovery may be used to check for losses of the element during sample digestion and subsequent processing, and to differentiate any matrix interferences in the elemental determinations. In this study, the spikes were planted in two ways. Prior to the digestion, selected soil samples were spiked with known aliquots of arsenic, cadmium and lead. This spike was to identify any losses of the element during sample processing as well as matrix interferences. The outcomes illustrated that the spike recoveries were all within 100 ± 10 per cent of the amounts added and the digestion process would not be a cause for error. Subsequently, samples were not spiked for the microwave digestions. However, the digested solutions were spiked prior to the elemental determination. The average spike recoveries for arsenic, cadmium and lead were 96, 99 and 103 per cent, respectively. No serious matrix interference was detected in the soils analyzed.

Accuracy of the Analysis - Recovery of Standard Reference Materials Two standard reference materials were used during the analyses. A NIST certified water standard

(NIST 1640) was used to check the accuracy of the calibration and the GFAAS instrument was programmed to reject a calibration curve if the outcome of the NIST water standard test exceeded 100 ± 10 per cent of the certified value. The instrument would then continue calibration curves until the criterion of the NIST water standard was met. The analyses using ICP-OES required a post-analysis examination of the readings on the water standard to see if the calibration curve met the desired requirements. If it failed, the analysis would be rejected and the entire batch would be rerun until the requirement was met.

The standard reference material NIST 2709 (a certified San Joaquin Soil) was included with every batch of the soils digested and analyzed. Figures 1 to 3 show in chronological order the recoveries of arsenic, cadmium, and lead for the 200 consecutive analyses of the NIST 2709 samples. They provide indications on the consistency of the accuracy of the determinations. Out of 200 determinations, 18, 20, and 22 determinations for arsenic, cadmium and lead, respectively failed to meet the quality assurance criteria. This equates approximately to a 10 per cent failure rate. The failed batches were rejected and the analysis repeated.

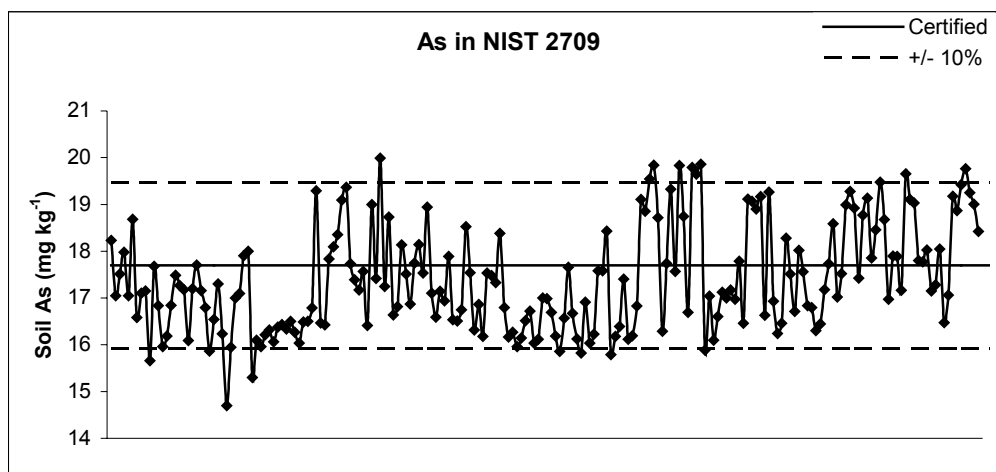


Figure 1. Chronological Recording of Arsenic Recovered from NIST 2709 during GFAAS

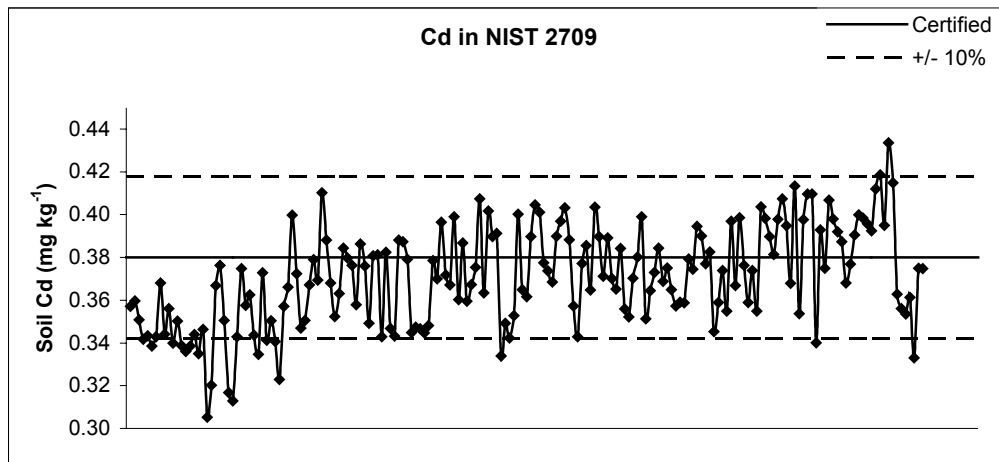


Figure 2. Chronological Recording of Cadmium Recovered from NIST 2709 during GFAAS

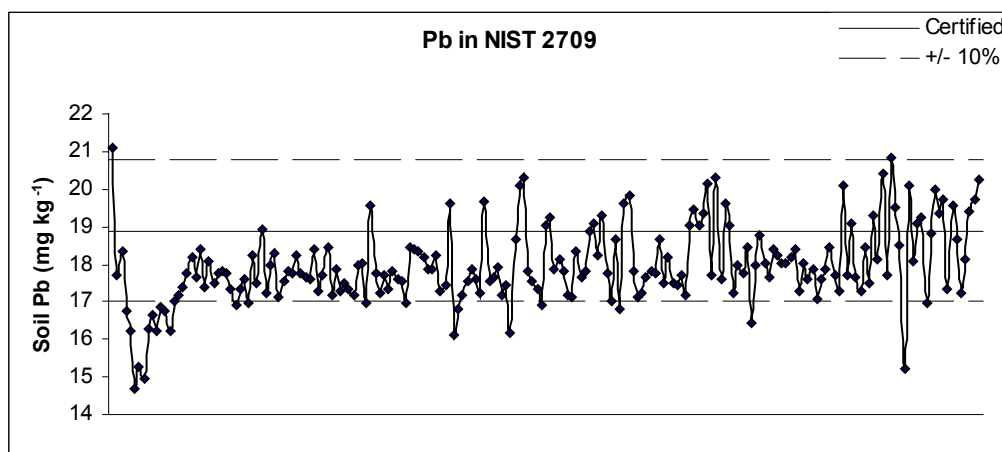


Figure 3. Chronological Recording of Lead Recovered from NIST 2709 during GFAAS

Judging from the data presented in the figures, more data points fell below the certified values. On the average, our determinations underestimated the arsenic, cadmium, and lead in NIST 2709 by 1.7, 2.5 and 5.0 per cent, respectively (Table 3). Consequently, we expect that the soil arsenic, cadmium and lead concentrations we reported would be underestimated by similar magnitudes. The certified values in NIST 2709 were obtained by the neutron activation

techniques, so the underestimations most likely reflected the differences in the characteristics of the instruments employed in the determinations.

Table 3. Recoveries of Arsenic, Cadmium, and Lead from NIST 2709 in GFAAS Analyses

Element	Average Recovery¹ (mg kg⁻¹)	Certified Value¹ (mg kg⁻¹)	Deviation² (%)
Arsenic	17.4 ± 1.1	17.7 ± 0.8	-1.7
Cadmium	0.37 ± 0.02	0.38 ± 0.01	-2.5
Lead	18.0 ± 1.1	18.9 ± 0.5	-5.0

¹Denote mean ± standard deviation

²Percent of deviation from the certified value

Benchmark Soils

In 2001, all but one of the 50 original locations of the benchmark soils was revisited and sampled. At each location five replicates of samples were taken, for a total of 245 samples. In this manner, the statistical inference of the spatial variability may be addressed. Because these samples were taken at a different depth (0 – 20 cm) than the ones in the 1967 sampling (0 – 50 cm), samples from 0 - 50 cm depth were also taken at 12 selected locations that were revisited. These samples were used to compare with the shallower samples to see if there were significant differences in the elemental concentrations between the 0 - 20 cm samples and the 0 - 50 cm sampling depths.

The archived samples of the benchmark soils, taken in 1967, were analyzed along with the samples collected in 2001 so the values reported were based on the same chemical analysis protocols. The SAS statistical software package was used to perform a Tukey test that compared the differences in concentrations of arsenic, cadmium, and lead in the 1967 and 2001 samples at both 95 per cent and 99 per cent confidence intervals. The statistical tests were also performed to compare the differences between the 0 – 20 cm and 0 - 50 cm samples taken at the first 12 locations.

Sampling Depths The 12 locations sampled at both the 0 - 20 cm and 0 - 50 cm depths during the 2001 survey represent soil series types found in four counties in the Central Valley of California. The texture of these soils range from clay and clay loam in the Merced and Panoche series to loam in the Fresno, Holland and San Joaquin series, and sandy loam in the Kettleman and San Joaquin series. The concentrations of arsenic, cadmium, lead, phosphorus and zinc in each layer of the soil were compared. For all of the elements, the sampling depth of 20 or 50 cm did not appear to significantly affect the outcomes.

The mean arsenic concentrations of the five 0 - 20 cm samples and the corresponding 0 – 50 cm samples at the 12 selected locations are summarized in Table 4. At $p < 0.01$, the arsenic concentrations of the 0 – 20 cm depth samples were not significantly different from the corresponding concentrations of the 0 – 50 cm depth samples. Among the locations, soils at site 10 exhibited the largest absolute difference in the arsenic concentrations (9.9 vs. 11.7 mg kg⁻¹) and the relative percentage difference between the 0 – 20 and 0 – 50 cm depth soil samples was approximately 17 per cent. The spatial variability of the field alone could account for this magnitude of difference. Therefore, the outcomes derived from 0 - 20 cm and 0 – 50 cm sampling depths would be comparable.

Table 4. Arsenic Concentrations of Soils of 0 to 20 and 0 to 50 cm Sampling Depths

Site Number	Soil Series ¹	County	0-20 cm (mg kg ⁻¹)	0-50 cm (mg kg ⁻¹)	RPD ² (%)
8	Fresno l	Kern	9.9	11.2	11
10	Fresno l	Merced	9.9	11.7	17
13	Holland l	Fresno	4.9	4.7	4
21	Kettleman sl	Fresno	9.9	9.1	8
23	Kettleman sl	Fresno	9.2	10.5	13
25	Lassen c	Tulare	11.6	10.8	7
32	Merced c	Kern	14.3	13.1	9
33	Merced c	Fresno	10.3	9.9	4
34	Merced cl	Merced	4.8	5.0	4
41	San Joaquin sl	Merced	3.4	3.2	6
42	San Joaquin l	Tulare	5.3	5.8	9
48	Panoche cl	Fresno	12.0	10.9	10

¹The abbreviations denote soil texture that c is clay; l is loam; sl is sandy loam; and cl is clay loam

²Relative percentage difference between the concentrations of the 0 – 20 and 0 – 50 cm depths

The mean cadmium concentrations at the 0 – 20 cm and 0 – 50 cm sampling depths are summarized in Table 5. Again, the mean cadmium concentrations of the 0 – 20 cm soil samples were not significantly different from the mean concentrations of the 0 - 50 cm soil samples at $p < 0.01$. More than likely, the differences exhibited in these sets of concentrations reflected simply field variability and sampling errors. The difference in concentrations at Site 33 (0.26 vs. 0.52 mg kg⁻¹), although not significantly different, was notable (Table 5). Numerically, the considerably higher average cadmium concentration of the 0 – 50 cm sampling depth was due to the unusually high concentration in one of the five sampling points. The high cadmium concentration in this sample was accepted because the determinations met all of the criteria specified in the quality control and quality assurance protocols.

Because of the low soil cadmium concentrations, small differences in the concentrations of these two sampling depths could result in large relative percent differences. Except for site 33, the relative percent differences for the remaining sites, however, were all reasonable. It is

imperative nevertheless that replicated samples be taken to account for the variability and sampling errors in the cadmium determinations.

Table 5. Cadmium Concentrations of Soils of 0 to 20 and 0 to 50 cm Sampling Depths

Site Number	Soil Series ¹	County	0-20 cm (mg kg ⁻¹)	0-50 cm (mg kg ⁻¹)	RPD ² (%)
8	Fresno l	Kern	0.47	0.43	4
10	Fresno l	Merced	0.13	0.14	7
13	Holland l	Fresno	0.24	0.24	0
21	Kettlemen sl	Fresno	0.26	0.21	21
23	Kettlemen sl	Fresno	0.41	0.36	13
25	Lassen c	Tulare	0.16	0.22	32
32	Merced c	Kern	0.31	0.28	10
33	Merced c	Fresno	0.26	0.52	67
34	Merced cl	Merced	0.19	0.20	5
41	San Joaquin sl	Merced	0.19	0.16	17
42	San Joaquin l	Tulare	0.33	0.27	20
48	Panoche cl	Fresno	0.27	0.27	0

¹The abbreviations denote soil texture that c is clay; l is loam; sl is sandy loam; and cl is clay loam

²Relative percentage difference between the concentrations of the 0 – 20 and 0 – 50 cm depths

The lead concentrations of the 0 - 20 cm vs. 0 - 50 cm soil samples are summarized in Table 6. The soil lead concentrations of the 0 - 20 cm depth were not significantly different from those of the 0 - 50 cm depth at the corresponding site at $p < 0.01$. Judging by the relative percentage differences, the magnitude of differences between the soil samples at the 0 – 20 cm and 0 – 50 cm sampling depths were rather small and were well within the range of spatial variability expected of the field sampling.

Table 6. Lead Concentrations of Soils of 0 to 20 and 0 to 50 cm Sampling Depths

Site Number	Soil Series ¹	County	0-20 cm (mg kg ⁻¹)	0-50 cm (mg kg ⁻¹)	RPD ²
8	Fresno l	Kern	15.7	15.8	1
10	Fresno l	Merced	13.5	14.4	6
13	Holland l	Fresno	21.6	18.2	17
21	Kettleman sl	Fresno	12.1	11.1	9
23	Kettleman sl	Fresno	16.0	15.7	2
25	Lassen c	Tulare	9.5	8.2	15
32	Merced c	Kern	17.5	14.6	18
33	Merced c	Fresno	15.9	11.7	24
34	Merced cl	Merced	11.7	11.0	6
41	San Joaquin sl	Merced	11.6	11.7	1
42	San Joaquin l	Tulare	16.0	15.7	2
48	Panoche cl	Fresno	11.9	12.8	7

¹The abbreviations denote soil texture that c is clay; l is loam; sl is sandy loam; and cl is clay loam

²Relative percentage difference between the concentrations of the 0 – 20 and 0 – 50 cm depths

The soil phosphorus concentrations at the 0 - 20 cm sampling depth were not significantly different from the corresponding concentrations of the 0 - 50 cm sampling depth at $p \leq 0.01$ (Table 7). The pattern for the soil phosphorus concentrations of the 0 – 20 cm and 0 – 50 cm sampling depths was similar to those established by the comparisons already made for arsenic, cadmium, and lead. The relative percentage differences of the soil phosphorus concentrations at these two sampling depths were within the range variations expected of the field sampling.

Table 7. Phosphorus Concentrations of Soils of 0 to 20 and 0 to 50 cm Sampling Depths

Site Number	Soil Series ¹	County	0-20 cm (mg kg ⁻¹)	0-50 cm (mg kg ⁻¹)	RPD ² (%)
8	Fresno l	Kern	1234	1054	16
10	Fresno l	Merced	288	335	38
13	Holland l	Fresno	886	953	7
21	Kettlemen sl	Fresno	781	726	7
23	Kettlemen sl	Fresno	702	709	1
25	Lassen c	Tulare	672	649	3
32	Merced c	Kern	571	558	2
33	Merced c	Fresno	240	213	12
34	Merced cl	Merced	633	620	2
41	San Joaquin sl	Merced	119	150	23
42	San Joaquin l	Tulare	573	402	35
48	Panoche cl	Fresno	555	491	12

¹The abbreviations denote soil texture that c is clay; l is loam; sl is sandy loam; and cl is clay loam

²Relative percentage difference between the concentrations of the 0 – 20 and 0 – 50 cm depths

The soil zinc concentrations at the 0 - 20 cm sampling depth were not significantly different from those of the 0 - 50 cm sampling depth (Table 8). With the exception of one site, the relative percentage differences of the soil zinc concentrations at these two depths were all less than 10 per cent.

Table 8. Zinc Concentrations of Soils of 0 to 20 and 0 to 50 cm Sampling Depths

Site Number	Soil Series ¹	County	0-20 cm (mg kg ⁻¹)	0-50 cm (mg kg ⁻¹)	RPD ² (%)
8	Fresno l	Kern	95.1	95.4	0
10	Fresno l	Merced	75.1	73.4	2
13	Holland l	Fresno	83.0	86.3	4
21	Kettlemen sl	Fresno	94.3	79.9	17
23	Kettlemen sl	Fresno	94.3	98.6	4
25	Lassen c	Tulare	70.5	69.8	1
32	Merced c	Kern	97.6	99.1	2
33	Merced c	Fresno	71.5	73.2	2
34	Merced cl	Merced	75.0	72.4	4
41	San Joaquin sl	Merced	34.2	34.7	1
42	San Joaquin l	Tulare	65.5	71.6	9
48	Panoche cl	Fresno	91.2	93.0	2

¹The abbreviations denote soil texture that c is clay; l is loam; sl is sandy loam; and cl is clay loam

²Relative percentage difference between the concentrations of the 0 – 20 and 0 – 50 cm depths

Based on the data presented in Tables 4 through 8, it is reasonable to conclude that the arsenic, cadmium, lead, phosphorus, and zinc concentrations of the benchmark soils were not affected by variations at the soil sampling depths of 0 – 20 cm or 0 – 50 cm. It would be acceptable to directly compare the outcomes from soil samples taken in 1967 of 0 – 50 cm sampling depth to those taken in 2001 of 0 – 20 cm sampling depth.

1967 vs. 2001 The descriptive statistics summaries of arsenic, cadmium, lead, phosphorus and zinc concentrations in benchmark soil sampled in 1967 and 2001 are presented in Tables 9 and 10, respectively. The respective elemental concentrations of the samples collected in 1967 and 2001 were not significantly different at $p \leq 0.01$.

Table 9. Descriptive Statistics Summary of Element Concentrations in Benchmark Soil Samples Collected in 1967

Element	Observations	Range (mg kg⁻¹)	Mean (mg kg⁻¹)	Median (mg kg⁻¹)
Arsenic	50	1.8 – 20.5	8.8 ± 4.3	8.5
Cadmium	50	0.03 – 0.44	0.18 ± 0.10	0.17
Lead	50	3.6 – 25.0	12.0 ± 5.3	11.4
Phosphorus	50	51 – 1127	520 ± 262	520
Zinc	50	21.8 – 142.7	69.2 ± 25.8	72.3

Table 10. Descriptive Statistics Summary of Element Concentrations in Benchmark Soil Samples Collected in 2001

Element	Observations	Range (mg kg⁻¹)	Mean (mg kg⁻¹)	Median (mg kg⁻¹)
Arsenic	50	1.8 – 16.6	7.6 ± 3.9	6.5
Cadmium	50	0.07 – 0.53	0.22 ± 0.11	0.19
Lead	50	4.9 – 26.8	14.6 ± 5.5	13.6
Phosphorus	50	124 – 1503	616 ± 342	564
Zinc	50	34.2 – 123.6	75.9 ± 21.8	75.7

The 1967 vs. 2001 medians for arsenic, cadmium, lead, phosphorus, and zinc were 8.5 vs. 6.5, 0.17 vs. 0.19, 11.4 vs. 13.6, 520 vs. 564, and 72.4 vs. 75.7 mg kg⁻¹, respectively. Overall, the baseline levels of these elements in the benchmark soils remained stable over the 35-year period. As a result, there was no need to correct for baseline changes due to increases in the background levels when the data from cropland soils was compared.

While the baseline levels across the state remained constant, the conditions at individual benchmark locations might have changed. In the 2001 soil sampling, five replicates of soil samples were obtained across a 50-meter transect. Based on the determinations of the replicates, the 99 per cent upper and lower confidence limits of the elemental concentrations were established. To illustrate the changes in elemental concentrations at each location, the mean elemental concentrations from the 2001 sampling, along with the 99 per cent confidence ranges, were plotted in ascending order (Figures 4 to 8). The corresponding mean concentrations from the 1967 sampling were then plotted accordingly at the same position along the horizontal axis. If the elemental concentration of the sample obtained in 1967 lay inside of or above the corresponding confidence range, it indicated that the trace element concentration at the site had not changed. If the 1967 mean was below the 2001 confidence range, the element concentration at this site most likely has risen over the sampling period. Based on this criterion, we determined that the arsenic, cadmium, lead, phosphorus, and zinc concentrations at 4, 14, 20, 8 and 14 sites, respectively, have been significantly increased. The symbols indicating these locations are marked in red in Figures 4 to 8.

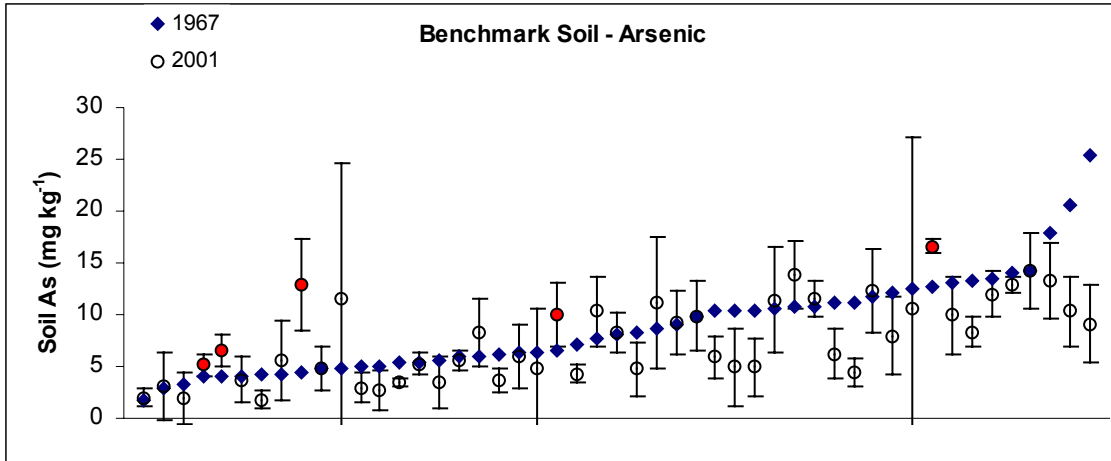


Figure 4. Arsenic Concentrations of Benchmark Soils, 1967 vs. 2001

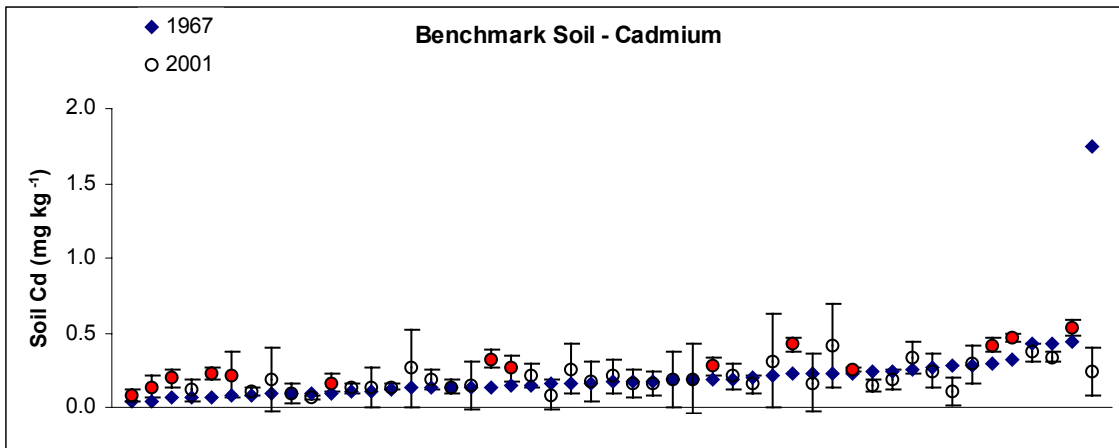


Figure 5. Cadmium Concentrations of Benchmark Soils, 1967 vs. 2001

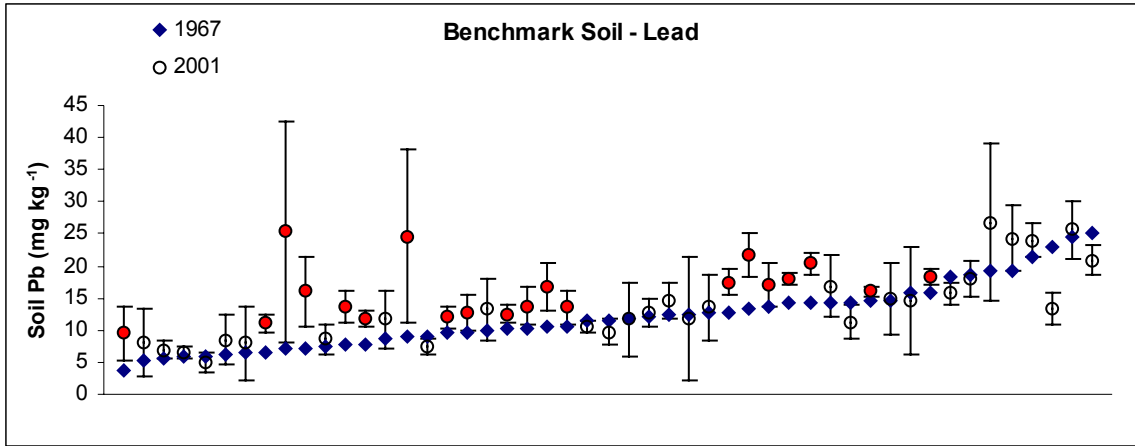


Figure 6. Lead Concentrations of Benchmark Soils, 1967 vs. 2001

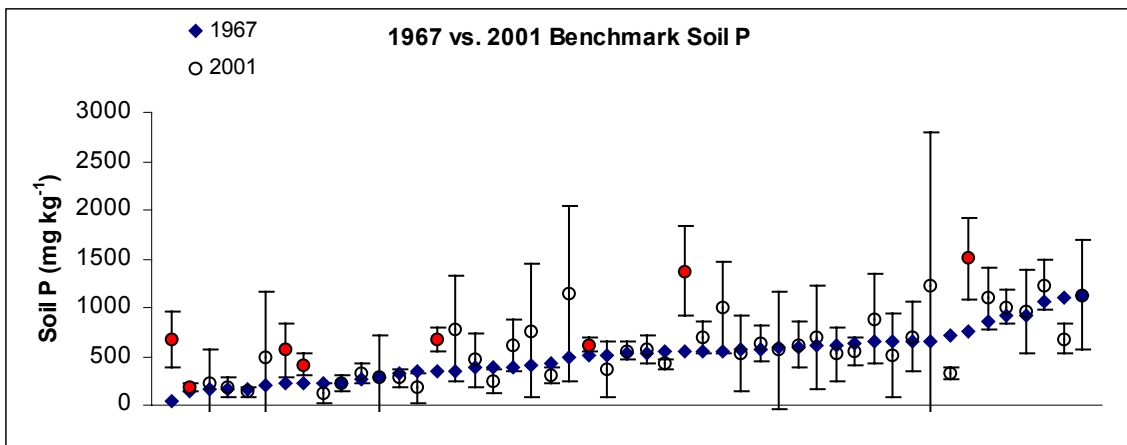


Figure 7. Phosphorus Concentrations of Benchmark Soils, 1967 vs. 2001

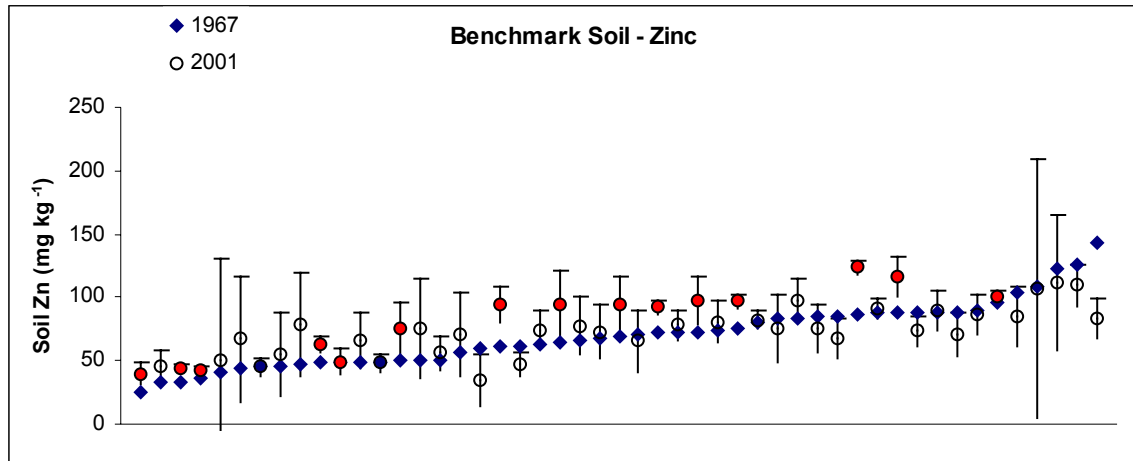


Figure 8. Zinc Concentrations of Benchmark Soils, 1967 vs. 2001

The soils at more benchmark sites were affected by cadmium, lead, and zinc. Except for lead, the magnitudes of increases were small. These three metallic elements have been common industrial metals for many years, and through long-term and widespread use have become the most common environmental pollutants. When leaded gasoline was prevalent, lead was emitted in automobile exhausts. Zinc is used in the vulcanization of rubber, while cadmium is a contaminant in zinc used in industrial manufacturing. Through these processes, cadmium, lead, and zinc may be released even at remote locations. In addition, these elements appear in consumer products.

