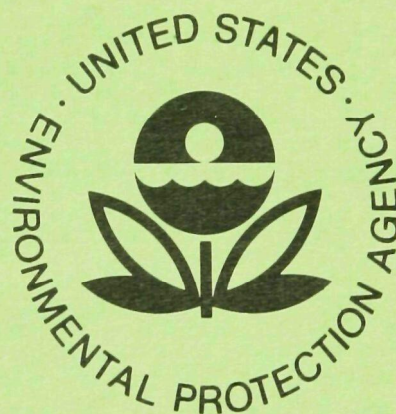


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PLANT UPTAKE OF CADMIUM FROM PHOSPHATE FERTILIZER



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PLANT UPTAKE OF CADMIUM FROM PHOSPHATE FERTILIZER

by

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CONTENTS

	<u>Page</u>
List of Figures	iv
List of Tables	v
Acknowledgements	vi
I Introduction	1
II Conclusions	2
III Recommendations	3
IV Materials and Methods	4
V Results and Discussion	9
VI References	24
VII Appendix A	25
Synthesis of Cadmium Dihydrogen Phosphate	
Appendix B	26
List of Data Tables	

LIST OF FIGURES

	<u>Page</u>
1. Cadmium concentration in radishes grown on Westport fine sand as a function of Cd in concentrated super phosphate fertilizer (CSP).	11
2. Cadmium concentration in lettuce grown on Westport fine sand as a function of Cd in concentrated super phosphate fertilizer (CSP).	12
3. Cadmium concentration in peas grown on Westport fine sand as a function of Cd in concentrated super phosphate fertilizer (CSP).	13
4. Cadmium concentration in radishes grown on Virtue silt loam as a function of Cd in concentrated super phosphate fertilizer (CSP).	14
5. Cadmium concentration in lettuce grown on Virtue silt loam as a function of Cd in concentrated super phosphate fertilizer (CSP).	15

LIST OF TABLES

		<u>Page</u>
1.	Characteristics of soils used in the Cd uptake experiment.	5
2.	Treatment materials, amounts and method of application for Cadmium uptake experiment.	6
3.	Cadmium levels resulting from treatments 1-7 of the Cd uptake experiment ($\mu\text{g Cd/g soil}$).	7
4.	Factors and levels used in Treatments 7-14.	7
5.	Dry matter percentage, dry weight yields, and plant P concentrations for treatments 1-7 of Cd uptake experiment. Values represent means of 14 pots.	10
6.	Summary of the slope and intercepts of the regression of plant Cd concentration on Cd added in fertilizer, and percentage of added Cd found in plants.	17
7.	Cadmium concentrations in plants grown on Westport fine sand as affected by fertilizer material, placement and source of Cd.	19
8.	Cadmium concentration in plants grown on Virtue silt loam soil as affected by fertilizer material, placement and source of Cd.	20
9.	Summary of means of major placement and fertilizer material effects on dry matter yields.	21
10.	Summary of means of major placement and fertilizer material effects on plant phosphorus concentrations.	22

ACKNOWLEDGEMENTS

This investigation was made possible by the contributions and support of many people. Among others we would like to acknowledge the help of Dr. Gerald Simmonson of the Oregon State University Soil Science Department and Fred Gilderman and Burrell Lovell of the USDA Soil Conservation Service for assistance in obtaining the soils.

We would particularly like to thank Dan Krawczyk and the personnel of the CERL Laboratory Services Branch for their effort in providing the analyses of the plant samples and Ron Silberman for his help with the statistical analyses.

The investigation was suggested by Region 10 personnel. Fertilizer samples were obtained by Carolyn Wilson of the Region 10 office, who also made valuable suggestions concerning the manuscript, as did Dr. Dave Tingey of the CERL. Fertilizer analyses were performed by the Region 10 laboratory. Seeds were furnished by Northrup King.

SECTION I

INTRODUCTION

The cadmium (Cd) content of phosphate ores used in fertilizer manufacture is highly variable. Values of 130 mg Cd per kg for ores from the western United States as compared to 9 mg/kg for Florida ores have recently been published (Anon. 1974). In 11 samples of 18-46-0 (N, P₂O₅, K₂O), presumably of Idaho origin, the Cd content ranged from 7.4 to 156 mg/kg.^{a/} Ten of the samples exceeded 50 mg/kg and 6 exceeded 125 mg/kg. Seven samples of 0-46-0 ranged from 86 to 114 mg Cd per kg.

A substantial body of literature is available concerning uptake of Cd by plants, but in most cases reported levels applied to the soil were much higher than would occur due to the Cd content of phosphate fertilizers. Reports of Schroeder and Balassa (1963) and Williams and David (1973) indicate that detectable amounts may be taken up from this source. This report describes an experiment conducted to evaluate uptake of Cd by some common food crop plants from phosphate fertilizers containing levels of Cd commonly encountered in materials manufactured from western ores. The work was undertaken in response to a request from the U.S. Environmental Protection Agency Region 10 personnel for assistance in evaluating the possibility of undesirable Cd levels in foodstuffs resulting from use of these fertilizers. Specific objectives of the project include:

- a. To provide information concerning the probability that plant Cd levels of biological significance to consuming organisms would occur as a result of use of high Cd fertilizers.
- b. To provide information concerning the effect of soil properties and the chemical form and placement of phosphate fertilizer on Cd uptake.

It was not possible to test a large number of soils for Cd uptake within the scope of this project. Therefore, it was decided to restrict these initial studies to two soils: (1) an acid coarse textured soil in which the activity of Cd²⁺ would remain relatively high and favor plant uptake and (2) a medium textured soil containing free CaCO₃ which would tend to depress Cd solubility and uptake.

The results reported here are preliminary and the data will be subjected to further analysis. Also considerable care is required in projecting greenhouse experiment results to field conditions.

^{a/} Unpublished data, U.S. Environmental Protection Agency, Region 10. Seattle.

SECTION II

CONCLUSIONS

1. Uptake of cadmium contained in phosphatic fertilizers by radish, lettuce and peas grown on a coarse textured acid soil was shown to be a linear function of the Cd concentration, at least over the range of 0.0 to 0.087 $\mu\text{g Cd per g soil}$. The Cd concentration in lettuce was over 6 $\mu\text{g/g dry weight}$ when fertilized at the rate of 100 $\mu\text{g P/g soil}$ with concentrated super phosphate (CSP) containing 174 $\mu\text{g Cd/g fertilizer}$ (0.087 $\mu\text{g Cd/g soil}$). Percentage of Cd in fertilizer recovered in the plants was 5.3, 9.0, and 2.0 for the radish (top plus root), lettuce (tops), and peas (foliage plus seeds), respectively. These uptakes may be of sufficient magnitude to be of biological significance to consumer organisms.
2. Uptake of Cd in fertilizer was also linear from a calcareous silt loam soil, but was much lower than from the acid sand. The Cd concentration in lettuce was 1.2 $\mu\text{g/g dry weight}$ when fertilized at the rate of 100 $\mu\text{g P/g soil}$ with CSP containing 174 $\mu\text{g Cd/g fertilizer}$ (0.087 $\mu\text{g Cd/g soil}$). Percentages of Cd recovered in the plants were 0.6 in radish and 0.8 in lettuce. Background levels on the calcareous silt loam soil were higher than those on the acid sand. Cd levels in peas grown on the calcareous soil were below the detection limit of 0.20 $\mu\text{g Cd/g dry weight}$.
3. Plant uptake of cadmium from di-ammonium phosphate (DAP) fertilizer on an acid coarse textured soil was markedly reduced when this material was applied in a single spot as compared to mixing throughout the pot. Cd uptake from mixed DAP was similar to that from CSP applied either mixed or in a spot. Placement effects in a calcareous silt loam were smaller than those in the acid coarse textured sand.

SECTION III

RECOMMENDATIONS

This investigation was intended to be preliminary in nature. Uptake of cadmium from phosphate fertilizer materials appears to be high enough to warrant further investigation. Results indicate three areas of particular interest.

(1) Uptake of Cd by food crops from phosphate fertilizers applied to acid soils of low cation exchange capacity.

(2) The effects of cumulative doses of high Cd fertilizers on acid soils and on soils that do not maintain high Cd activity such as the calcareous silt loam used in this study is not known and should be investigated.

(3) The reduced Cd uptake by spot (or band) placement of di-ammonium phosphate fertilizer should be further investigated. The results shown here suggest that this placement might have potential as a management technique to reduce Cd uptake on coarse textured soils. The theoretical soil chemistry of this effect should be understood as well as possible field applications.

SECTION IV

MATERIALS AND METHODS

The two soils selected for the experiment were (1) Westport fine sand (Typic udipsamment), an acid dune soil from near Bandon, Oregon; and (2) Virtue silt loam (Xerollic durargid), a calcareous soil from near Nyssa, Oregon.

