CALIFORNIA DEPARTMENT OF FOOD & AGRICULTURE ▪ DIVISION OF INSPECTION SERVICES ▪ AGRICULTURAL COMMODITIES AND REGULATORY SERVICES BRANCH

Evaluation of HEAVY METALS & DIOXIN in Inorganic Commercial Fertilizers and California Cropland Soils

CALIFORNIA DEPARTMENT OF FOOD & AGRICULTURE

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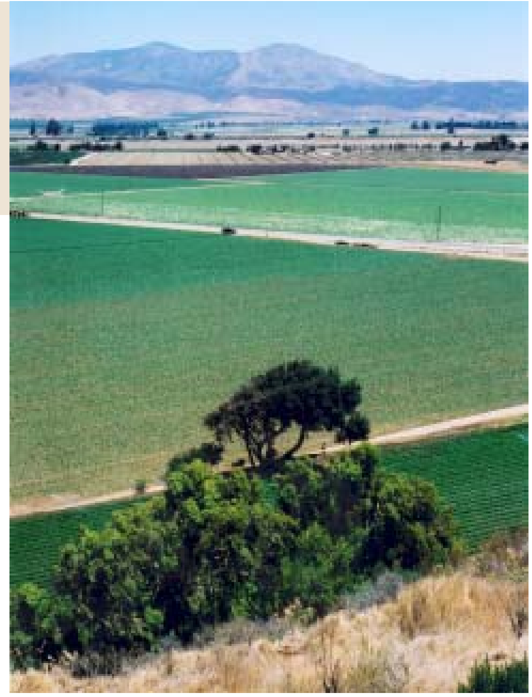
in Inorganic Commercial Fertilizers and California's Cropland Soils



Looking eastward across the Salinas Valley.

Executive Summary

In January 2002, the California Department of Food and Agriculture (CDFA) implemented regulations limiting the addition of arsenic (As), cadmium (Cd), and lead (Pb) to cropland through applications of inorganic commercial fertilizers containing micronutrients (iron [Fe], manganese [Mn], and zinc [Zn]) and phosphate.

These regulations were prompted by concerns about human health and the environment arising from the use of fertilizers that could contain excessive amounts of As, Cd, and Pb. In setting the regulatory limits, the department utilized outcomes of risk-based estimates and relevant data in the technical literature.

The risk assessment process, the model, and the assumptions were peer reviewed twice and found to be acceptable, with the caviat that modeling did not use soil data that were fully representative of California's agricultural soils. There was a concern that background soil concentrations of As, Cd, and Pb measured in 1967 did not necessarily account for the intensely cultivated and fertilized cropland soils found in California today. Concerns were expressed by environmental groups that As, Cd, and Pb might have accumulated in cropland soils through applications of phosphate fertilizers and micronutrients, allowing their concentrations to increase since the 1967 measurements were taken. Therefore, they contended, the harvested crops could have contained higher amounts of the contaminants than the outcomes predicted by the model.

In estimating soil solution concentrations, the department used assumptions based on highly contaminated, non-agricultural soils. These concentrations, in turn, were used to estimate how much of the three contaminants plants would draw from the soil (plant uptake factors). Because they could not be certain how much As, Cd, and Pb were in soils, the risk assessors assumed that the cropland soils were comparable to the heavily contaminated soils represented in a worst-case scenario. The assessors concluded that the outcomes produced under this assumption would be protective when crops raised on these soils were consumed by humans and animals. This assumption was deemed overly conservative.

However, the plant uptake factors (PUFs) used in the risk assessment model did not correspond to high concentrations of metals in the soil solution for plant uptake. There were concerns that the data employed in the risk-based assessment were not representative of agricultural soils and that risk would be overestimated.

Since completing the regulations, CDFA has validated assumptions used in the risk assessment model by field research. Studies of crops and cropland soils by UC Riverside indicate that the actual concentrations of metals in the soil and plant tissues are considerably lower than those used in the risk assessment model. Therefore, the research suggests that the actual risks should be significantly lower than the risks expressed in the risk assessment model.