When the benchmark soils were initially selected, the locations represented undisturbed soil profiles. During the course of time, land uses have changed at the locations and/or the nearby vicinities in many cases. These changes might have affected the trace element contents of soils at specific locations. According to the 2001 survey, the land uses at the benchmark soil areas can be divided into four general categories. The first land use category includes soils that remained in undisturbed and minimally disturbed conditions (Sites 3, 5, 6, 8, 21, 24, 25, 30, 31, 39, 40 and 44). These were forests, wild lands, and rangelands that have not been cultivated and are unlikely

to have undergone significant changes in the 34 years between samplings. The second category includes soils that are now under cultivation. These soils may be further divided into those used for low-intensity agriculture (i.e. non irrigation winter grains, grazing pastures, etc.), orchards (Sites 11, 38, 42 and 46), and those used for higher-intensity agriculture, such as vegetable production (Sites 9, 10, 12, 18, 19, 20, 32, 33, 47, 49 and 50). The third category includes soils now situated near roads (Sites 2, 4, 7, 13, 15, 16, 26, 28, 29 and 35) or in midst of developed urban areas (Sites 1, 14, 36, and 37). The three locations in category four were no longer accessible as they were completely taken over by other activities such as subdivisions (Sites 17, 22, and 45).

In analysis, all of the soils at the orchard sites exhibited increases in arsenic and lead content, reflecting the legacies of lead arsenic sprays used as insecticides. The increase in soil phosphorus content occurred primarily at sites that are in agricultural production. There did not appear to be a pattern in those sites exhibiting increases in cadmium, lead and zinc, and the rising concentrations in the soil did not appear to be related to the land uses.

In the sampling at the agricultural production fields, we purposely avoided orchards and roadside locations. In this manner, we hoped to minimize external influences on identifying the role of fertilizers on the trace element accumulations in cropland soils.

Cropland Soils

The amounts of arsenic, cadmium, and lead added to cropland soils with each fertilizer and/or micronutrient application is characteristically small. With repeated applications over time, however, these elements could build up in the soil. Experimentally, we could proceed by establishing the baseline levels in the soils prior to the applications, keeping track of the quantities of materials applied, and returning years later to assess the buildup by sampling the

soils and determining the resulting concentration increases. Comparing the final results with the baseline would then reveal the magnitude of any changes that had occurred. To authenticate the findings, the same experiment should be replicated and must be repeated in different geographic regions. In reality, this approach is not practical as it will take much time and a great deal of effort to obtain the desirable data. Instead, a different approach was employed in this study. The soil conditions, cultural practices, and supplies of fertilizers and micronutrients are relatively homogeneous in a production region. Under the circumstances, all of production fields would have started with the same baseline conditions. As the trace element buildup occurred after periods of land cultivation, the arsenic, cadmium, and lead concentrations of the cropland soils in the region would rise in proportion to the amounts of fertilizers or micronutrients applied. Records of fertilizer and micronutrients applications, or of the length of time the land has been under cultivation, usually do not exist. Other means must be used to indicate the magnitude of fertilizer and micronutrients inputs, and therefore of trace elements inputs.

When the phosphorus fertilizers and micronutrients were applied, the amounts applied invariably exceed the amounts taken up by plants. In addition, parts of plant biomass are reincorporated into the soil after the crop harvests, thus recycling part of the nutrients and contaminants. Therefore, phosphorus and micronutrient ingredients (zinc, iron and manganese) are expected to accumulate in the cropland soils receiving routine applications. The phosphorus contents of the cultivated soils would invariably increase with amounts of fertilizers used. Because iron and manganese are abundant in soil, the increase in their concentrations would be difficult to distinguish from the already high background levels. However, zinc contents of the soil would be sensitive to the inputs and may be used as an indicator of micronutrient inputs. The longer the land has been cultivated, the greater the accumulation. The total phosphorus and zinc

contents of the soils in a production region therefore are indicative of the amount of fertilizer and micronutrient additions to the soils. If arsenic, cadmium and lead were introduced into cropland soils by the fertilizer applications, their concentrations in the soil of a production region would increase in proportion to the corresponding soil phosphorus and zinc concentrations. To assess the effects of the fertilizer applications, the arsenic, cadmium and lead values of soils collected in one region were plotted versus the phosphorus and zinc concentrations. If a sufficient number of samples were collected and analyzed to cover the ranges, trends would emerge. Such trends are based on the attributes exhibited by the entire group and not affected by a small numbers of outliers, because the number of data points on each graph would be large. The baseline concentrations of arsenic, cadmium and lead for that region were also on the same graph as references. All of the graphs for an element were set to the same scale to illustrate differences between the various locations.

Four possible patterns may emerge from the comparisons (Table 11). In the first scenario, the trace element concentrations of the surface soils in a production region showed no elevation in comparison with the baseline concentrations. In this case, the trace element concentrations of the soils have not been affected by cultivation and they remained at the baseline range regardless of the phosphorus and zinc concentrations of the soils. In the second scenario, the trace elements in the surface soils in the region were elevated in comparison with the baseline concentrations, but they exhibited no increasing trend in relation to the phosphorus or zinc concentrations of the soils. If this is the case, the trace element concentrations of the soils have increased but the increase could not be attributed to the phosphorus fertilizer or micronutrients applications. Therefore, the trace element inputs that affected the contents in the soils were from diffuse sources such as pesticides, irrigation water, etc. In the third scenario, the trace elements in the

surface soils of the region were elevated in comparison with the baseline concentrations and they exhibited an increasing trend in relation to the phosphorus or zinc content in the soils. Under this scenario, the trace element concentrations increased in proportion with the phosphorus or zinc concentrations of the soils. This indicates that the phosphorus fertilizer or micronutrients inputs in the past have caused increases in the trace element concentrations of the soils.

Table 11. Trends of Arsenic, Cadmium and Lead Concentrations of Soils in a Region with Respect to the Corresponding Phosphorus and Zinc Concentrations

Scenario	Description of Trend	Interpretation
1	Soil trace element concentrations of the region remained within the baseline range regardless of the phosphorus or zinc concentration of the soils.	Soils in the region were not affected by the fertilizer or micronutrient applications.
2	Soil trace element concentrations of the region exceeded or were exceeding the baseline but their concentrations did not rise in proportion to the phosphorus or zinc concentrations of soils.	Trace element contents of the soils in the region were affected by diffuse sources other than phosphorus fertilizers and micronutrients.
3	Soil trace element concentrations of the region exceeded or were exceeding the baseline but their concentrations increased in proportion to the phosphorus or zinc concentrations of soils.	The phosphorus fertilizers or micronutrients applications had caused the trace element contents of soils in the region to increase.
4	Soil trace element concentrations of the region exceeded the baseline for the entire range as indicated by phosphorus or zinc concentrations of the soils and showed a rising trend.	The trace element contents of soil in the region were affected by the combination of diffuse sources and fertilizers.

In the fourth scenario, a combination of diffuse sources and fertilizer and micronutrient inputs affected the soil arsenic, cadmium and lead concentrations in the region. In this case, the trace element concentrations were above the baseline and take a general rising trend with respect to the increase of either phosphorus or zinc in soils. As the concentration of phosphorus or zinc increases, this relationship becomes more apparent.

In the following, we elaborate on the patterns that emerged from each case we examined.

Oxnard and Ventura Area A total of 65 samples were collected in vegetable production fields in the Ventura and Oxnard area. This production region was relatively small and was rapidly becoming urbanized. All of the soils sampled in this region were taken between the latitudes of 34°11'00" and 34°15'00" N and between the longitudes of 119°05'00" and 119:15:00" W. Almost all of the production fields were surrounded by urban developments of one kind or another. However, there had been a long history of vegetable production, thus fertilizer inputs were expected to be significant. The fields sampled were planted with beans (*Phaseolus vulgaris L.*), four were peppers (*Capsicum annuum L.*), and one each of lettuce (*Lactuca sativa L.*) and celery (*Apium graveolens L.*).

In the agricultural production regions, it is difficult if not impossible to locate sites that have not been affected by cultivation or other types of disturbance. As the elements of interest (arsenic, cadmium, lead, phosphorus and zinc) are relatively immobile in arid zone soils, professional opinions indicated and initial investigations confirmed that the soil at a depth of 1 m or more was not affected by inputs of these elements at the surface. For this reason, it was reasonable to assume that the soil at a depth greater than 1 m below the surface could be used to represent the baselines. Throughout this study, the concentrations in the soil at the 1.5 m sampling depth were used to represent the baseline levels of the elements of interests. The baseline concentrations of arsenic, cadmium, lead, phosphorus, and zinc of soils in the Ventura and Oxnard area are summarized in Table 12.

Table 12. Baseline Concentrations of Arsenic, Cadmium, Lead, Phosphorus and Zinc of Soils, Oxnard and Ventura Area

Element	Number of Observations	Minimum (mg kg⁻¹)	Maximum (mg kg⁻¹)	Mean (mg kg⁻¹)	CV (%)
Arsenic	7	5.3	9.8	7.4	21
Cadmium	7	0.27	0.77	0.45	38
Lead	7	10.6	14.2	12.7	9
Phosphorus	7	584	1335	838	40
Zinc	7	45.5	92.3	69.2	25

These levels were established by analyzing the soils collected at the 1.5 m soil depth at selected fields where the surface soil samples were collected. They defined the domains within which the trace elements and phosphorus contents of the soils would be considered at the background level.

Table 13 summarizes the arsenic, cadmium, lead, phosphorus, and zinc concentrations of the cropland soils in the Ventura/Oxnard area. The difference in trace element concentrations between the baseline levels and those in the production soils was tested using a Tukey test.

Table 13. Concentrations of Arsenic, Cadmium, Lead, Phosphorus and Zinc of Cropland Soils, Oxnard and Ventura Area

Element	Number of Observations	Minimum (mg kg⁻¹)	Maximum (mg kg⁻¹)	Mean (mg kg⁻¹)	CV (%)
Arsenic	65	4.7	11.0	7.7	18
Cadmium	65	0.45	2.38	1.05	59
Lead	65	14.5	38.9	20.0	24
Phosphorus	65	805	2536	1377	32
Zinc	65	57.8	149.1	89.6	21

The results showed that the arsenic and zinc concentrations of the cropland soils in the Ventura/Oxnard area were not significantly different from their respective baseline concentrations. This indicated that the soils had not received significant amounts of

micronutrients inputs and the arsenic contents of the cropland soils have not been affected by cultivations. The cadmium and phosphorus concentrations of the cropland soils were significantly higher than their respective baseline concentrations at $p \leq 0.05$, indicating that both cadmium and phosphorus concentrations of the production soils have been affected by external inputs. The lead concentrations of the cropland soils in this area were significantly higher than the baseline concentrations, at $p \leq 0.01$, indicating that lead contents in the soils have been affected by external inputs.

The causes of the cadmium and lead accumulations were deduced from the patterns which emerged from the soil trace elements vs. soil phosphorus or zinc plots. The arsenic, cadmium, and lead concentrations of the cropland soils in the Oxnard and Ventura Area were plotted against the corresponding soil phosphorus and zinc concentrations (Figures 9 – 14). On the graphs, the baseline of the trace element was also expressed in terms of the mean, marked as a solid line. The ranges of the baseline values are marked by dashed lines, indicating the minimum and maximum. The trends were interpreted according to the criteria outlined in Table 11.

1. Arsenic. The arsenic concentrations of soils in the vegetable production fields sampled in the Oxnard and Ventura Area were not elevated when compared to the established baseline levels (Table 11 and Figures 9 and 10). The arsenic concentrations of 65 cropland soil samples remained in the range defined by the minimum and maximum values of the baseline. The trends exhibited by soil arsenic concentrations and the corresponding phosphorus and zinc concentrations of the soils followed Scenario 1 described in Table 11. It appeared that the arsenic concentrations of the cropland soils in

the Oxnard and Ventura area have not been affected by crop production practices or other external inputs.

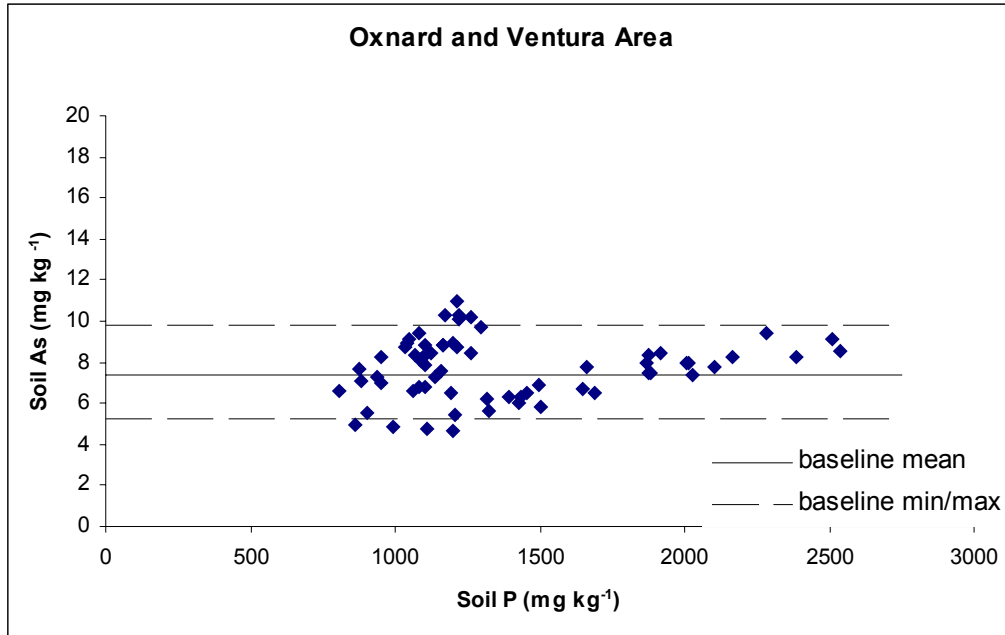


Figure 9. Arsenic vs. Phosphorus Contents of Cropland Soils, Oxnard and Ventura Area

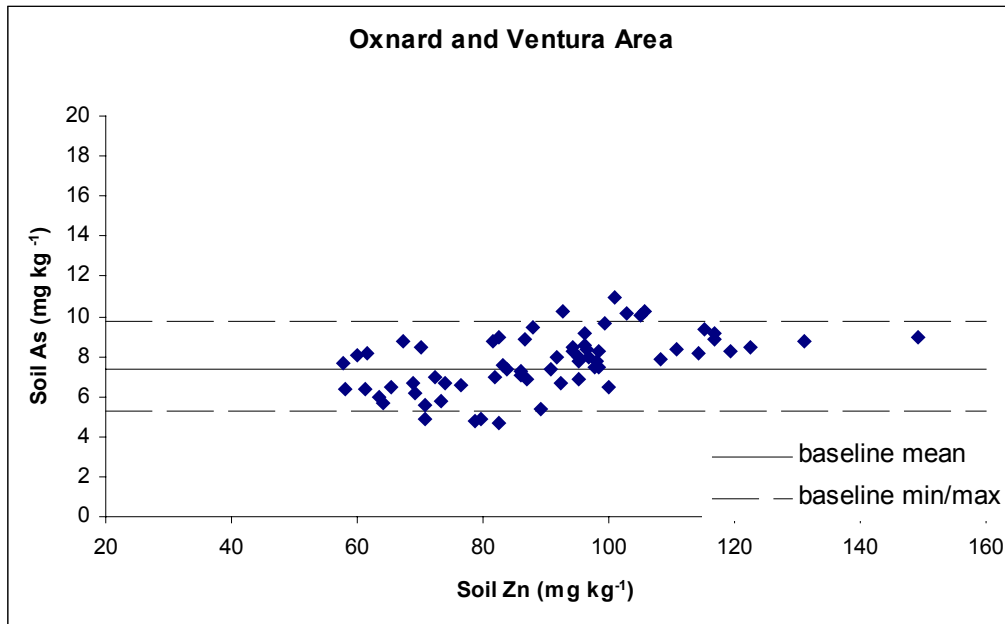


Figure 10. Arsenic vs. Zinc Contents of Cropland Soils, Oxnard and Ventura Area

2. Cadmium. Figures 11 and 12 illustrate the relationships of cadmium concentrations with respect to the phosphorus and zinc concentrations for cropland soils in the Oxnard and Ventura area, respectively. In that area, the phosphorus concentrations of the cropland soils reached as high as 2,500 mg kg⁻¹, far exceeding the baseline level. This indicates that some parts of the land have either been cultivated for a long time or received large inputs of phosphorus fertilizers.

The trend emerging from the plot of the soil cadmium vs. soil phosphorus (Figure 11) exhibited the pattern of Scenario 3 outlined in Table 11. The cadmium concentrations of the cropland soils increased with the corresponding phosphorus concentrations. Therefore, it was concluded that in the Ventura/Oxnard area, the cadmium contents of the cropland soils have increased due to the phosphorus fertilizer applications. However, it was not certain how much phosphorus fertilizer had been applied to result in this level of accumulation, nor do we know the cadmium concentrations of the fertilizers used in the past. The data indicated that when the concentrations of phosphorus were between 750 – 1,250 mg P kg⁻¹, the corresponding cadmium concentrations of the soils were well within the range of the baseline. However, once the soil phosphorus exceeded 1,250 mg P kg⁻¹, the cadmium concentrations were consistently above the baseline values and increased in proportion to the phosphorus concentrations of the soils. The data in Figure 11 indicate that the soil cadmium concentrations are increasing as the soil phosphorus concentrations increase, and they follow the linear regression that:

$$Y = 0.0013 * X - 0.8208, R^2 = 0.89$$

where Y represents the cadmium concentration of the soil (in mg kg⁻¹) and X represents the phosphorus concentration of the soil (mg kg⁻¹).

When the cadmium concentrations were plotted against the corresponding zinc concentrations for soils in the Oxnard and Ventura area, the results showed that cadmium contents of the soils in this region had exceeded the baseline range. The remaining data points in this population fell between the baseline mean and maximum. Under normal circumstances, the data points in a population should be centered around the mean and evenly distributed between the minimum and the maximum. The uneven distribution of the cadmium concentrations above the mean indicate that the mean of the population is moving upward (Figure 12). However, the increases were not related to the zinc contents of the soils. Essentially, the trend fit the pattern of Scenario 2 as described in Table 11. Inputs from phosphorus fertilizers caused the highest cadmium concentrations in the population of the outliers, as illustrated in Figure 11.

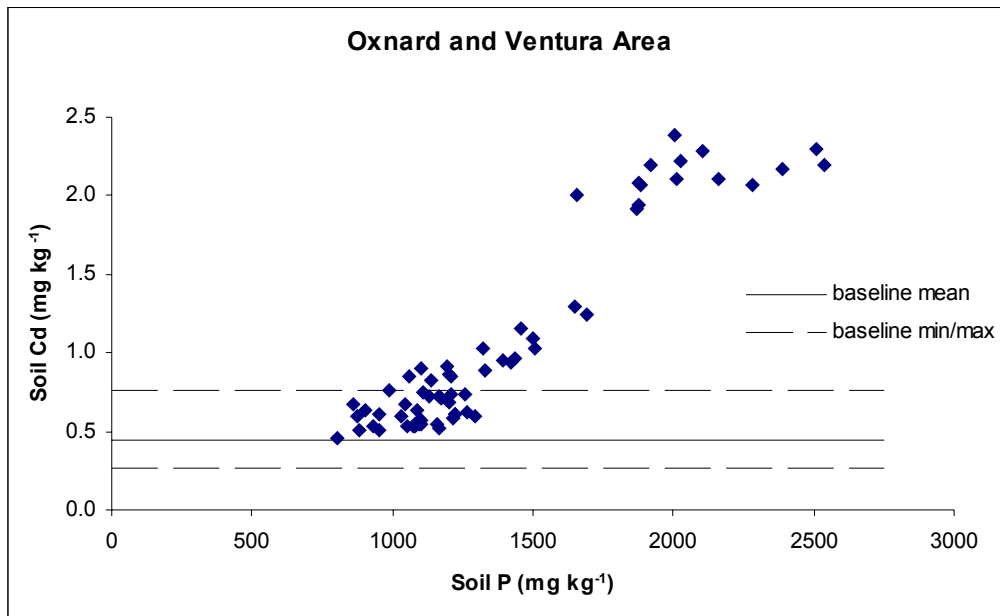


Figure 11. Cadmium vs. Phosphorus Contents of Cropland Soils, Oxnard and Ventura Area

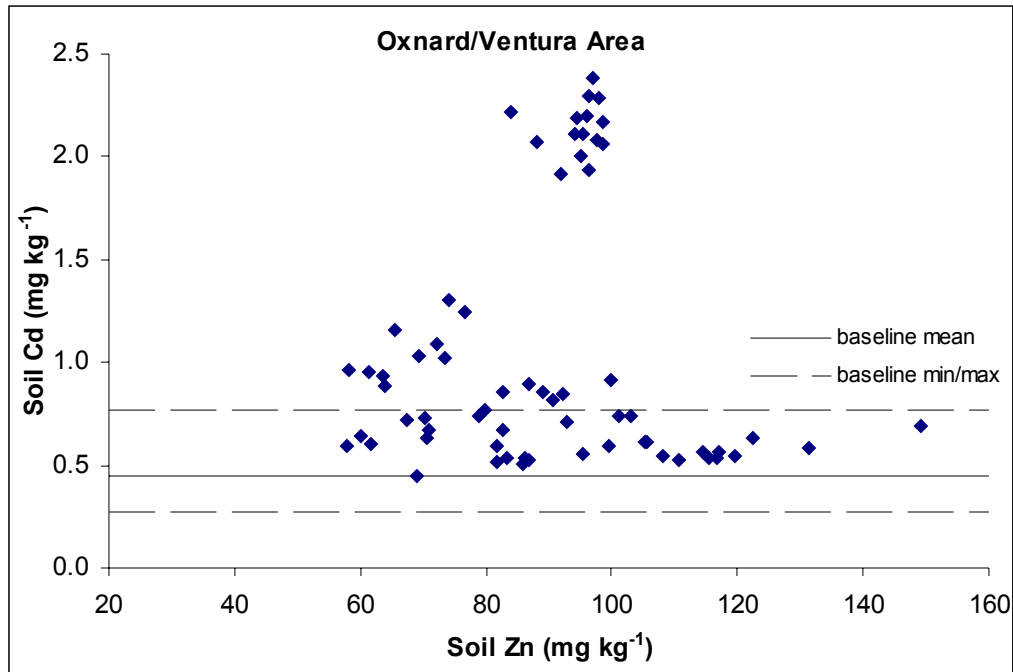


Figure 12. Cadmium vs. Zinc Contents of Cropland Soils, Oxnard and Ventura Area

3. **Lead** Figures 13 and 14 illustrate the lead concentrations of soils in the Ventura/Oxnard area with respect to the corresponding phosphorus and zinc concentrations. It was obvious that the lead concentration of every cropland soil analyzed exceeded the baseline range. The concentration range for lead in these soils was between 35 and 40 mg Pb kg⁻¹ soil, in contrast with the 11 – 14 mg Pb kg⁻¹ for the baseline range. However, there is no apparent trend showing that lead concentrations increase with the soil phosphorus or zinc concentrations. Considering that the crop production fields in the Oxnard and Ventura area were frequently sandwiched between urban developments, it is not uncommon for lead concentrations in the urban soils to become elevated due to emissions from the automobile exhaust emissions or other sources. As leaded gasoline has not been used for more than 30 years, the lead undoubtedly has accumulated in these soils for a long time.

