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THE EFFECT OF PHOSPHATE FERTILIZER CADMIUM ON CADMIUM IN SOILS AND CROPS

by

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CONTENTS

1. INTRODUCTION

Cadmium is known to present a potential hazard to human and animal health. Therefore, entry into the food chain, by uptake in food crops and fodder, should be restricted as much as possible. One of the ways in which soils are contaminated, thus promoting cadmium uptake by crops, is application of phosphate fertilizer, which contains various amounts of this heavy metal. Cadmium concentration varies with the source of phosphate rock and the amount removed during processing in the manufacture of phosphate fertilizer.

The present study was conducted to determine the rise in soil cadmium as related to the amount of cadmium applied to Dutch arable soils when given phosphate fertilizer. A large number of stored soil samples from at least ten-year old phosphate fertilizer experiments were selected for supplemental Cd determinations. Cadmium accumulation in phosphate-fertilized soils was estimated by comparing Cd concentrations of control and phosphate-treated plots at various time intervals. In some current experiments crop Cd was determined as well, to study plant-availability of Cd in phosphate fertilizer.

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2. MATERIALS AND METHODS

The present study included 18 long-term experimental fields of varying phosphate status, where various rates of phosphate have been, or still are, applied annually. The P-source was mainly superphosphate, except in trials ZWZH 1355, OB 3049 and IB 0013 where triple superphosphate has been used. Some soil characteristics are presented in table I. Soil samples from the control (no P) and the phosphate-treated plots (highest P rate), taken at two- to eight-year intervals, were analyzed for total Cd. Likewise samples of the phosphate fertilizer used, if still available, were analyzed for Cd. Supplemental Cd analyses were obtained from samples of phosphate fertilizer used in other field experiments in the period 1947-1964. In some current phosphate fertilizer experiments crops were also analyzed for Cd.

Soil samples were taken from the top 0-20 cm. Organic matter, pH-KCl, fraction of soil particles < 16 µm and $CaCO_3$ were determined according to the normal procedures used by the Institute for Soil Fertility (Vierveijzer *et al.*, 1979). Water-soluble P (Pw) was estimated according to Sissingh (1971); a concentration of 30 mg/l is considered adequate. Citric-acid (1%)-soluble P was determined in a soil suspension at a 5:50 W/V extraction ratio, after shaking the suspension for two hours at ambient temperature and allowing it to settle for 24 hours.

Great care was taken to prevent contamination of soil and plant samples with heavy metals during preparation for Cd-analysis, e.g. by using a titanium mill or mixer and aluminium sieves.

TABLE 1. Characteristics of soils in long-term phosphate fertilizer experiments used for soil Cd determinations.

Reg.number	Soil type	pH-KCl	Org.matter	Particles < 16 µm	$CaCO_3$	$P_{citr.acid}$	P_{water}	Date of first sampling	Ann. P_2O_5 appl.
			%	%	%	mg/100 g	mg/l		kg/ha
OB 3049	sand	4.7	3.0	8.1	-	25.1		13/ 4/48	200
IB 1920	sand	4.9	4.7	-	-		19.0	24/10/72	240
WB 1435	sand	4.5	5.5	6.0	-	61.5		26/ 3/47	200
D 179	sand	4.2	5.5	4.0	-	46.0		26/ 4/44	200
OGe 80	sand	4.5	4.3	-	-	45.0		16/ 9/42	136
NGe 846	sand	4.4	8.5	-	-	49.0		15/ 8/41	144
Pr 87	reclaimed peat	5.4^{x}	6.5	-	-	6.0		'42	200
ZGr 1	reclaimed peat	4.2	13.7	-	-	18.5		8/25	100
WR 16	loess	6.2	2.0	28.0	-		30.0	20/ 3/69	480
WM 611	marine clay	7.4	2.1	22.0	15.3	23.0		9/ 3/48	100
IB 0013	marine clay	7.3	2.5	30.0	11.0	9.0	5.0	29/10/71	240
ZHE 282	marine clay	7.6	1.5	26.0	7.4	32.0		24/ 2/38	140
ZWZH 1355	marine clay	7.4	2.7	43.0	9.5		22.0	3/ 4/69	480
ZHE 294	marine loam	7.1	1.7	18.4	1.2	36.0		11/10/42	200
ZHE 241	marine clay	7.4	1.7	41.0	6.3	40.0		4/ 8/41	200
WF 387	marine clay	6.4	2.5	35.0	0.2	41.5		8/ 3/43	200
ZGe 384	fluvial clay	4.1	2.9	34.3	-	14.5		22/ 4/47	200
ZGe 836	fluvial clay	4.4	3.3	33.0	-	20.0		20/ 3/52	200