Soils were dried, mixed, and crushed to pass a 1/2 cm screen prior to potting. Plants were grown in paraffin coated paper containers approximately 20 cm in diameter and each containing 4 kg air dry soil. Selected soil properties are shown in Table 1. Due to the low organic matter content, 2 1/2 percent by weight of an acid peat was mixed with the Westport soil to improve water holding capacity. Analyses of the Westport soil shown in Table 1 were from samples taken after the peat was added. Measured pH of the Westport soil varied from 4.5 to 5.3 when sampled at different times. These differences were apparently due to low buffering capacity.

Fertilizer materials used in this study were obtained by Region 10 EPA personnel. They included concentrated superphosphate (CSP) and diammonium phosphate (DAP) with a low and high cadmium level sample of each (Table 2). While both CSP samples were nominally 0-46-0 (N, P_2O_5 , K_2O) and both DAP samples were nominally 18-46-0, they were from entirely different sources.

The treatment set utilized is shown in Table 2. In addition to the above materials, reagent grade monocalcium phosphate dihydrate (MCP), and cadmium dihydrogen phosphate prepared in the laboratory (Appendix A), were utilized in selected treatments. The ammonium nitrate (AN) added to the CSP treatments supplies the same total N as the DAP treatments. All treatments supply a total of 100 $\mu\text{g P}$ (245 $\mu\text{g P}_2\text{O}_5$) per g of soil. In addition to the materials shown in Table 2, 0.39 g KNO_3 and 0.34 g K_2SO_4 were mixed with the soil in each pot to supply K, S, and additional N.

The treatment set shown in Table 2 contains two subsets, each designed to yield specific information. Treatments 1-7 supply increasing amounts of Cd in the range of 0 to .087 $\mu\text{g Cd}$ per g soil as shown in Table 3. All treatments in this subset utilize CSP as a fertilizer source and all treatments were thoroughly mixed with the soil utilizing a twin shell blender. Treatments 7-14 comprise a 2^3 factorial experiment with factors and levels as shown in Table 4. This set is designed to evaluate the effect of cadmium source, fertilizer material (CSP vs DAP), and mix vs spot application, on uptake of Cd by the plants. The spot application is intended to simulate band application in the field. In this method all treatment materials were placed in a single spot located at the center of the pot and 5 cm below the soil surface. Lateral distance from the seeds to the spot was also approximately 5 cm.

TABLE 1. CHARACTERISTICS OF SOILS USED IN THE Cd UPTAKE EXPERIMENT.

		Westport Fine Sand	Virtue Silt Loam
pH			
1:2 Soil:water		4.5	8.4
Organic matter	Percent		
Wet digestion		0.6	1.19
Total Nitrogen	Percent		
Kjeldahl		.01	.08
Cation exch. Cap.	m. eq/100g		
Neutral $\underline{\text{N}}$ $\text{NH}_4\text{O Ac}$		2.2	20.0
Extractable $\text{P}^{\text{a/}}$	$\mu\text{g/g}$	11	13
Free carbonates	Percent as CaCO_3	0.0	2.2
Total Cadmium	$\mu\text{g/g.}$	<0.5	0.6
Soluble Cadmium $^{\text{b/}}$	$\mu\text{g/g.}$	0.05	0.1

$\underline{\text{a/}}$ NaHCO_3 extraction for Virtue soil, dilute $\text{HCl-NH}_4\text{F}$ for Westport soil

$\underline{\text{b/}}$ Total Ammonium Acetate Extractable.

TABLE 2. TREATMENT MATERIALS, AMOUNTS AND METHOD OF APPLICATION
FOR CADMIUM UPTAKE EXPERIMENT

Treatment No.	Materials						Cd-P µg/pot	Method
	MCP	CSP		DAP		AN		
		Low	High	Low	High			
		-----g/pot-----						
1	1.64					1.03		Mix
2		2.0	--	--	--	1.03		Mix
3	--	1.6	.4	--		1.03		Mix
4	--	1.2	.8	--		1.03		Mix
5	--	.8	1.2	--		1.02		Mix
6	--	.4	1.6	--		1.03		Mix
7	--	--	2.0	--		1.03		Mix
8	--	--	2.0	--		1.03		Spot
9	--	--	--	--	2.0	--		Mix
10	--	--	--	--	2.0	--		Spot
11	--	2.0	--	--	--	1.03	840	Mix
12	--	2.0	--	--	--	1.03	840	Spot
13	--	--	--	2.0	--	--	790	Mix
14	--	--	--	2.0	--	--	790	Spot

MCP - Monocalcium phosphate, reagent

CSP (low) - concentrated super phosphate, 0-46-0 12 ppm Cd

CSP (high) - concentrated super phosphate, 0-46-0, 174 ppm Cd

DAP (low) - Di-ammonium phosphate, 18-46-0, 7 ppm Cd

DAP (high) - Di-ammonium phosphate, 18-46-0, 157 ppm Cd

Cd-P - Cadmium phosphate, $\text{Cd}(\text{H}_2\text{PO}_4)_2$, 39% Cd by analysis

AN - Ammonium nitrate, reagent.

TABLE 3. CADMIUM LEVELS RESULTING FROM TREATMENTS 1-7 OF THE Cd UPTAKE EXPERIMENT ($\mu\text{g Cd/g SOIL}$)

Treatment	Cd Concentration $\mu\text{g Cd/g}$
1	0
2	.0065
3	.0226
4	.0387
5	.0548
6	.0709
7	.0870

TABLE 4. FACTORS AND LEVELS USED IN TREATMENTS 7-14

Fertilizer Material	Placement	Cd Source
1. Concentrated super phosphate, 0-46-0	1. Mixed with soil	1. High Cd fertilizer
2. Di-ammonium phosphate, 18-46-0	2. Spot application	2. Cd $(\text{H}_2\text{PO}_4)_2$ added to low Cd fertilizer

The Cd source comparison is intended to evaluate the effect of adding $\text{Cd}(\text{H}_2\text{PO}_4)_2$ as compared to a similar amount of native Cd in the fertilizer. In the factorial subset all DAP treatments contain a total of .080 μg Cd per g soil while all CSP treatments contain .087 $\mu\text{g/g}$.

Three common garden crops were grown: garden peas, *Pisum sativum* L. cultivar Little Marvel; radish, *Raphanus sativus* L., cult. early Scarbet Globe; and leaf lettuce, *Lactuca sativa* L., var. *crispa* cult. Oak Leaf. Two replications were placed in a completely random arrangement. Total pots in the experiment numbered 168. Pots were planted March 27, 1975 with the exception of the garden peas on the Westport soil which were planted April 4. Plants were thinned to 6 plants per pot for radishes and lettuce and 3 plants per pot for peas shortly after emergence. Daytime temperature in the greenhouse were $75^\circ\text{F} \pm 5^\circ$; and night temperatures were $65^\circ \pm 5^\circ$.

Field capacity moisture percentages (W/W) were determined for each soil by applying water to the surface of a soil column and gravimetrically determining the soil water content above the wetting front after allowing a 24 hour equilibration period. Pots were weighed daily and deionized distilled water added to replace loss by evapotranspiration. Initially the total weight maintained corresponded to about 75 percent of field capacity. This total weight increased to field capacity as roots were established and evaporative demand increased.

Radishes were harvested May 1. The edible root portions and the tops were harvested separately. Plants were rinsed with deionized water, fresh weight determined and dry weight determined after freeze drying. Lettuce was harvested May 8. The tap root constituted only a very small portion of the total weight and this was not included in the foliar sample. Peas were harvested May 28 from the Virtue soil and June 2 from the Westport soil. Samples from these crops were handled in the same manner as the radishes. Pea materials were not rinsed except for a few basal portions of the stems that were contaminated with soil.

For total Kjeldahl nitrogen and total phosphorus determinations 50 mg plant samples were digested in a block digester using H_2SO_4 and HgO (Kjeldahl method). Colorimetric determinations were then carried out with an automated analyzer. For total Kjeldahl nitrogen, NH_4^+ was determined using the indophenol blue color formed from reaction with sodium phenate and hypochlorite ion. Phosphorus was determined using molybdo-phosphoric acid reduced to molybdenum blue complex with ascorbic acid.

Cadmium analyses were carried out using approximately a 1 g sample digested in a block digester with 2:1 nitric-perchloric acid, followed by Cd determination on an atomic adsorption spectrophotometer. Zinc analyses are in progress and will be reported later.

SECTION V

RESULTS AND DISCUSSION

REPLACEMENT SERIES TREATMENTS

Results from the two treatment subsets were quite different and will be discussed separately. The progressive replacement of the low Cd CSP source with the high Cd CSP did not detectably affect dry matter yields for any of the crops on either soil. Mean dry matter yields and percentages are summarized in Table 5. Treatment means and standard errors are included in Appendix B. Plants in treatments 1-7 generally appeared healthy and grew well with the exception that the pea vines in some pots exhibited early senescence and yields of both pea foliage and seeds was highly variable. This was apparently unrelated to treatment. The lack of any growth effects due to treatments simplifies interpretation of the cadmium concentration data as dilution or concentration effects due to growth differences are not likely to be important.