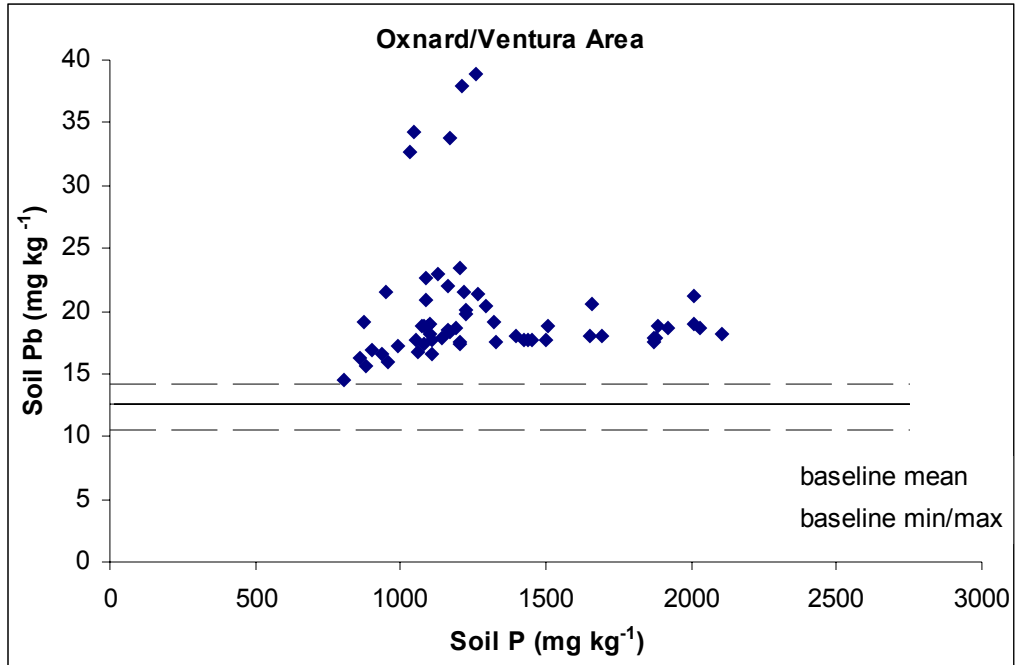


Figure 13. Lead vs. Phosphorus Contents of Cropland Soils, Oxnard and Ventura Area

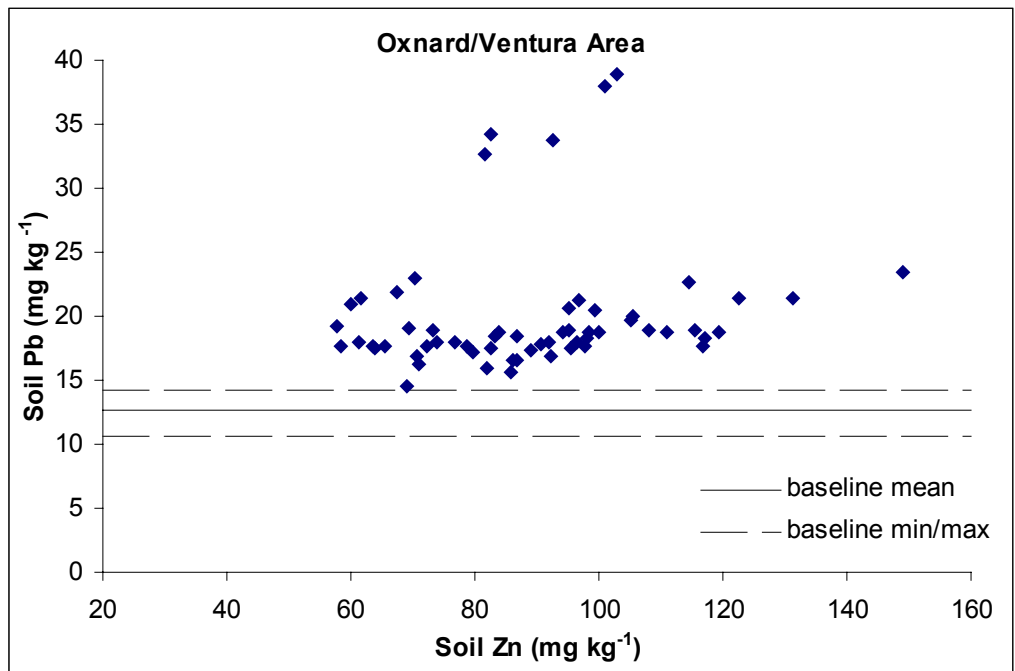


Figure 14. Lead vs. Zinc Contents of Cropland Soils, Oxnard and Ventura Area

Santa Maria and San Luis Obispo Valley In the Santa Maria and San Luis Obispo Valley, 34 production fields were sampled, totaling 170 soil samples. At the time of sampling, they were planted with broccoli (*Brassica oleracea L.*), lettuce (*Lactuca sativa L.*), cauliflower (*Brassica oleracea L.*), spinach (*Spinacia oleracea L.*), cabbage (*Brassica oleracea L.*), Napa cabbage, corn (*Zea mays L.*) and celery (*Apium graveolens L.*). The soils sampled in this region were taken between the latitudes of 34°54'00" and 35°02'00" N and the longitudes of 120°20'00" and 120°35'30" W. The baseline concentrations of the elements of interest were obtained from soils at the 1.5 m depth, collected in this valley in the 1970s (Table 14). The baseline phosphorus concentrations of the soils in the Santa Maria and San Luis Obispo Valley showed the lowest minimum concentrations and the narrowest range in all of the regions sampled. This clearly showed the homogeneous nature of the soils in this region. Yet the phosphorus concentrations of the cropland soil samples from this region spanned a wide range. The phosphorus concentrations cover a range of nearly 1,000 mg P kg⁻¹ soil (Table 15). This broad range of concentrations indicates a wide spectrum of fertilizer applications.

Table 14. Baseline Concentrations of Arsenic, Cadmium, Lead, Phosphorus and Zinc of Soils, Santa Maria and San Luis Obispo Valley

Element	Number of Observations	Minimum (mg kg ⁻¹)	Maximum (mg kg ⁻¹)	Mean (mg kg ⁻¹)	CV (%)
Arsenic	60	1.3	6.7	4.0	38
Cadmium	60	0.21	0.84	0.45	34
Lead	60	5.8	18.8	13.9	14
Phosphorus	60	122	717	376.9	38
Zinc	60	4.4	103.3	40.3	50

Table 15. Concentrations of Arsenic, Cadmium, Lead, Phosphorus and Zinc of Cropland Soils, Santa Maria and San Luis Obispo Valley

Element	Number of Observations	Minimum (mg kg ⁻¹)	Maximum (mg kg ⁻¹)	Mean (mg kg ⁻¹)	CV (%)
Arsenic	169	3.3	13.1	6.6	24
Cadmium	169	0.31	1.67	0.73	33
Lead	169	11.4	22.0	16.5	15
Phosphorus	169	206	1206	710	35
Zinc	169	21.4	83.8	52.3	28

When the differences of the population means of the cropland soils and the baselines were tested using the Tukey test, the results showed that, for all of the elements of interest, the concentrations in the cropland soils were significantly higher than the baseline at $p \leq 0.01$. It was obvious that that the trace element concentrations of cropland soils in the Santa Maria and San Luis Obispo Valley had been affected by external factors.

- 1. Arsenic.** The arsenic concentrations in majority of the cropland soils in the Santa Maria and San Luis Obispo Valley either exceeded the baseline range or fell above the baseline mean (Figure 15). In fact, only five of the samples were below the mean baseline concentration. It was indicative that the arsenic concentrations of the soils in this region have been rising across the board. However, when the soil's arsenic concentration is plotted versus its phosphorus concentration, there is no apparent trend suggesting that the arsenic concentrations were rising in step with the increasing phosphorus concentrations in the soils (Figure 15). The data fit Scenario 2 described in Table 11, in which the arsenic concentrations in this region have increased, but the increase is not related to phosphorus fertilizer applications. When the arsenic is plotted versus the soil zinc concentration (Figure 16), a similar conclusion can be reached.

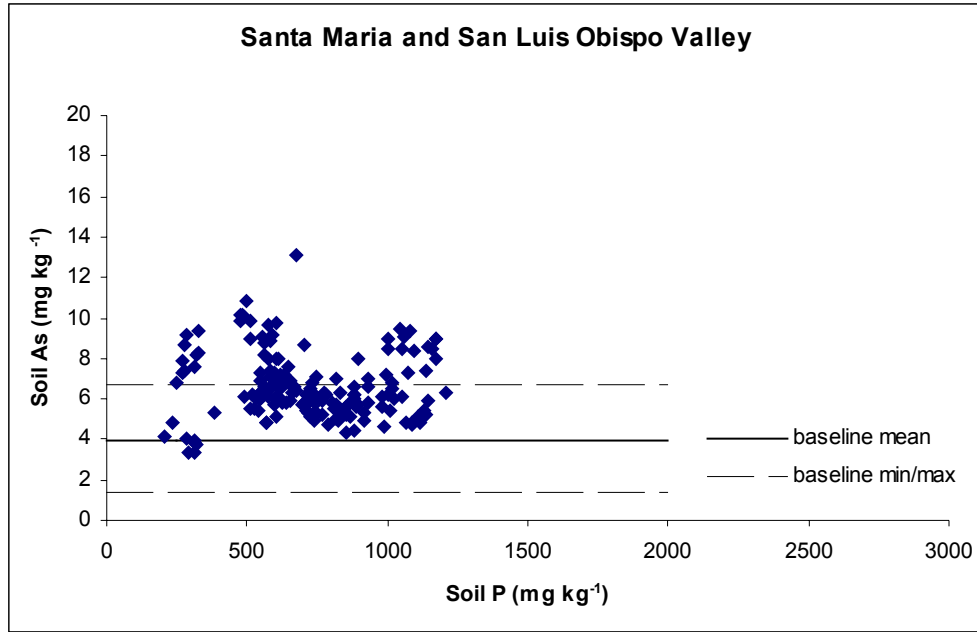


Figure 15. Arsenic vs. Phosphorus Contents of Cropland Soils, Santa Maria and San Luis Obispo Valley

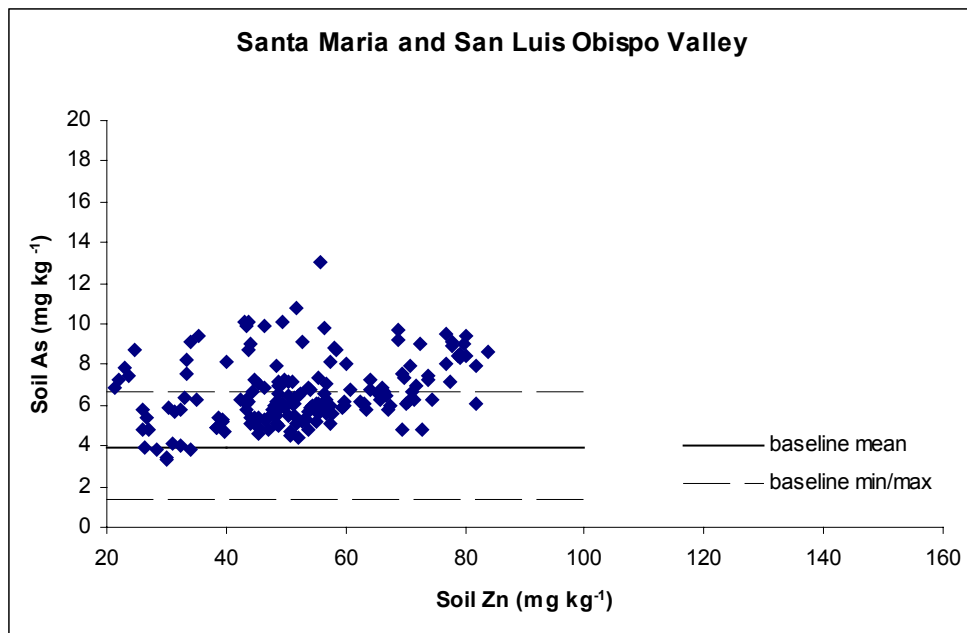


Figure 16. Arsenic vs. Zinc Contents of Cropland Soils, Santa Maria and San Luis Obispo Valley

Therefore, although arsenic concentrations of the cropland soils in the Santa Maria and San Luis Obispo Valley have exceeded the baseline levels in this region, the increase could not be related to applications of phosphorus fertilizer or zinc amendments.

2. Cadmium The cadmium concentrations of cropland soil samples from the Santa Maria and San Luis Obispo Valley varied from 0.31 to 1.67 mg Cd kg⁻¹ soil. However, less than half of the samples exceeded the baseline concentration range for this region. Among those that were within the range of the baseline, a relatively small proportion of those were still below than the baseline mean (Figure 17). This appeared to indicate that a considerable portion of the soils have been affected by the anthropogenic inputs of cadmium, and that cadmium concentrations had risen although not all exceeded the baseline. When the cadmium concentrations of the soils were plotted against corresponding phosphorus concentrations, the trend that emerged from the plot in Figure 17 fit Scenario 2 outlined in Table 11.

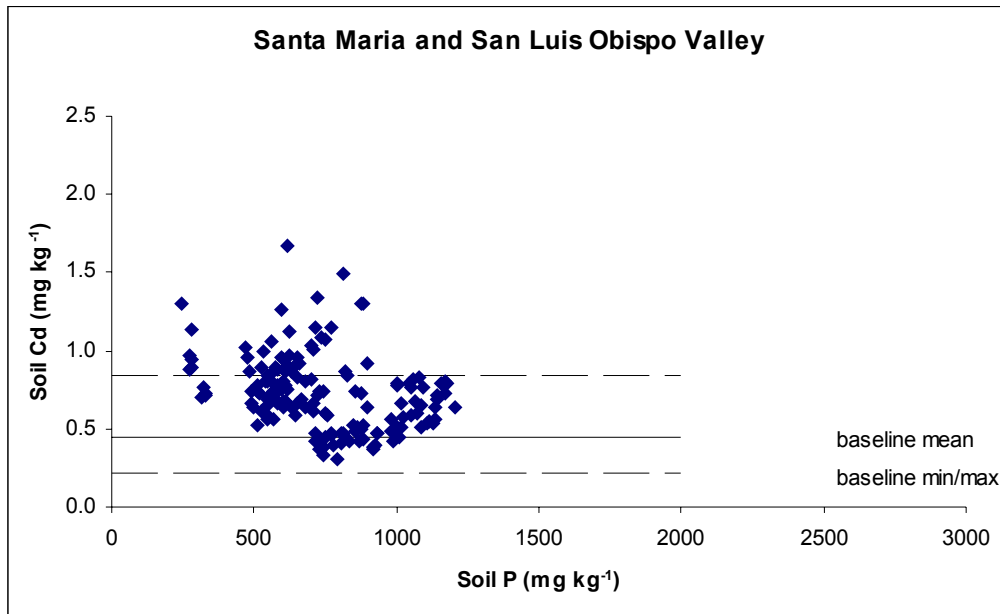


Figure 17. Cadmium vs. Phosphorus Contents of Cropland Soils, Santa Maria and San Luis Obispo Valley

There is no indication that the cadmium concentration of the soils increased along with the phosphorus concentrations. In fact, for those soils whose cadmium concentrations exceeded the baseline, their phosphorus concentrations were relatively moderate.

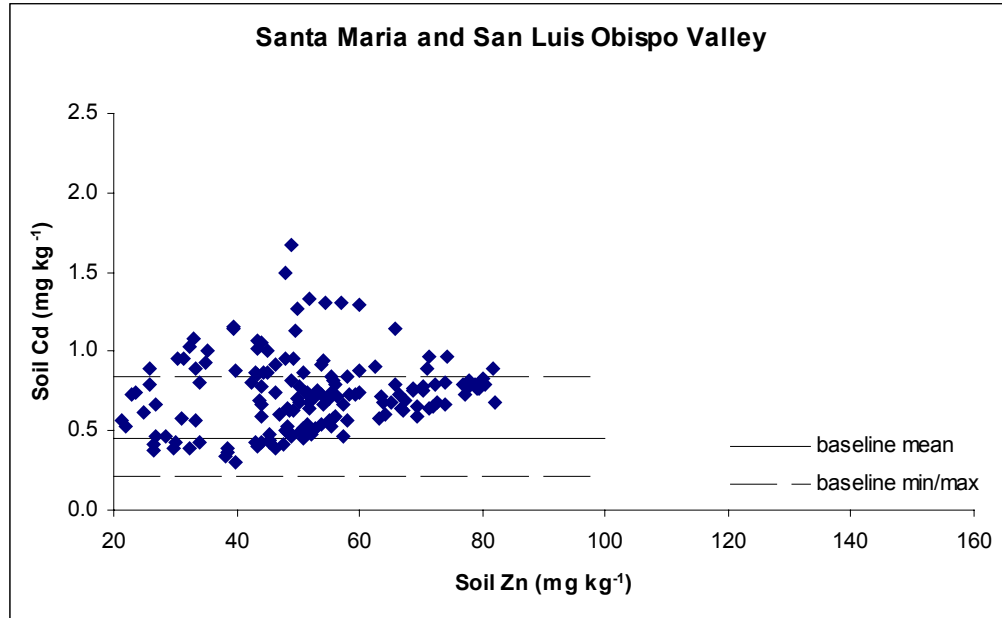


Figure 18. Cadmium vs. Zinc Contents of Cropland Soils, Santa Maria and San Luis Obispo Valley

When the cadmium concentrations are plotted versus the zinc content in the soil, the same conclusions can be drawn (Figure 18). Cadmium concentrations of the cropland soils in Santa Maria and San Luis Obispo Valley have increased. However, the increase cannot be attributed to the applications of phosphorus fertilizers or micronutrients.

- 3. Lead.** The lead concentrations of cropland soils in the Santa Maria and San Luis Obispo Valley fell within a rather narrow range of 11.4 to 22.0 mg Pb kg⁻¹ soil (Figure 19 and 20). Though only a small number of samples in this population exceed the baseline maximum concentration for lead, the lead concentrations have risen, since nearly all of them were equal to or greater than the mean baseline level (Figures 19 and 20).

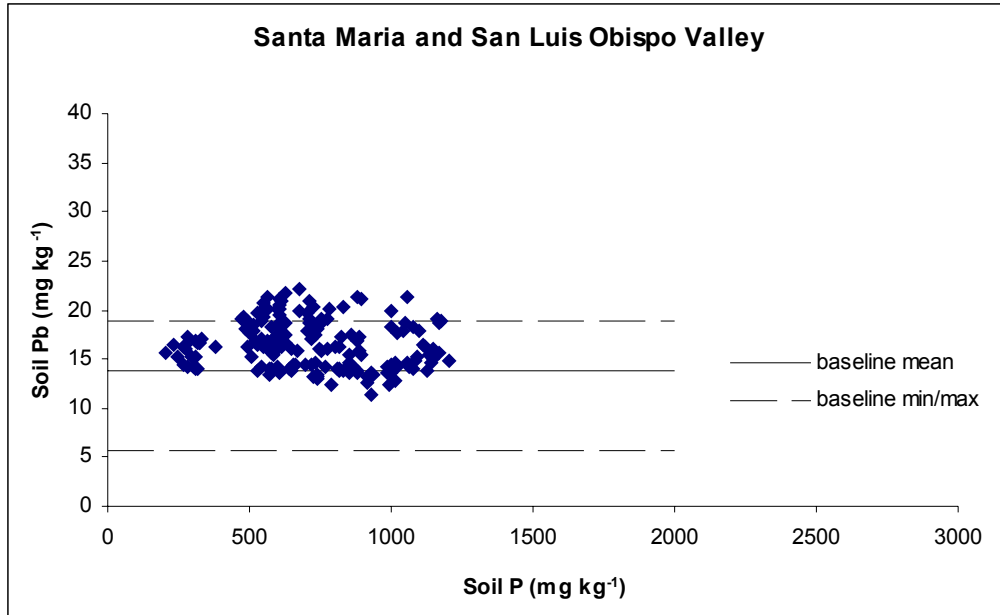


Figure 19. Lead vs. Phosphorus Contents of Cropland Soils, Santa Maria and San Luis Obispo Valley

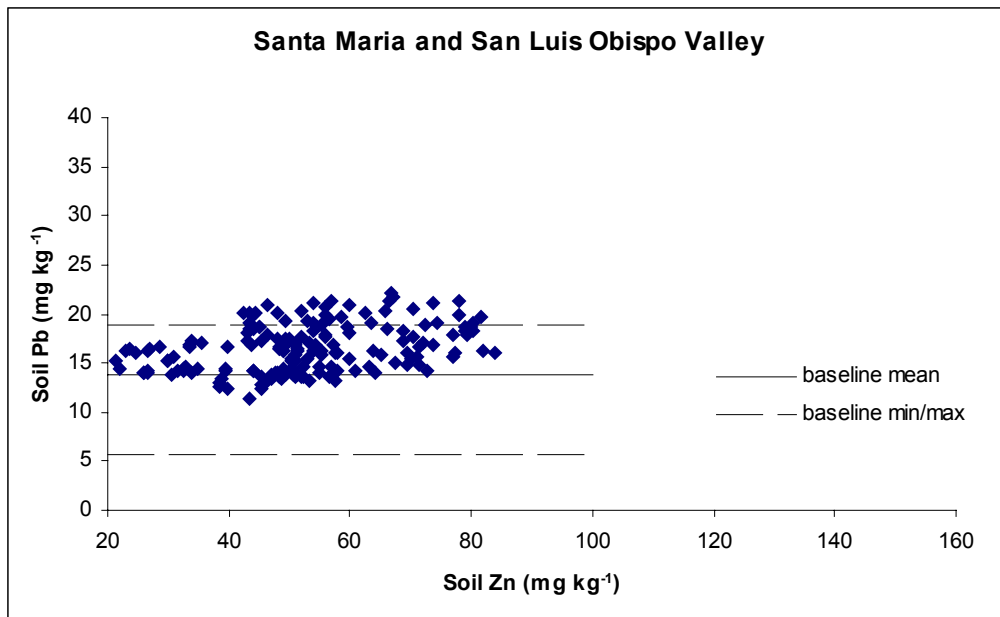


Figure 20. Lead vs. Zinc Contents of Cropland Soils, Santa Maria and San Luis Obispo Valley

When the lead concentrations were plotted versus the soil phosphorus or zinc concentrations, the data distribution reflected the pattern of Scenario 2 described in Table

11. Though the lead concentrations in the Santa Maria and San Luis Obispo Valley soils were elevated, this elevation was not related to applications of phosphorus fertilizer or micronutrient amendments.

Colusa/Glen County In Colusa/Glen County, 17 fields were sampled, totaling 85 samples. All of the soils sampled in this region were taken between the latitudes of 39°00'29.8" and 39°19'55.4" N and the longitudes 121°53'21.8" and 122°15'42.4" W. No sample was collected to establish the baseline levels, and the concentrations of the 1967 benchmark soils (Table 9) were used as the reference points. The mean concentrations of arsenic, cadmium and lead in the cropland soils in the Colusa/Glen County area were 11.1, 0.23 and 8.5 mg kg⁻¹ soil, respectively. They were comparable to the respective means of the 1967 benchmark soils (Table 9). The concentration ranges for arsenic, cadmium, and lead varied from 6.1 to 18.4, 0.15 to 0.35, and 6.0 to 17.0 mg kg⁻¹, respectively. The means and the ranges were well within those defined by the 1967 benchmark soils.

In this region, we expect the concentration ranges of the baselines to be rather narrow as the soils are homogeneous. Assuming that the minimum concentrations were still within the baseline, the concentration ranges of the soils could be indicators of whether the maximum concentrations could have exceeded the baseline. In this regard, the range for soil arsenic concentrations, 12.3 mg kg⁻¹, was comparable to the regions where the arsenic concentrations of soils had risen to exceed the baseline levels, namely the Santa Maria and San Luis Obispo Valley. For cadmium and lead, the concentration ranges of the soils were 0.20 and 11.0 mg kg⁻¹, respectively, and are comparable to the regions where cadmium and lead concentrations had not exceeded the baseline levels. The phosphorus concentrations of soils in this region were lower compared with other regions, and they covered a narrower range, indicating that the phosphorus

inputs in these soils have been moderate (Table 20). The zinc mean concentrations of the soils and the concentration ranges were similar to those observed in other regions. For soils from the same region, a zinc concentration range from 56.1 – 111.7 mg kg⁻¹, clearly indicates that zinc has been added to the soil from external sources.

Table 16. Concentrations of Arsenic, Cadmium, Lead, Phosphorus and Zinc of Cropland Soils, Colusa/Glen County

Element	Number of Observations	Minimum (mg kg⁻¹)	Maximum (mg kg⁻¹)	Mean (mg kg⁻¹)	CV (%)
Arsenic	85	6.1	18.4	11.1	27
Cadmium	85	0.15	0.35	0.23	17
Lead	85	6.0	17.0	8.5	20
Phosphorus	85	214	849	469	30
Zinc	85	56.1	111.7	82.9	14

1. **Arsenic.** The soil samples collected in the Colusa/Glen County area recorded the highest arsenic concentrations, and the data also covered the broadest range of any of the regions sampled (Figures 21 and 22). Even though the baseline level could not be clearly defined, it is reasonable to deduce that the arsenic concentrations in cropland soils in Colusa/Glen County had shifted upward. When they are plotted against the soil phosphorus concentrations, the distribution of arsenic concentrations followed the pattern of Scenario 2 outlined in Table 11 (Figure 21) – namely, that the arsenic concentrations of the cropland soils in Colusa/Glen County had increased due to factors other than the phosphorus fertilizer applications.