x) = $pH.H_2O$

3. RESULTS

Most field experiments have been conducted for 10-15 and some for (over) 20 years. Figures 1a, b, c, show soil Cd trends for the control (no P) and phosphate-treated plots at two-to eight-year intervals. Apart from some trials on marine clay and on sand, there is no definite rise in soil Cd in plots repeatedly given Cd-containing phosphate fertilizer. However, trends are difficult to interpret, also because of the erratic pattern shown by the untreated plots. In fact, trends are affected by gains in soil Cd from atmospheric deposition, apparent losses by "dilution" of the topsoil following deeper ploughing and sampling, and real losses due to leaching and removal with crops. Nevertheless the overall picture is for soil Cd to be highest in the phosphate-treated plots.

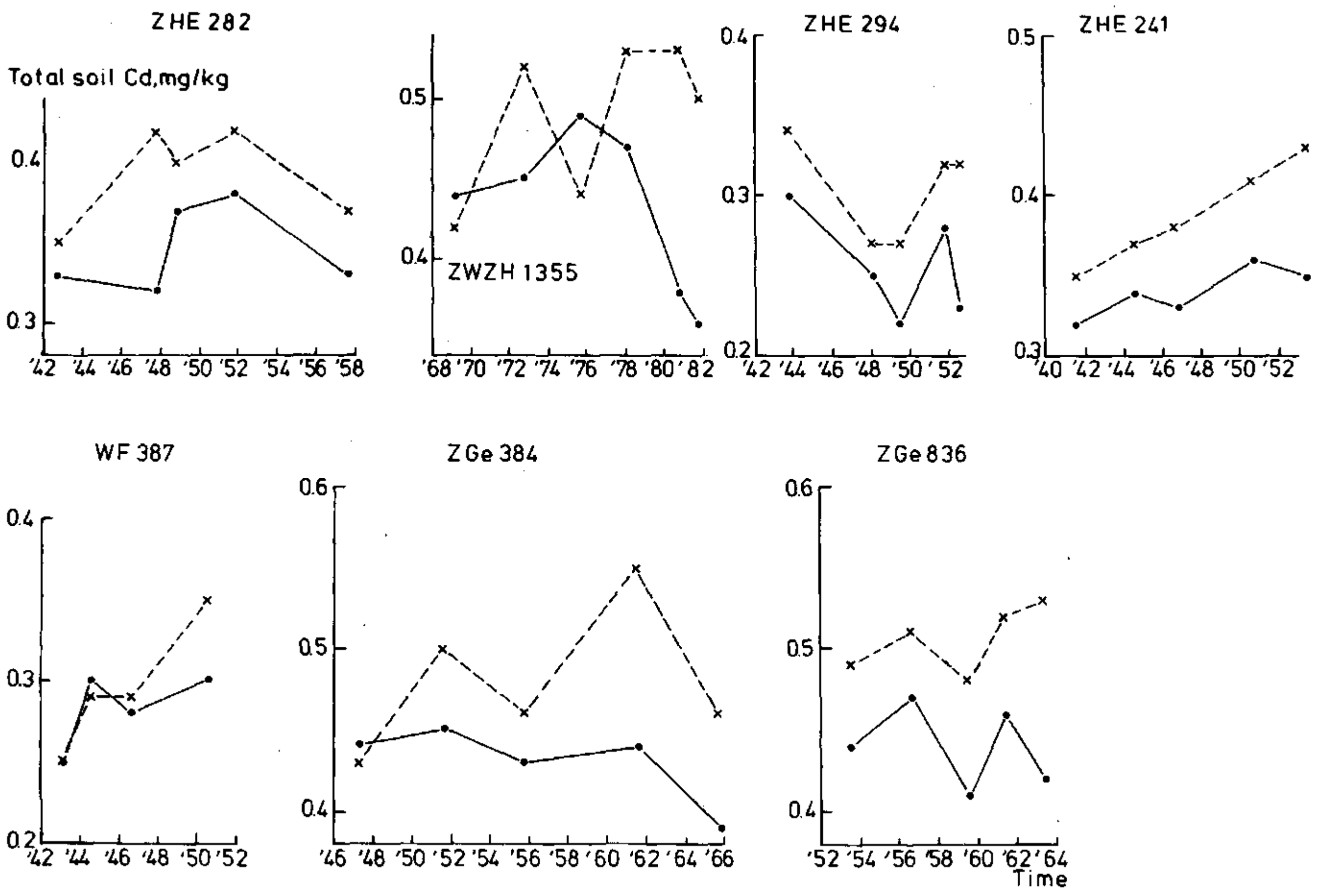

Figure 1a. Trends in (total) soil Cd in long-term phosphate fertilizer experiments. Marine and fluvial clay or loam soil; • = without P, × = with P.