Mean plant phosphorus concentrations are shown in Table 5. Phosphorus concentrations by individual treatments are included in Appendix B. In most cases, the phosphorus concentrations in the plants were not affected by treatment, but on the Virtue silt loam soil the probability of no effects was $<.05$ for radish tops and $<.01$ for pea foliage. The pattern for the radish tops was not consistent, so the results may be spurious, but in pea foliage on this soil the P concentration was depressed slightly when the proportion of high Cd CSP was increased. This was probably related to the chemical properties of the fertilizers from the two sources rather than any effect related to the Cd level. These few apparent effects on phosphorus concentration are probably not important in terms of interpreting Cd effects in this portion of the experiment.

The Cd concentrations in plants grown on Westport fine sand increased markedly when high Cd CSP was substituted for low Cd CSP. The results were highly significant and could generally be represented by a linear regression. Plots and regression lines for the Westport soil are shown in Figures 1-3. Individual treatment means are included in Appendix B. Some difficulty was encountered with the regression analysis of the pea data from the Westport soil, where the low levels of fertilizer Cd resulted in plant levels below the analytical detection limit of $0.20 \mu\text{g/g}$. In this case the value for the highest Cd treatment registering at or below the detection limit was assumed to be $0.20 \mu\text{g/g}$ and values from the lower treatment levels were not included in the regression. This procedure resulted in 6 treatments being used to determine the regression for pea seeds and 5 treatments for pea foliage.

The effect on plant Cd concentration on the Virtue soil was not as dramatic but was measurable for the radish and lettuce plots and regression lines for the Virtue soil are shown in Figures 4 and 5. Pea seeds and foliage from this soil were almost all below the detection limit of

TABLE 5. DRY MATTER PERCENTAGE, DRY WEIGHT YIELDS, AND PLANT P CONCENTRATIONS FOR TREATMENTS 1-7 OF Cd UPTAKE EXPERIMENT. a/

	Westport fine sand			Virtue silt loam		
	Percent	Dry	Plant	Percent	Dry	Plant
	Dry Matter	Matter	P	Dry Matter	Weight	P
	%	g/pot	%	%	g/pot	%
Radish						
Root	5.27	3.67	.66	5.88	4.49	.35
Top	5.63	3.84	1.10	7.15	2.11	.37
Lettuce	5.25	5.52	.46	4.82	5.99	.49
Pea						
Seeds	26.6	4.80	.68	31.5	6.41	.62
Foliage	21.9	8.77	.35	48.1	5.81	.19

a/ Values represent means of 14 pots.

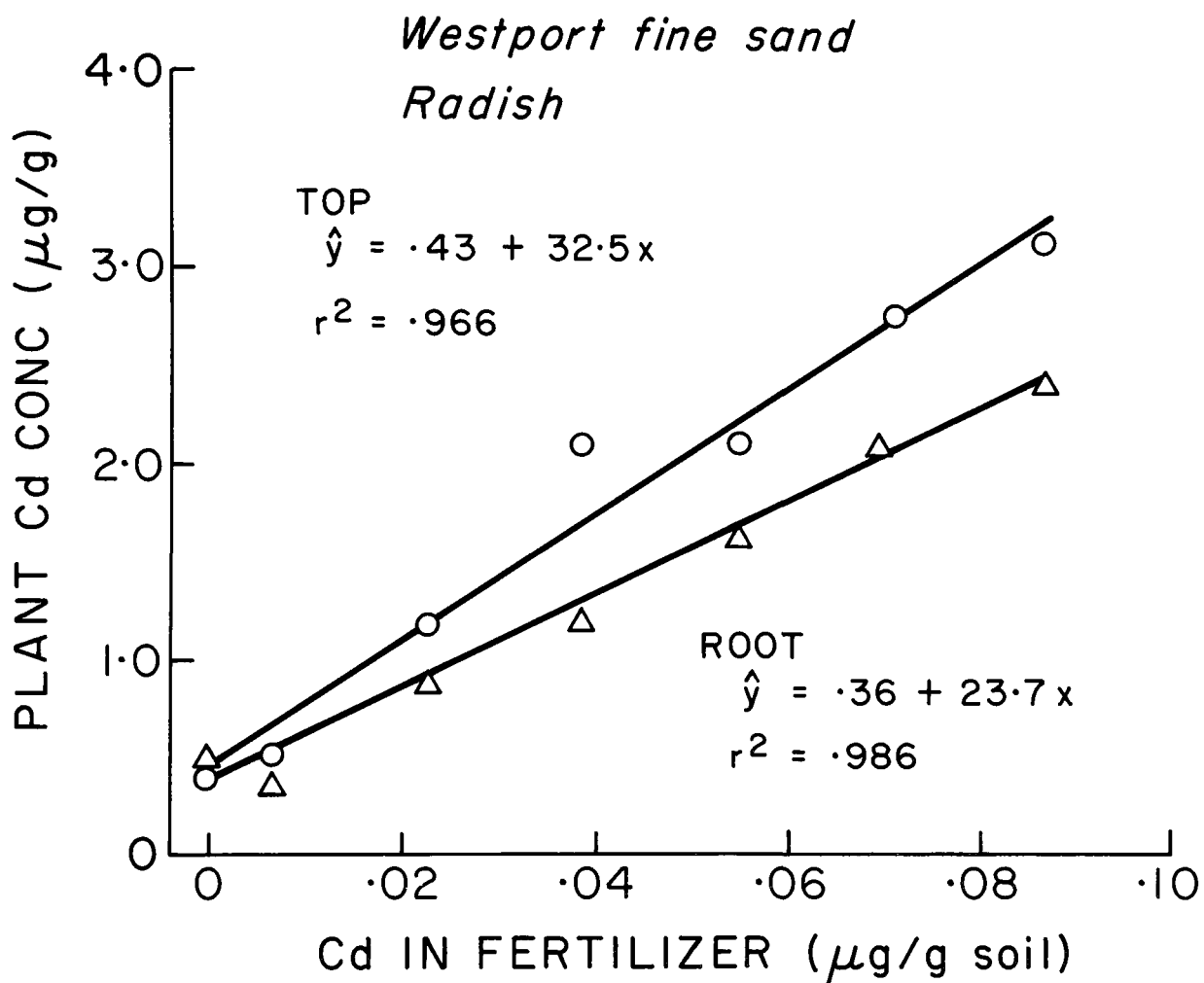


Figure 1. Cadmium concentration in radishes grown on Westport fine sand as a function of Cd in concentrated super phosphate fertilizer (CSP).

