

Long-Term Effect of Phosphate Fertilization on Cadmium Uptake by Oat and its Accumulation in Soil

Bal Ram Singh*, Dependra KC and Asgeir RA

Faculty of Environmental Sciences and Natural Resource Management, Norwegian University of Life Sciences, Box 5003, 1430 Aas, Norway

Abstract

Phosphate fertilizers contain varying amounts of cadmium (Cd) and other heavy metals as contaminants from phosphate rock (PR). Periodic applications of these fertilizers could result in measurable accumulations of Cd in soils and in harvested crops. A long term field study for fifteen cropping seasons (1992-2006) was conducted on an experimental plot located at the Norwegian University of Life Sciences (Ås, Norway) to evaluate the effect of application of cadmium enriched phosphate fertilizer on Cd uptake by Oat (*Avena sativa*) and its accumulation and availability in soil. Treatments consisted of three NPK fertilizer sources containing 1, 90, 381 mg Cd kg⁻¹ P and applied at the rate of 0.03, 2.7, 11.43 g Cd ha⁻¹yr⁻¹, respectively. Surface soil samples (0-20 cm), collected after harvesting of oat in 1992, 1995, and 2006, and were analyzed for total and extractable Cd, pH, dissolve organic carbon (DOC) and PO₄³⁻. Plant samples collected in 1992, 1995, 1997, 2002 and 2006 were analyzed total Cd. Plant Cd generally decreased with increased soil pH throughout the experimental period except 1992. Increased input of Cd through fertilizers increased the Cd concentration in soil but the Cd concentration in oat grain remained unaffected. Ammonium nitrate (NH₄NO₃)⁻¹ extractable Cd in the soil increased with increasing rate of Cd through different sources but it decreased with increased pH throughout the experimental period with minor exceptions. Plant Cd did not show any significant correlation with extractable Cd in soil and hence the Cd input through fertilizers did not significantly affect the concentration of Cd in oat grain. Model (WHAM) prediction of Cd uptake by plants showed that crop yield, pH and DOC in combination explained about 57% of the variation in Cd uptake and DOC (r²=0.47, p<0.0001) was the most important factor. However, in individual years (e.g.2006) the combination of FA-Cd and yield did in fact explain 92% of the Cd-uptake.

Keywords: Cadmium; Cd uptake; Extractable Cd; NPK fertilizers; Oats; Plant Cd; Phosphate fertilizers; Soil pH; Soil solution; Modelling

Introduction

Since the middle of the last century, commercial fertilizers have played a critical role in increasing food and fiber production around the world. However, these fertilizers may also contain some nonessential and harmful elements such as cadmium, lead and/or arsenic [1]. There is a concern that continuous use of such fertilizers over a long period may cause an accumulation of trace elements to high levels, which ultimately increases the risk to environmental and human health [2]. Cadmium (Cd), in addition to its natural presence in soils, can be introduced through anthropogenic activities, e.g. Fertilization, organic waste disposal and atmospheric deposition [3]. Although P fertilizers represent the major anthropogenic input of phosphorus to agricultural soils, both inorganic P fertilizers and organic P sources (sewage, sludge and manure) contain Cd₃ [3]. In addition to direct inputs of Cd, phosphorus fertilizer can indirectly affect Cd accumulation in crops through its effects on soil chemistry, crop growth, and microbial interactions [4]. Most of trace elements are persistent in soil because of their relative immobility in soils. However, Cd is more mobile and soluble than other trace elements contained in fertilizers [5]. Cadmium is present in plant materials due to its uptake from soil [6]. The availability of Cd in soil and its uptake by plant depend on several soil and plant factors. Cadmium enters human body from environment through ingestion via food (especially plant-based food) mechanism [7].