A soil survey by UC Riverside reassessed the concentrations of As, Cd, and Pb in the benchmark soils in 2001. The results indicate that increased levels of metals are insignificant and the use of 1967 data is still valid, so there is no need to correct the baseline concentrations used in the risk assessment model. In addition, micronutrient fertilizers and soils were tested for dioxins. Testing was performed by the Department of Toxic Substances Control at its Hazardous Materials Laboratory. The results indicate that regulations are not necessary to set standards limiting dioxin-like (PCDD/Fs) compounds.

The department also has surveyed the presence of six other metals (cobalt, copper, mercury, molybdenum, nickel, and selenium) in phosphates, micronutrients and their blends to assess the necessities of limiting addition of these metals to cropland soils. The results indicate that concentrations of these metals are low in the products and there is no need to limit their addition to cropland soils.

CDFA considers the regulations to be protective of human health and the environment. Results of field research indicate that the risk-based concentrations are valid and the regulatory limits adopted in 2001 should remain in effect.

Rationale Employed in the Risk Assessment

As, Cd, and Pb Concentrations in Benchmark Soils

In the following tables, the arsenic, cadmium, and lead concentrations of benchmark soils collected in 1967 and 2001 were compared. The paired sets of data offer snapshots showing the changes over a 35-year period. Results of statistical analysis showed that the arsenic, cadmium, and lead concentrations of benchmark soils in 2001 were not significantly different from those of the 1967. Therefore, CDFA concludes that the benchmark soil concentrations in 1967 are still valid and there is no need to correct for the baselines.

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

Fog sets in on a Northern California hayfield.

As, Cd, and Pb Accumulation in soils of Vegetable Production Regions in California

A survey of As, Cd, and Pb concentration in soils of seven vegetable-production regions of California indicates the following:

- The As concentrations are mostly within the baseline concentrations. Only in two regions, Santa Maria/San Luis Obispo valley and Colusa/Glen County, As concentrations exceed the baseline concentrations due to inputs other than phosphorus and micronutrient sources (diffused sources).
- The Cd concentrations have increased in five out of seven regions and remained within baseline in two regions in California. The elevated concentrations, however, are due to other inputs in four regions (diffused sources). Only in the Oxnard/Ventura region, the elevated concentrations are from phosphorus fertilizer addition.
- The Pb concentrations are mostly within the baseline concentrations. Only in three regions did Pb concentrations exceed the baseline concentrations due to inputs other than phosphate and micronutrients.
- Even in regions where the arsenic, cadmium, and lead contents of the cropland soils have shifted upwards in reference to the baseline, concentrations in a majority of the samples examined remained within the background ranges.

Contaminant Concentrations

Production Region	Arsenic	Cadmium	Lead
Oxnard/Ventura Area	Baseline	P Fertilizer	Diffuse Sources
Santa Maria/ 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

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

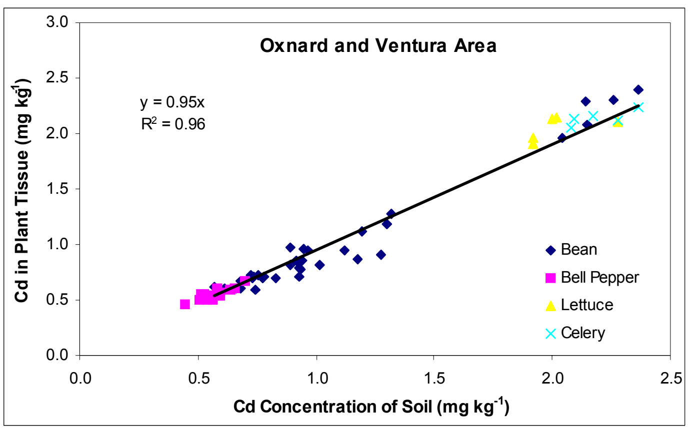
The concentrations of As, Cd, and Pb in the cropland soils are well within the range of soil concentrations used by Sauve et al. in determining the Kd for soils (Sauve, Sebastien; Hendershot, William; and Allen, Herbert E. Solid-solution Partitioning of Metals in Contaminated Soils: Dependence on pH, Total Metal