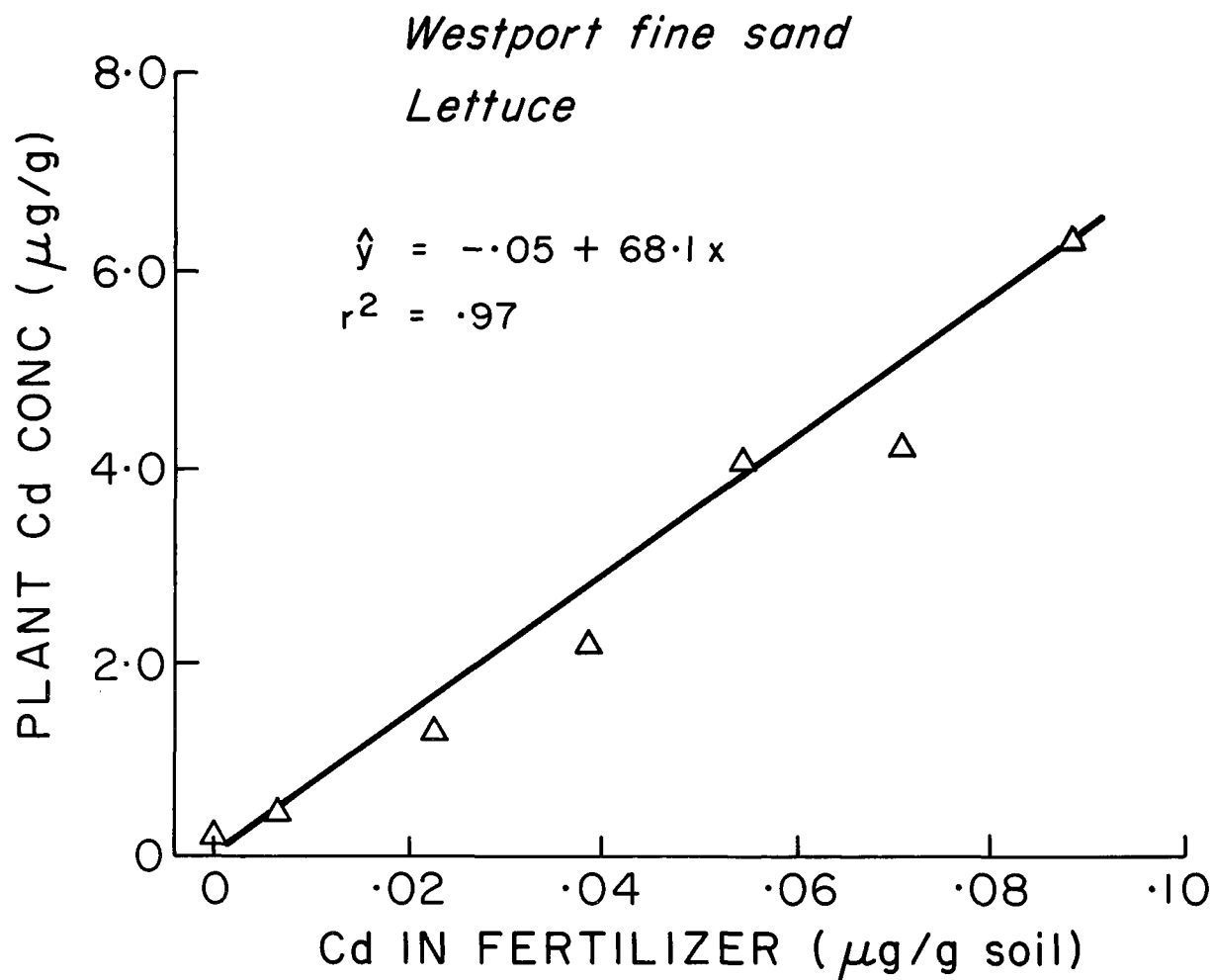


Figure 2. Cadmium concentration in lettuce grown on Westport fine sand as a function of Cd in concentrated super phosphate fertilizer (CSP).

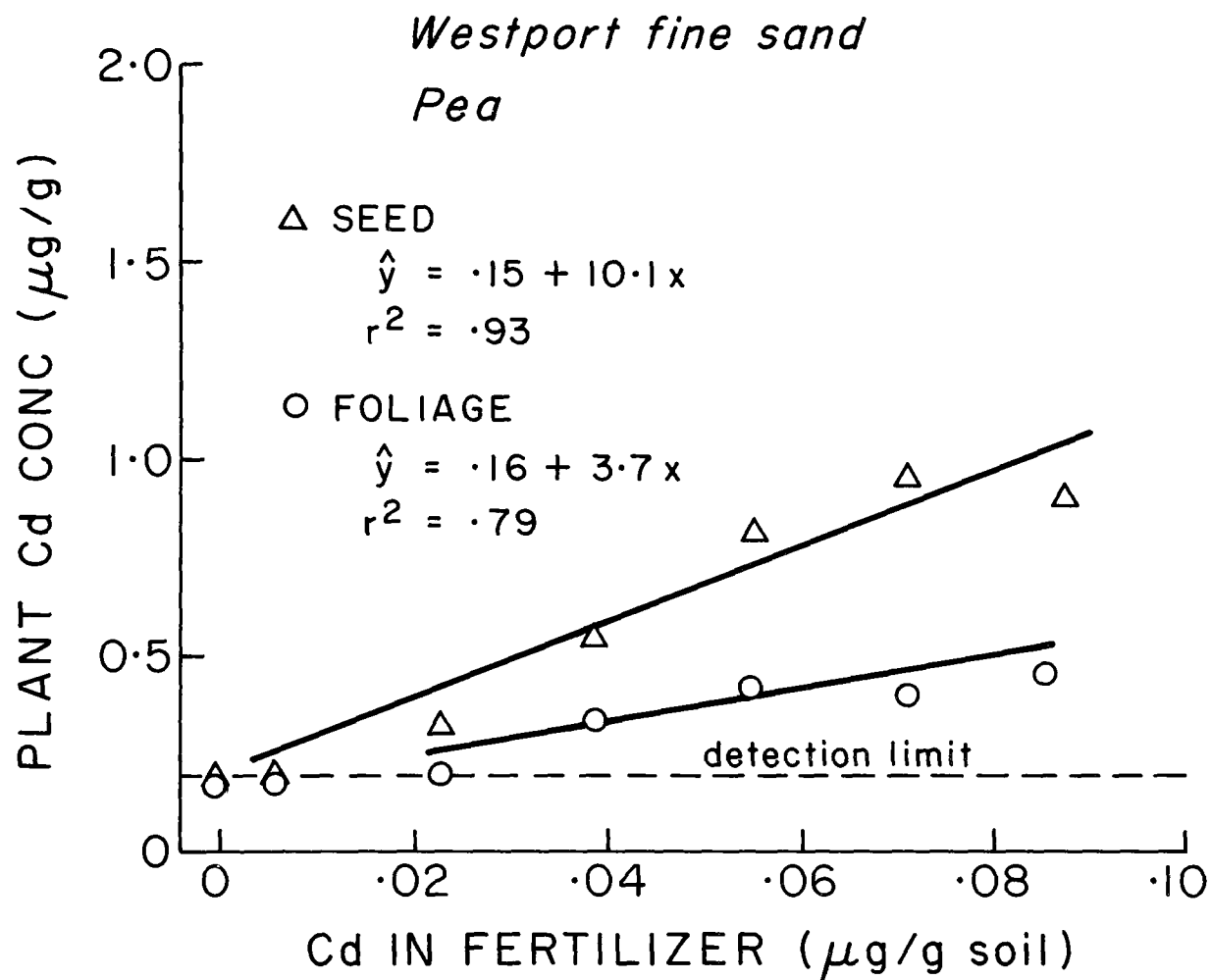


Figure 3. Cadmium concentration in peas grown on Westport fine sand as a function of Cd in concentrated super phosphate fertilizer (CSP).

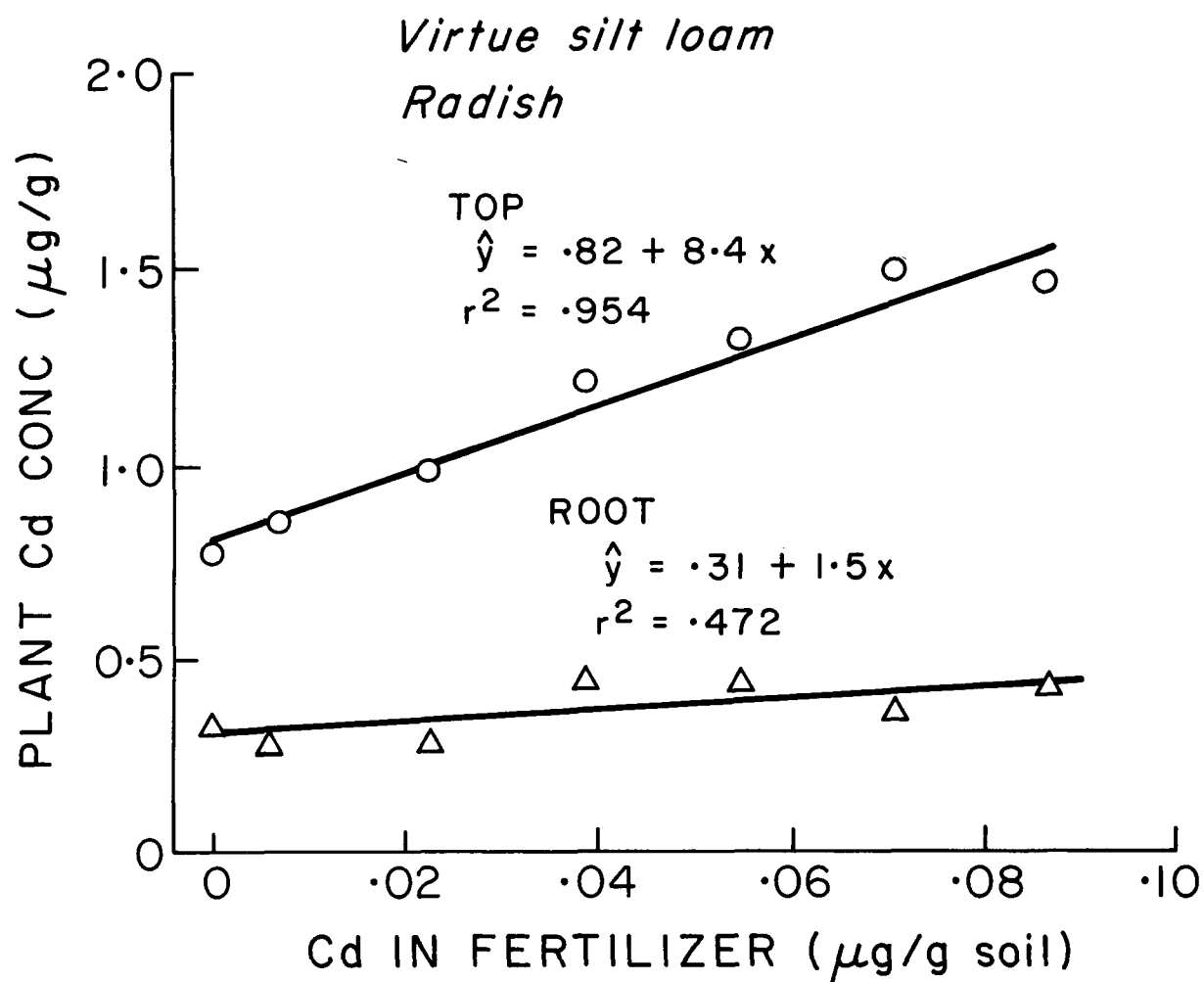


Figure 4. Cadmium concentration in radishes on Virtue silt loam as a function of Cd in concentrated super phosphate fertilizer (CSP).