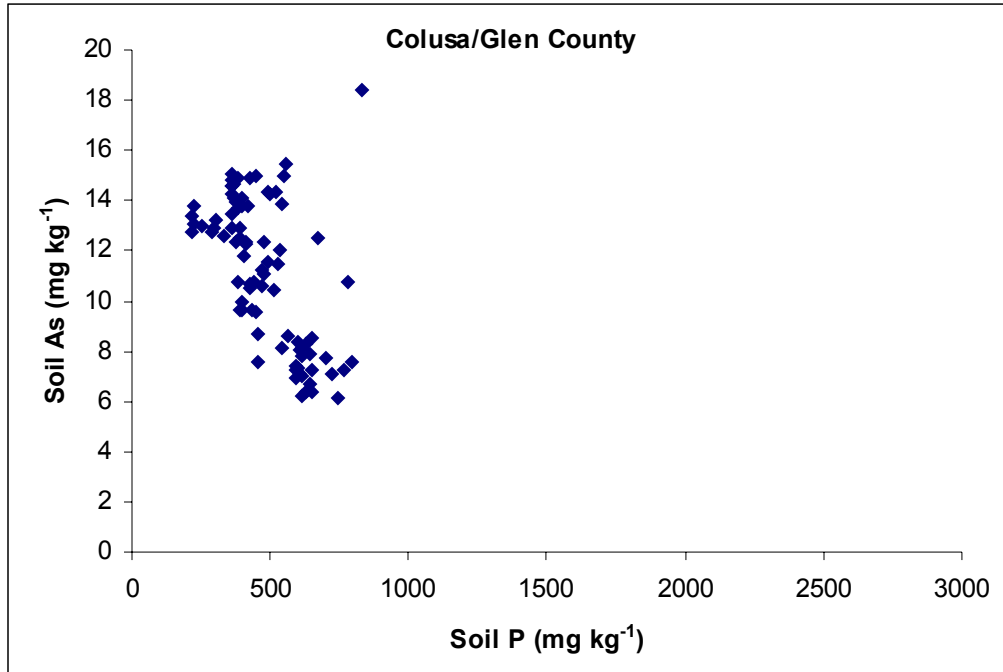


Figure 21. Arsenic vs. Phosphorus Contents of Cropland Soils, Colusa/Glen County

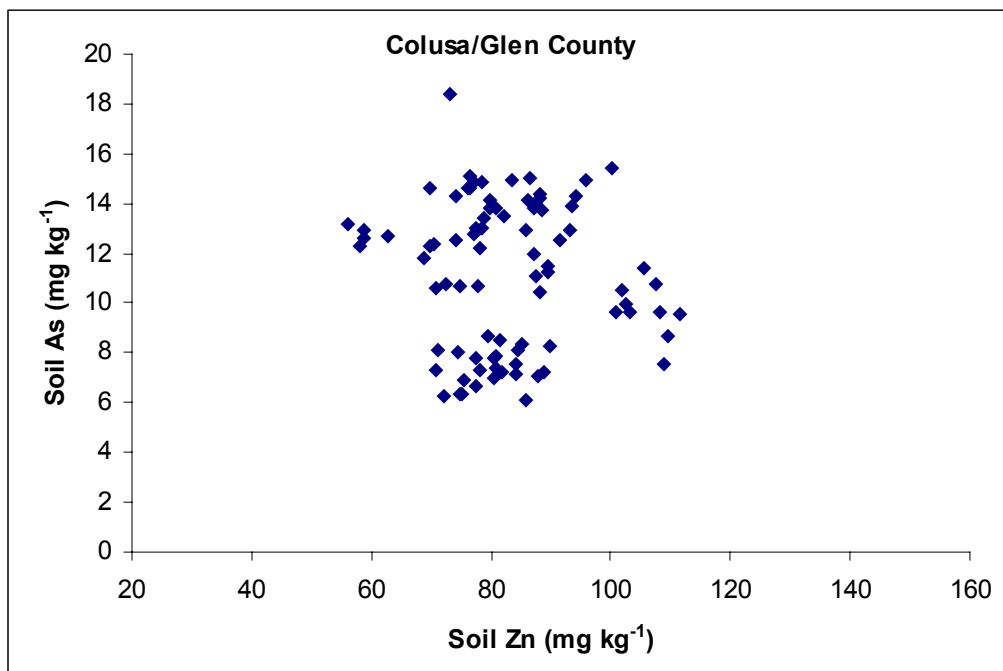


Figure 22. Arsenic vs. Zinc Contents of Cropland Soils, Colusa/Glen County

When the arsenic concentrations of the soils were plotted against the corresponding zinc concentrations, the trend again followed the pattern of Scenario 2 outlined in Table 11 (Figure 22). The concentration range for zinc spanned a wide horizon, from 56.1 to 111.7 mg kg⁻¹ obviously indicating the presence of external inputs. Even under these circumstances, there is no indication that the apparently elevated arsenic concentrations of the cropland soils were influenced by the zinc concentrations in the soil. The accumulation of arsenic in cropland soils in the Colusa/Glen County area could not be attributed to the application of phosphorus fertilizer and micronutrient supplements.

2. **Cadmium.** The range of cadmium concentrations of soils in the Colusa/Glen County is narrow and the mean cadmium concentration is also low compared to findings of the other regions (Figures 23 and 24). In fact, the soils in this region recorded the lowest

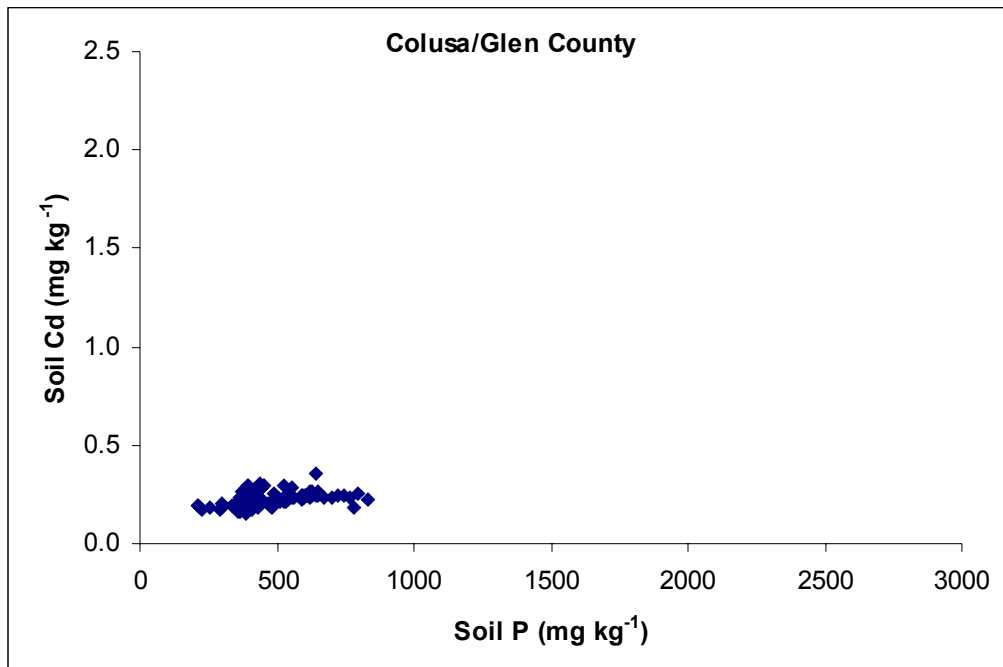


Figure 23. Cadmium vs. Phosphorus Contents of Cropland Soils, Colusa/Glen County

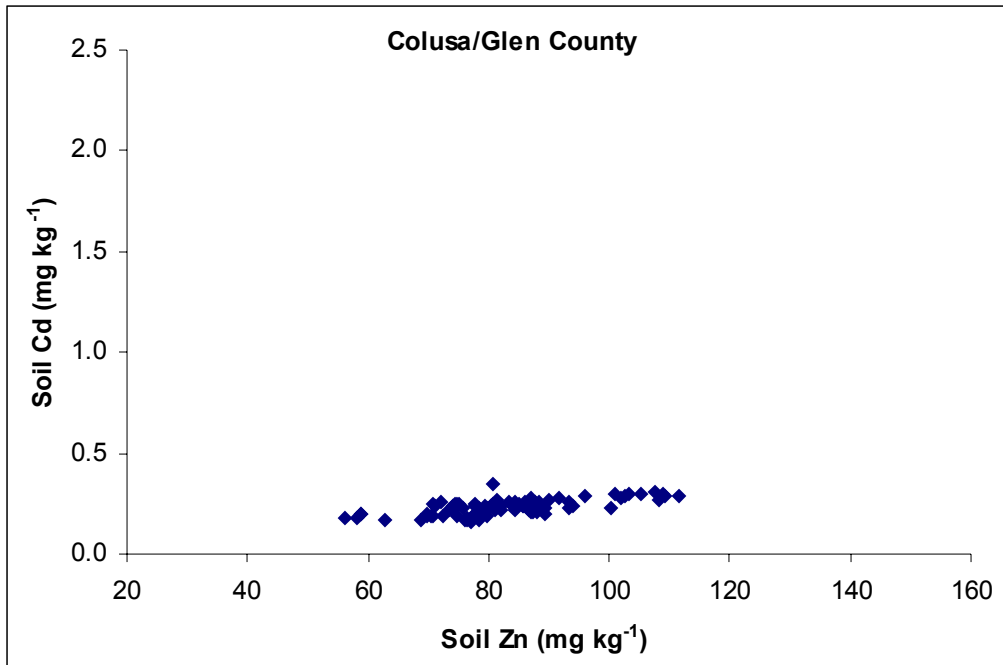


Figure 24. Cadmium vs. Zinc Contents of Cropland Soils, Colusa/Glen County

mean cadmium concentration, 0.23 mg kg⁻¹, among all of the regions sampled. Even though there is no baseline data, it is reasonable to assume that the cadmium concentrations of soils in Colusa/Glen County have not exceeded the baseline levels. When the cadmium values were plotted versus the phosphorus or the zinc content in the soil, their distributions followed the pattern of Scenario 1 from Table 11 (Figures 23 and 24). This further confirmed that cadmium concentrations of cropland soils in the Colusa/Glen County area remained in the baseline range and had not been affected by phosphorus fertilizer and micronutrients applications.

3. **Lead.** Like cadmium, the range of lead concentrations of the cropland soils in Colusa/Glen County, from 6.0 to 17.0 mg kg⁻¹, was narrow compared to those of the cropland soils in the other surveyed regions. Had the outlier of 17.0 mg kg⁻¹ been removed, the lead concentrations of the soils would all be less than 12 mg kg⁻¹, in the lower 50th percentile of the 1967 benchmark soils. The mean lead concentration, 8.5 mg

kg⁻¹, was low in comparison to the findings of the other surveyed regions (Table 20). When the lead concentrations of the soils were plotted versus the corresponding phosphorus or the zinc concentrations, there was no indication that the soil lead concentrations changed with the increasing phosphorus or zinc contents in the soils (Figures 25 and 26).

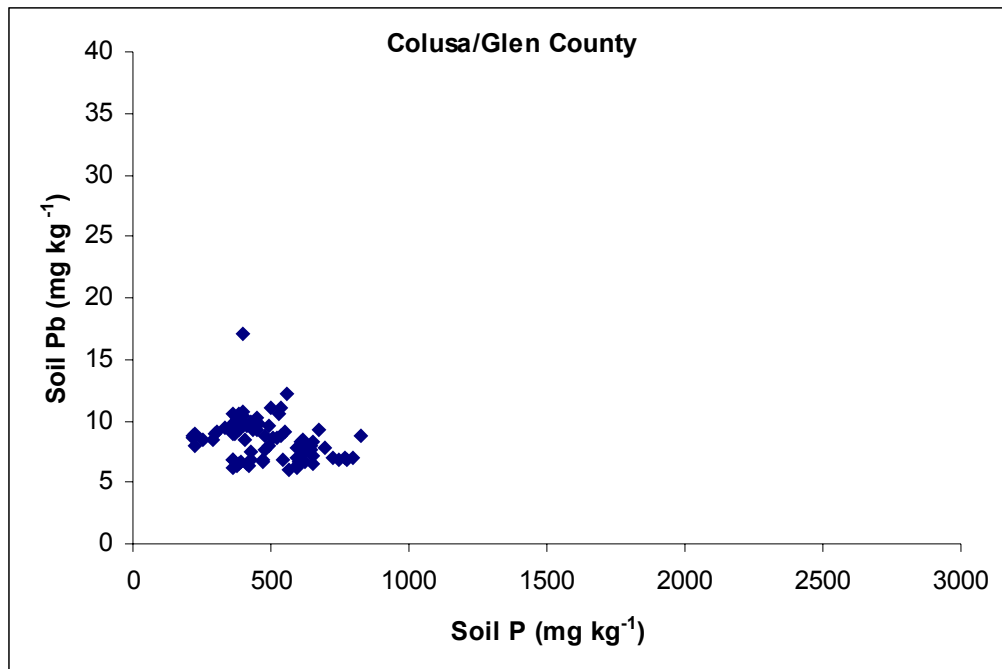


Figure 25. Lead vs. Phosphorus Contents of Cropland Soils, Colusa/Glen County

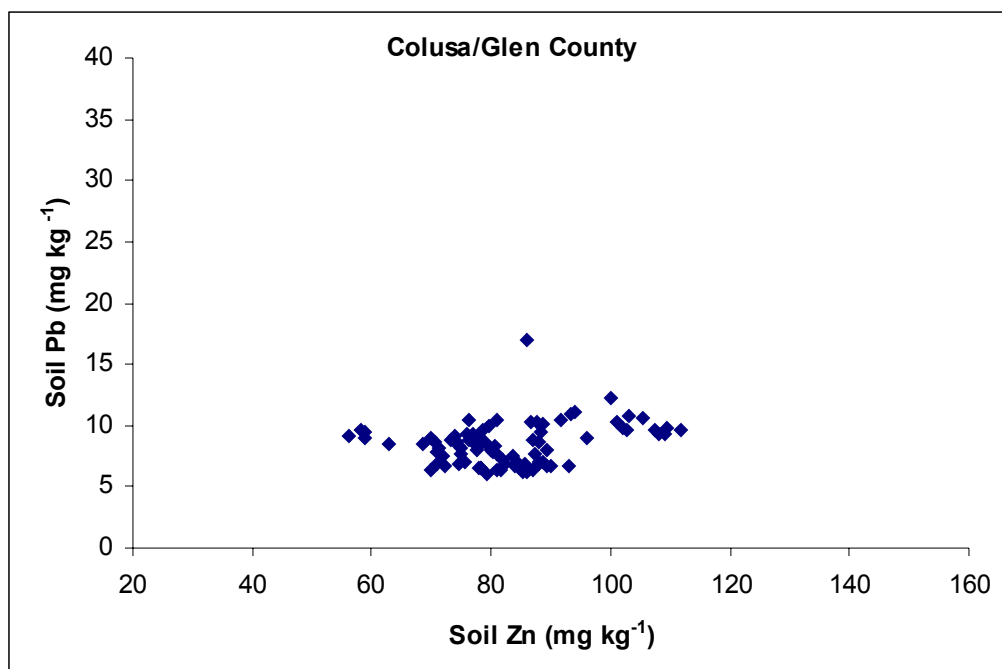


Figure 26. Lead vs. Zinc Contents of Cropland Soils, Colusa/Glen County

The trends emerging from Figures 25 and 26 fit the pattern of Scenario 1 as outlined in Table 11. Apparently, the lead concentrations of cropland soils in Colusa/Glen County remained at the baseline level and had not been affected by the application of phosphorus fertilizers and micronutrients.

Fresno Area In the Fresno area, 13 fields were sampled, totaling 65 samples. The sampling locations were located on the west side of the San Joaquin Valley and were not intensively cultivated until water from the State Water Project became available for irrigation in the early 1970s. Both the phosphorus and zinc concentration ranges of the soils (356 – 870 and 48.3 – 76.8 mg kg⁻¹, respectively) were narrow, compared to regions with a longer history of intensive cultivations (Table 17). The mean concentrations were also low compared to the other regions that were sampled. The means and ranges of arsenic, cadmium, and lead concentrations of the soils in the Fresno area were well within those defined by the 1967 benchmark soils. Like

the cropland soils in Colusa/Glen County, the arsenic concentrations of the soils showed signs of shifting upwards and possibly exceeding the baseline toward the upper end of the range. The cadmium and lead concentrations of the soils remained at the baseline levels.

Table 17. Concentrations of Arsenic, Cadmium, Lead, Phosphorus and Zinc of Cropland Soils, Fresno Area

Element	Number of Observations	Minimum (mg kg ⁻¹)	Maximum (mg kg ⁻¹)	Mean (mg kg ⁻¹)	CV (%)
Arsenic	65	8.2	13.6	11.0	11
Cadmium	65	0.20	0.43	0.28	19
Lead	65	7.8	15.0	10.1	13
Phosphorus	65	356	870	500	20
Zinc	65	48.3	76.8	62.4	11

1. **Arsenic.** The arsenic concentrations of the soils, ranging from 8.2 to 13.6 mg kg⁻¹, were all in the upper 50th percentile of the 1967 benchmark soils. Like the cropland soils in the Colusa/Glen County area, the arsenic concentrations of the soil in the Fresno area as a whole showed signs of shifting upward. Judging by the range, the extent of the accumulations was probably minimal, as the concentrations toward the upper end of the range were considerably lower than maximum of the 1967 benchmark soils. When the soil arsenic concentrations of the soils were plotted against the corresponding phosphorus or zinc concentrations (Figures 27 and 28), the arsenic concentrations of the soils were positively correlated to both phosphorus and zinc concentrations. This indicates that the application of both phosphorus fertilizers and micronutrients had influenced the arsenic concentrations of the cropland soils. .

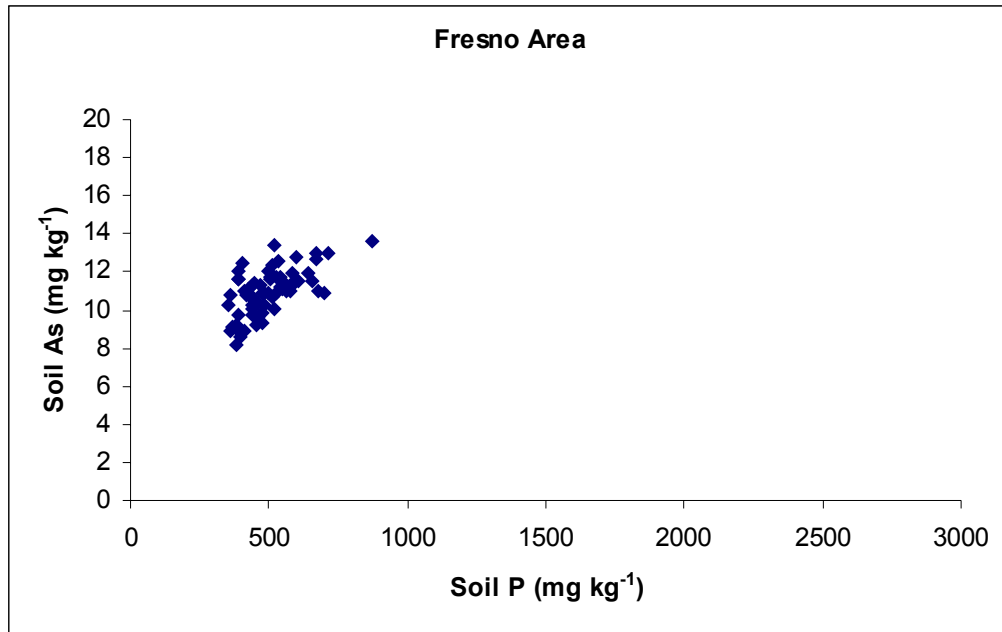


Figure 27. Arsenic vs. Phosphorus Contents of Cropland Soils, Fresno Area

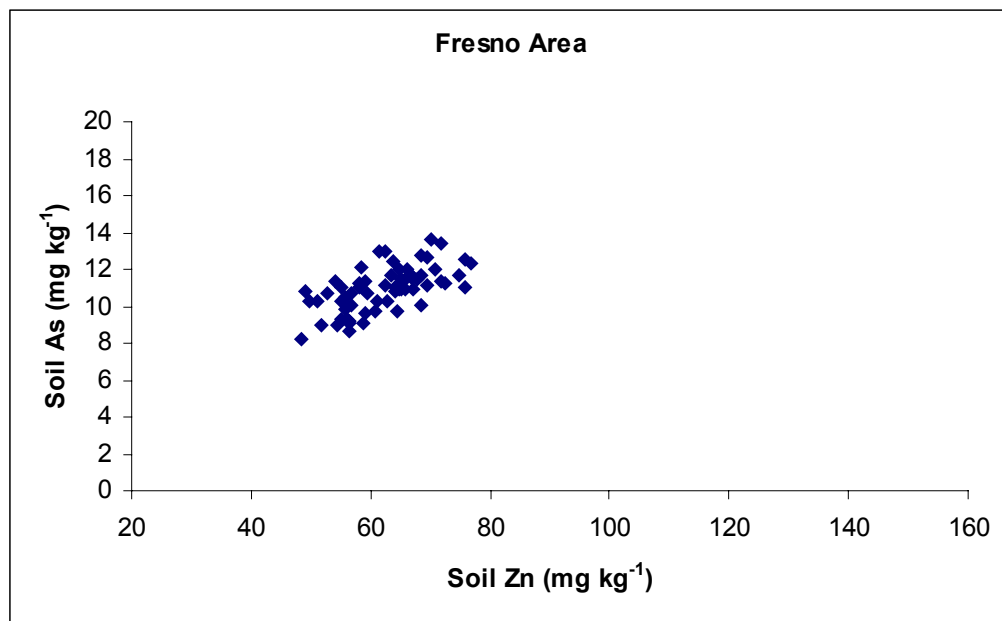


Figure 28. Arsenic vs. Zinc Contents of Cropland Soils, Fresno Area

2. **Cadmium.** The range of cadmium concentrations ($0.23 - 0.47 \text{ mg kg}^{-1}$) of the soil samples obtained in the Fresno area was narrow compared to that of the other regions sampled. The mean cadmium concentration of 0.28 mg kg^{-1} was comparable

to those of the regions where cadmium concentrations were at the baseline levels. Even though no data was available to establish the baseline levels for this region, it was reasonable to assume that the cadmium concentrations of these soils remained at the baseline level. When the cadmium concentrations were plotted against the phosphorus concentrations in the soils (Figures 29), the data showed the pattern of Scenario 3 as outlined in Table 11 with the cadmium concentrations positively correlated to the corresponding phosphorus. Although the cadmium concentrations had not exceeded the baseline, they nevertheless exhibited signs that applications of phosphorus fertilizer had started to affected cadmium concentrations.

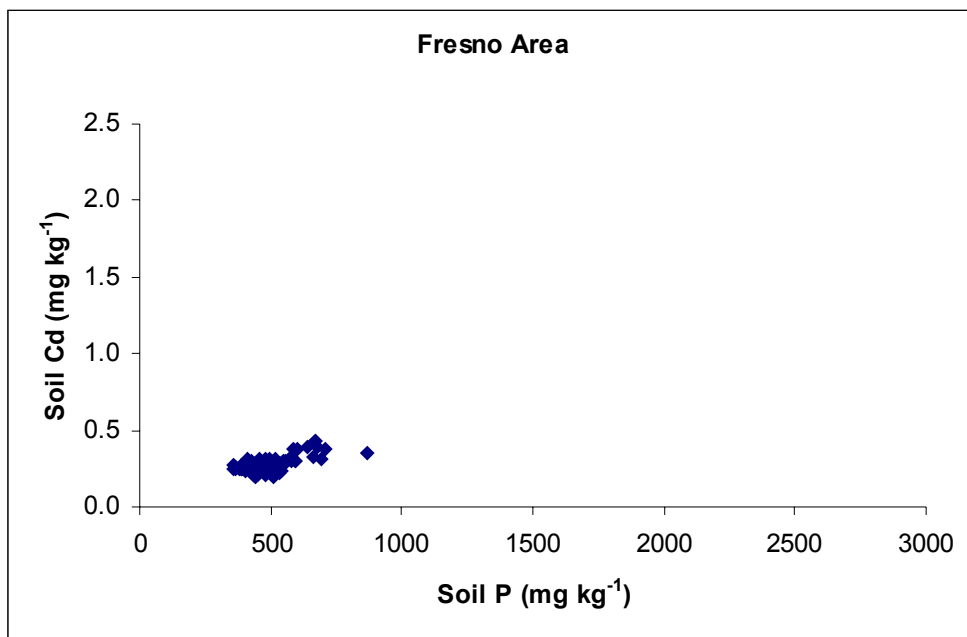


Figure 29. Cadmium vs. Phosphorus Contents of Cropland Soils, Fresno Area

When the cadmium concentrations of the soils were plotted against the corresponding zinc concentrations (Figure 30), it was obvious that the zinc concentration had no effect on the cadmium contents of the cropland soils in the Fresno area.

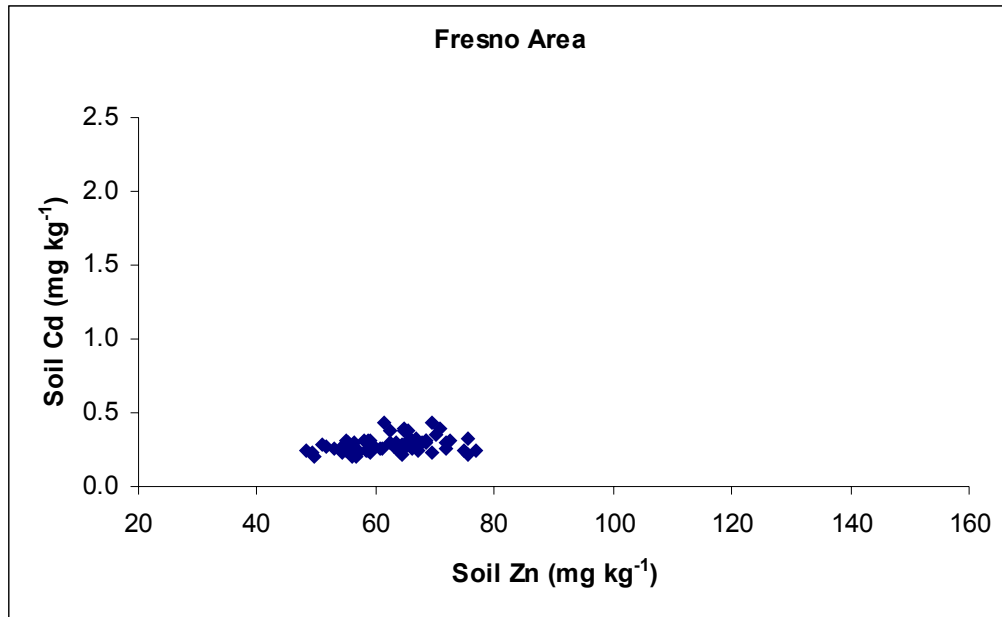


Figure 30. Cadmium vs. Zinc Contents of Cropland Soils, Fresno Area

3. **Lead.** Although there was no data to define the baseline concentrations in this region, the range of lead concentrations is low (7.7 – 15.0 mg kg⁻¹) compared to those of the other regions. The majority of the data points fell in the lower 50th percentile of lead concentrations for the 1967 benchmark soils. The range of lead concentrations (7.3 mg kg⁻¹) is considerably narrower than those regions where the lead concentrations of the soil had been elevated by external inputs (Table 21). It is reasonable to conclude that the lead concentrations of the soils in the Fresno area had not been affected by anthropogenic activities and still remain at the baseline levels. The lead concentrations were plotted against the corresponding phosphorus and lead concentrations in the soils (Figures 31 and 32).