When we apply phosphorus fertilizer to our cropland, trace element, especially Cd, also enter soil as fertilizer contaminants [8,9]. The amount of Cd taken up by an individual plant depends on the amount of bioavailable Cd present in the soil [10] and the physiological and morphological characteristics of the plant [11]. In a short-term growth chamber study, increase in Cd concentration in durum wheat by P fertilization was caused by increased uptake and translocation by decreasing Zn accumulation by P fertilization rather than direct

addition of Cd [12]. For a single or few applications, Cd addition will be insignificant compared with total volume of receiving soil but repeated application may lead to a gradual buildup of Cd in agricultural soils over time [13]. In long-term field studies in USA, UK and Norway, no significant change in the Cd content of soils was found from the application of phosphorus fertilizer [14]. However, researchers in Australia and the U.K. reported that long-term applications of P fertilizers increased concentration of Cd in surface soil [15,16]. Increased Cd accumulation in oat, ryegrass, carrot, and spinach was reported in response to the application of P or NPK fertilizer containing 1 to 400 mg Cd kg⁻¹ P [17].

Assessing the impact of phosphate fertilization on the accumulation of Cd in soils and its transfer to plants requires adequate knowledge of how various factors affect Cd phytoavailability. Soil properties that can influence Cd availability include pH, clay type, chloride content and the content of soil organic matter and Fe and Mn oxides [18]. Of these soil properties, soil pH is often the most important factor in regulating the availability of Cd in soil and its uptake by plants [11,19]. However, increasing soil pH does not always reduce Cd availability in soils and plant uptake, because this relationship depends on other factors such as soil characteristics, plant species and field conditions [20]. Singh et al. [19] found that the decrease in Cd concentration was not consistent

*Corresponding author: Bal Ram Singh, Faculty of Environmental Sciences and Natural Resource Management, Norwegian University of Life Sciences, Box 5003, 1430 Aas, Norway, Tel: +4773595000; E-mail: balram.singh@nmbu.no

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at pH levels beyond 6.5. Besides the soil and plant factors, the field conditions can change the Cd availability to plants, due to a better plant root system induced by liming or environmental conditions [20].

The impact of P fertilization has mostly been evaluated under growth chamber studies and relatively few information are available on long-term effects of repeated application of Cd through P fertilizers. The hypothesis is that i) long-term use of Cd-rich P- fertilizers increase the total and labile concentrations of Cd in soil, and ii) that the uptake of Cd have increased as a function of the long-term applications of Cd rich P to soils. Hence, a long-term experiment was conducted at the experimental farm of the Norwegian University of Life Sciences Ås, southeastern Norway. This area is one of the most productive Norwegian agriculture regions, and is characterized by slightly acid soils. The study was designed to investigate the effect of P fertilizers containing varying amounts of Cd, based on the origin of rock phosphate, on total and extractable Cd in soils and its uptake by plants at different pH levels during a period of 15 years under field conditions.

Material and Methods

Field experiment

A long-term fertility experiment was initiated in 1992 at the experimental farm of Department of Environment Sciences, Norwegian University of Life Sciences, Ås, on a loam soil (39% sand, 40% silt and 21% clay), classified as Fluventic Humaquept [21]. The soil contained 2.4% organic carbon, 0.19 mg Cd kg⁻¹ and 82 mg extractable P kg⁻¹. Prior to initiation of this experiment, the field was used for a liming experiment with different pH levels over a long period. The cadmium (Cd) experiment was imposed on this liming experiment. The experiment was a factorial randomized block design with 18 plots (2 replicates, 3 initial pH levels and 3 Cd-treatments). Each plot was 4.5 m × 10 m=45 m², with the harvesting area of 2 × 8=16 m². Before conducting the experiment, the plots were treated with lime (dolomite 31.5 %) to achieve soil pH₁=5.0 (no lime), pH₂=5.6 and pH₃=6.0. However, that pH range not successfully obtained (Table 1). The liming was thus repeated during the course of the study to keep the pH levels near to the initial values set. Phosphorus fertilizers were applied at the rate of 30 kg ha⁻¹ and three different NPK fertilizers with different Cd concentration were used. The first fertilizer (NPK with 17%, N 5% P, and 13%K) contained 1 mg Cd kg⁻¹ P, and supplied about 0.03 g Cd ha⁻¹ yr⁻¹. The second fertilizer (15% N, 15%P, and 15% K) contained 90 mg Cd kg⁻¹ P and supplied 2.7 g Cd ha⁻¹ yr⁻¹ and the third fertilizer (15% N, 15% P, and 15% K), contained about 381 mg Cd kg⁻¹ P and supplied 11.43 g Cd ha⁻¹ yr⁻¹. YARA Norge AS, based on rock phosphate of different origins, manufactured these fertilizers. All fertilizers were applied as basal dose before sowing oat.