Burden, and Organic Matter. Environmental Science and Technology 34(7), 1125-1131, 2000). Therefore, the department concludes that the Kd constants used to calculate risk-based concentrations are valid at this time and protective of human health and the environment. The department has, however, commissioned a study to determine Kds for California cropland soils. A re-evaluation of risk-based concentration would be in order upon completion of the study.

As, Cd, and Pb Uptake by Crops in Vegetable Production Regions in CA

A limited number of leaf tissue samples of the crops were collected along with the soil samples in two of the seven regions, namely the Oxnard and Ventura Area, and Santa Maria and San Luis Obispo Valley. The limitations were a result of the crops not being available during soil sampling or growers not granting access for crop sampling. In terms of the As, Cd, and Pb contents in soils, these two regions are representative of farmland soils in California, since the As, Cd, and Pb concentrations in soils are mostly elevated relative to their respective baselines.

Plant Uptake of Cadmium



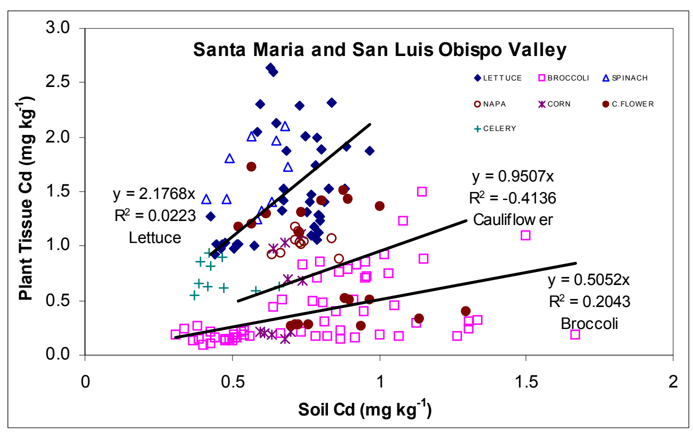
The plant tissue concentration of Cd in broad beans (n=35), bell pepper (n=20), lettuce (n=5), and celery (n=5) in the Oxnard/Ventura region indicates that:

- Plant uptake of Cd (Y) is linearly related to soil Cd (X) that (Y)= 0.95(X) with R^2= 0.96. Four different plant species sampled all lined up along the same regression line. The regression line provides the plant uptake factors for these crops. A comparison of the slope of this line (0.95) to the PUFs used in the risk assessment model reveals that the uptake of Cd by these crops is well within the range of values used to calculate the risk-based concentrations (Appendix D in the risk assessment study).

Rows of iceburg lettuce near Monterey.

The plant tissue concentration of Cd in lettuce (n=40), broccoli (n=60), spinach (n=10), Napa Cabbage (n=10), sweet corn (n=10), cauliflower (n= 20), and celery (n=10) in Santa Maria/San Luis Obispo indicates:

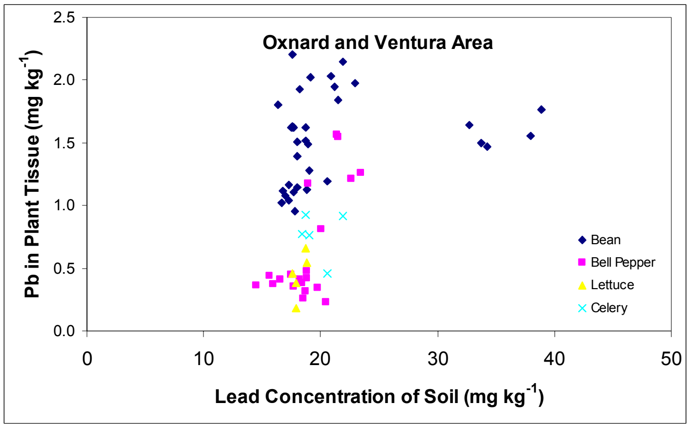
- Plant uptake of Cd (Y) is not linearly correlated to the soil Cd (X). The tissue concentration fell in a rather narrow range and did not allow the trend to be fully established. However, if the lettuce data from this study is pooled with the USDA Holgrem data to redo the regression calculation, a correlation becomes apparent. The plant tissue (Y) = 2.17(X) with R^2=0.49. The linear regression is considered to be significant since the range of soil Cd was much wider. A comparison of the slope of this line (2.17) as plant uptake factors for these crops, with the PUFs used in the risk assessment model, reveals that the uptake of Cd by these crops is well within the range of values used to calculate the risk-based concentrations.