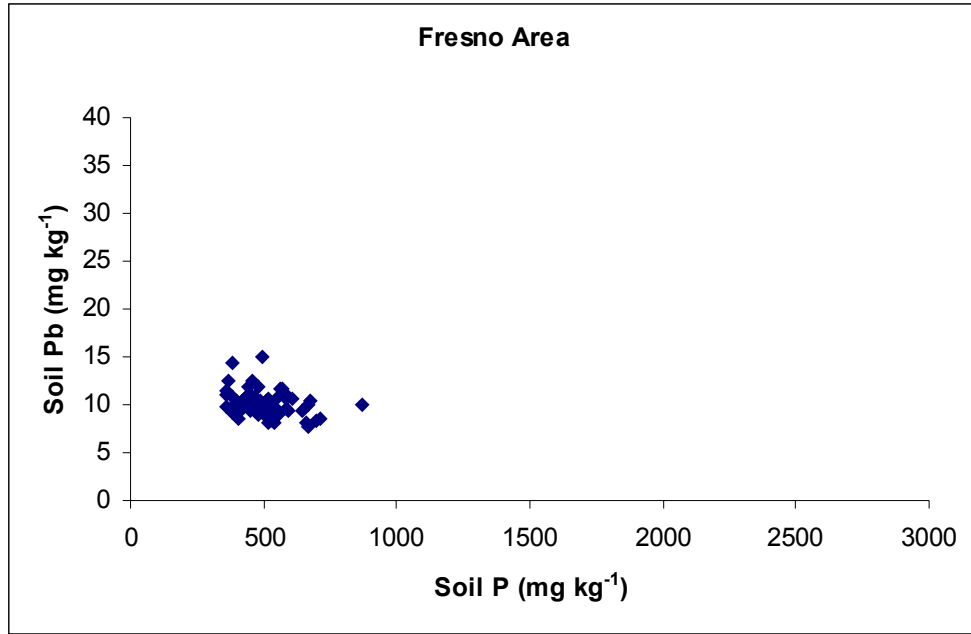


Figure 31. Lead vs. Phosphorus Contents of Cropland Soils, Fresno Area

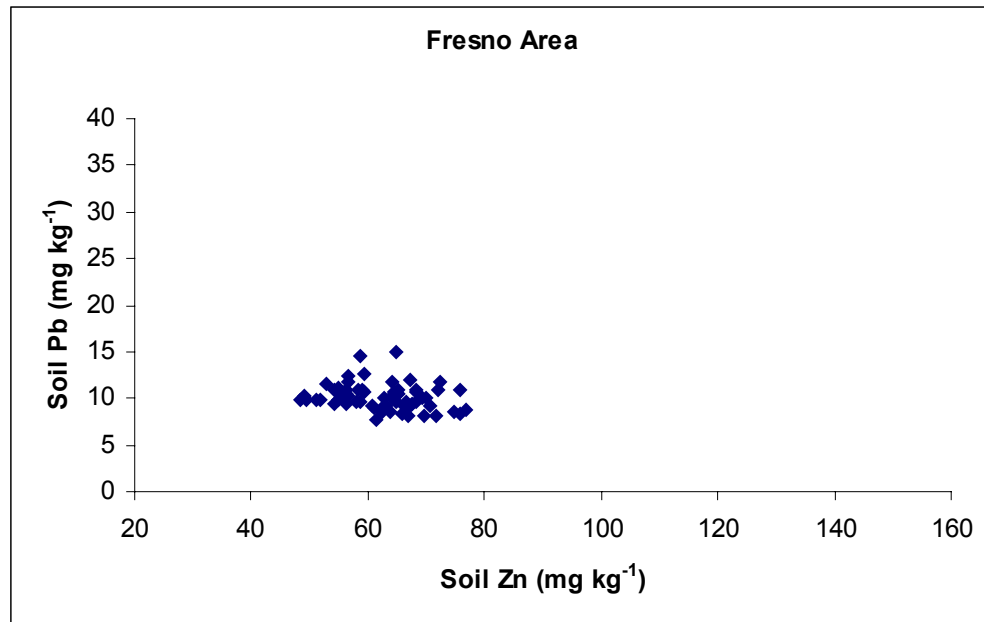


Figure 32. Lead vs. Zinc Contents of Cropland Soils, Fresno Area

The trends emerging from the data in Figures 31 and 32 showed no relationship between the lead-to-phosphorus and lead-to-zinc contents in the soils. Therefore, the lead contents

of cropland soils in the Fresno area had not been affected by applications of phosphorus fertilizer and micronutrients.

Coachella Valley In the Coachella Valley, 16 fields were sampled, totaling 80 samples. All of the soils sampled in this region were taken between the latitudes of 33°31'19.3" and 33°32'16.6" N and the longitudes of 116°01'37.2" and 116°09'29.4" W. The baseline ranges for arsenic, cadmium, lead, phosphorus and zinc established by concentrations at the 1.5 m soil depth are summarized in Table 18.

Table 18. Baseline Concentrations of Arsenic, Cadmium, Lead, Phosphorus and Zinc of Soils, Coachella Valley

Element	Number of Observations	Minimum (mg kg⁻¹)	Maximum (mg kg⁻¹)	Mean (mg kg⁻¹)	CV (%)
Arsenic	6	3.4	5.5	4.2	22
Cadmium	6	0.11	0.18	0.16	19
Lead	6	14.3	30.2	17.7	35
Phosphorus	6	368	1416	876	59
Zinc	6	34.0	77.1	61.3	25

The concentrations of the same elements of cropland soils in Coachella Valley are summarized in Table 19. The data for this region showed that the range of soil phosphorus concentrations, which varied from 500 to greater than 2,500 mg P kg⁻¹ soil, was considerably wider than those found in the other regions. The range of zinc concentrations of cropland soils in the Coachella Valley, varying from 53.8 to 128.3 mg kg⁻¹ soil, was also much wider than the other regions surveyed (Table 18). Wide ranges of both elements were indicative of heavy fertilizer and micronutrient inputs through cultivation.

Table 19. Concentrations of Arsenic, Cadmium, Lead, Phosphorus and Zinc of Cropland Soils, Coachella Valley

Element	Number of Observations	Minimum (mg kg ⁻¹)	Maximum (mg kg ⁻¹)	Mean (mg kg ⁻¹)	CV (%)
Arsenic	80	1.2	5.4	3.0	32
Cadmium	80	0.19	0.90	0.32	43
Lead	80	9.2	21.7	12.0	17
Phosphorus	80	527	2623	1196	46
Zinc	80	53.8	128.4	82.9	20

1. **Arsenic.** The concentration of arsenic in the baseline soil samples was numerically higher than in most of the samples taken from the agricultural fields. However, there was an overlap in the concentration range of these two populations, 3.4 – 5.5 and 1.2 – 5.4 mg kg⁻¹ for the baseline and the production fields, respectively (Figure 33). None of the samples taken from the agricultural fields was higher than the baseline maximum concentration, and more than half of the soils had arsenic concentrations below the baseline minimum (Figures 33 and 34). There was not a significant difference between the means of these two populations at $p \leq 0.01$. Although the range of phosphorus concentration in these soils was wide, indicating potentially heavy phosphorus fertilizer inputs, there was no apparent relationship between the arsenic concentration and the corresponding phosphorus content in the soil (Figure 33). Therefore, it might be concluded the arsenic concentrations of the cropland soils in the Coachella Valley appeared to remain at the baseline levels and seemingly heavy phosphorus fertilizer applications had not affected the outcomes.

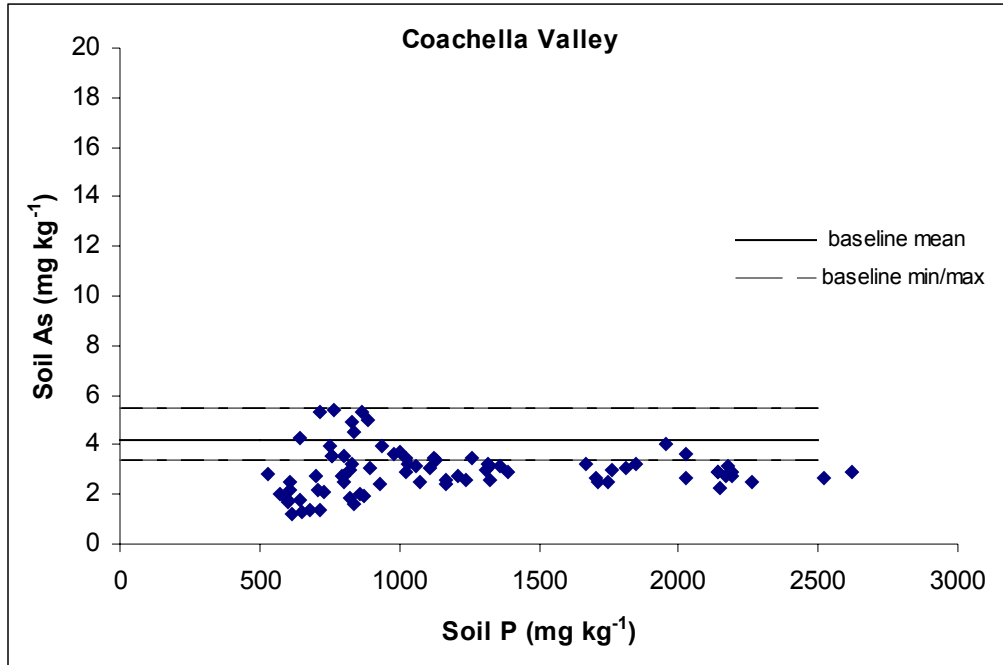


Figure 33. Arsenic vs. Phosphorus Contents of Cropland Soils, Coachella Valley

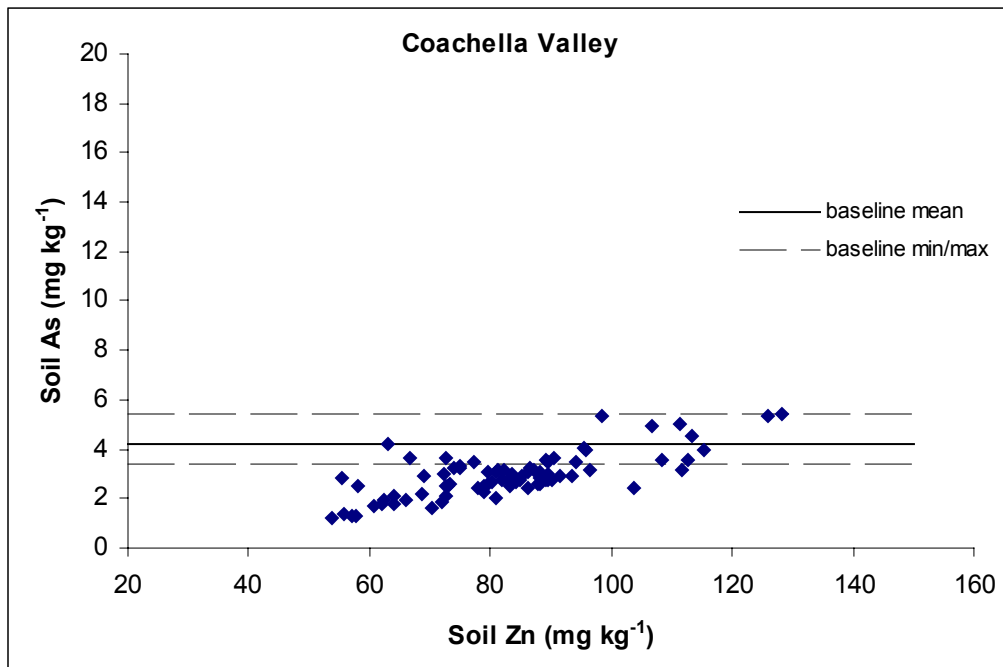


Figure 34. Arsenic vs. Zinc Contents of Cropland Soils, Coachella Valley

When they are plotted against the zinc concentrations in the soils, the arsenic concentrations, though remaining below the baseline maximum, appeared to increase as the zinc concentrations of the soils increased (Figure 34). As the zinc concentrations of the soils indicated potentially significant inputs of micronutrients, the trend observed in Figure 34 would be an indication that the micronutrient inputs potentially affected the arsenic concentrations of the cropland soils in the Coachella Valley. However, they had not risen beyond the baseline level.

2. **Cadmium.** The cadmium concentrations of nearly all of the cropland soil samples obtained in the Coachella Valley exceeded the narrow cadmium baseline levels for the region. The cadmium contents of the soils were unequivocally affected by external cadmium inputs, some of them by rather wide margins. The trend that emerged from the plotting of soil cadmium concentrations against the corresponding phosphorus concentrations followed the pattern of Scenario 2 from Table 11, with no relationship between the concentrations of these two elements in the soils (Figure 35). A similar trend emerged from the plotting the cadmium concentrations of the soils against the corresponding zinc concentrations (Figure 36). Therefore, the cadmium concentrations of the cropland soils in the Coachella Valley exceeded the baseline levels. However, the elevation of cadmium concentrations in these soils is not related to the applications of phosphorus fertilizers and micronutrients.

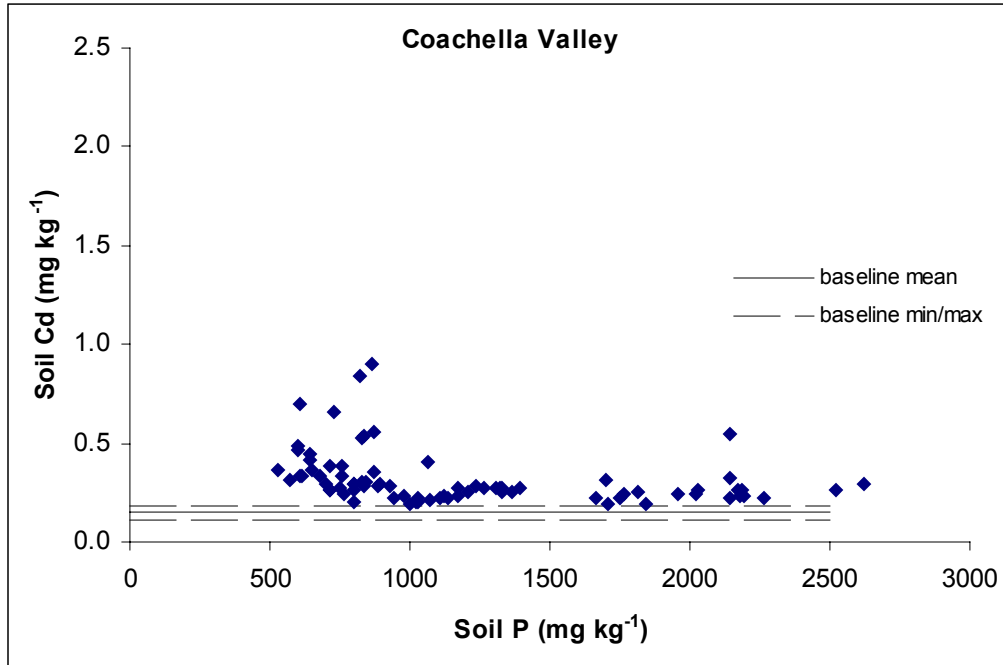


Figure 35. Cadmium vs. Phosphorus Contents of Cropland Soils, Coachella Valley

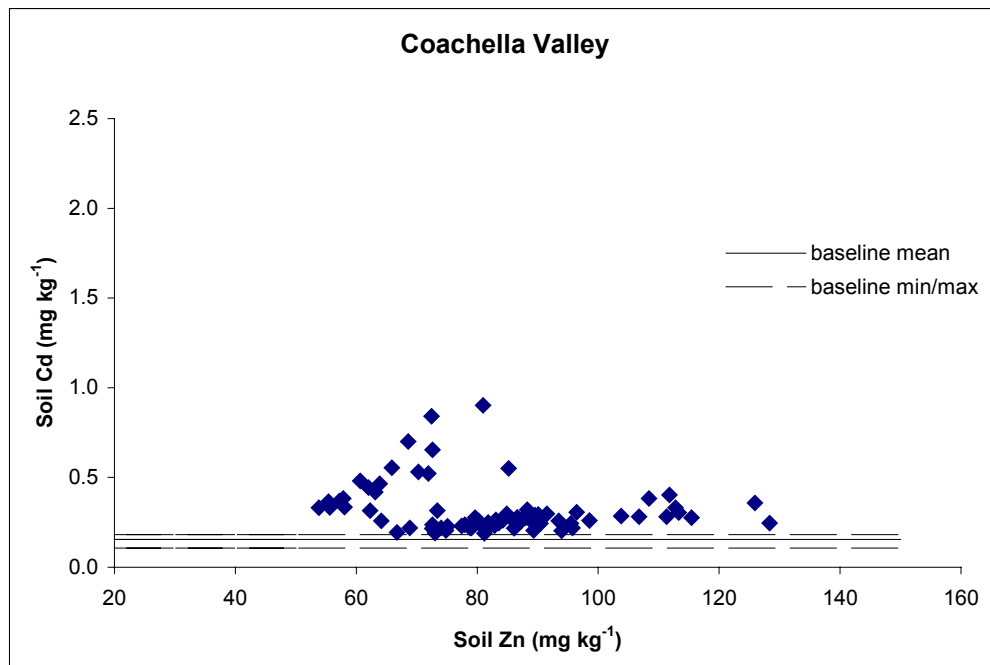


Figure 36. Cadmium vs. Zinc Contents of Cropland Soils, Coachella Valley

3. **Lead** The baseline lead levels of soils in the Coachella Valley were the highest among any of the regions sampled, and the range was also wider than other surveyed regions (Table 18). Except for one soil, the lead concentrations of the cropland soils were below the baseline mean concentration. Judging from the data in Table 18, the mean of the baseline was considerably closer to the minimum than the maximum of the baseline. This indicates that the data followed a lognormal distribution, in that majority of the data points were expected to fall close to the mean value, yet the range was significantly expanded by the presence of a few high values. In fact, all but one of the baseline measurements was between the range of 14 and 17 mg Pb kg⁻¹. If the outlier of the lead baseline measurements (30 mg kg⁻¹) was excluded, the range of lead concentrations for cropland soils (9.2 – 21.7 mg kg⁻¹) overlapped the adjusted baseline levels. It was therefore reasonable to conclude that the lead concentrations of the cropland soils in Coachella Valley were within the baseline levels.

When the soil lead concentrations of the soils were plotted against the corresponding phosphorus and zinc concentrations, they showed that the lead contents were not related to phosphorus and zinc concentrations of the soils. Therefore the lead concentrations of cropland soils in the Coachella Valley remained at the baseline level and had not been affected by applications of phosphorus fertilizers and micronutrients.

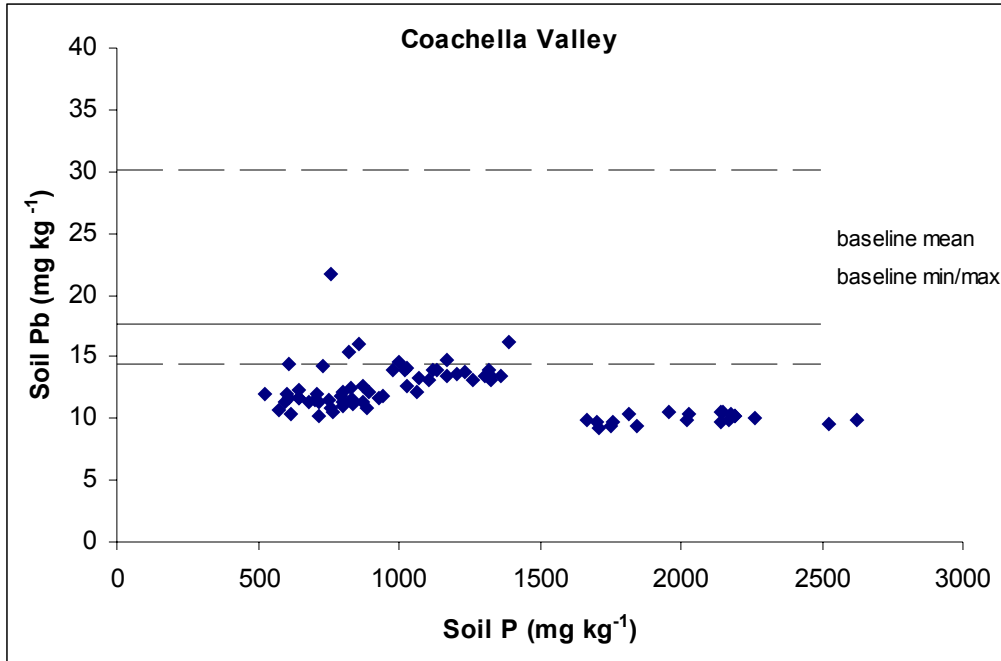


Figure 37. Lead vs. Phosphorus Contents of Cropland Soils, Coachella Valley

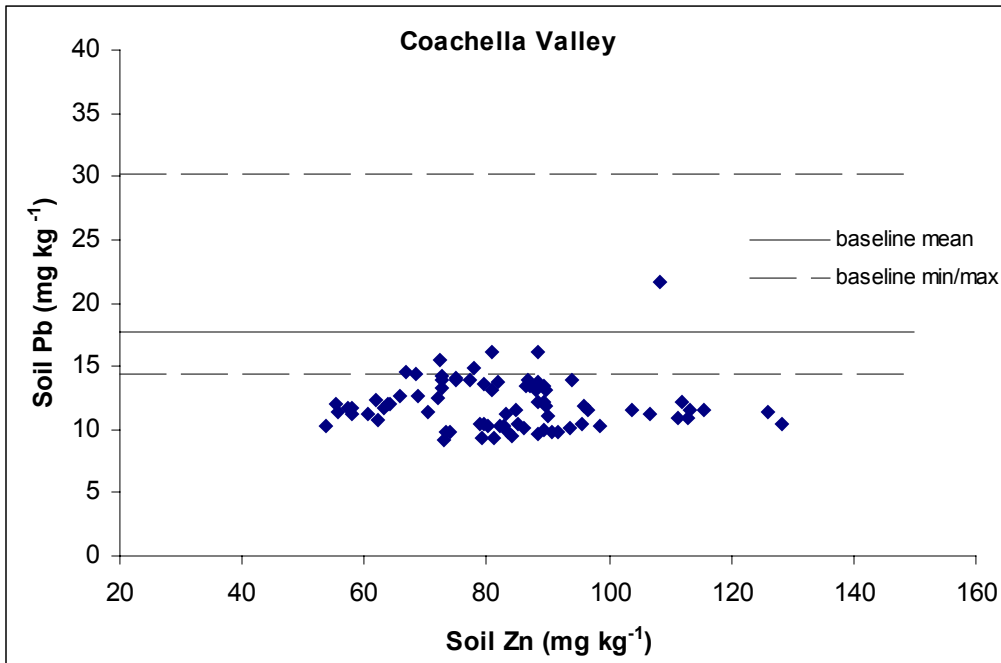


Figure 38. Lead vs. Zinc Contents of Cropland Soils, Coachella Valley

Imperial Valley In the Imperial Valley, 16 fields were sampled, totaling 80 samples. All of the soil samples in this region were taken between the latitudes of 32°46'13.1" and 32°57'30.6" N and the longitudes of 115°18'13.6" and 115°20'27.6" W. Samples were taken at a 1.5 m depth to establish the baseline concentrations for trace elements in the region (Table 19). The baseline phosphorus concentration of the soils in the Imperial Valley was between 472 – 847 mg P kg⁻¹. The phosphorus concentrations of cropland soils were between 832 – 1,519 mg P kg⁻¹. The range for the cropland soils showed an upward shift and almost completely exceeded the baseline, indicating rather heavy phosphorus fertilizer inputs through cultivation (Tables 20 and 21). The range for zinc concentrations of the cropland soils and the baseline levels overlapped, indicating that micronutrients supplements have not been significant in these soils.

Table 20. Baseline Concentrations of Arsenic, Cadmium, Lead, Phosphorus and Zinc of Soils, Imperial Valley

Element	Number of Observations	Minimum (mg kg ⁻¹)	Maximum (mg kg ⁻¹)	Mean (mg kg ⁻¹)	CV (%)
Arsenic	7	3.8	10.9	7.6	34
Cadmium	7	0.17	0.32	0.25	23
Lead	7	14.0	31.7	19.1	31
Phosphorus	7	473	848	654	21
Zinc	7	33.0	75.5	57.8	24

Table 21. Concentrations of Arsenic, Cadmium, Lead, Phosphorus and Zinc of Cropland Soils, Imperial Valley

Element	Number of Observations	Minimum (mg kg ⁻¹)	Maximum (mg kg ⁻¹)	Mean (mg kg ⁻¹)	CV (%)
Arsenic	80	4.9	11.5	7.6	20
Cadmium	80	0.25	0.50	0.38	16
Lead	80	13.5	24.0	17.0	12
Phosphorus	80	832	1,519	1,125	13
Zinc	80	39.1	80.6	59.8	15

Although significant amounts of phosphorus fertilizer had been used on these cropland soils, the means and ranges of arsenic, cadmium and lead concentrations for the cropland soils in the Imperial Valley were comparable to those of the baseline levels.

1. **Arsenic.** The arsenic concentrations of the cropland soils in the Imperial Valley were evenly distributed within the baseline range. Only two data points exceeded the baseline maximum. The trend that emerged from plotting the arsenic concentrations of the soils against the corresponding phosphorus and zinc concentrations showed that they followed the pattern of Scenario 1 as outlined in Table 11 (Figures 39 and 40). The arsenic concentrations remained well within the baseline levels and had not been influenced by the applications of phosphorus fertilizers and micronutrients.