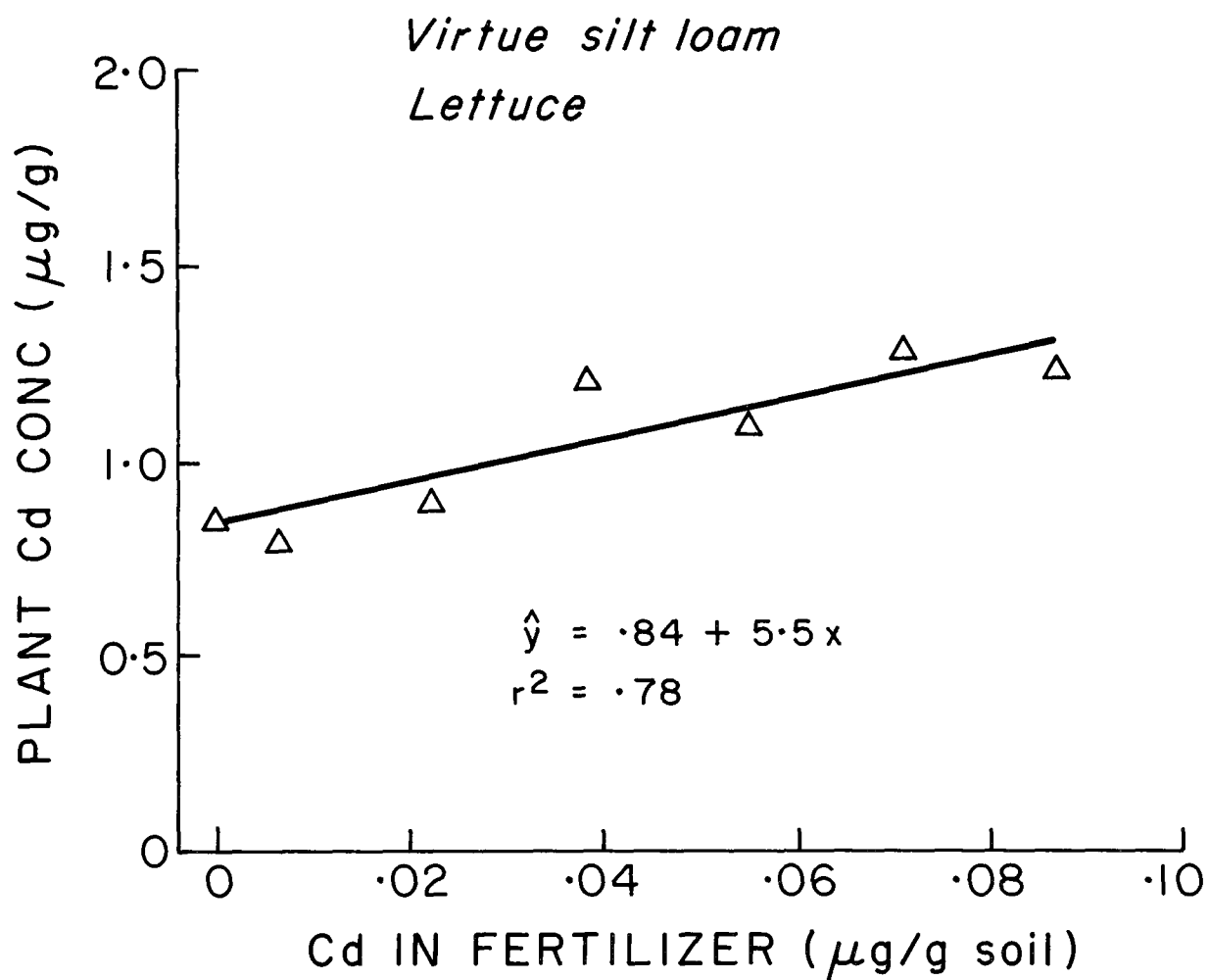


Figure 5. Cadmium concentration in lettuce grown on Virtue silt loam as a function of Cd in concentrated super phosphate fertilizer (CSP).

0.20 $\mu\text{g Cd/g}$ and are not reported. Cadmium concentrations in radish tops and lettuce increased substantially as the proportion of high Cd CSP was increased, but at a much lower rate than for the Westport soil. Radish roots apparently increased slightly in Cd, but the hypothesis of a zero slope could only be rejected at the 0.1 probability level and not at the 0.05 level.

The effect of soils and crops can probably best be evaluated from Table 6. With the exception of radish roots the intercepts were much lower on the Westport fine sand than the Virtue silt loam, indicating a higher background level from the Virtue soil as collected. The Westport soil was from a dune area and undoubtedly had never been fertilized. The Virtue soil was from just outside a cultivated field near a country road and while it apparently had not been fertilized, its history is less clear. The total cadmium concentration for the Westport fine sand was $<0.5 \mu\text{g/g}$ and for the Virtue silt loam was $0.6 \mu\text{g/g}$. The exchangeable (ammonium acetate extractable) cadmium concentration for Westport fine sand was $0.05 \mu\text{g/g}$ and for Virtue silt loam was $0.1 \mu\text{g/g}$.

The most striking effects are in the slope and in the percentages of the Cd applied in fertilizer that was found in the plant. For radish plants this was 5.29% on the Westport fine sand compared to 0.61% for the Virtue silt loam. For lettuce the values were 9.40% and 0.82% (Table 6). This calculation was based on the slope of the regression line, the mean dry matter produced and the amount of Cd contained in the fertilizer. The higher uptake for lettuce than radish is in agreement with the results of Haghiri (1973) even though he applied much higher levels of Cd than are found in fertilizers.

Cadmium concentrations and percentage uptake was less for peas than radishes or lettuce. The 5.3 and 2.0 percent of applied Cd found in the radishes and pea plants respectively grown in Westport fine sand (Table 6) are similar to the result of Williams and David (1973) who found 6.3 and 3.3% of the Cd applied in single superphosphate taken up by these crops from podzolic soil with a cation exchange capacity (CEC) of 5.3 millequivalents per 100 g.

The difference in uptake by the soils is exactly what would have been expected as the high pH associated with the free CaCO_3 as well as the higher CEC in the Virtue soil would tend to lower uptake (Williams and David, 1973, Haghiri, 1974). These two soils should represent near maximum and minimum uptake conditions.

The biological significance to consumer organisms is not clear, but it does not appear that it can be dismissed as unimportant. The accumulation of $6.3 \mu\text{g/g}$ Cd in lettuce on a dry weight basis is only about $.315 \mu\text{g/g}$ on a fresh weight basis at 5.25 percent dry matter (94.75% water). However, a relatively small amount of wilting to 90% water would result in $0.63 \mu\text{g Cd/g}$ on a fresh weight basis. It would appear that the Cd uptakes found here, particularly on the coarse textured acid

TABLE 6. SUMMARY OF THE SLOPE AND INTERCEPTS OF THE REGRESSION OF PLANT Cd CONCENTRATION ON Cd ADDED IN FERTILIZER AND PERCENTAGE OF ADDED Cd FOUND IN PLANTS

Plant	Westport fine sand			Virtue silt loam		
	Intercept $\mu\text{g/g}$	Slope <u>a/</u>	Uptake % <u>b/</u>	Intercept $\mu\text{g/g}$	Slope <u>a/</u>	Uptake % <u>b/</u>
Radish						
Root	.36	23.7	2.17	.31	1.5 (NS)	.17
Top	.43	32.5	3.12	.82	8.38	.44
			<u>5.29</u>			<u>.61</u>
Lettuce	-.05	68.1	9.40	.84	5.5	.82
Pea						
Seed	.15	10.1	1.21	--	--	--
Foliage	.16	3.7	.81			
			<u>2.02</u>			

a/ $\mu\text{g Cd/g plant per } \mu\text{g fertilizer Cd/g soil}$

b/ Percent of Cd in fertilizer found in plant

soil, would justify further investigation in regards to uptake of Cd from fertilizer in soils in which Cd is likely to remain active. Virtually nothing is known concerning effects from repeated dosage, and this aspect should be studied in calcareous as well as acid soils.

The effect of treatment on plant nitrogen were generally small and statistical significance could not be demonstrated in most cases. These data are not included in the report.