Parameters	1992	1995	2006
Soil pH ₁	4.5 (0.02)	4.4 (0.04)	5.1 (0.04)
Soil pH ₂	5.1 (0.06)	5.0 (0.50)	5.6 (0.18)
Soil pH ₃	5.7 (0.12)	5.8 (0.07)	5.9 (0.15)
DOC (mg l ⁻¹)	115 (29.9)	112 (32.1)	36 (5.8)
P-AL, (mg kg ⁻¹)	82		91
PO ₄ ³⁻ (mg kg ⁻¹)	0.17 (0.06)	0.15 (0.02)	0.12 (0.01)
CEC (1M NH₄AC):			
Ca ²⁺ (mg kg ⁻¹)	4.9		7.3
Mg ²⁺ (mg kg ⁻¹)	0.62		0.87
Na ⁺ (mg kg ⁻¹)	0.05		0.09
K ⁺ (mg kg ⁻¹)	0.3		0.5

Table 1: Chemical properties of soil collected in 1992, 1995 and 2006.

Collection of soil and plant sample

The surface soil samples (0-20 cm) for this study were collected from three years 1992,1995 and 2006, while those of grain samples from five years 1992, 1995, 1997, 2002 and 2006. In each plot, 6-8 subsamples were collected from 0-20 cm depth with soil auger, which were made into a composite sample. During soil sampling, a grid pattern with Zig-Zag line was followed so that the composite sample represents the entire plot. This stratified random method increases the precision for the field as well as it increases the accuracy of soil tests. This composite sample was then air dried, ground and passed through a 2 mm sieve prior to analysis. Crop harvested at maturity was separated into grain and straw but only grain samples were used for Cd analysis.

Soil analysis

Soil samples were analyzed for “total” and extractable Cd, cation exchange capacity, dissolved organic carbon, PO₄³⁻ and soil pH as described below.

Total and extractable Cd: Estimation of the apparent total concentration of Cd in soil (from now on coined total Cd) was conducted after decomposing the soil by concentrated strong acid as outlined here: 1 g of soil sample was placed into a Teflon tube with 5 ml of freshly sub boiled ultra-pure nitric acid, and the digestion was performed with an Ultraclave. The start pressure was 50 bars and the Ultraclave temperature was 250°C for about 25 minutes. The digested samples were diluted to 50 ml by adding double de-ionized water. The same soil samples were also extracted with 30 ml of 0.01M NH₄NO₃, having soil solution ratio of 1:10. This solution was mixed with 3 g of soil and shaken overnight. The next day, the solution was centrifuged for 30 min. The suspension was passed through a Blue Ribbon (diameter 125 mm) filter, and kept overnight at room temperature. The concentration of Cd in the digested and extracted solutions was determined by ICP-MS (Perkin Elmer Sciex Elan 6000) using Rh (Rhodium) as internal standard. Here, we use the term extractable Cd for NH₄NO₃ extractable Cd.

Soil chemical parameters: For the determination of dissolved organic carbon (DOC) and phosphate ions (PO₄³⁻), soil samples were extracted with 30 ml of 0.01 M KNO₃, having a soil solution ratio of 1:10. The suspensions were filtered through “Blue ribbon” filters and the PO₄³⁻ ions in filtrates were determined by a Lachate IC500 Ion Chromatography analyzer. For the determination of DOC, the filtrates were passed through 0.45 μm membrane filters and analyzed by a Shimadzu TOC-V analyzer with Pt-catalyzed combustion. Experimental blanks were provided. Soil pH was measured at a soil-water ratio of 1:2.5 w/v by glass electrode (Orion pH-instrument model SA 720 with combination pH electrode) [22]. 1M ammonium acetate (NH₄AC) at neutral pH was used to determine soil cation exchange capacity (H⁺, Ca²⁺, K⁺, Mg²⁺, and Na⁺) (CEC). Three g of soil was mixed with 20 ml of 1 M NH₄AC and shaken on an end over end shaker overnight. The next day, the suspension was passed through a Blue Ribbon (Dia 125 mm) filter, and made to 25 ml with NH₄AC [23]. The extracted solution was analyzed for cations by using an ICP-OES analyzer (Perkin Elmer, Optima 5300 DV) and H⁺ by titration with NaOH.