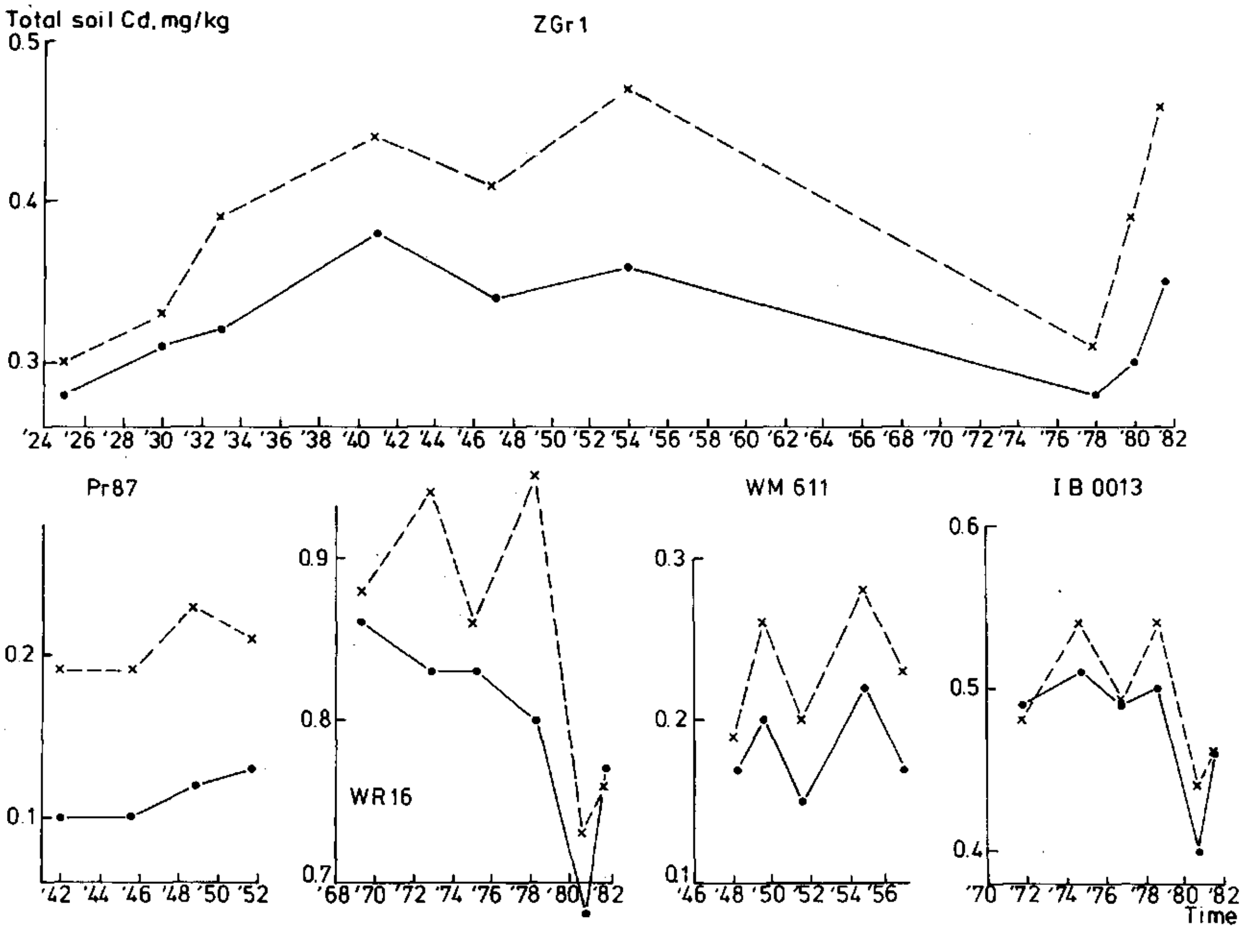

Figure 1b. Trends in (total) soil Cd in long-term phosphate fertilizer experiments. Marine clay, reclaimed peat and loess soil; · = without P, × = with P.

A better insight into soil Cd accumulation, following annual application of Cd-containing phosphate fertilizers, is obtained by plotting the *differences* in soil Cd between phosphate-treated and control plots against sampling dates. In this way the effects of atmospheric deposition and ploughing depth, which may be considered similar for phosphate-treated and untreated plots within one trial field, are eliminated. However, the effects of leaching and removal with the crop, which tend to be higher on phosphate-treated plots, remain.

The data from the various experiments have been assembled in one figure (fig. 2), adjusted to a standard annual application rate of 200 kg P_2O_5 per ha. It is assumed that differences in soil Cd between