PLACEMENT AND SOURCE EFFECTS

The results of treatments 7-14 (Table 2) clearly show that fertilizer materials and placement affect the Cd uptake, and that this effect is not the same on the two soils. The most striking effect is the lack of Cd uptake from spot placed DAP on the Westport fine sand soil (Table 7). Even though approximately the same total amount of Cd was applied in all treatments in this subset, the Cd uptake is very low wherever DAP was applied in a spot treatment. This was generally true whether the Cd was native in the fertilizer or added to the fertilizer as Cd $(\text{H}_2\text{PO}_4)_2$. By contrast the spot placement of CSP on this soil did not generally reduce Cd uptake as compared to CSP mixed with the soil, nor did the use of DAP instead of CSP reduce Cd uptake when the fertilizers were mixed with the soil. The reason for the marked decrease in Cd uptake due to the spot placement of DAP on the acid soil is not known, but it is probably related to the neutral or slightly basic reaction of DAP as compared to the acid CSP.

The dramatic decrease due to spot placement of DAP did not occur on the Virtue silt loam soil (Table 8), where significant treatment effects could only be discerned in the lettuce and radish tops. In both these cases Cd uptake appeared to be slightly decreased by spot placement of DAP and increased by spot placement of CSP. Mixed treatments of both fertilizers resulted in similar levels in the plant.

Cadmium uptake in radishes grown on Westport fine sand (Table 7), with added Cd $(\text{H}_2\text{PO}_4)_2$ was slightly higher than that from Cd found in the fertilizer. In all other cases no differences could be detected between native Cd and Cd added to the fertilizer. This would indicate that if this material were used to artificially increase the Cd level of fertilizers the uptake would probably be at least as great as that from fertilizers containing a similar amount of native Cd.

The possibility that differences in Cd levels could be due to different growth effects of the various fertilizers, or simple lack of uptake due to positional unavailability must be considered. The treatments did affect plant dry weight and phosphorus levels in a number of cases. Summaries of significant effects are shown in Tables 9 and 10. Data from individual treatments are included in Appendix B, Tables 8-11.

TABLE 7. CADMIUM CONCENTRATIONS IN PLANTS GROWN ON WESTPORT FINE SAND AS AFFECTED BY FERTILIZER MATERIAL, PLACEMENT AND SOURCE OF Cd

Placement	Treatment		Radish		Lettuce	Pea	
	Material	Cd Source	Root	Top	Top	Seed	Foliage
μg Cd per g dry weight							
Mix	CSP (high)	fertilizer	2.40	3.12	6.35	.46	.91
Spot	CSP (high)	fertilizer	1.92	2.88	4.35	.46	1.05
Mix	DAP (high)	fertilizer	3.55	2.24	6.01	.53	1.07
Spot	DAP (high)	fertilizer	.20	<.19	.28	<.19	<.19
Mix	CSP (low)	added	3.53	4.61	5.32	.67	.81
Spot	CSP (low)	added	3.20	7.33	5.98	.69	.93
Mix	DAP (low)	added	4.05	2.71	3.61	.60	.92
Spot	DAP (low)	added	.42	<.19	1.14	<.19	<.19
Summary of significant effects							
	Mix CSP		2.97	3.87	5.79	5.66	.81
	Spot CSP		2.56	5.10	5.17	5.78	.93
	Mix DAP		3.80	2.47	4.81	5.66	.92
	Spot DAP		.31	<.19	.71	<.19	<.19

Cd source effect (P < .05)

In fertilizer	2.01	2.11
Added	2.80	3.71

Probability of Type I error for main effect and interaction <.01.

TABLE 8. CADMIUM CONCENTRATION IN PLANTS GROWN ON VIRTUE SILT LOAM SOIL AS AFFECTED BY FERTILIZER MATERIAL, PLACEMENT AND SOURCE OF Cd

Treatment			Radish		Lettuce	Peas	
Placement	Material	Cd Source	Root	Top	Top	Seed	Foliage
			$\mu\text{g Cd per g dry weight}$				
Mix	CSP (high)	fertilizer	.43	1.72	1.23	Below detection limit of 0.20	
Spot	CSP (high)	fertilizer	.77	2.53	2.41		
Mix	DAP (high)	fertilizer	.37	1.46	1.25		
Spot	DAP (high)	fertilizer	.44	1.00	.81		
Mix	CSP (low)	added	.45	1.48	1.07		
Spot	CSP (low)	added	1.12	3.22	3.49		
Mix	DAP (low)	added	.47	1.49	1.38		
Spot	DAP (low)	added	.57	1.03	1.08		
Summary of significant effects							
	Mix CSP			1.60	1.15		
	Spot CSP			2.87	2.94		
	Mix DAP			1.47	1.31		
	Spot DAP			1.02	.94		

Main effects and interaction shown significant probability of Type I error <.01

TABLE 9. SUMMARY OF MEANS OF MAJOR PLACEMENT AND FERTILIZER MATERIAL EFFECTS ON DRY MATTER YIELDS.

<u>Treatment</u>	<u>Radish</u>		<u>Lettuce</u>		<u>Peas</u>	
	<u>Roots</u>	<u>Tops</u>	<u>Tops</u>	<u>Seed</u>	<u>Foliage</u>	
g dry weight per pot						
Westport fine sand						
Mix		3.22	4.68			
Spot		2.62	1.07			<u>a/</u>
CSP	3.56	3.45				
DAP	2.24	2.39				<u>a/</u>
Virtue silt loam						
Mix	4.27	2.09	5.42		5.91	
Spot	2.76	1.64	2.07		5.27	<u>b/</u>

a/ Interaction present, but relatively minor compared to main effect

b/ Complex interaction with fertilizer source.

TABLE 10. SUMMARY OF MEANS OF MAJOR PLACEMENT AND FERTILIZER MATERIAL EFFECTS ON PLANT PHOSPHORUS CONCENTRATIONS.

<u>Treatment</u>	<u>Radish</u>		<u>Lettuce</u>	<u>Peas</u>	
	<u>Roots</u>	<u>Tops</u>	<u>Tops</u>	<u>Seeds</u>	<u>Foliage</u>
	percent of dry weight				
Westport fine sand					
CSP	.58	.88	.51		.34
DAP	.70	1.55	.60		.57
Virtue silt loam					
CSP					
Mix	.35	.36	.48	.64	.18
Spot	.30	.36	.44	.50	.13
DAP					
Mix	.39	.42	.48	.66	.22
Spot	.19	.27	.38	.51	.10

On the Westport soil radishes root and top weights are decreased by use of DAP fertilizer as compared to CSP, and radish tops and lettuce were depressed by spot application of either fertilizer. The reason for these effects were not completely clear but the DAP did increase plant P concentrations in most plants (Table 10) independent of placement. This indicates that phosphorus from the spot placed DAP was utilized even though on this soil Cd was not. While these growth effects do complicate interpretation they simply do not account for the nearly complete lack of Cd uptake from spot placed DAP.

The effects of treatment on dry matter yields and phosphorus concentration was quite different on the calcareous Virtue soil (Table 9 and 10). Here yields were consistently depressed by spot placement of fertilizer. This is probably due to lower availability of phosphorus as phosphorus concentrations were depressed by spot placement on this soil, particularly in the case of the DAP.

These effects of placement and fertilizer material on yield and plant phosphorus concentration may be of agronomic interest but we are concerned with them here in relation to interpretation of the Cd uptake data. It should not be implied that these effects are related to the Cd in the fertilizer. They are useful in evaluating whether the plant was utilizing the nutrients supplied by a particular material and placement.

The most important effect noted in this section of the experiment was the lack of Cd uptake from spot placement of DAP on the acid soil. This effect may have important implications as a management technique, and therefore should be further investigated from both theoretical and application standpoints. Effects of material and placement on Cd uptake on the calcareous soil were less dramatic but may still warrant further investigation.

SECTION VI

REFERENCES

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SECTION VII

APPENDIX A

Synthesis of Cadmium Dihydrogen Phosphate (Preparation of $\text{Cd}(\text{H}_2\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$.)

We were unable to obtain this salt through normal commercial channels so the compound was synthesized in the following manner using the Parker Rust Proof Company Patented procedure (1926).

The salt was synthesized in the following manner: approximately 1 gram of 100 mesh cadmium metal was allowed to react with 20 ml of 75% phosphoric acid held at $80-85^\circ\text{C}$. Two more 10 ml portions of 75% phosphoric acid were added at intervals of several hours. When all of the cadmium metal was consumed (visual examination), the reaction mixture was allowed to cool. The white crystals which formed were separated from the mother liquor by filtration. They were washed with absolute ethanol to remove any unreacted phosphoric acid and allowed to air dry for several hours. The crystals were then analyzed via atomic absorption and found to contain 39% cadmium. The predicted value for cadmium in this compound is 33%. The 6% difference might well be due to a small amount of unreacted cadmium metal remaining with the crystals.