Analysis of plant samples

To determine dry matter yield, grain samples were oven dried at 105°C and weighed. The grain samples were digested by dry-ashing the plant samples at 450°C with treatment of 1:2 conc. HCL: HNO₃ mixture. The heating and acid digestion step was done twice and the

collected residue was then dissolved in 5 ml of HNO₃ and finally diluted to 50 ml by double distilled water prior to analysis of Cd by an ICP-OES analyzer (Perkin Elmer, Optima 5300 DV).

WHAM modelling

The speciation of Cd in the 0.01M NH₄NO₃ extracts was calculated using WHAM/Model VII version 7.0.4 for waters [24]. Input values (Cd, pH, DOC, PO₄³⁻), are shown in Tables 1 and 2. The 0.01 M concentrations of NH₄⁺ and NO₃⁻ from the extract solution was also included. We treated the system as being in equilibrium with the atmosphere (p CO₂=3.9 × 10⁻⁴ atm.). We also assumed dissolved organic matter (DOM) to have the ion binding properties of 'default' fulvic acid, FA, as defined in WHAM/Model VI, and that the DOM is 50% carbon by weight. As suggested by the software guide, we let 50% of the acid groups of FA being active in proton/metal binding. The free ion activity of (FIA) Cd or Cd bound to dissolved organic matter (DOM) is quoted as Cd-FIA and Cd-DOM, respectively.

Statistical analysis

All statistical analysis were conducted using JMP Pro v 13.0.0 [25]. The models included were analysis of variance, stepwise-, linear- and multiple regression. The level of statistical significance relative to P values is hereafter referred to as P <0.05 or P > 0.05, being statistically significant or non -significant, respectively.

Results and Discussion

Total and extractable Cd concentration

The liming treatments had forced the soil pH to near the three desired levels, but soil pH increased slightly with years (Table 1). At least in the most acid soils. Although the Cd-application rates increased with two folds from lowest to highest, there was no significant increase in CdHNO₃ ("total") before 2006 (Table 2). Neither within treatments nor as compared to the inherent CdHNO₃ before initiation of experiment (0.19 mg/kg). In soils from 2006, the repeated application rates had created a minor, but corresponding increase with the CdHNO₃. The little effect of Cd input on soil Cd (total or extractable) is partly assigned to relatively minor contribution of Cd input (0.03-11.43 g/ha), and from the literature, the effect of low application rates of Cd to cultivated soils vary. Jeng and Singh [14] found only minor changes in Cd content of soil samples from the treated plots with organic and inorganic fertilizers during a long-term experimental period from 1963 to 1991. The results reported by Sato et al. [26] and Meers et al.

[27] also support this finding. Others have reported some increase of Cd resulting from long-term applications of Cd-rich P-fertilizers. In a long-term mineral fertilization experiment carried out in Germany, it was found that aqua-regia extractable Cd in soils increased due to long-term application of commercial fertilizer as compared to control plots [28]. Similarly, Loganathan et al. [29] and Gray et al. [30] found marked increase in acid-extractable Cd in surface soils after long-term fertilization in pasture systems in New Zealand. From a greenhouse experiment, He and Singh [17] reported that increasing the Cd input from 2,7 µg Cd kg⁻¹ soil to 12,5 µg Cd kg⁻¹ soil through P fertilizers, resulted in an increase in acid-extractable Cd in a loam soil from 18,7 µg Cd pot⁻¹ soil to 87,0 µg Cd pot⁻¹.