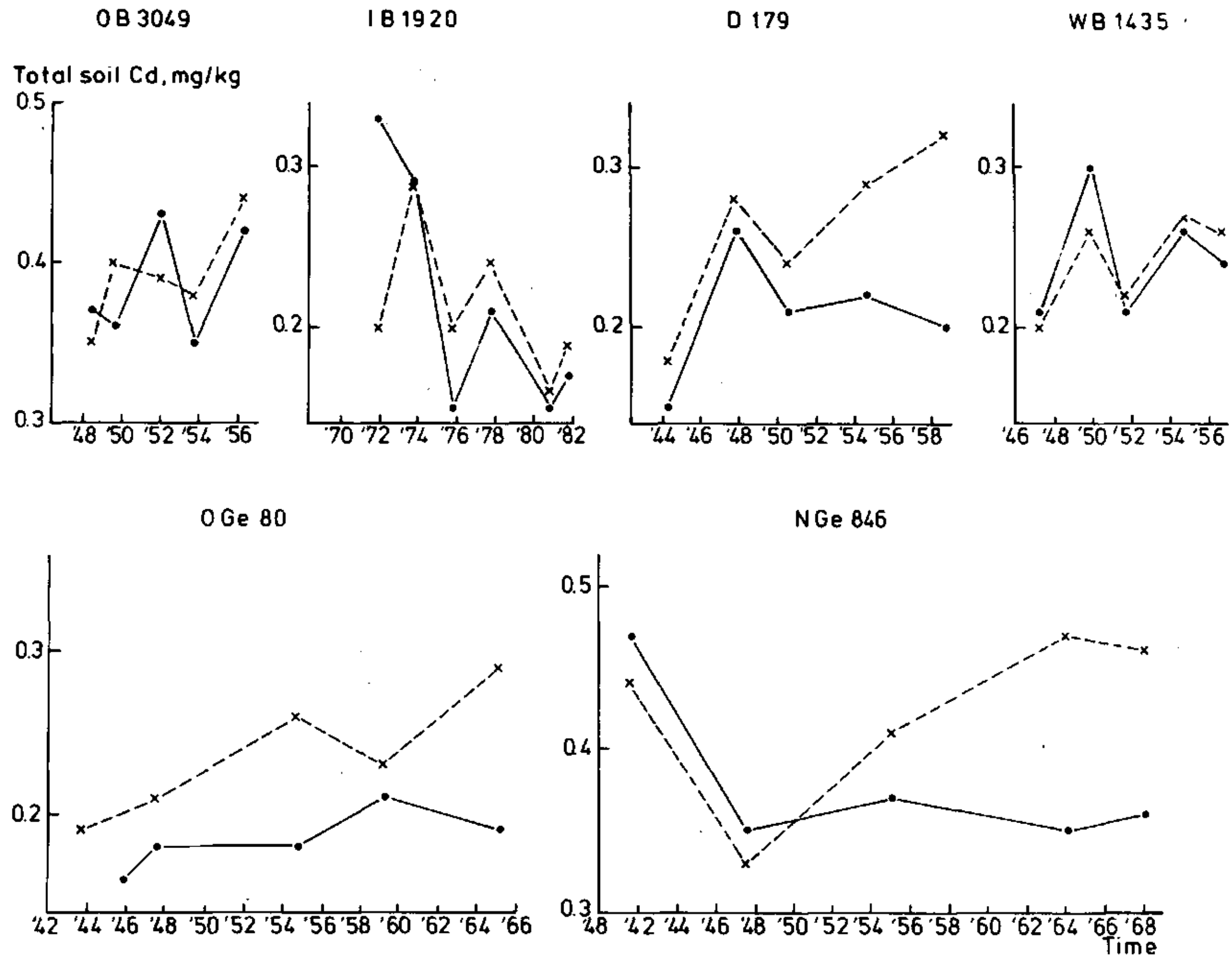

Figure 1c. Trends in (total) soil Cd in long-term phosphate fertilizer experiments. Sand; · = without P, × = with P.

phosphate-treated and control plots are proportional to phosphate application rate. For convenience, incidental differences in soil Cd existing before phosphate treatment started ($y \neq 0$ at $x = 0$, fig. 2) were eliminated by moving the curves parallel to the ordinate to the origin ($x = 0$, $y = 0$).

According to fig. 2, soil Cd accumulation amounted to 0.02 - 0.10 and 0.07 - 0.19 mg/kg in the experiments running for 10 and 20 years, respectively, i.e. a maximum annual Cd accumulation of 0.01 mg/kg. Unfortunately, a possible relation between soil Cd and fertilizer Cd cannot be determined as in most cases no fertilizer samples had been kept for subsequent (Cd) analysis. Cadmium concentrations of phosphate fertilizers used in the 1947-1964 period, ranging from 12-36 mg/kg (63-190 mg Cd/kg P_2O_5) and 9-60 mg/kg (21-140 mg Cd/kg P_2O_5) for super-