APPENDIX B
LIST OF DATA TABLES

- B-1. Cadmium and Zinc concentrations in fertilizer material used in Cd uptake experiment (mean of 4 replications).
- B-2. Dry matter yields from Westport fine sand soil in pots treated with MCP or CSP fertilizers from two sources. Rates calculated to supply 100 μg P/g soil.
- B-3. Dry matter yields from Virtue silt loam soil in pots treated with MCP or CSP fertilizer from two sources (mean of 2 replications). Rates calculated to supply 100 μg P/g soil.
- B-4. Phosphorus concentration in plants grown on Virtue silt loam soil with MCP or CSP fertilizer from two sources (mean of 2 replications). Rates calculated to supply 100 μg P/g soil.
- B-5. Phosphorus concentration in plants grown on Westport fine sand soil treated with MCP or CSP fertilizer from two sources (mean of 2 replications). Rates calculated to supply 100 μg P/g soil.
- B-6. Cadmium concentration in plants grown on Westport fine sand as affected by Cd in phosphate fertilizer (mean of 2 replications). Low and high sources of CSP contain 12 and 174 ppm μg Cd/g respectively.
- B-7. Cadmium concentration in plants grown on Virtue silt loam soil as affected by Cd in phosphate fertilizer (mean of 2 replications). Low and high sources of CSP contain 12 and 174 μg Cd/g respectively.
- B-8. Dry matter yields of plants grown on Westport fine sand as affected by fertilizer materials and placement (mean of 2 replications).
- B-9. Mean dry matter yield of plants grown on Virtue silt loam as affected by fertilizer material and placement (mean of 2 replications).
- B-10. Mean phosphorus concentration in plants grown on Westport fine sand as affected by fertilizer material and placement (mean of 2 replications).
- B-11. Mean phosphorus concentration of plants grown on Virtue silt loam as affected by fertilizer material and placement (mean of 2 replications).

TABLE B-1. CADMIUM AND ZINC CONCENTRATIONS IN FERTILIZER MATERIAL USED
IN Cd UPTAKE EXPERIMENT (MEAN OF 4 REPLICATIONS).

Material	<u>Cd</u>	<u>Zn</u>
	µg/g	µg/g
CSP - low Cd	12	78
CSP - high Cd	174	1564
DAP - low Cd	7.0	114
DAP - high Cd	157	1385

TABLE B-2. DRY MATTER YIELDS FROM WESTPORT FINE SAND SOIL IN POTS TREATED WITH MCP OR CSP FERTILIZERS FROM TWO SOURCES (MEAN OF 2 REPLICATIONS). RATES CALCULATED TO SUPPLY 100 μg P/g SOIL.

CSP Source Low-High %	Final Cd Concentration Fertilizer (Soil) $\mu\text{g/g}$	Radish		Lettuce	Peas	
		Root	Top g/pot	Top	Seed	Foliage
100-0 (MCP)	0 (0) ^{a/}	3.90	3.84	6.00	5.45	8.74
100-0	13 (0.0065)	3.08	3.99	5.81	4.44	9.48
80-20	45 (.023)	3.61	3.52	5.60	4.52	7.65
60-40	77 (.039)	3.66	3.78	5.38	5.55	7.91
40-60	110 (0.055)	3.64	3.90	4.54	4.98	8.83
20-80	142 (0.071)	3.45	3.94	5.82	4.08	9.85
100-0	174 (.087)	4.33	3.93	5.50	4.60	8.93
Standard Error		.421	.363	.351	.584	1.20
Mean		3.67	3.84	5.52	4.80	8.77
Percent dry matter		5.27	5.63	5.25	26.6	21.9

^{a/} $< 4 \times 10^{-4} \mu\text{g/g}$.

TABLE B-3. DRY MATTER YIELDS FROM VIRTUE SILT LOAM SOIL IN POTS TREATED WITH MCP OR CSP FERTILIZER FROM TWO SOURCES (MEAN OF 2 REPLICATIONS). RATES CALCULATED TO SUPPLY 100 μg P/g SOIL.

CSP Source low-High %	Final Cd Concentration Fertilizer (Soil) $\mu\text{g/g}$	Radish		Lettuce	Peas	
		Root	Top g/pot	Top	Seed	Foliage
100-0 (MCP)	0 (0) ^{a/}	3.71	1.93	5.58	6.54	5.50
100-0	13 (.0065)	4.35	2.05	5.55	5.31	5.67
80-20	45 (.023)	4.74	1.98	7.05	6.03	5.63
60-40	77 (.039)	4.10	2.19	5.61	5.42	6.85
40-60	110 (.055)	4.67	2.23	7.10	7.18	6.21
20-80	142 (.071)	4.96	2.16	5.94	7.49	5.37
100-0	174 (.087)	4.87	2.21	5.08	6.84	5.43
Standard Error		.412	.177	.712	.457	.692
Mean		4.49	2.11	5.99	6.41	5.81
Percent dry matter		5.88	7.15	4.82	31.5	48.1

^{a/} $< 4 \times 10^{-4} \mu\text{g/g}$

TABLE B-4. PHOSPHORUS CONCENTRATION IN PLANTS GROWN ON VIRTUE SILT LOAM SOIL WITH MCP OR CSP FERTILIZER FROM TWO SOURCES (MEAN OF 2 REPLICATIONS). RATES CALCULATED TO SUPPLY 100 $\mu\text{g P/g SOIL}$.

CSP Source low-High %	Final Cd Concentration Fertilizer (Soil) $\mu\text{g/g}$	Radish		Lettuce Top % P	Peas	
		Root	Top		Seed	Foliage
100-0 (MCP)	0 (0) ^{a/}	.36	.43	.60	.64	.20
100-0	13 (.0065)	.34	.41	.51	.59	.29
80-20	45 (.023)	.32	.35	.46	.62	.21
60-40	77 (.039)	.38	.35	.48	.60	.24
40-60	110 (.055)	.36	.36	.45	.64	.15
20-80	142 (.071)	.33	.35	.47	.64	.15
100-0	174 (.087)	.35	.39	.49	.65	.14
Standard Error		.025	.014	.047	.021	.0199
Mean		.349	.374 *	.492	.619	.193 **

*Significant at .05 level

**Significant at .01 level

^{a/} $< 4 \times 10^{-4} \mu\text{g/g}$

TABLE B-5. PHOSPHORUS CONCENTRATION IN PLANTS GROWN ON WESTPORT FINE SAND SOIL TREATED WITH MCP OR CSP FERTILIZER FROM TWO SOURCES (MEAN OF 2 REPLICATIONS). RATES CALCULATED TO SUPPLY 100 $\mu\text{g P/g SOIL}$.

CSP Source low-High %	Final Cd Concentration Fertilizer (Soil) $\mu\text{g/g}$	Radish		Lettuce Top	Peas	
		Root	Top % P		Seed	Foliage
100-0 (MCP)	0 (0) ^{a/}	.75	1.04	.45	.69	.35
100-0	13 (.0065)	.70	1.08	.45	.66	.36
80-20	45 (.023)	.65	1.04	.44	.67	.35
60-40	77 (.039)	.64	1.04	.47	.73	.31
40-60	110 (.055)	.66	1.06	.47	.66	.39
20-80	142 (.071)	.62	.91	.47	.69	.38
100-0	174 (.087)	.59	.93	.50	.70	.35
Standard Error		.031	.023	.025	.046	.042
Mean		.656	1.10	.462	.682	.352

^{a/} $< 4 \times 10^{-4} \mu\text{g/g}$

TABLE B-6. CADMIUM CONCENTRATION IN PLANTS GROWN ON WESTPORT FINE SAND AS AFFECTED BY Cd IN PHOSPHATE FERTILIZER (MEAN OF 2 REPLICATIONS). LOW AND HIGH SOURCES OF CSP CONTAIN 12 AND 174 ppm $\mu\text{g Cd/g}$ RESPECTIVELY.

CSP Source Low-High %	Final Cd Concentration Fertilizer (Soil) µg/g	Radish		Lettuce	Peas	
		Root	Top	Top	Seed	Foliage
		µg Cd/g dry wt.				
100-0 (MCP)	0 (0) ^{a/}	.50	.38	.20	<.19	<.19
100-0	13 (.0065)	.37	.47	.44	<.19	<.19
80-20	45 (.023)	.90	1.18	1.34	.33	<.19
60-40	77 (.039)	1.21	2.11	2.20	.55	.35
40-60	110 (.055)	1.64	2.12	4.08	.81	.42
20-80	142 (.071)	2.10	2.76	4.18	.95	.40
100-0	174 (.087)	2.41	3.12	6.33	.91	.46
Standard Error (log normal distribution)		.157	.133	.088	.082	.079
Linear regression (soil Cd vs plant Cd)						
Slope		23.7	32.5	68.1	10.1	3.7
Intercept		.356	.433	-0.49	.149	.163
S.E. yx		.0987	.218	.438	.094	.056
r ²		.986**	.966**	.969**	.929**	.789*

a/ $< 4 \times 10^{-4} \mu\text{g/g}$

** significant at .01 level

*sig. at .05 level

TABLE B-7. CADMIUM CONCENTRATION IN PLANTS GROWN ON VIRTUE SILT LOAM SOIL AS AFFECTED BY Cd IN PHOSPHATE FERTILIZER (MEAN OF 2 REPLICATIONS). LOW AND HIGH SOURCES OF CSP CONTAIN 12 AND 174 µg Cd/g RESPECTIVELY.