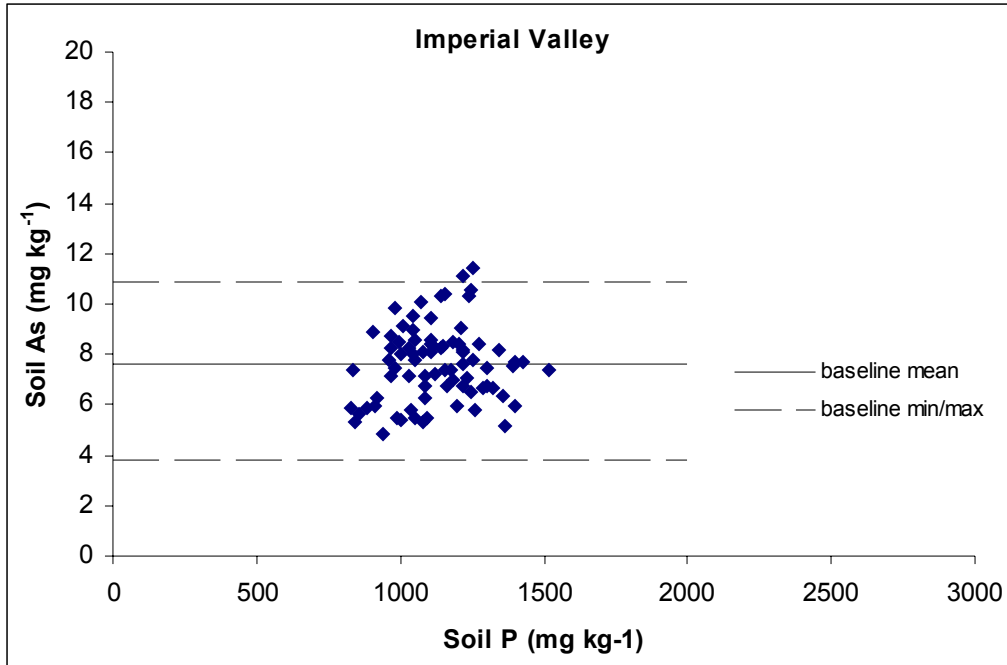


Figure 39. Arsenic vs. Phosphorus Contents of Cropland Soils, Imperial Valley

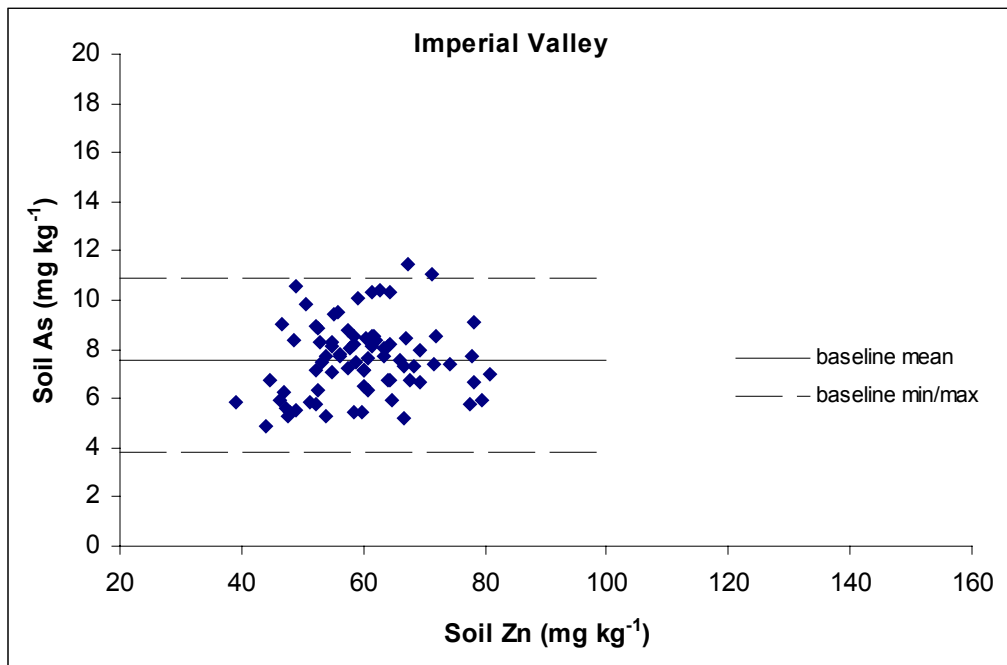


Figure 40. Arsenic vs. Zinc Contents of Cropland Soils, Imperial Valley

2. **Cadmium.** The baseline range for cadmium concentrations of soils in the Imperial Valley was narrow, 0.17 to 0.32 mg kg⁻¹. For the cropland soils, the cadmium concentrations were either in the upper 50th percentile of the baseline levels or exceeded it. Although the actual concentrations were low in comparison to those in the other regions, there was a clear indication that the cadmium contents of the soils in this region had shifted upward across the board, and cadmium had accumulated in the soils. However, the range of cadmium concentrations in these cropland soils, from 0.25 to 0.50 mg kg⁻¹, was rather narrow. When they were plotted against the phosphorus and zinc concentrations in the soils, the data showed the pattern of Scenario 2 as described in Table 11. Cadmium concentrations of the cropland soils in the Imperial Valley were not correlated with the phosphorus and zinc concentrations (Figure 41 and 42). These were indications that the increases in the cadmium concentrations in the soil were not related to applications of phosphorus fertilizers and micronutrients.

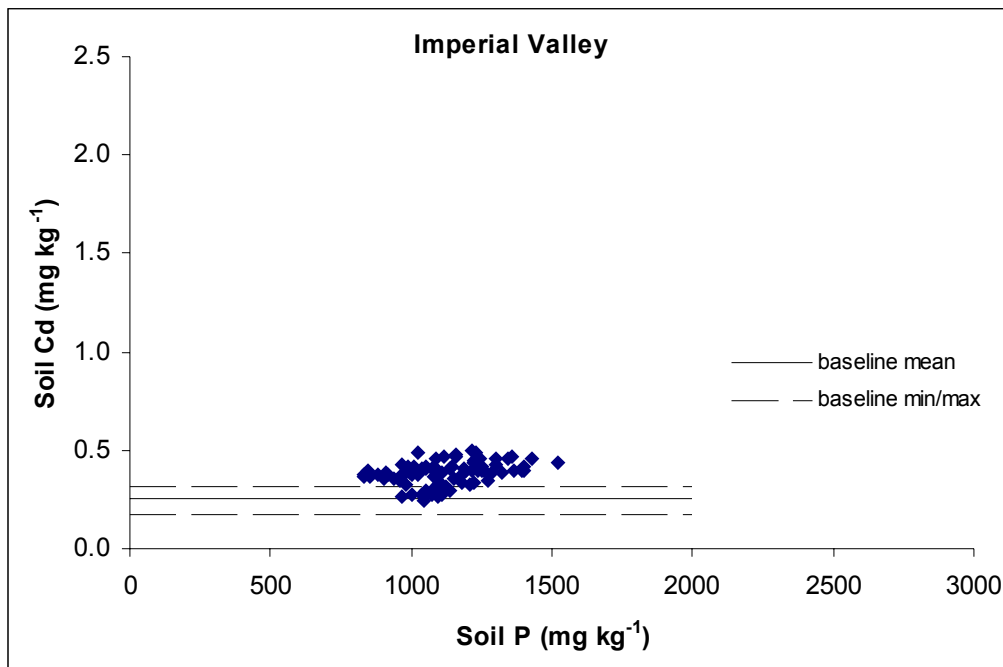


Figure 41. Cadmium vs. Phosphorus Contents of Cropland Soils, Imperial Valley

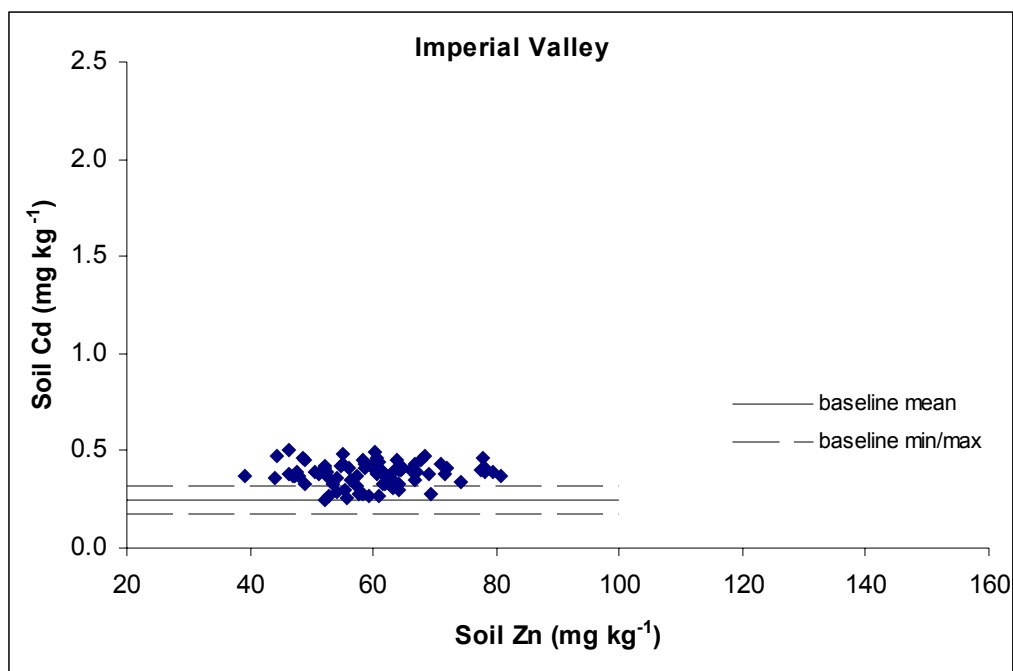


Figure 42. Cadmium vs. Zinc Contents of Cropland Soils, Imperial Valley

3. **Lead.** Soils in the Imperial Valley recorded the highest baseline lead concentration of any of the regions sampled. The distribution of baseline lead concentrations in this region was similar to that of the Coachella Valley. The baseline mean was considerably closer to the minimum rather than the maximum baseline level. The Coachella Valley and the Imperial Valley are situated on the north and south end of the Salton Sea, respectively. Both are part of bottom of the same ancient water body. It would be logical that the lead distributions in these two regions should be similar, as they were derived from the same sediment sources. All of the lead concentrations in the agricultural soils were within the baseline range. In fact, the majority of them fell between the baseline minimum and mean concentrations (Figures 43 and 44). When the lead concentrations are plotted against the phosphorus and zinc concentrations in the soils, the results show that the lead concentrations of the soils were not influenced by the

corresponding phosphorus and zinc concentrations (Figures 43 and 44). The lead accumulation in the Imperial Valley cropland soils is not significant. Their concentrations remained at the baseline levels and had not been affected by applications of phosphorus fertilizers and micronutrients.

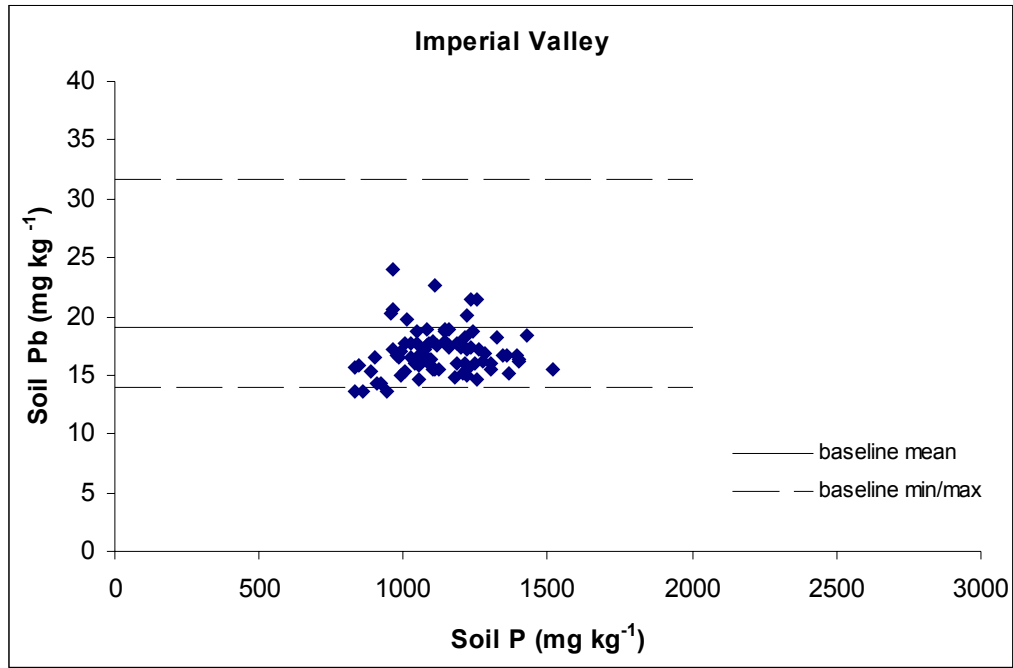


Figure 43. Lead vs. Phosphorus Contents of Cropland Soils, Imperial Valley

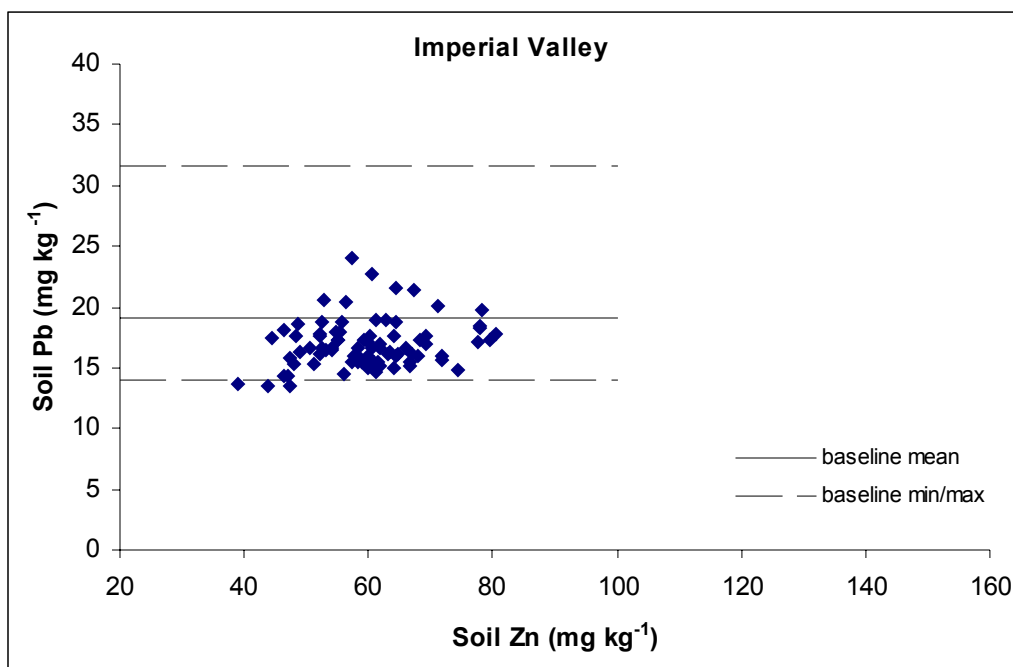


Figure 44. Lead vs. Zinc Contents of Cropland Soils, Imperial Valley

Monterey/Salinas Valley In the Monterey/Salinas Valley, 24 fields were sampled, with a total of 120 samples. All of the soils sampled in this region were taken between the latitudes of 36°31'54.4" and 36°36'42.8" N and the longitudes of 121°25'37.3" and 121°32'56.0" W. In this case, we purposely avoided the west side of valley known for soils naturally high in cadmium. Samples were taken at the 1.5 m depths to establish the baseline concentrations for trace elements in that region (Table 22). Table 23 summarizes the arsenic, cadmium, lead, phosphorus, and zinc contents of the cropland soils in the Monterey/Salinas Valley

Table 22. Baseline Concentrations of Arsenic, Cadmium, Lead, Phosphorus and Zinc of Soils, Monterey/Salinas Valley

Element	Number of Observations	Minimum (mg kg ⁻¹)	Maximum (mg kg ⁻¹)	Mean (mg kg ⁻¹)	CV (%)
Arsenic	4	4.7	11.8	8.9	34
Cadmium	4	0.13	0.28	0.18	36
Lead	4	13.4	16.3	15.1	9
Phosphorus	4	242	582	367	42
Zinc	4	47.5	77.8	65.2	23

Table 23. Concentrations of Arsenic, Cadmium, Lead, Phosphorus and Zinc of Cropland Soils, Monterey/Salinas Valley

Element	Number of Observations	Minimum (mg kg ⁻¹)	Maximum (mg kg ⁻¹)	Mean (mg kg ⁻¹)	CV (%)
Arsenic	120	3.0	14.5	7.0	33
Cadmium	120	0.25	0.65	0.40	20
Lead	120	13.6	62.2	21.6	31
Phosphorus	120	442	1,115	761	26
Zinc	120	42.6	104.0	67.1	19

The cadmium, lead, and phosphorus concentrations of the cropland soils in the Monterey/Salinas Valley were significantly higher than those of the baselines, at $p \leq 0.01$ (Tables 22 and 23). For the other elements, the concentrations of the cropland soils were not significantly different from their respective baselines. Consequently, the phosphorus contents of the soils had shifted upwards due to the application of phosphorus fertilizers. However, the micronutrients inputs were relatively insignificant as the zinc concentrations of the cropland soils were statistically not different from the baseline values. While the cadmium and lead contents of the soils had exceeded the baseline, the arsenic concentrations of the soils did not.

1. **Arsenic.** In the Monterey/Salinas Valley, the arsenic concentrations of the cropland soils varied from 3.0 to 14.5 mg kg⁻¹. However, majority of data points fell inside the baseline range and were evenly distributed within it. When the arsenic concentrations of the soils were plotted against the corresponding phosphorus and zinc concentrations, the results showed that the phosphorus and zinc concentrations had no effect on arsenic concentrations of the soils (Figures 45 and 46). Therefore, in Monterey/Salinas Valley, the arsenic contents of the cropland soils remained within the baseline range and the

applications of phosphorus fertilizers had no effect on them. The micronutrient inputs do not appear significant and they did not affect the cadmium concentrations of the soils.

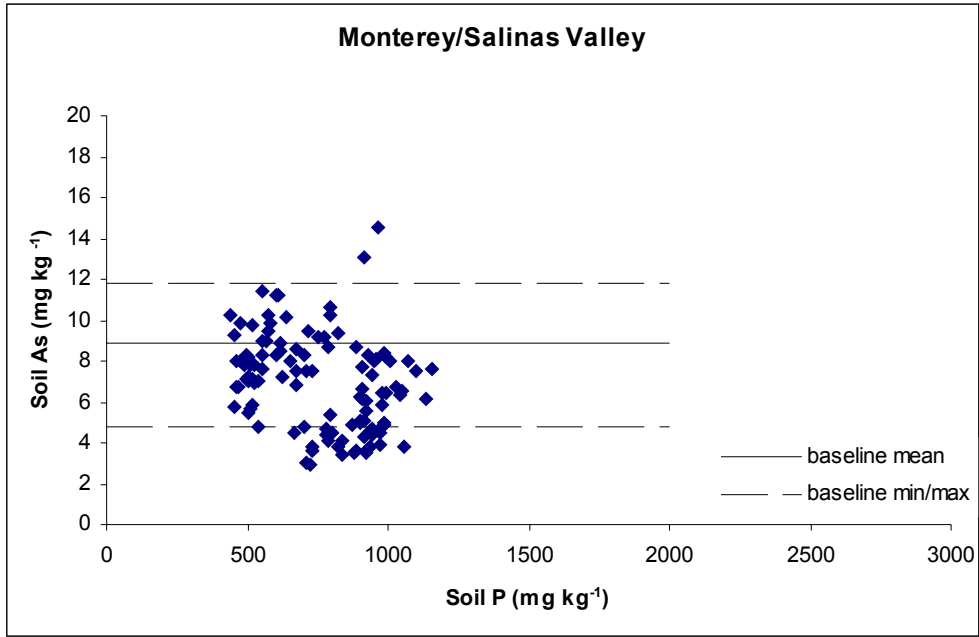


Figure 45. Arsenic vs. Phosphorus Contents of Cropland Soils, Monterey/Salinas Valley

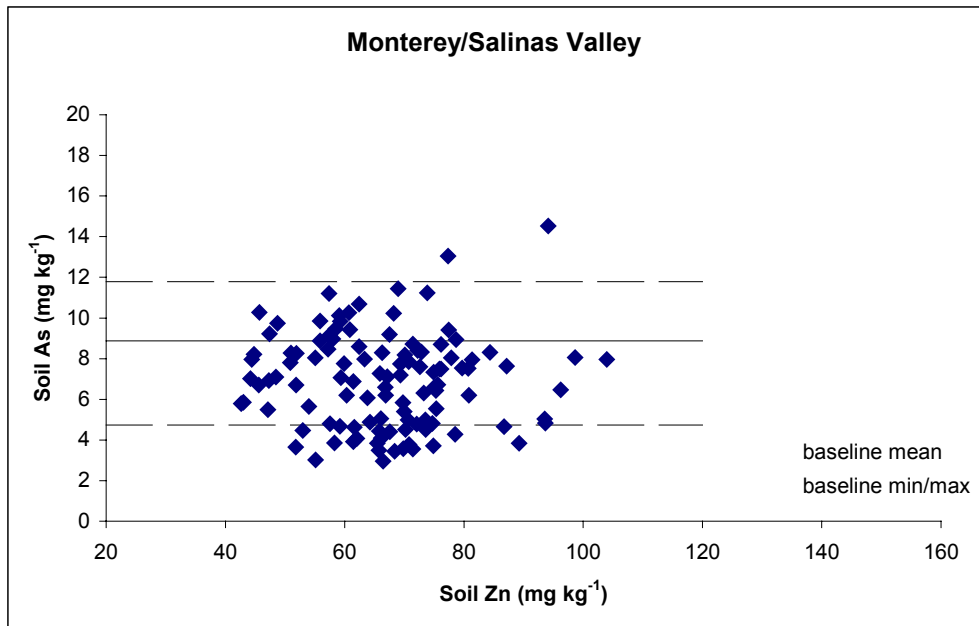


Figure 46. Arsenic vs. Zinc Contents of Cropland Soils, Monterey/Salinas Valley

2. **Cadmium.** In this region, we purposely avoided the areas where the soil cadmium concentrations were naturally 1 mg kg^{-1} and upwards, out of concern that a small amount of accumulation might be masked by the high background levels. In the sampled areas, nearly all of the cadmium concentrations in the cropland soils exceeded the baseline concentrations, though the concentrations, $0.25 - 0.65 \text{ mg kg}^{-1}$, were rather low. This magnitude of change most likely would not be detectable if it were measured for soils in the high cadmium areas. When the cadmium concentrations of the cropland soils in the surveyed areas were plotted against the corresponding phosphorus and zinc concentrations, the results showed that the cadmium concentrations of the soils had exceeded the baseline but were not in step with phosphorus and zinc concentrations (Figures 47 and 48).

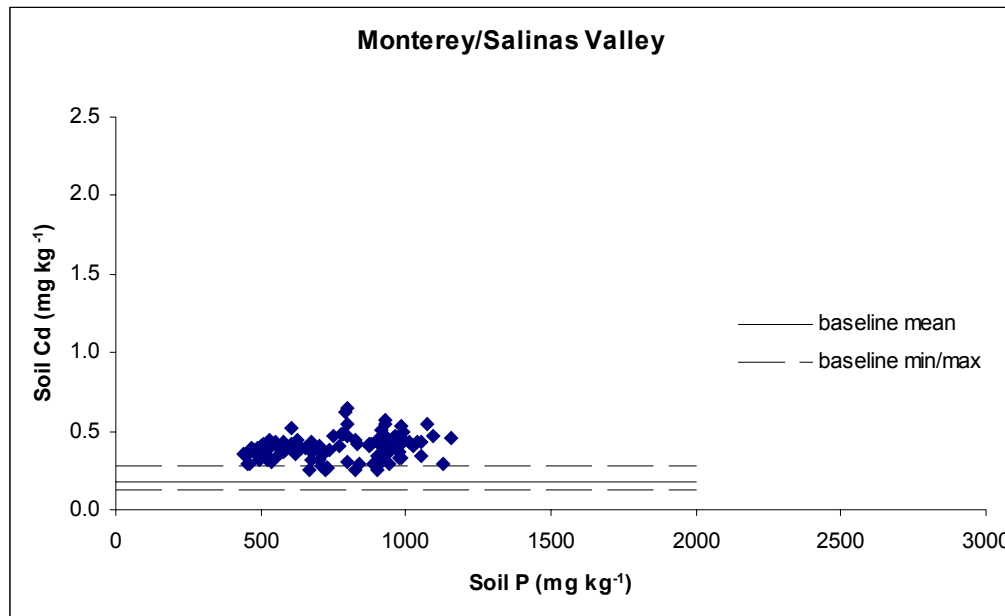


Figure 47. Cadmium vs. Phosphorus Contents of Cropland Soils, Monterey/Salinas Valley

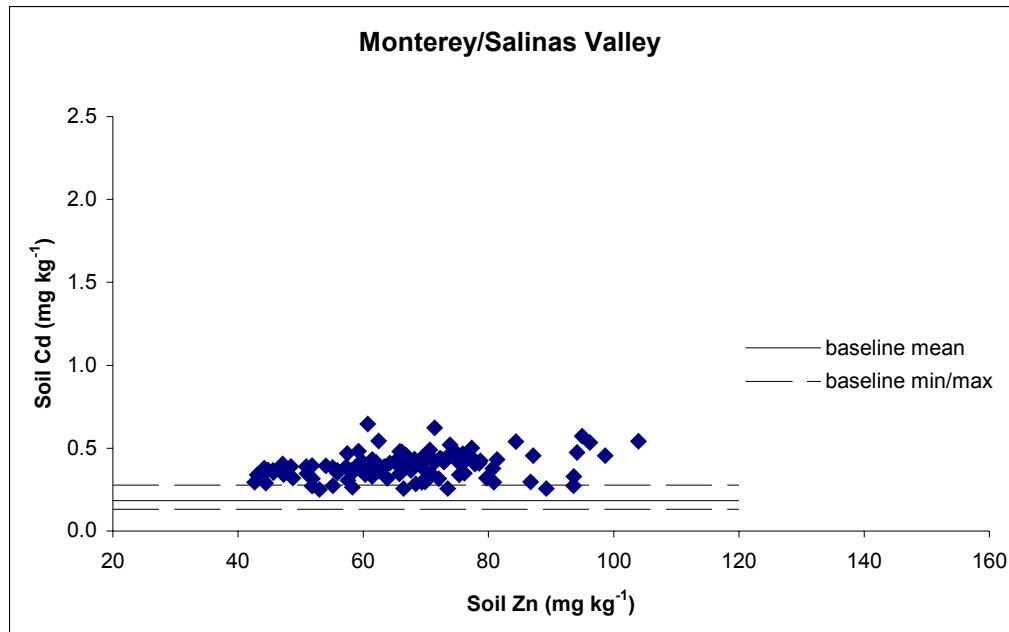


Figure 48. Cadmium vs. Zinc Contents of Cropland Soils, Monterey/Salinas Valley

In the areas where the cadmium concentrations of the soils were not naturally high, the soil cadmium contents had exceeded the baseline. In this case, the elevated concentrations could be attributed to applications of fertilizers and micronutrients.

4. **Lead.** The lead concentrations of the surveyed cropland soils in the Monterey/Salinas Valley covered a wide range, from 13.6 to 62.2 mg kg⁻¹ and included the highest concentrations among all of the soils sampled. When the lead concentrations of the soils were compared, approximately 50 per cent of the soils examined had lead concentrations exceeding the baseline levels. However, the lead concentrations of the soils were not affected by the corresponding phosphorus and zinc concentrations. In all, while the trace element concentrations exceeded the baseline levels, the accumulations were not related to the applications of phosphorus fertilizers and micronutrients (Figures 49 and 50).