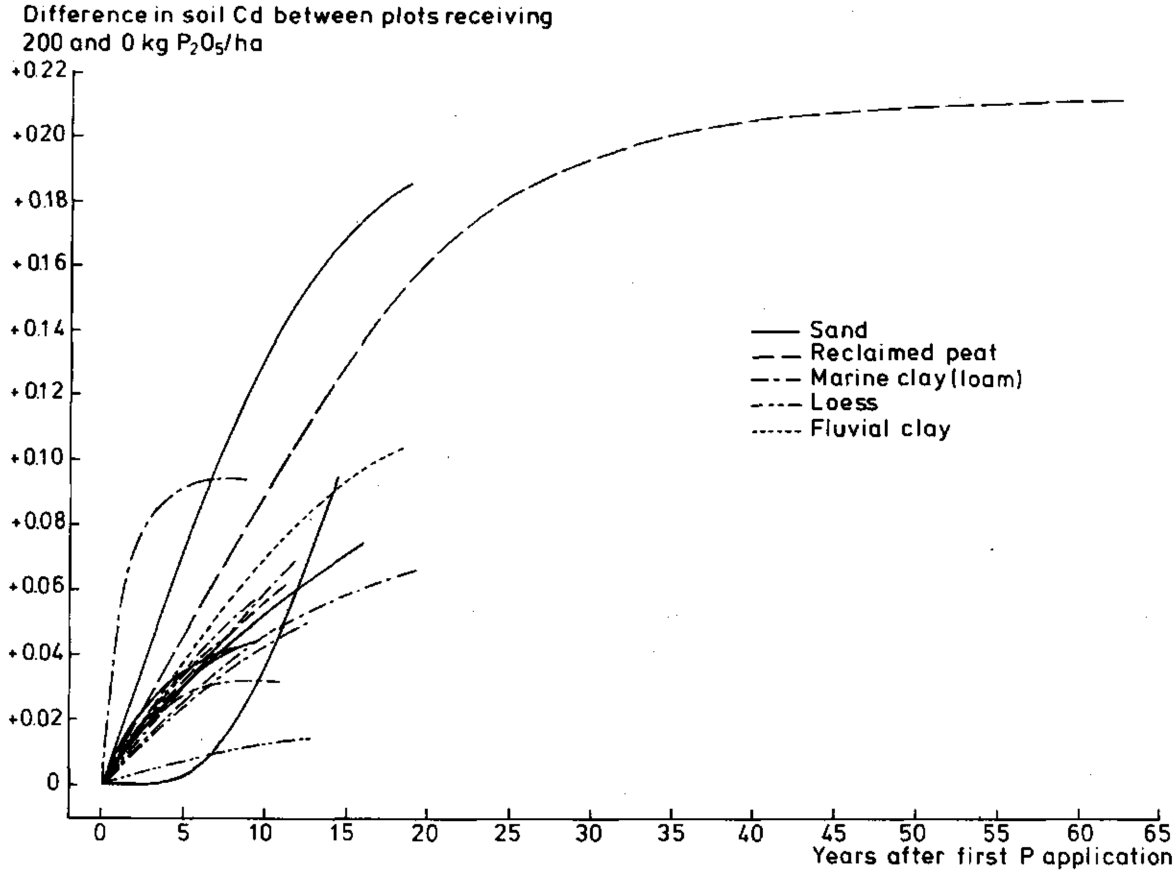

Figure 2. Trends shown by differences in soil Cd between plots given phosphate fertilizer (adjusted to 200 kg P_2O_5/ha) and control (0-P) plots in long-term phosphate fertilizer experiments.

phosphate and triple superphosphate, respectively, may be used as a reference.

In two, more recent, field experiments (IB 0013 and IB 1920), theoretical increases in soil Cd can be calculated (Table II), amounting to 0.09 and 0.04 mg/kg in 10 years, respectively, if annual phosphate application rates are adjusted to 200 kg P_2O_5 per ha. This is rather low as compared with the actual rise in soil Cd in the various experiments, i.e. 0.02 - 0.10 mg/kg in 10 years, as derived from fig. 2. There is some indication that at least the superphosphate used in one of the IB experiments contained relatively little Cd.

In table III data are given on Cd concentrations of crops grown in

TABLE II. Supply of Cd contained in phosphate fertilizer in a 10-year period in field experiments IB 0013 (marine clay; bulk density 1.2 g cm^{-3}) and IB 1920 (sand; bulk density 1.35 g cm^{-3}) given 240 kg P_2O_5/ha annually.

IB 0013	Triple superphosphate						
Year	sample	% P_2O_5	mg/kg Cd	mg Cd/kg P_2O_5	kg P_2O_5/ha	g Cd/ha	mg Cd/kg soil
1972	a	43.7	50	115	240	27.6	0.0115
1973	a	43.7	50	115	240	27.6	0.0115
1974	b	43.7	51	117	240	28.1	0.0117
1975	c	42.2	54	128	240	30.7	0.0128
1976	c	42.2	54	128	240	30.7	0.0128
1977	d	43.2	41	95	240	22.8	0.0095
1978	d	43.2	41	95	240	22.8	0.0095
1979	e	42.9	50	117	240	28.1	0.0117
1980	f	44.0	45	102	240	24.5	0.0102
1981	g	44.5	32	72	240	17.3	0.0072
Total					2400	259,8	0.1084