The NH₄NO₃ extractable Cd (CdNH₄NO₃) in our field trial was controlled by other factors than the application rates, and most evident is the pH. Even if it seems from Table 2 that the CdNH₄NO₃ in 2006 is controlled by the application rates, the statistical tests show a very strong correlation with pH for that year. The pH was negatively correlated with CdNH₄NO₃ in 1992 (r²=0.88, p<0.001) and 2006 (r²=0.89, p<0.001), but not correlated in 1995. Such pH-effect have also been reported by Wang et al. [31], who found significant increase of extractable Cd with decrease in soil pH for plant *Thalspi caerulescens*. Similar results have been reported by several others [19,32,33]. The positive and non-significant relationship between NH₄NO₃ extractable Cd and Cd input through fertilizers have earlier been reported [14,34-36]. The year 1995 was an exceptional year, with for instance very high plant yield (Table 3), and for that year the DOC was positively correlated with CdNH₄NO₃, (r²=0.71, p<0.001). The DOC extracted from the 1995 soils was, however, not exceptionally high compared to 1992 sampling. It can be seen in Table 1 that the DOC is remarkably much lower in 2006 compared to 1992 and 1995, and the concentrations of CdNH₄NO₃ were reduced to almost half compared to the earlier samplings. This is partly related to the increased pH in 2006 and possibly the low DOC. A combined regression model containing pH and DOC described 42% of the variation in CdNH₄NO₃ significantly (p<0.001) across the three years, where pH is negatively related and DOC positively related to CdNH₄NO₃. From a batch titration study conducted by Almås et al. [37], the same solubility controlling mechanisms were observed and described by WHAM/Model VI [24] making use of a parameterized version of the SCAMP sub-model [38]. These were mostly cultivated soils, and the solution pH was controlled by an active soil Ca pool (soils were frequently limed). When the pH control was optimized, the soluble cations were mostly well predicted. Moreover, the optimized model predicted solid phase metals predominantly bound to soil

Parameters	Cd-rate g ha ⁻¹ y ⁻¹	1992	1995	2006
Cd _{HNO3} (mg/kg)	0.03	0.17 (± 0.01)	0.19 (± 0.01)	0.19 (± 0.02)
	2.70	0.19 (± 0.01)	0.19 (± 0.01)	0.21 (± 0.01)
	381	0.17 (± 0.01)	0.18 (± 0.01)	0.22 (± 0.02)
Cd _{NH4NO3} (µg/kg)	0.03	7.0 (± 5.6)	8.1 (± 7.5)	4.3 (± 3.0)
	2.70	6.6 (± 5.4)	8.3 (± 7.5)	3.8 (± 3.3)
	381	7.0 (± 5.5)	7.5 (± 6.7)	5.6 (± 4.2)

Table 2: Cadmium in soil and soil extracts in 1992, 1995 and 2006. The inherent CdHNO₃ was 0.19 mg/kg before initiation of experiment (Std.dv. are shown, n=6).

pH treatment level	Grain yield kg ha ⁻¹				
	1992	1995	1997	2002	2006
5.0	773 (± 54)	na	2972 (± 333)	2614 (± 58)	1188 (± 40)
5.6	1178 (± 137)	4628 (± 209)	3383 (± 206)	2855 (± 109)	1247 (± 33)
6.0	1027 (± 60)	4973 (± 13)	3046 (± 76)	2589 (± 219)	1127 (± 24)

Table 3: Long -term pH-effect on grain yield of plant in different years (Std.dv. are shown, n=6).

organic matter and insignificantly to clays and iron/aluminum oxides. We assume that the same mechanisms control Cd solubility in this field trial as both pH and DOC plays a role.

Grain yield

Except from the harvest in 1995, for all the other years plants were harvested, pH treatment 5.6 resulted in the highest grain yields (Table 3). In general, grain yield increased from year 1992 to 1995 and then it decreased significantly from 1995 to 2006. There was no significant difference comparing grain yields of 1992 with 2016. The Cd treatment had no significant effect on yield and hence annual yields are grouped for each pH treatments. Grant et al. [8] also did not find any effect of moderate Cd applications on grain yield of durum wheat or flax. The exceptional high yield in 1995 was compared with meteorological data from the area, and generally was the summer 1992 dry (average 2.0 mm during June and July) and temperature low during growth season (June and July, oscillating around 16.8°C). In 2006 the precipitation (average 1.7 mm during June and July) was less than in 1995 (average 4.8 mm during June and July). It seems, however, to be important that in 1995 there were frequent episodes of short but heavy summer rain (episodes of 20, 40 to 80 mm/day) during June and July. Those heavy summer showers have likely humidified the whole root zone better, resulting in higher yields. Average temperature in 1995 and 2005 were 15.3°C and 17.2°C, respectively.