CSP Source low-High %	Final Cd. Concentration Fertilizer (Soil) µg/g	Radish		Lettuce	Peas	
		Root	Top	Top	Seed	Foliage
		µg Cd/g dry wt.				
100-0 (MCP)	0 (0) ^{a/}	.33	.78	.85		
100-0	13 (.0065)	.28	.87	.79	Below detection limit	
80-20	45 (.023)	.28	.98	.92	of 0.20	
60-40	77 (.039)	.44	1.21	1.23		
40-60	110 (.055)	.43	1.31	1.08		
20-80	142 (.071)	.36	1.48	1.28		
100-0	174 (.087)	.43	1.45	1.24		
Standard Error		.036	.093	.091		
Linear regression (soil Cd vs plant Cd)						
Slope		1.48	8.38	5.50		
Intercept		.305	.819	.836		
S.E. y.x		.056	.066	.103		
r ²		.472	.954*	.784*		

^{a/} < 4 x 10⁻⁴ µg/g

* Sig. at .01 level.

TABLE B-8. DRY MATTER YIELDS OF PLANTS GROWN ON WESTPORT FINE SAND AS AFFECTED BY FERTILIZER MATERIALS AND PLACEMENT (MEAN OF 2 REPLICATIONS).

<u>Placement</u>	<u>Treatment</u>		<u>Radish</u>		<u>Lettuce</u>	<u>Peas</u>	
	<u>Material</u>	<u>Cd Source</u>	<u>Root</u>	<u>Top</u>	<u>Top</u>	<u>Seed</u>	<u>Foliage</u>
Mix	CSP (high)	fertilizer	4.33	3.92	5.49	4.59	3.93
Spot	CSP (high)	fertilizer	2.99	2.65	.38	5.21	7.19
Mix	DAP (high)	fertilizer	1.61	2.20	5.07	3.50	3.92
Spot	DAP (high)	fertilizer	2.59	2.18	1.36	2.65	3.77
Mix	CSP (low)	added	3.72	3.87	3.71	3.73	3.66
Spot	CSP (low)	added	3.22	3.37	1.19	4.35	5.58
Mix	DAP (low)	added	2.20	2.90	4.48	3.82	3.90
Spot	DAP (low)	added	2.55	2.30	1.34	1.97	1.94
Summary of significant effects							
<u>Placement</u>	Mix			3.22	4.68		
	Spot			2.62	1.07		
<u>Material</u>	CSP		3.56	3.45	b/	4.47	
	DAP		2.24	2.39		2.99	
				a/		c/	

Probability of Type I error <.01 except as noted.

a/ Small placement X material interaction

b/ Complex interaction, but much smaller than placement effect

c/ P <.07

TABLE B-9. MEAN DRY MATTER YIELD OF PLANTS GROWN ON VIRTUE SILT LOAM AS AFFECTED BY FERTILIZER MATERIAL AND PLACEMENT (MEAN OF 2 REPLICATIONS).

Placement	Treatment	Cd Source	Radish		Lettuce	Peas	
	Material		Root	Top	Top	Seed	Foliage
g/pot							
Mix	CSP (high)	fertilizer	4.87	2.12	5.08	5.43	6.84
Spot	CSP (high)	fertilizer	3.14	1.72	2.04	7.12	4.84
Mix	DAP (high)	fertilizer	4.12	1.86	6.27	6.27	4.08
Spot	DAP (high)	fertilizer	2.69	1.60	1.36	1.36	6.24
Mix	CSP (low)	added	3.70	2.00	5.24	5.17	5.58
Spot	CSP (low)	added	2.70	1.56	2.01	4.65	4.94
Mix	DAP (low)	added	4.44	2.28	5.11	5.30	7.14
Spot	DAP (low)	added	2.53	1.67	2.87	3.95	5.13
Summary of significant effects							
		Mix	4.27	2.09	5.42		5.91
		<u>Spot</u>	2.76	1.64	2.07		5.27
							<u>a/</u>

Probability of Type I error <.01 except as noted.

a/ Main effect probability complicated by interaction. Spot placement lower than mix except for the low Cd DAP.

TABLE B-10. MEAN PHOSPHORUS CONCENTRATION IN PLANTS GROWN ON WESTPORT FINE SAND AS AFFECTED BY FERTILIZER MATERIAL AND PLACEMENT (MEAN OF 2 REPLICATIONS).

Placement	Treatment		Radish		Lettuce	Peas	
	Material	Cd Source	Root	Top	Top	Seed	Foliage
			% P				
Mix	CSP (high)	fertilizer	.58	.93	.50	.70	.35
Spot	CSP (high)	fertilizer	.49	.73	.45	.70	.36
Mix	DAP (high)	fertilizer	.71	1.46	.68	.61	.47
Spot	DAP (high)	fertilizer	.72	1.66	.55	.63	.74
Mix	CSP (low)	added	.66	1.04	.56	.60	.27
Spot	CSP (low)	added	.57	.82	.53	.62	.35
Mix	DAP (low)	added	.72	1.56	.60	.65	.56
Spot	DAP (low)	added	.73	1.41	.56	.61	.49
Summary of significant effects							
		CSP	.58	.88	.51	a	.34
		DAP	.70	1.55	.60		.57

Probability of Type I error of main effects shown <.01.

a/ Main effect not significant; interaction with source <.05.

TABLE B-11. MEAN PHOSPHORUS CONCENTRATIONS OF PLANTS GROWN ON VIRTUE SILT LOAM AS AFFECTED BY FERTILIZER MATERIAL AND PLACEMENT (MEAN OF 2 REPLICATIONS).

Placement	Treatment	Cd Source	Radish		Lettuce	Peas	
	Material		Root	Top	Top	Seed	Foliage
				% P			
Mix	CSP (high)	fertilizer	.35	.37	.48	.65	.14
Spot	CSP (high)	fertilizer	.28	.29	.42	.49	.15
Mix	DAP (high)	fertilizer	.39	.36	.47	.66	.28
Spot	DAP (high)	fertilizer	.17	.28	.38	.51	.08
Mix	CSP (low)	added	.35	.36	.47	.63	.22
Spot	CSP (low)	added	.32	.42	.46	.52	.11
Mix	DAP (low)	added	.38	.48	.48	.65	.17
Spot	DAP (low)	added	.21	.26	.38	.51	.17
Summary of significant effects							
		Mix CSP	.35	.36	.48	.64	.18
		Spot CSP	.30	.36	.44	.50	.13
		Mix DAP	.39	.42	.48	.66	.22
		Spot DAP	.19	.27	.38	.51	.10
					a/	b/	a/

Probability of Type I error.

<.01 for placement, <.05 for material and interaction except as noted.

a/ Additional interaction with sources.

b/ Only placement effect significant.

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/3-76-053		2.		3. RECIPIENT'S ACCESSION NO.	
4. TITLE AND SUBTITLE Plant Uptake of Cadmium from Phosphate Fertilizer				5. REPORT DATE May 1976	
				6. PERFORMING ORGANIZATION CODE	
7. AUTHOR(S) John Reuss, H. L. Dooley, and William Griffis				8. PERFORMING ORGANIZATION REPORT NO.	
9. PERFORMING ORGANIZATION NAME AND ADDRESS U. S. Environmental Protection Agency Corvallis Environmental Research Laboratory, EERD,TEB Corvallis, Oregon 97330				10. PROGRAM ELEMENT NO. 1AA602	
				11. CONTRACT/GRANT NO.	
12. SPONSORING AGENCY NAME AND ADDRESS U. S. Environmental Protection Agency Corvallis Environmental Research Laboratory Corvallis, Oregon 97330				13. TYPE OF REPORT AND PERIOD COVERED Final--FY1970-1976	
				14. SPONSORING AGENCY CODE EPA/ORD	
15. SUPPLEMENTARY NOTES					
16. ABSTRACT A preliminary investigation of selected crop plants for Cadmium uptake from various sources of commercially available fertilizer was conducted under controlled greenhouse conditions in Corvallis, Oregon. Results indicated statistically significant differences in Cadmium content of plant tissue as functions of fertilizer source, mode of application, tissues analyzed, and soil type. The highest level of Cadmium accumulation (6 µg/g dry weight) was found in lettuce grown on a coarse textured acid soil and fertilized at the rate of 100 µg P/g soil with concentrated super phosphate (CSP) containing 174 µ Cd/g fertilizer (0.087 µ Cd/g soil). It was concluded that these uptakes may be of sufficient magnitude to be of biological significance to consumer organisms. Further study was recommended.					
17. KEY WORDS AND DOCUMENT ANALYSIS					
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS		c. COSATI Field/Group	
		Cadmium, bioaccumulation and phosphate fertilizer			
18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC		19. SECURITY CLASS (This Report) UNCLASSIFIED		21. NO. OF PAGES 43	
		20. SECURITY CLASS (This page) UNCLASSIFIED		22. PRICE	