IB 1920	Normal superphosphate						
Year	sample	% P_2O_5	mg/kg Cd	mg Cd/kg P_2O_5	kg P_2O_5/ha	g Cd/ha	mg Cd/kg soil
1972	a	19.4	7.1	37	240	8.9	0.0033
1973	b	18.7	13.0	69	240	16.6	0.0061
1974	b	18.7	13.0	69	240	16.6	0.0061
1975	c	20.1	9.9	49	240	11.8	0.0044
1976	c	20.1	9.9	49	240	11.8	0.0044
1977	c	20.1	9.9	49	240	11.8	0.0044
1978	c	20.1	9.9	49	240	11.8	0.0044
1979	d	19.6	12.0	61	240	14.6	0.0054
1980	d	19.6	12.0	61	240	14.6	0.0054
1981	d	19.6	12.0	61	240	14.6	0.0054
Total					2400	133.1	0.0493

TABLE III. Cd concentrations of soil and crops in phosphate fertilizer experiments (mg/kg d.m.).

			Cd mg/kg soil				Cd mg/kg crop				P_2O_5	Cd
			without P_2O_5		with P_2O_5		without P_2O_5		with P_2O_5		kg $ha^{-1}year^{-1}$	g ha^{-1}
			1980	1981	1980	1981	1980	1981	1980	1981		until 1982
IB 0013	(1972)x)	sugar beet foliage	0.40	-	0.44	-	0.01	-	0.17	-	240	260
" "	"	spring barley (grain)	-	0.46	-	0.46	-	0.04	-	0.04		
" "	"	spring barley (straw)	-	0.46	-	0.46	-	0.13	-	0.11		
IB 1920	(1972)	sugar beet foliage	0.15	-	0.16	-	0.44	-	0.56	-	240	133
" "	"	potato tuber	-	0.17	-	0.19	-	0.08	-	0.13		
WR 16	(1969)	sugar beet foliage	0.68	-	0.73	-	0.45	-	0.37	-	480	250-450xx)
" "	"	onion bulb	-	0.77	-	0.76	-	0.24	-	0.26		
" "	"	onion foliage	-	0.77	-	0.76	-	0.28	-	0.33		
ZGr. 1	(1918)	potato tuber	0.30	-	0.39	-	0.06	-	0.15	-	100	250-450xx)
" "	"	winter barley (grain)	-	0.35	-	0.46	-	0.09	-	0.09		
ZWZH 1355	(1969)	sugar beet foliage	0.38	-	0.53	-	0.15	-	0.16	-	480	250-450xx)
" "	"	winter wheat (grain)	-	0.36	-	0.50	-	0.11	-	0.11		
" "	"	winter wheat (straw)	-	0.36	-	0.50	-	0.14	-	0.15		

x) year of first phosphate application   xx) estimation, assuming 40-70 mg Cd/kg P_2O_5 (normal superphosphate) long-term phosphate fertilizer experiments. There is no distinct difference in crop Cd between the phosphate-treated and control plots. A strong response in dry-matter yield to applied phosphate may lower crop Cd because of "dilution", and this may outweigh the effect of applied Cd.

4. DISCUSSION

According to published reports, part of the cadmium contained in phosphate fertilizers accumulates in the soil. This may or may not induce elevated crop Cd concentrations, depending on the following factors:

a. Cd content and amount of fertilizer used,
b. soil pH and chemical characteristics of the fertilizer,
c. crop response to phosphate: a strong response may result in a decrease in crop Cd ("dilution"),
d. the crop's ability to absorb Cd.

Trends in soil/crop Cd can be studied more comprehensively in experiments with various rates of phosphate (Cd) - see for instance Williams and David (1976), Andersson and Hahlin (1981), Mortvedt *et al.* (1981), Reuss *et al.* (1978) - than in those with a single phosphate (Cd) application rate, e.g. Mulla *et al.* (1980), Poletschny (1981), and the work presented here.

Williams and David (1976) report a considerable increase in (wheat) grain Cd in a field experiment on clay soil (pH 5.5), following application of 340 kg P_2O_5 per ha as superphosphate (183 mg Cd/kg P_2O_5) in a five-year period. In this experiment a total of 62 g Cd per ha was applied.

Andersson and Hahlin (1981) found a significant increase in (barley) grain Cd on a heavy clay following application of 1650 kg P_2O_5 per ha as superphosphate (52 mg Cd/kg P_2O_5) in 16 years. In this case a total of 86 g Cd per ha was applied.

