POTENTIAL ROLES OF FERTILIZER AND MICRONUTRIENT SUPPLEMENT APPLICATIONS ON PCDD/Fs AND TRACE ELEMENTS IN CALIFORNIA AGRICULTURAL SOILS.

Myrto Petreas[1], Charlie Li[1], Joginder Dhaliwal[1], F.Reber Brown[1], N.J. Krage[2], Maryam Khosravifard[3], Andrew Chang[2]

[1]Hazardous Materials Laboratory, California Department of Toxic Substances Control, Berkeley, CA 94704
[2]Department of Environmental Sciences, University of California, Riverside, CA 92521
[3]Agricultural Commodities & Regulatory Services, California Department of Food and Agriculture, Sacramento, CA 95814

Introduction

Concerns have been raised on whether trace elements and dioxins associated with waste-derived fertilizer and micronutrient supplement products may, upon long term use, pose a threat to human health and the environment. There are reports[1] showing dioxins in micronutrient supplements and liming products made from recycled industrial wastes. In 2002, the USEPA issued regulations limiting PCDD/F content in waste derived micronutrient products to 8 pg/g TEQ. Also in 2002, California issued regulations limiting the levels of As, Cd, and Pb in fertilizer products, while efforts in developing national standards are pending. In this study we examined the potential contribution of waste-derived fertilizers and micronutrient supplements to PCDD/F, As, Cd, and Pb concentrations in California agricultural soils.

Methods

We determined As, Cd, and Pb concentrations in surface soil samples from 50 benchmark locations sampled throughout California in 1967 and again in 2001. Benchmark soils are representative of soils in California and sampling locations were identified in the 1950s as sites undisturbed by intensive cultivations. In addition to benchmark soils, trace elements were measured in over 650 surface soil samples (0-20 cm in depth) collected from vegetable production fields in seven agricultural regions in 2001. Fertilizer and micronutrient applications vary by region and crop and there are no reporting requirements for their use. Concentrations of P and Zn were used as indicators of the amount of fertilizers and micronutrient supplements that had been applied. Concentrations of PCDD/Fs were determined in a subset of 50 composite samples, selected among the benchmark soils and the agricultural regions, based on high/low content of indicator elements (P, Zn). Additionally, 15 samples of commercial micronutrient supplements (Zn-enriched) were analysed for trace elements, and 5 of these samples were also analysed for PCDD/Fs. All the micronutrient supplement samples were manufactured prior to 2002, the year regulations were introduced. PCDD/Fs were determined by standard HRMS methods (HML SOP 880)[3]. For trace element determinations, aliquots of soils were dissolved by microwave assisted acid digestion following US EPA Method 3052[4] and the elemental contents in the solution were determined by graphite furnace atomic absorption spectroscopy.

Results and Discussion

The levels detected in these micronutrient supplement products are in agreement with results from similar work conducted by the State of Washington[1]. Overall, very low levels of PCDD/Fs were found in micronutrient supplement products (Table 1). One of the micronutrient supplement samples, however, exceeded the recently introduced regulatory limit of 8 pg/g. The sample with the highest PCDD/Fs (17.4 pg/g I-TEQ, mostly furans) also had the highest As (44 ug/g) and Pb (3000 ug/g) content, but its Zn content was near the median of all the 15 samples analysed so far. Additional work is under way to determine whether manufacturers have modified their products since the introduction of regulations. Concentrations of PCDD/Fs in agricultural and benchmark soil samples (preliminary data, Table 2) were very low ranging from 1.8 pg/g to 5.5 pg/g. Concentrations of PCDD/Fs in this cross sectional survey of California agricultural soils appear to be well within the USEPA's estimates for rural soils[5].

In cropland production systems, there are many potential sources of contaminant inputs namely irrigation, pesticide application, waste disposal, and atmospheric fallout, and their contributions to the build-up in soils may be far more significant than fertilizer applications[2]. Our data showed that the As, Cd, and Pb levels in the benchmark soils in California have not changed significantly from 1967 to 2001 (Table 3). The comparison of the 1967 and 2001 samples provides a snapshot on changes in trace element concentrations in California soils over the last 34 years. While soil trace element contents in most agricultural production sites investigated are well within the ranges of their respective baselines (i.e., background concentrations at 1.5-2 m soil depth of respective sites), As, Cd and Pb concentrations in some sites of the more intensely cultivated agricultural regions have risen above the background (Table 4). The trace element concentrations in these soils would rise in proportion to the soil P and/or Zn concentrations if the accumulations were the result of applying phosphate fertilizers and/or Zn micronutrient supplements. When this hypothesis was tested separately against the data collected in each agricultural region, there was little evidence that the fertilizer and micronutrient supplements have caused the increases.

References

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Acknowledgement

This work was partially funded by the California Department of Food and Agriculture (CDFA). We thank Mr. Stephen Mauch of CDFA for overseeing this project. The Center for Analytical Chemistry of CDFA performed the elemental analysis of the soil amendments. The authors' views do not necessarily express the views of the California State Government.

Table 1. Levels of As, Cd, Pb, Zn and I-TEQ in Micronutrient Supplements

	As (μg g^{-1})	Cd (μg g^{-1})	Pb (μg g^{-1})	Zn (μg g^{-1})	I-TEQ (pg/g)
n	15	15	15	15	5
Mean	5.3	11.6	521	226,415	5.2
SD	12.6	17.7	1077	201,555	6.8
Median	0.1	4.0	6	179,000	2.2
Min	<0.1	<1	<1	20	1.9
Max	44	70	3000	793,000	17.4

Table 2. I-TEQ Levels (pg/g) in California Agricultural Soils (n=15)

Mean	SD	Median	min	max
2.88	1.05	2.61	1.77	5.51

Table 3. As, Cd, and Pb Concentrations of California Benchmark Soils

Year	As (μg g^{-1})		Cd (μg g^{-1})		Pb (μg g^{-1})	
	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD
1967	1.8 – 20.5	8.8 ± 4.3	0.03 – 0.44	0.18 ± 0.10	3.6 – 25.0	12.0 ± 5.3
2001	1.8 – 16.6	7.6 ± 3.9	0.07 – 0.53	0.22 ± 0.11	4.9 – 26.8	14.6 ± 5.5

Table 4. **As, Cd, and Pb levels in California Agricultural Soils (0-20 cm bgs) and Baseline soils (1.5 m bgs) from the same region**

A. Arsenic

Region	Baseline (μg g^{-1})	Agricultural Soils (μg g^{-1})
A	5.3 – 9.8	4.7 – 11.0
B	1.3 – 6.7	3.3 – 13.3
C	3.4 – 5.5	1.2 – 5.4
D	3.8 – 10.9	4.9 – 11.5
E	4.7 – 11.8	3.0 – 14.5

B. Cadmium

Region	Baseline (μg g^{-1})	Agricultural Soils (μg g^{-1})
A	0.27 – 0.77	0.45 – 2.38
B	0.21 – 0.84	0.31 – 1.67
C	0.11 – 0.18	0.19 – 0.90
D	0.17 – 0.32	0.25 – 0.50
E	0.13 – 0.28	0.25 – 0.65

C. Lead

Region	Baseline (μg g^{-1})	Agricultural Soils (μg g^{-1})
A	10.6 – 14.2	14.5 – 38.9
B	5.8 – 18.8	11.4 – 22.0
C	14.3 – 30.2	9.2 – 21.7
D	14.0 – 31.7	13.5 – 24.0
E	13.4 – 16.3	13.6 – 62.2