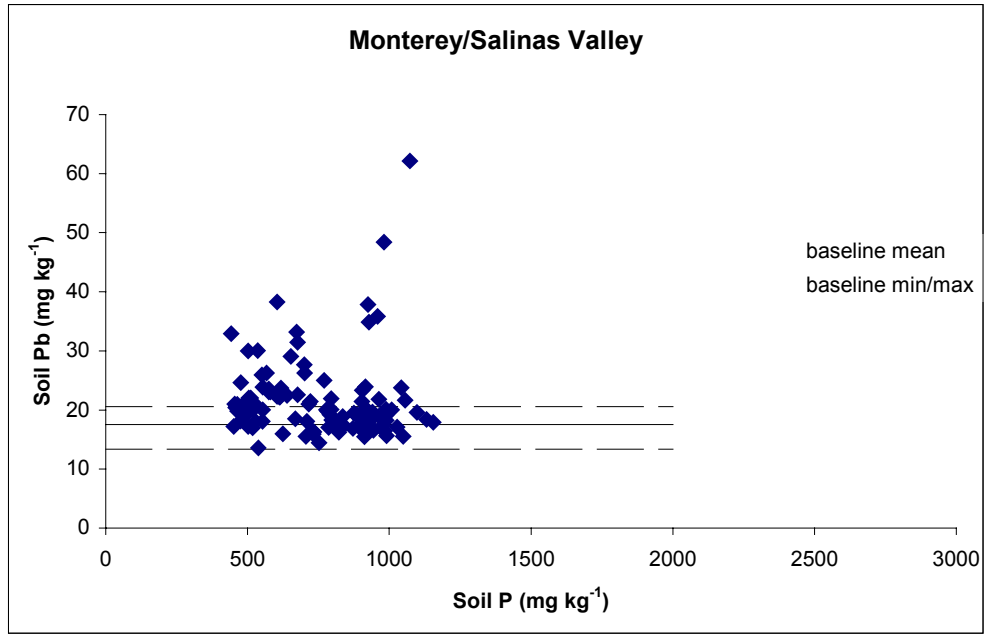


Figure 49. Lead vs. Phosphorus Contents of Cropland Soils, Monterey/Salinas Valley

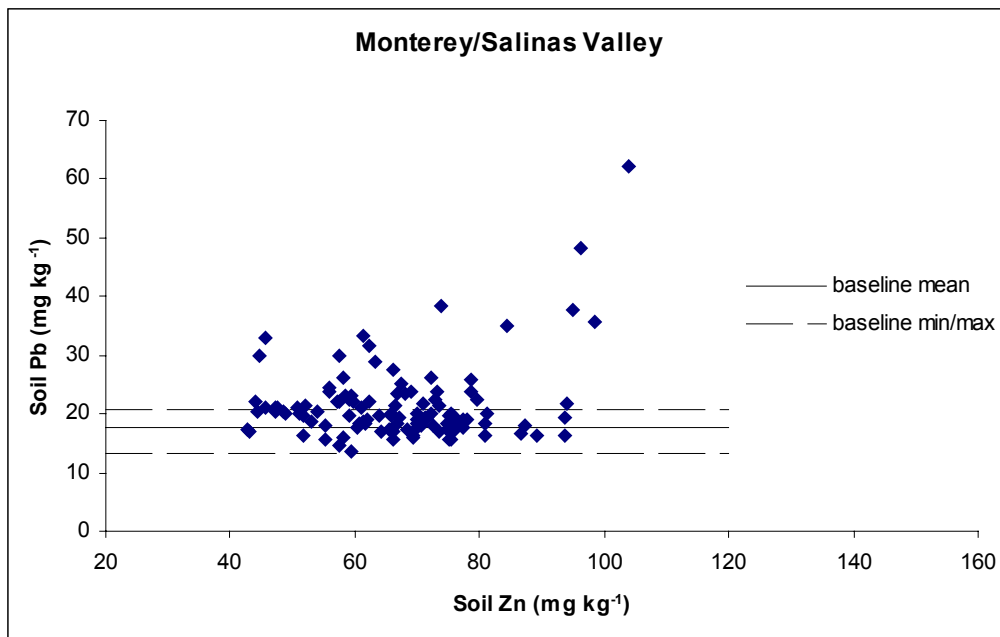


Figure 50. Lead vs. Zinc Contents of Cropland Soils, Monterey/Salinas Valley

Summary In the previous sections, the impact of the phosphorus fertilizers and micronutrients on the arsenic, cadmium and lead accumulations in the California cropland soils were elaborated separately, region by region. The outcomes are compiled in Tables 24 and 25 for comparison.

Table 24. Role of Phosphorus Fertilizers on Arsenic, Cadmium and Lead Contents of Cropland Soils in California

Production Region	Arsenic	Cadmium	Lead
Oxnard and Ventura Area	Baseline	P Fertilizer	Diffuse Sources
Santa Maria and San Luis Obispo Valley	Diffuse Sources	Diffuse Sources	Diffuse Sources
Colusa/Glen County	Diffuse Sources	Baseline	Baseline
Fresno	Baseline ¹	Baseline	Baseline
Coachella Valley	Baseline	Diffuse Sources	Baseline
Imperial Valley	Baseline	Diffuse Sources	Baseline
Monterey/Salinas Valley	Baseline	Diffuse Sources	Diffuse Sources

¹While remaining in the baseline range, the arsenic contents of soils showed a rising trend.

Table 25. Role of Micronutrients on Arsenic, Cadmium and Lead Contents of Cropland Soils in California

Production Region	Arsenic	Cadmium	Lead
Oxnard and Ventura Area	Baseline	Diffuse Sources	Diffuse Sources
Santa Maria and San Luis Obispo Valley	Diffuse Sources	Diffuse Sources	Diffuse Sources
Colusa/Glen County	Diffuse Sources	Baseline	Baseline
Fresno	Baseline ¹	Baseline	Baseline
Coachella Valley	Baseline	Diffuse Sources	Baseline
Imperial Valley	Baseline	Diffuse Sources	Baseline
Monterey/Salinas Valley	Baseline	Diffuse Sources	Diffuse Sources

¹While remaining in the baseline range, the arsenic contents of soils showed a rising trend.

Arsenic In five of the seven production regions surveyed in California, the arsenic contents of the cropland soils remained within the baseline ranges. In the remaining two

production regions, the arsenic concentrations of the soils shifted upward across the board. Either the entire population, or at least the upper end of the concentration range, exceeded the baseline level. However, the accumulations in the soils could not be attributed to the applications of phosphorus fertilizers or micronutrients and were from diffuse sources.

Cadmium The cadmium concentrations of cropland soils in one of the seven surveyed production regions exceeded the baseline and showed clear signs of rising with respect to the phosphorus content of the soils. We can conclude that the phosphorus fertilizer applications had caused the cadmium concentrations of the soils to rise. In four of the remaining six production regions, the cadmium concentrations in the cropland soils shifted upward across the board. Either the entire population, or at least the upper end of the concentration range, exceeded the baseline level. In these cases, the elevated lead concentrations in the soils were caused by diffuse sources rather than phosphorus fertilizers and micronutrients. For the remaining two production regions, the cadmium contents of the soils remained within the baseline. The applications of phosphorus fertilizers and micronutrients did not affect the cadmium contents of soils in these two regions.

Lead Applications of phosphorus fertilizers and micronutrients had no effect on the lead concentrations of the cropland soils in California. In four of the seven production regions, the lead concentrations remained within the baseline range. In remaining three production regions, the lead concentrations had shifted upward across the board. Either the entire population, or at least the upper end of the concentration range, exceeded the baseline level. In these cases, the elevated lead concentrations in the soils were caused by diffuse sources rather than phosphorus fertilizers and micronutrients.

Arsenic, Cadmium, Lead, and Zinc in Plant Tissue

The primary sources of trace elements in plant tissues are those present in the growth media. How did the accumulation of arsenic, cadmium, and lead in cropland soils affect the concentration of these elements in plant tissue? Generally, plants are expected to absorb trace elements that are present in the soil solution, namely in ionic and complex forms. Arsenic, cadmium and lead, once they enter the soil, readily react with clays, organic matter, and other reactive components of the soils. They are adsorbed by the solid phases and/or form sparingly soluble precipitates in the soil. However, the extent of the absorption and precipitation is dependent on the characteristics of the plants and properties of the soils. If all other conditions are equal, the trace element concentrations are invariably higher in the leaves as compared to the fruits, seeds, and other above-ground biomass. Also, plants grown on soils with heavier texture, higher organic matter content, and a more alkaline pH tend to absorb less of the trace metals of interest. Even at rather low concentrations in the solution phase, plants absorb trace elements at noticeable rates, and often the amounts absorbed are in proportion to the amounts present in the soils.

This investigation focused on field sampling of the cropland soil cultivated for vegetable production. At the time of sampling, plants were not always available for collection. Additionally, the same crop species were not found at all of the sampling locations. As the leaf tissue would be most sensitive to the presence of trace elements in the soils, we collected leaf tissue samples of crops grown at the same locations where soils samples were taken whenever they were available. In this manner, plant tissue samples were obtained from fields in the Oxnard and Ventura Area and Santa Maria and San Luis Obispo Valley.

The plant tissue samples were washed with non-ionic detergents, rinsed with de-ionized water, dried at 65°C, and ground to pass a screen with 0.1 mm diameter openings. Aliquots of plant tissue were digested with nitric and hydrochloric acid mixtures and diluted to volume for analysis of arsenic, cadmium, lead, phosphorus, and zinc content. For the analysis, we used graphite furnace atomic absorption spectroscopy (GF-AAS) or inductive capillary plasma optical emission spectroscopy (ICP-OES). For a crop production region where general conditions such the soil and fertilizer management were comparable, the trace element concentrations in leaf tissue should be correlated to those of the soil, if the plant uptake has been affected by the trace element accumulation.

Arsenic We were unable to measure arsenic concentrations of the plant tissue with confidence as the concentrations of the element were frequently below the detection limits, and we were therefore unable to establish a data set that met the quality control and quality assurance criteria outlined on page 35 of this report. We concluded that the arsenic concentrations of the leaf tissues were less than 0.1 mg kg⁻¹ dry weight.

Cadmium In Oxnard and Ventura Area, the cadmium concentrations of the soils were elevated by the applications of phosphorus fertilizers. There is a positive correlation between the cadmium concentrations in the leaf tissue and the cadmium concentrations in the corresponding soils (Figure 51). The linear regression representing the showed that the cadmium in plant tissue (Y) is related to the cadmium concentration of soil (X), such that $Y = 0.95 * X$ with $R^2 = 0.96$ and the cadmium concentration in the leaf tissue of broad bean, bell pepper, lettuce and celery were plotted on the same graph and the data points lined up along the same linear regression line. The slope of this regression line would be the plant uptake factor for cadmium expressed as mg kg⁻¹ in plant tissue per mg kg⁻¹ in soil. This clearly demonstrates that

cadmium, if it accumulates in the soils, will be transferred to growing crops. The cadmium content of the plant tissue is also correlated to the phosphorus concentration of the soil (Figure 52). The linear regression showed that the cadmium in plant tissue (Y) is related to the phosphorus concentration of soil (X), such that $Y = 0.0014 * X - 0.8387$ with $R^2 = 0.88$. This further illustrates the impact of phosphorus fertilizer applications on cadmium buildup in receiving soils and crops.

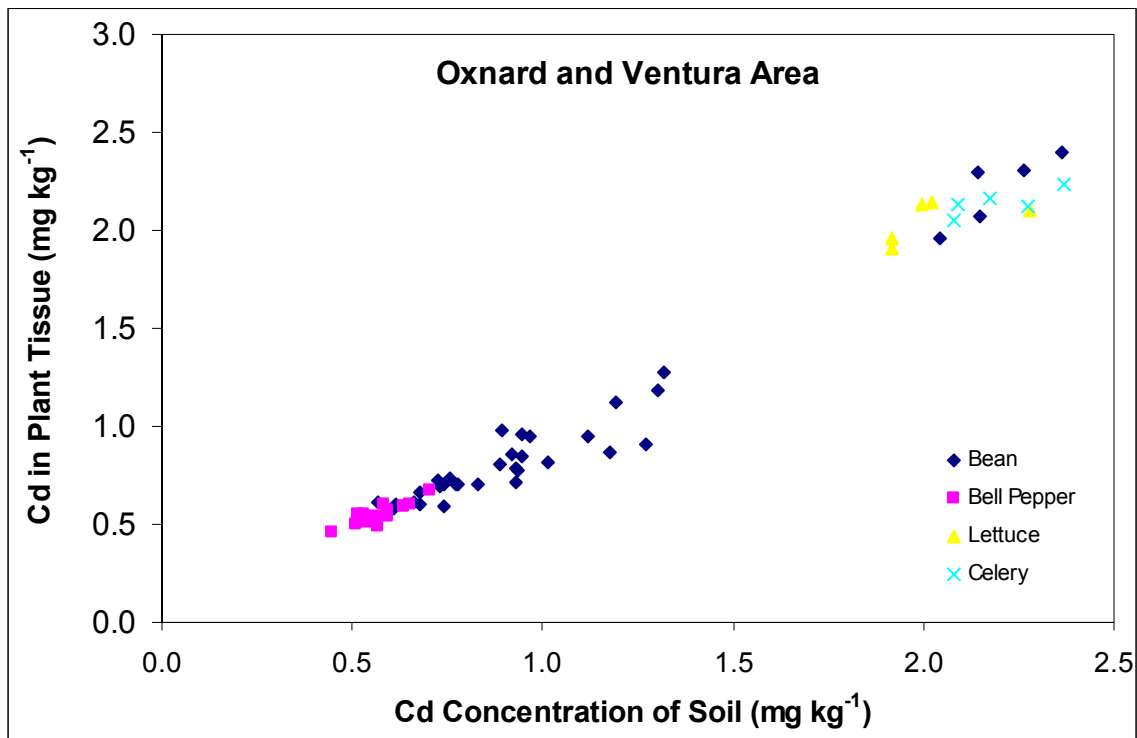


Figure 51. Cadmium Concentration of Plants (leaf tissue) in Relation to the Cadmium Concentrations of Soils, Oxnard and Ventura Area.

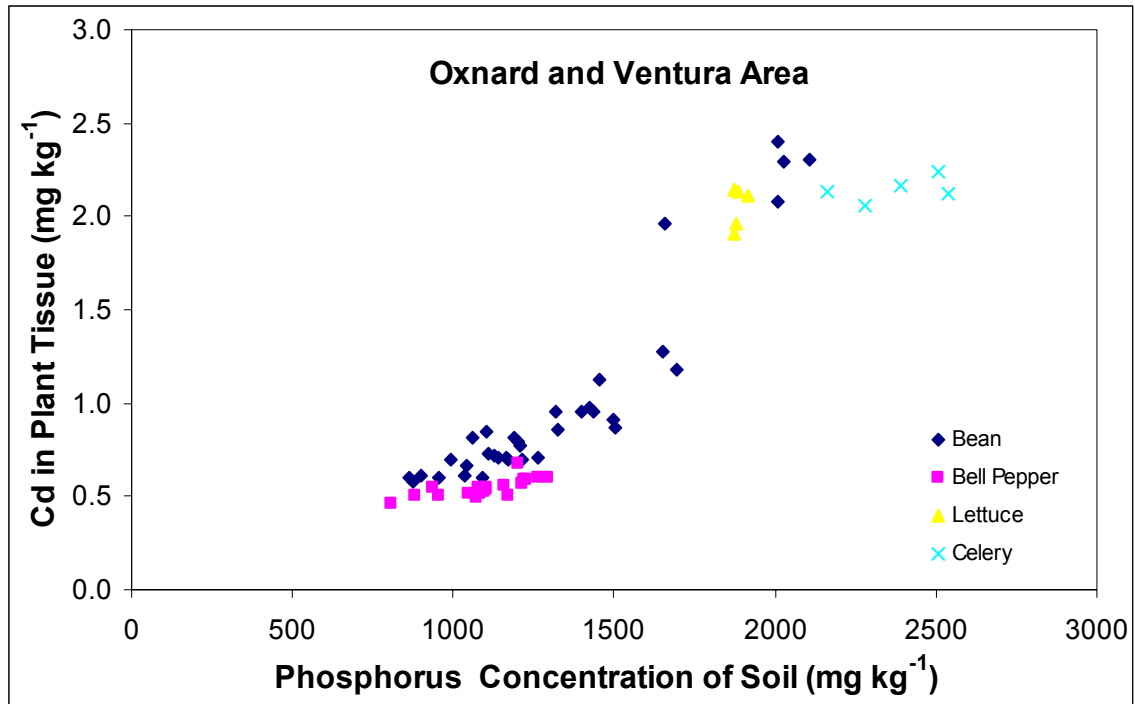


Figure 52. Cadmium Concentration of Plants (leaf tissue) in Relation to the Phosphorus Concentrations of Soils, Oxnard and Ventura Area

As the cadmium concentrations were not affected by the zinc content of the soils, which represented the micronutrient inputs, the cadmium contents of the plant tissues were also not affected by the zinc content of the soils (Figure 53).

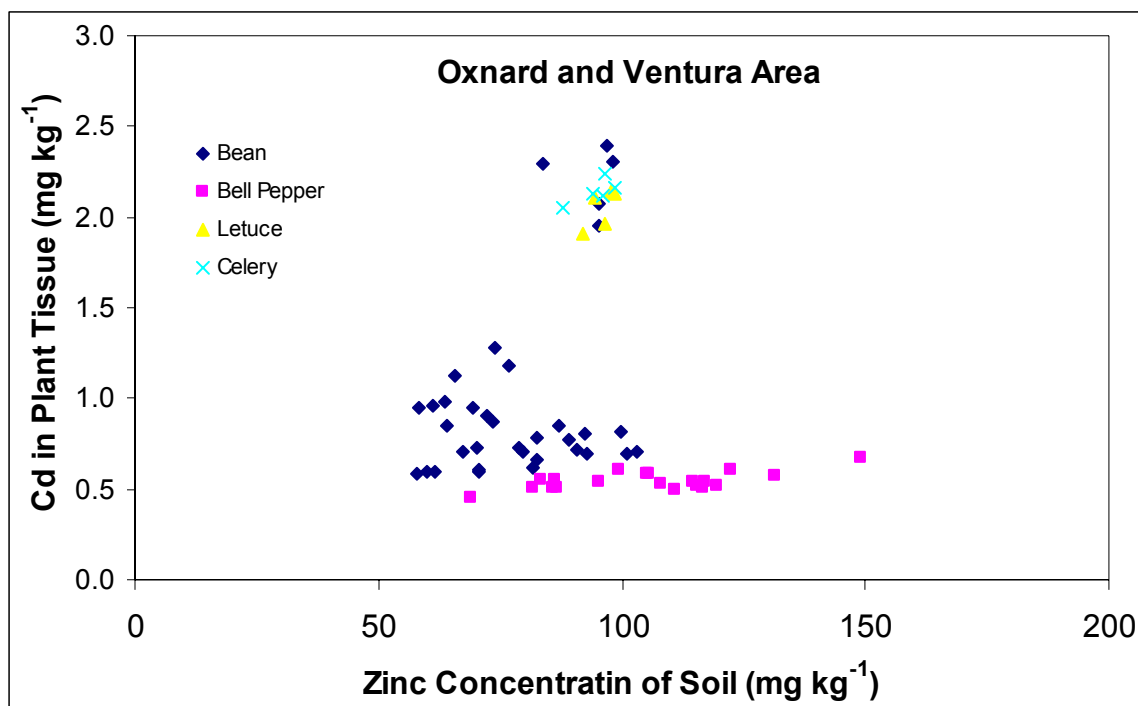


Figure 53. Cadmium Concentration of Plants (leaf tissue) in Relation to the Zinc Concentrations of Soils, Oxnard and Ventura Area

In the Santa Maria and San Luis Obispo valleys, the cadmium contents of the cropland soils have shifted upward. However, the increases in cadmium concentrations in the soils were not caused by the applications of phosphorus fertilizers and/or micronutrients. While cadmium contents in a portion of the soils exceeded the baseline maximum, the soil cadmium in the majority of the sampled fields remained within the upper end of the baseline concentration range. In this case, the cadmium contents of plants did not appear to be related to the phosphorus concentration of the soil (Figure 54). The cadmium concentrations of lettuce, spinach, and cauliflower were invariably greater than 1 mg kg^{-1} even when the soil cadmium contents were between the mean (0.45 mg kg^{-1}) and maximum (0.84 mg kg^{-1}) of the baseline range, while the cadmium concentrations of broccoli leaves generally were less than 1 mg kg^{-1} even when the soil cadmium content reached more than 1.5 mg kg^{-1} (Figure 55).

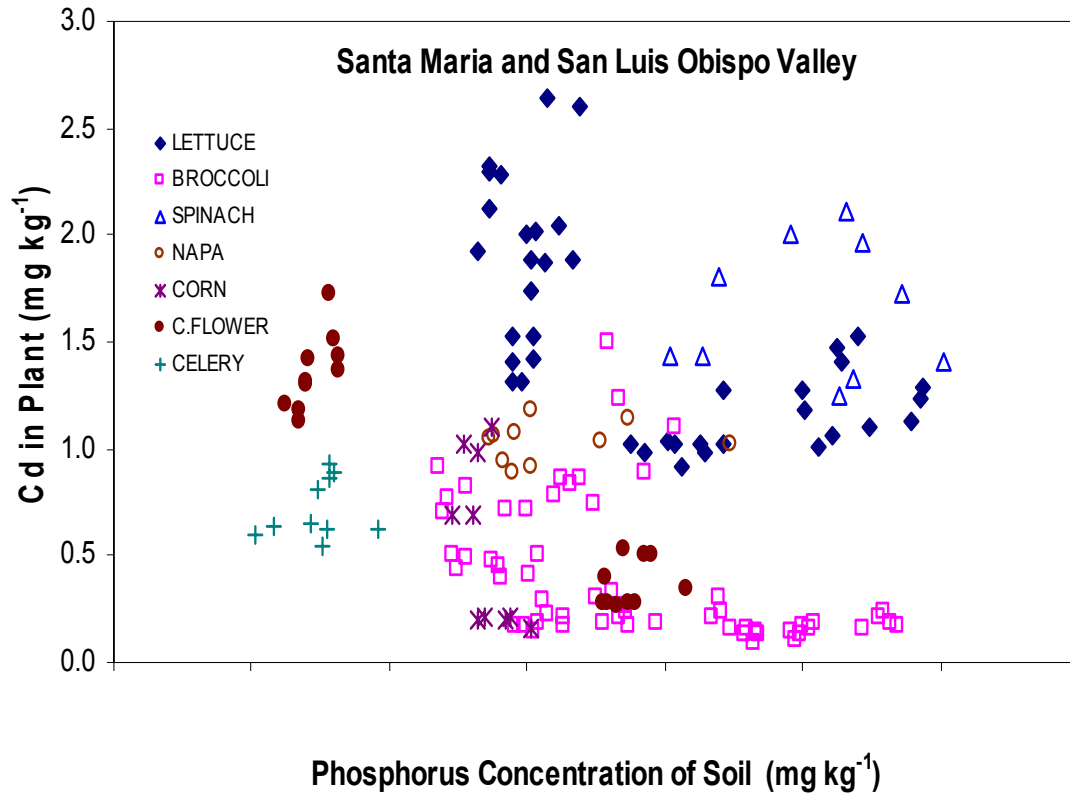


Figure 54. Cadmium Concentration of Plants (leaf tissue) in Relation to the Phosphorus Concentrations of Soils, Santa Maria and San Luis Obispo Valley

The linear regression relationship of the cadmium concentrations in plant tissue (Y) versus cadmium concentrations in soils (X) for lettuce, broccoli, and cauliflower were as follows:

$$Y = 0.51 * X, \quad R^2 = 0.20 \quad \text{for broccoli}$$

$$Y = 0.95 * X, \quad R^2 = -0.41 \quad \text{for cauliflower}$$

$$Y = 2.18 * X, \quad R^2 = 0.02 \quad \text{for lettuce}$$

In general, in Santa Maria and San Luis Obispo Valley, the plant tissue concentration data scattered widely (approximately 0.1 to 2.5 mg kg⁻¹) over a rather narrow range of cadmium concentrations (approximately 0.5 to 1.0 mg kg⁻¹). As a result, the linear regression relationships were very weak or non-existing. To obtain a statistically significant regression relationship, the data needed to be expanded to cover a wider range of soil cadmium concentrations.

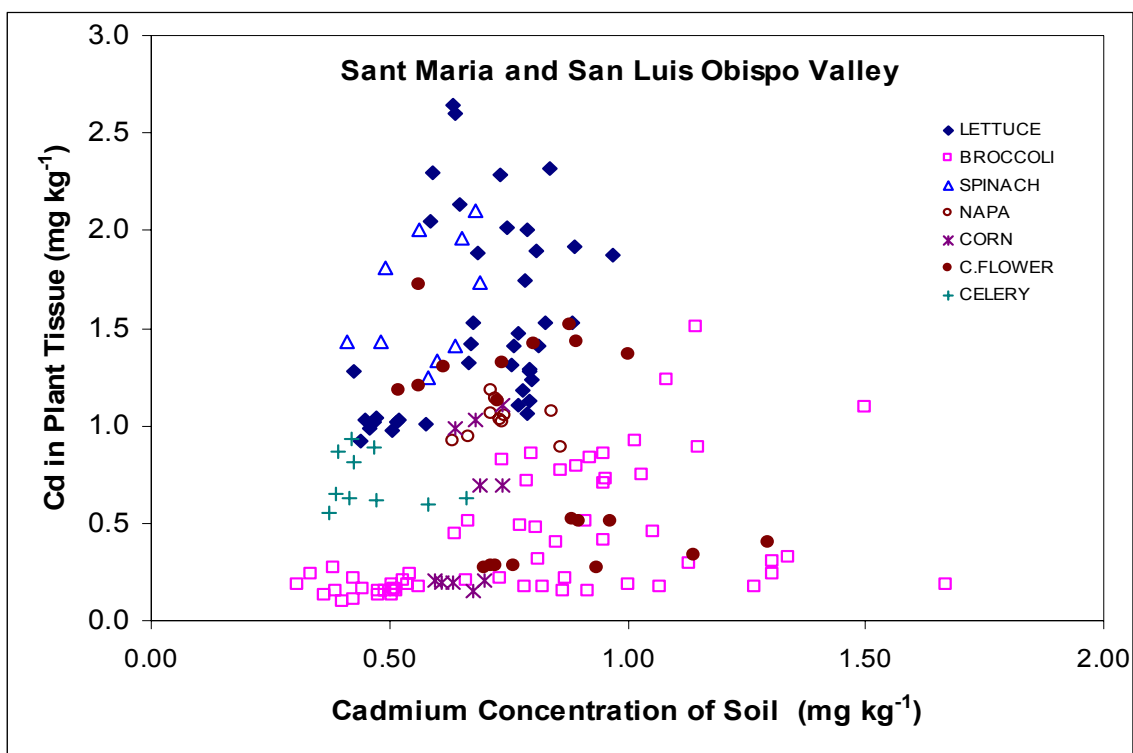


Figure 55. Cadmium Concentration of Plants (leaf tissue) in Relation to the Cadmium Concentrations of Soils, Santa Maria and San Luis Obispo Valley

In 1975, U.S. Department of Agriculture conducted a nationwide survey of trace elements in cropland soils and harvested crops (Wolnik et al., 1983ab). In which, the soils and plants in California were included. We pooled the data for California lettuce in that survey and the lettuce data we obtained in Santa Maria and San Luis Obispo Valley. In this manner, the range of soil cadmium concentrations expanded from approximately <0.1 to 1.0 mg kg^{-1} (Figure 56). The linear regression between cadmium concentration in lettuce (Y) and cadmium concentrations of soils (X) that $Y = 2.17 * X$ with $R^2 = 0.49$ is significant.