Mortvedt *et al.* used three diammonium phosphate fertilizers, containing 4,154 and 318 mg Cd per kg P_2O_5, at a rate of 115 kg P_2O_5 per ha in a field experiment with winter wheat on a silt loam soil (pH 4.7). Grain Cd was only increased by the high-Cd phosphate fertilizer, supplying 37 g Cd per ha. The effect was eliminated by liming the soil. Grain Cd was lower in the low-Cd fertilizer treatment than in the control (no phosphate) because of the strong response of the crop to applied phosphate ("dilution").

Reuss *et al.* (1978) added 100 mg P per kg soil (about 620 kg P_2O_5/ha) as triple superphosphate with either 380 or 26 mg Cd per kg P_2O_5, to lettuce, radish and peas grown in pots in an acid sand (pH 4.5) or a heavy clay (pH 8.4) soil. The extra addition of 220 g Cd per ha with the high-Cd fertilizer was clearly reflected in crop Cd in the sand, but not in the clay soil.

In a field experiment with barley on silt loam (pH 6.7), Mulla *et al.* (1980) found no rise in crop Cd following 36 annual applications of 400 kg P_2O_5 per ha, as triple superphosphate containing 387 mg Cd/kg P_2O_5. This is rather surprising as a total of 5570 g Cd per ha was applied. However, in a pot experiment with Swiss chard (*Beta vulgaris*) grown in the phosphate-treated soil there was a distinct increase in crop Cd level compared with that in the control soil.

According to Poletschny (1981), Cd applications of up to 450 g per ha, contained in various phosphate fertilizers totaling 2875 kg P_2O_5 per ha over a period of 22 years, neither increased soil (loess, silt clay) nor crop Cd significantly.

Andersson (1976), Gunnarsson (1980) and Kloke (1980) postulate that soil Cd supply (via P fertilizers) and losses (by crop removal and by leaching) balance if the fertilizer contains no more than 35-70 mg Cd per kg P_2O_5 and normal rates of, say, 60 kg P_2O_5 per ha per annum are not exceeded. However, in this balance sheet atmospheric Cd is not accounted for.

Jung *et al.* (1979) conclude that there is hardly any effect on crop cadmium to be expected on "normal" soils, containing 0.1 - 1.0 mg/kg Cd, at "normal" rates of phosphate, i.e. 120 kg P_2O_5 per ha as a maximum. Low-Cd fertilizers alone are no guarantee that elevated crop Cd levels will not occur, according to these authors.

Sauerbeck and Rietz (1980) argue that restrictions on phosphate fertilizer Cd are not opportune as yet and that technical implications are complex. Moreover, low-Cd phosphate ores are not plentiful. In this context it should be stated that in Germany a maximum of 3 mg/kg (total) soil Cd is still widely accepted. In contrast, in the Netherlands a maximum value of 1.0 mg/kg (total) soil Cd is suggested, based on data from polluted fluvial sediments (Smilde *et al.*, 1982).

5. SUMMARY AND CONCLUSIONS

Cd-accumulation in soil, resulting from the use of phosphate fertilizer, was studied in 18 long-term field experiments, by comparing trends in soil Cd in the phosphate-treated and control plots. The effect of atmospheric Cd deposition can thus be eliminated.

Soil Cd accumulation amounted to 0.002 - 0.010 mg/kg per annum at a phosphate rate of 200 kg P_2O_5 and an estimated Cd rate ranging from 8 to 26 g (± 50%) per ha. There were no distinct differences among soil types.

It is postulated that applying, as an average, 70 kg P_2O_5 per ha per annum, and along with it 2.8 - 9.1 g (± 50%) Cd, does not result in an inadmissible rise in soil Cd in the first 100 to 200 years to come.

A Cd dose estimated at 135 - 450 g per ha, applied over the years in five long-term field experiments, did not significantly increase Cd concentrations of wheat (grain), barley (grain), potato (tuber), sugar beet (leaf) and onion (bulb). This was true for various soil types.

The experimental data would have been more valuable if Cd contents of all phosphate fertilizers used had been known, and also if soil/crop Cd concentrations had been determined for various phosphate rates within each experiment.

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