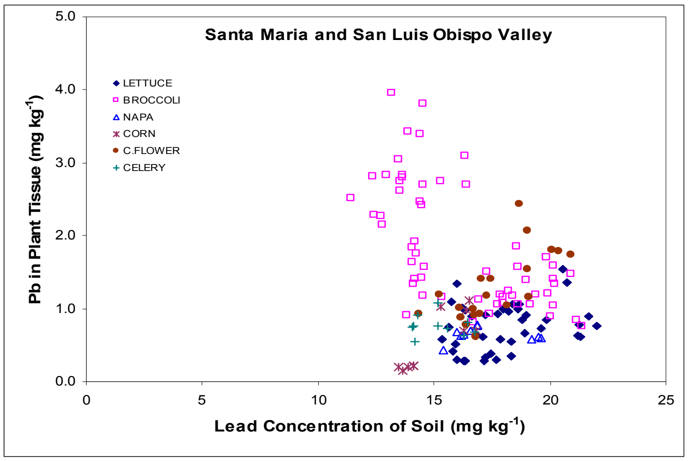


Plant Uptake of Arsenic

The arsenic concentrations of the leaf tissues were less than 0.1 mg kg^{-1} dry weight. Therefore, crops do not take up significant amounts of As.

Plant Uptake of Lead





The Pb concentration of Oxnard and Ventura soils has increased because of input from diffused sources not related to fertilizer and micronutrient applications. The crop tissue tests, however, indicate that Pb concentration in plant tissue of crops does not correlate to Pb concentration in soils, and on the graph the data for plant species tended to form clusters of their own. It appeared that the Pb concentration in plant tissue is species-specific and not significantly related to the lead contents of soils.

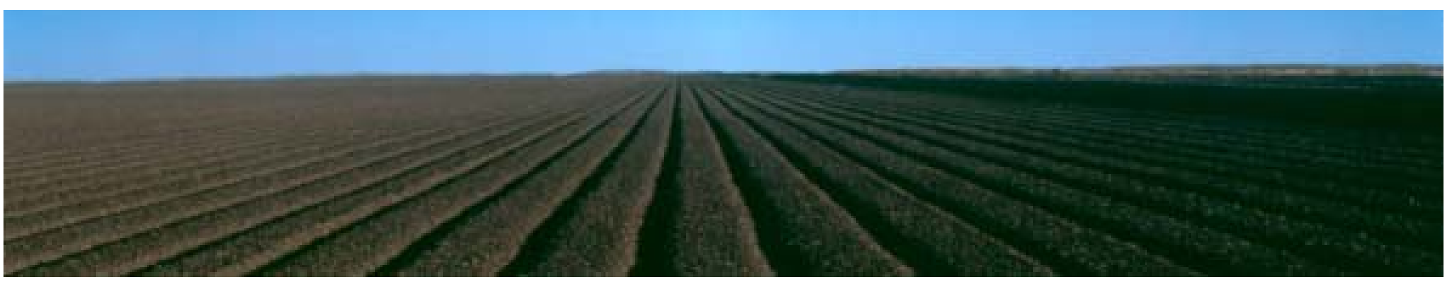
Therefore, the department concludes that the PUFs used to calculate risk-based concentration are valid at this time and protective of human health. The department has, however, commissioned a study to determine PUFs utilizing California cropland soils. A reevaluation of risk-based concentration will be done once the PUFs are available.