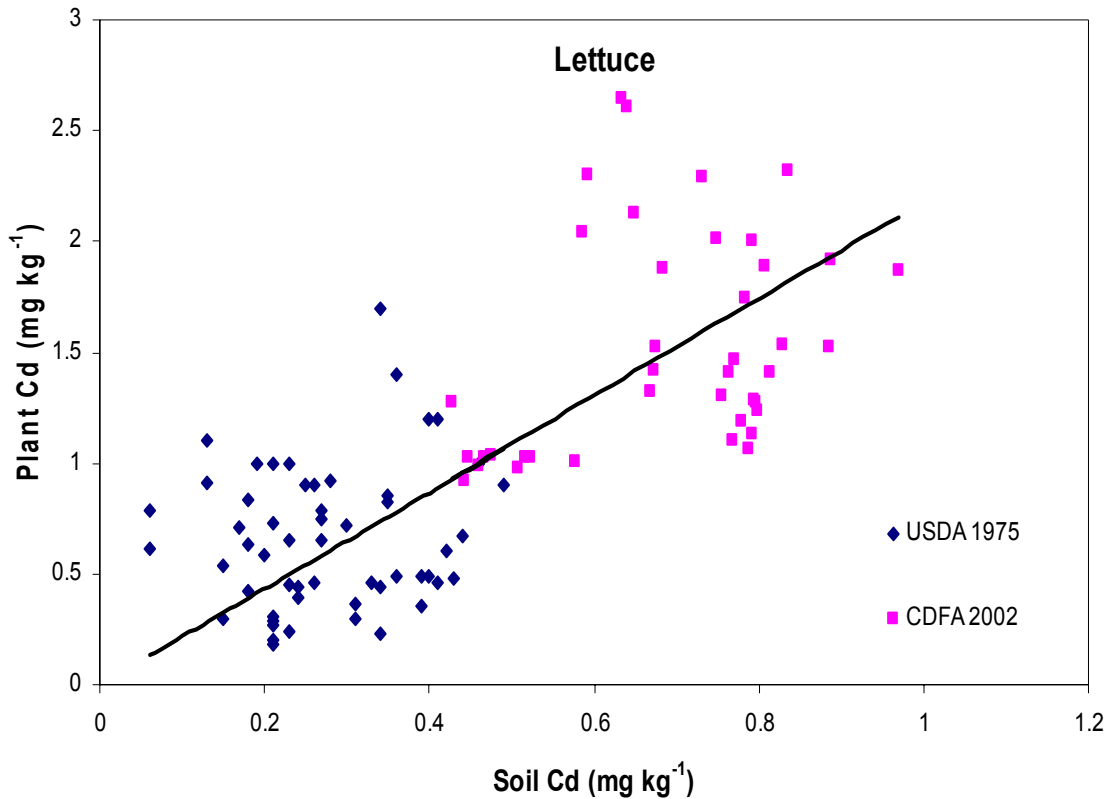


Figure 56. Linear Regression of cadmium concentration in lettuce and cadmium concentration in soils for data derived from Wolnik (1983ab) (USDA1975) and Figure 55 (CDFA2002)

Lead In the Oxnard and Ventura Area, the lead content of soils had been affected by inputs from diffuse sources. The lead content of plant tissues varied from 0.18 mg kg⁻¹ in lettuce to over 2 mg kg⁻¹ in leaves of broad beans and their concentrations in the leaf tissue were not correlated to the phosphorus and zinc concentrations of the soils (Figure 57). In the figure, the concentrations of each plant species appeared to form a cluster of its own. Nevertheless, the concentrations were within the range we normally expect to find in plant tissues (Kabata-Pendias, 2001).

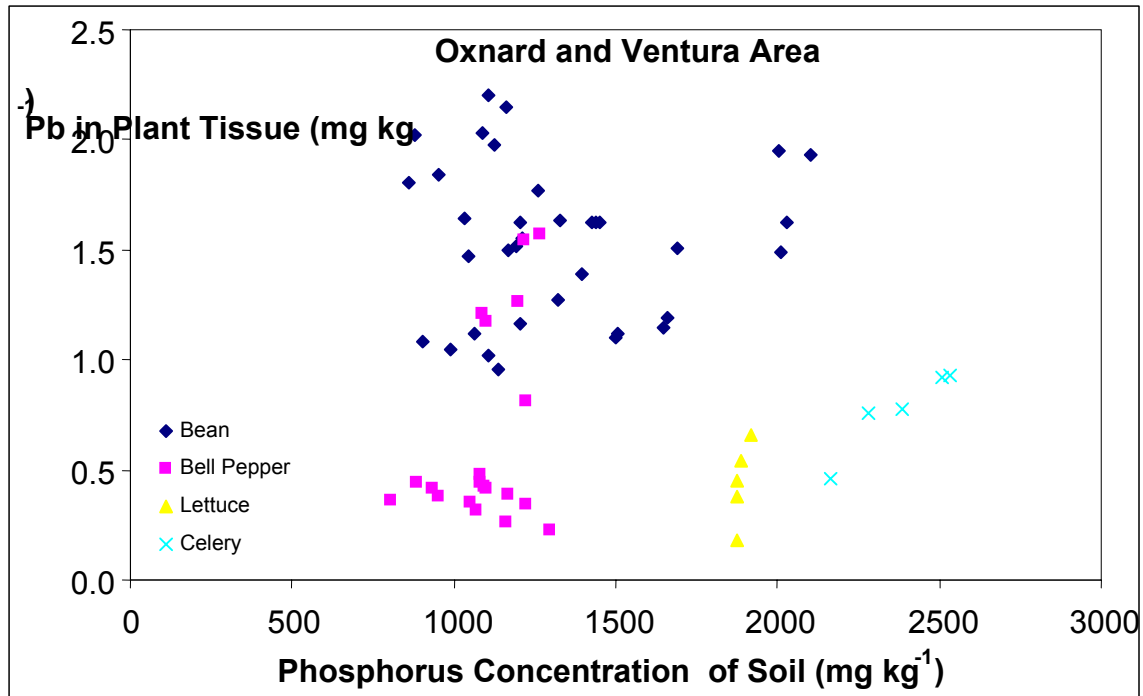


Figure 57. Lead Concentration of Plants (leaf tissue) in Relation to the Phosphorus Concentrations of Soils, Oxnard and Ventura Area

It is obvious that the lead content of sampled plants have not been affected by the applications of phosphorus fertilizers and micronutrients. Even when the lead contents of plant tissue were plotted against the soil lead concentrations, there was little evidence that they might be affected by the soil lead levels (Figure 58).

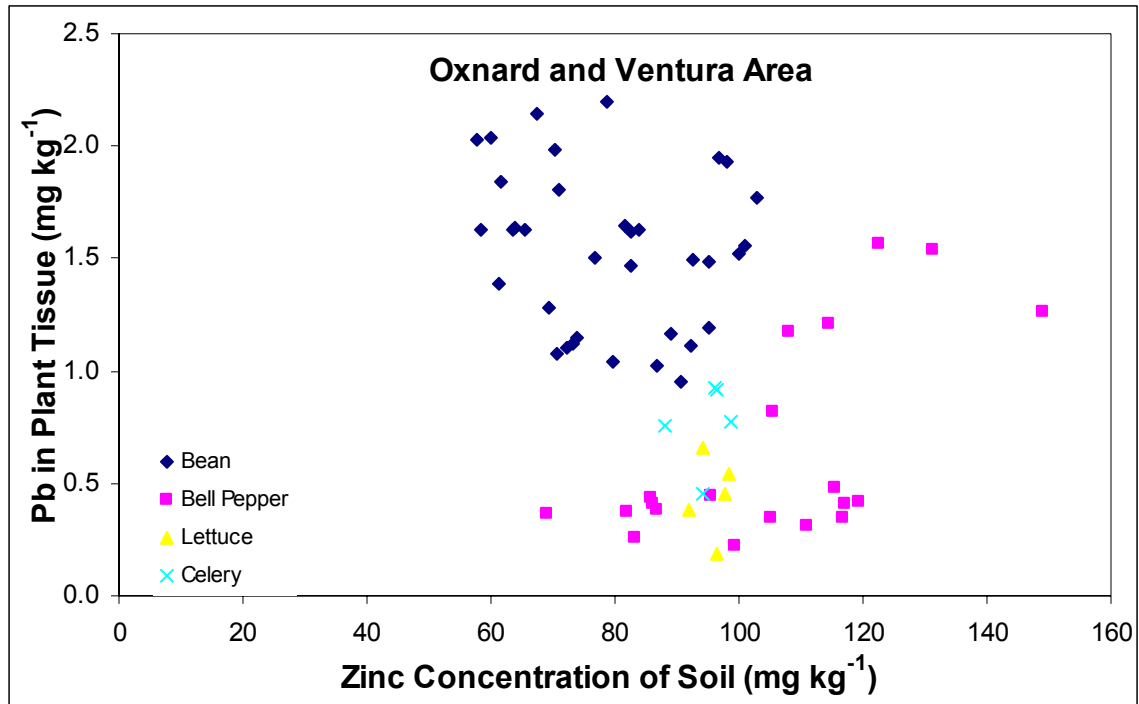


Figure 58. Lead Concentration of Plants (leaf tissue) in Relation to the Zinc Concentrations of Soils, Oxnard and Ventura Area

Like the Oxnard and Ventura Area, the lead content of the soils in the Santa Maria/ San Luis Obispo Valley had been affected by diffuse sources, and as a group shifted upward against the baseline levels. At present, the lead levels in some of the soils had exceeded baseline range while a majority of the population remained within the baseline range. The lead content of the plant tissues varied from approximately 0.2 mg kg⁻¹ for leaves of sweet corn to >4 mg kg⁻¹ for broccoli leaves. The concentrations were within the range normally expected for the plant tissues, and there is no indication that the phosphorus fertilizer and micronutrient applications affected the outcomes (Figures 60 and 61). The lead content of the plant tissues also were not related to the lead concentrations of the soils (Figure 62).

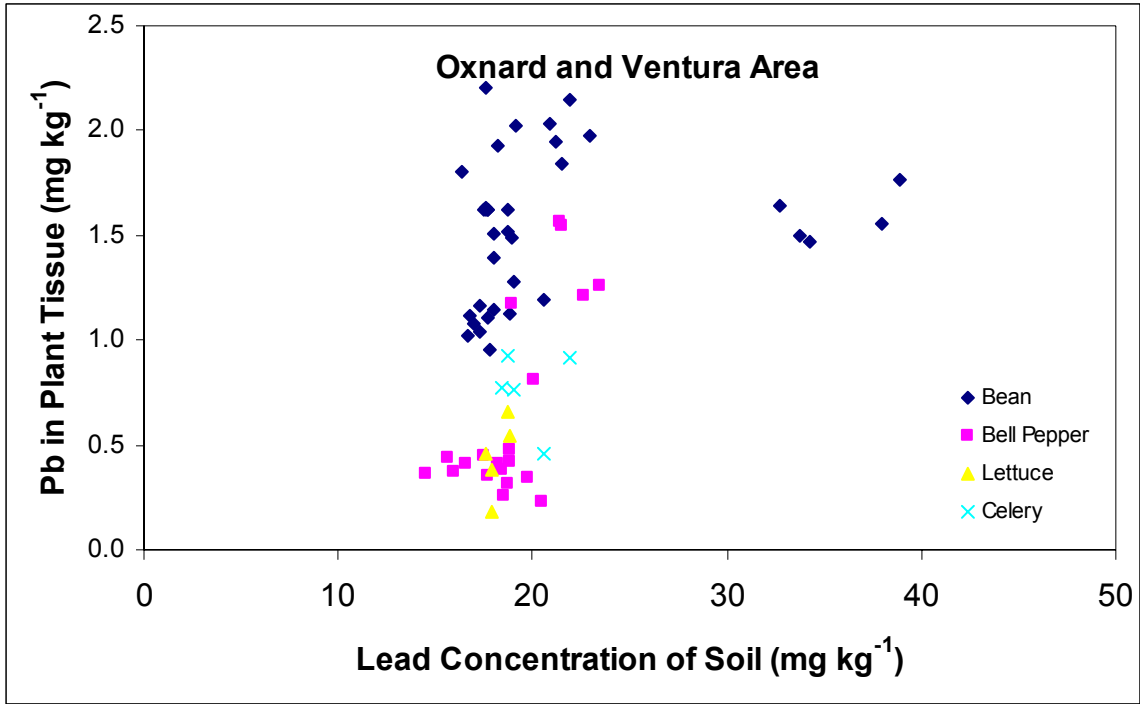


Figure 59. Lead Concentrations of Plants (leaf tissue) in Relation to the Lead Concentrations of Soils, Oxnard and Ventura Area

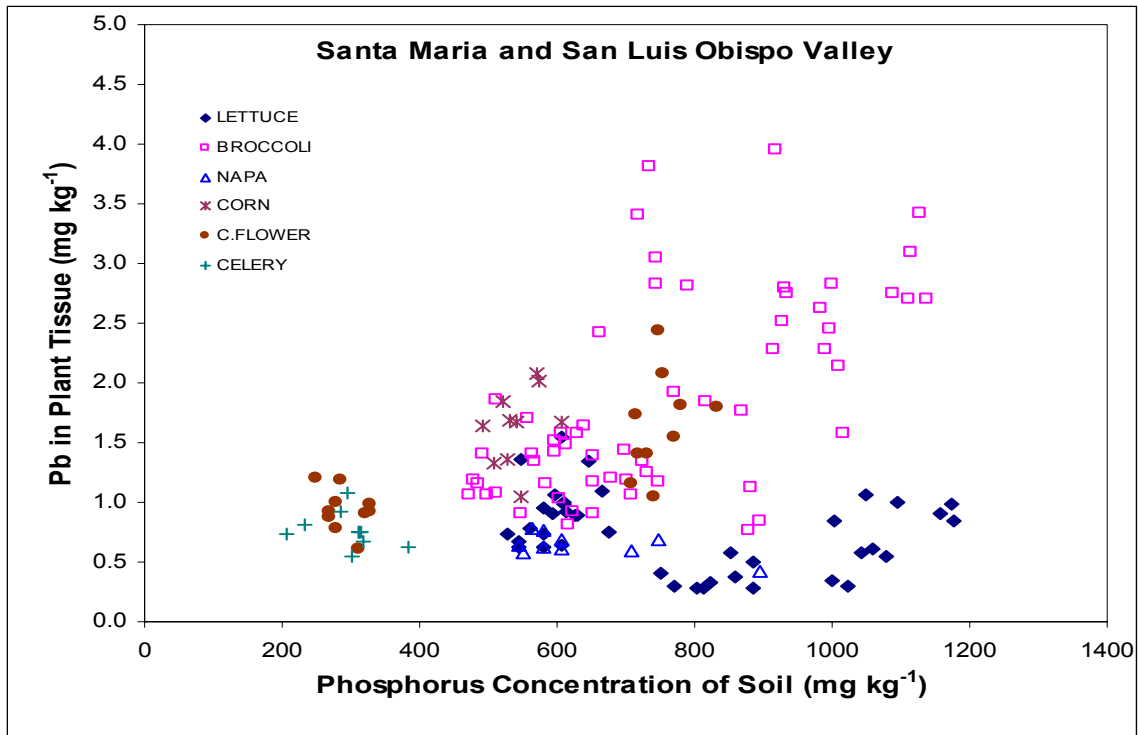


Figure 60. Lead Concentrations of Plants (leaf tissue) in Relation to the Phosphorus Concentrations of Soils, Santa Maria and San Luis Obispo Valley

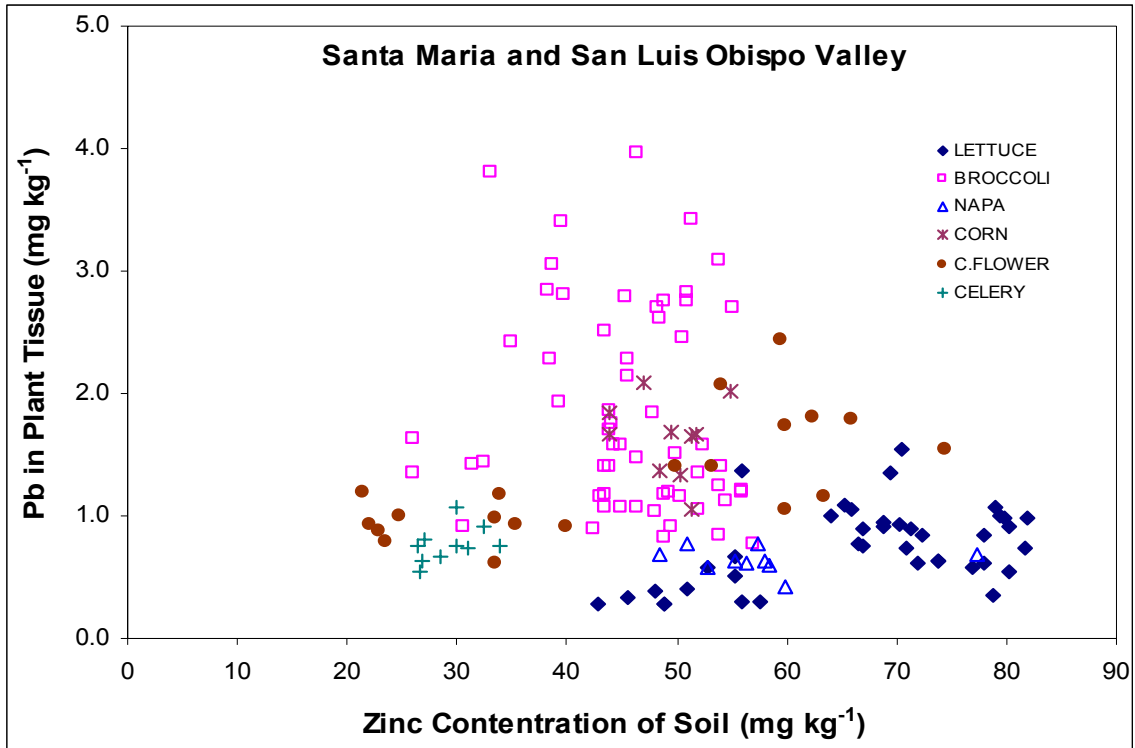


Figure 61. Lead Concentrations of Plants (leaf tissue) in Relation to the Phosphorus Concentrations of Soils, Santa Maria and San Luis Obispo Valley

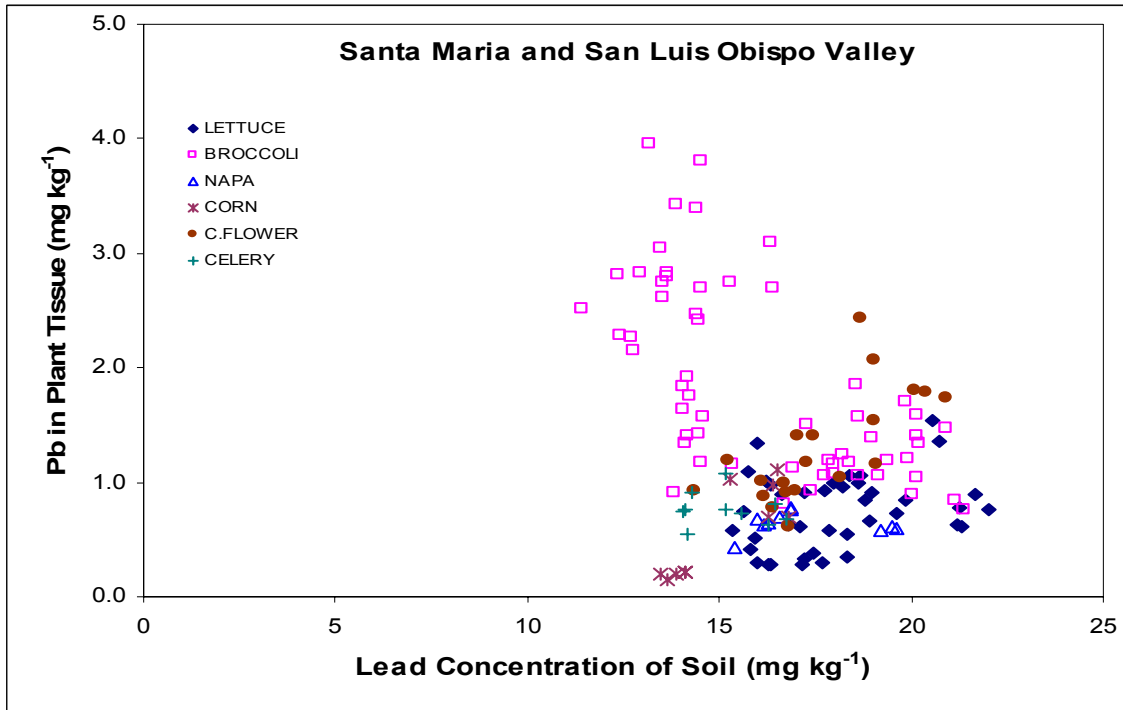


Figure 62. Lead Concentrations of Plants (leaf tissue) in Relation to the Lead Concentrations of Soils, Santa Maria and San Luis Obispo Valley

Zinc Zinc is a primary ingredient in micronutrient supplements used in crop production. In both the Oxnard and Ventura Area and the Santa Maria and San Luis Obispo Valley, the zinc contents of plant tissues were not related to the zinc concentrations of soils (Figures 63 and 64). It appeared that the concentrations of a plant species form a cluster of their own and for the same plants, their concentrations were different in the two production regions.

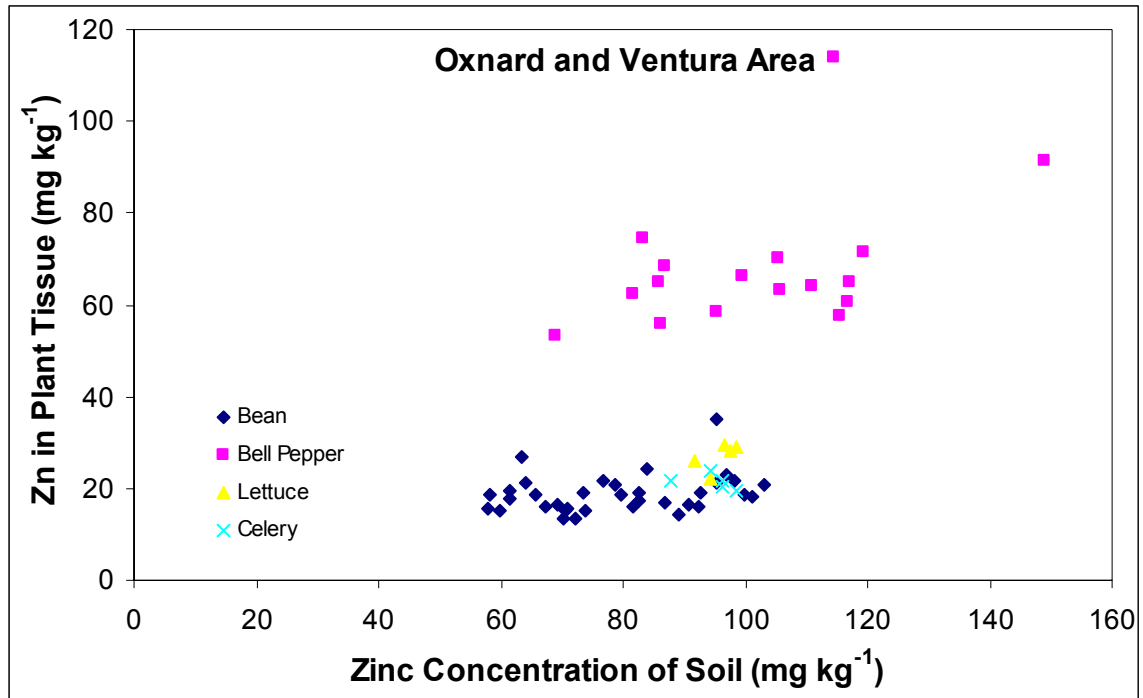


Figure 63. Zinc Concentrations of Plants (leaf tissue) in Relation to the Zinc Concentrations of Soils, Oxnard and Ventura Area

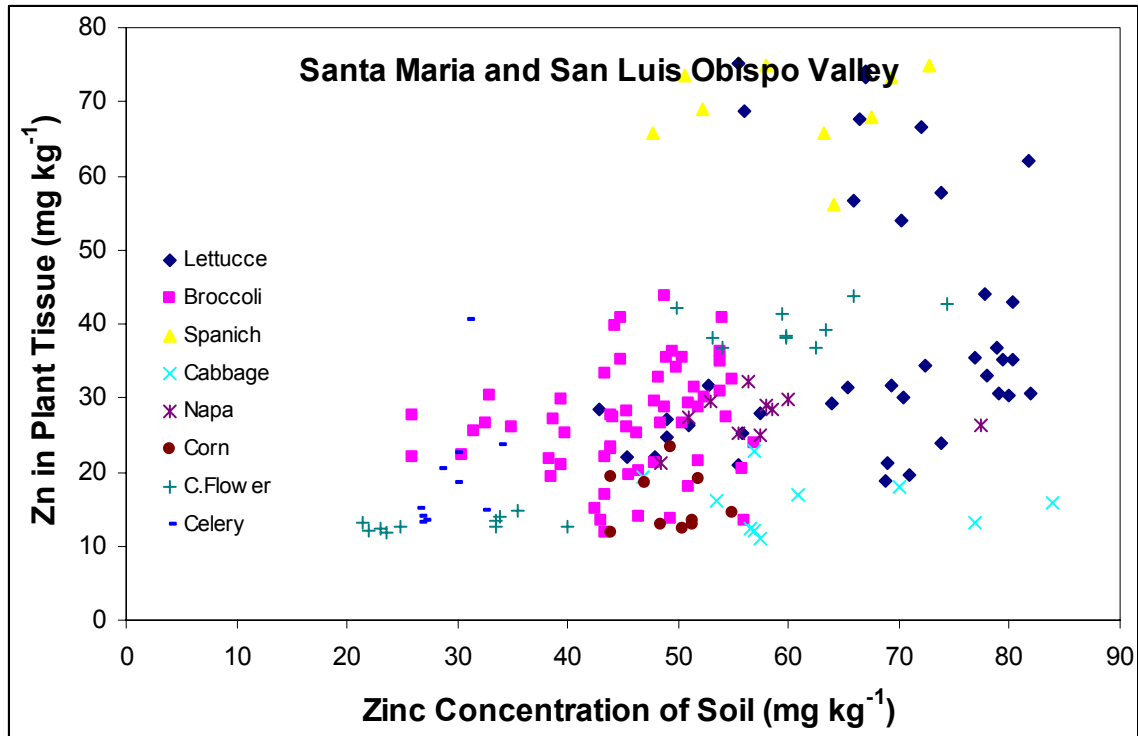


Figure 64. Zinc Concentrations of Plants (leaf tissue) in Relation to the Zinc Concentrations of Soils, Santa Maria and San Luis Obispo Valley

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