As, Cd, and Pb, in Phosphate, Iron, Manganese, and Zinc Products

The CDFA has monitored the concentrations of As, Cd, and Pb in phosphate, micronutrients, and their blended products, totaling 721 samples during 1999 to 2004. The data is very skewed (see the distribution table). Thus, the distributions are described in terms of median and percentiles. The median value for As in all products is 2 ppm, Cd in all products is 4 ppm, and Pb in all products is <10 ppm. These concentrations are relatively low, and consistent with industry's practice of distributing cleaner phosphate sources for California, as well as the elimination of the K061 (Electric Arch Furnace Dust) recycled hazardous waste for manufacturing of zinc products. Also, the U.S. Environmental Protection Agency has promulgated threshold limits for As, Cd, and Pb in Zn fertilizers derived from hazardous waste. Therefore, the department believes that the standards adopted in 2002 over-estimates the risk to human health and the environment because the metals additions to soils are at a much lower rate than accounted for in the original risk assessment study. Even though phosphate, iron, manganese, and zinc products were not responsible for the elevated concentrations of As, Cd, and Pb in most of the regions studied, the department wants to safeguard against further addition of metals to cropland soils. The regulatory limits adopted in 2002 are valid and there is no need to make adjustments based upon metals loading rates.

As, Cd, Pb Distributions During 1999-2004

Metal/Product	# Samples	Median	Percentile				
			75%	90%	95%	99%	100%
			parts per million, ppm				
As Blend	381	2	4	6	8	13	33
As Micronutrient	211	<1	1	9	24	80	3400
As Phosphate	128	7	13	18	23	36	190
As All	720	2	5	11	16	37	3400
Cd Blend	381	6	30	50	67	90	100
Cd Micronutrient	212	<2	9	23	40	160	4200
Cd Phosphate	128	27	115	150	170	230	270
Cd All	721	4	28	67	113	180	4200
Pb Blend	381	<10	<10	16	70	440	2500
Pb Micronutrient	212	<10	11	200	550	7900	27900
Pb Phosphate	128	<10	<10	<10	14	33	40
Pb All	721	<10	<10	28	120	2900	27900



Central Valley soil.

Dioxin in Iron, Manganese, and Zinc Products and Soils in California

Very low levels of PCDD/Fs were found in micronutrient supplement products (only one sample exceeded EPA's 8 pg/g I-TEQ). The levels detected in these micronutrient products are in agreement with results from similar work conducted by the State of Washington. The sample with the highest PCDD/Fs (17.4 ug/g I-TEQ, mostly furans) had the highest As (44 ug/g) and Pb (3000 ug/g) content but its Zn content was near the median of all the 10 samples analyzed. Zinc is not a good indictor for dioxin in micronutrients. However, Pb and As might be.

PCDD/Fs in this cross-sectional survey of California soils showed that the concentrations of dioxin-like compounds of benchmark soils and cropland soils were comparable. In both cases, the concentration in one of the soils exceeded the US EPA's threshold of 8 pg g^{-1}. For the benchmark soils, the concentrations did not appear to be related to the proximity of urban and industrial developments. The site with the higest I-TEQ concentration (24.40 pg g^{-1}) was located in the Mojave Desert while the I-TEQ concentration of soil at a site in the midst of San Diego's high tech industrial park was measured as 4.30 pg g^{-1}. For the cropland soils, the I-TEQ concentrations were not related to either phosphorus or Zn contents of the soils. The soils with the highest phosphorus (2233 mg kg-1) and Zn (118 mg kg^{-1}) contents had I-TEQ concentrations of 5.46 and 7.82 pg g^{-1}, respectively. The highest I-TEQ concentration (17.30 pg g^{-1}) was associated with the soil that contained 571 and 67 mg kg^{-1} of phosphorus and Zn, respectively. Based upon this analysis, levels of dioxin in soils are not affected by use of micronutrients.

Levels of As, Cd, Pb, Zn, and I-TEQ in Micronutrient Supplements

Constituent	As (ug g^{-1})	Cd (ug g^{-1})	Pb (ug g^{-1})	Zn (ug g^{-1})	I-TEQ (pg g^{-1})
Number of Observations	20	20	20	20	10
Mean	4	12	404	275,160	4.27
Minimum	<0.1	<1	<1	20	1.2
Maximum	**44**	**70**	**3000**	**800,000**	**17.4**

Ranges of Typical Background Levels of Dioxin-like Compounds (I-TEQ) in Various Environmental Media

Media	I-TEQ (pg g^{-1})
Rural Soils	1 to 6
Urban Soils	7 to 20
Sediments	1 to 60

Concentration of Compounds (I-TEQ) in CA Soils

Category	Benchmark Soil	Cropland Soil
Number of Observations	10	20
Minimum (pg g^{-1})	2.48	1.77
Maximum (pg g^{-1})	24.40	17.30
Median (pg g^{-1})	5.73	4.52
Mean (pg g^{-1})	7.44	5.04
Standard Deviation (pg g^{-1})	6.51	3.56

Therefore, the department does not anticipate any adverse impact from the addition of such low dioxin levels to cropland soils, and regulations need not be established to set standards for dioxin.

Chemist Charlie Li of the California Department of Toxic Substances Control's Hazardous Materials Laboratory performs soxhlet extraction.

Carrots harvested near Coachella, CA.

Distribution of Cobalt, Copper, Mercury, Molybdenum, Nickel, and Selenium in Products

Phosphate, micronutrient, and blended products (381 samples total) were surveyed during 1999-2001 for concentration of six other metals of potential concern. The survey reveals that these metals are present at low concentrations in products (see distribution table). The median concentration in all products for cobalt is 1 ppm, for copper is 13 ppm, for mercury <0.1 ppm, for molybdenum is <10 ppm, for nickel is 9 ppm, and for selenium is 0.2 ppm. The analysis of these results indicates that there is no potential concern from addition of these metals to cropland soils. Therefore, regulations need not be established to set standards for these metals.

Heavy Metals Distributions During 1999-2001

Metal/Product	# Samples	Median	Percentile				
			75%	90%	95%	99%	100%
			parts per million, ppm				
Co Blend	209	<1	3	8	23	180	800
Co Micronutrient	112	3	22	72	92	1000	1700
Co Phosphate	60	2	4	5	7	10	12
Co All	381	1	4	23	40	380	1700
Cu Blend	209	15	84	600	1000	6000	21000
Cu Micronutrient	112	6	30	380	2100	26800	48800
Cu Phosphate	60	19	60	80	90	530	6900
Cu All	381	13	60	500	1100	11200	48800
Hg Blend	209	<0.1	<0.1	<0.1	<0.1	4	0.5
Hg Micronutrient	108	<0.1	<0.1	<0.1	0.1	3	3
Hg Phosphate	60	<0.1	<0.1	<0.1	<0.1	0.1	0.3
Hg All	374	<0.1	<0.1	<0.1	<0.1	0.5	3
Mo Blend	209	<10	<10	10	17	60	1100
Mo Micronutrient	112	<10	<10	<10	10	120	260
Mo Phosphate	60	10	15	20	20	22	23
Mo All	380	<10	<10	13	20	60	1100
Ni Blend	209	4	23	80	110	150	1813
Ni Micronutrient	112	15	45	130	190	530	990
Ni Phosphate	60	31	139	200	230	260	270
Ni All	381	9	44	120	170	350	1813
Se Blend	209	0.2	0.4	2	5	30	120
Se Micronutrient	112	0.3	2	10	20	70	80
Se Phosphate	60	0.2	0.6	1	4	22	29
Se All	373	0.2	0.8	4	10	44	120

Harvesting sweet corn for sale at a farmers market.

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