Plant cadmium concentration

Increase in Cd input through fertilizers from 0.03 g/ha/yr to 11.43 g/ha/yr did not significantly affect the Cd concentration in plant within the trial period (Table 4). Neither did the application doses affect the uptake. The lack of direct relationship between moderate Cd application to soil and uptake in plants have also been reported by others [32,36,39-41]. Guttormsen et al. [42] did however, report significant increase of plant Cd concentration with increase in Cd input, using the same range of Cd input through P fertilizers. In that experiment, however, Perriguet et al. [43] found increased Cd concentration in roots of maize plant with increasing concentrations of Cd in nutrient solution. The transport to the rest of the plant was not affected equally. The phytoavailability of Cd in soil depends upon the plant species [44] and its physiological status [45,46], but also on the geochemistry of Cd in soil solution and the ability of the solid phase to replenish Cd removed from soil solution during the plant uptake period. The geochemistry of trace metals in soils are mostly controlled by the pH, soil organic material (SOM) and OC, whereas the level of concentration is determined by the inherent total concentration in soil [37,47-49].

The statistical relationship between concentration of Cd in plant, yield and some geochemical parameters was tested. These were pH, DOC, Cd-FIA, Cd-DOM, CdHNO₃, CdNH₄NO₃, and PO₄³⁻. Yield was very different between years and the total uptake, or offtake, is higher in years of good yield (all three years, r²=0.50, p<0.0001). Soil pH is a major factor influencing Cd solubility and mobility in soils. Cd Solubility and ion activity decreases with increasing pH that finally increases Cd sorption. Therefore, the soil distribution coefficient (K_d),

increases with increasing pH, while phytoavailability correspondingly decreases [50,51]. Low soil pH contribute to greater plant availability of the Cd present in the soil [8]. Since pH is an important factor controlling the geochemistry of Cd, pH was tested against Cd uptake. The relationship was insignificant for all years, and significantly negative only for the 2006 year data (r²=0.82, p<0.0001). After an initial stepwise regression exercise containing the above mentioned parameters, we tested a multivariate regression model on the Cd uptake. The uptake was controlled by yield, pH and DOC (r²=0.75, p<0.0001). When the exceptional year 1995 was removed from the data, yield and DOC were still significantly controlling the uptake (r²=0.68, p<0.0001). Since however, uptake is the product of yield and concentration, the Cd uptake was tested without yield, and then pH and DOC in combination explained about 57% of the variation in Cd uptake. The most significant parameter was DOC (r²=0.47, p<0.0001) all the three years included. When every year was investigated separately, yield was always the most significant parameter. One year in company with pH (1992), or PO₄³⁻ (1995) or FA-Cd (2006). In 2006, the combination of FA-Cd and yield did in fact explain 92% of the Cd-uptake. In sum for this soil type, the yield seems to be the most important factor controlling the Cd uptake from a soil amended with moderate amounts of Cd through inorganic fertilizer. McLaughlin et al. [52] reported that Cd concentrations in potato tubers were positively related to the degree of Cd-Cl complexes in solution. Despite that Cd form complexes with Cl, the Cl concentrations in soil solution in this soil are too low to have an impact as there is an excess of rain water preventing accumulation of Cl in the root zone. Increase in soil pH decreased plant cadmium concentration. These results are in accordance with those reported by several investigators [34,42,53]. Cieccko et al. [54] reported ten folds decrease in plant Cd concentration with liming in their experiment on Triticale and oil rapeseed.

Long-term effects

The same three doses of Cd concentration (0.03, 2.7 and 11.43 g/ha) were applied through P fertilizer during 15 years of the experiment. The observed changes in total and extractable Cd in the soil and concentration and uptake of Cd in plant during the entire experimental period are described below.

Changes in total and extractable Cd concentration in soil

Total cadmium concentration varied differently during the experimental years for each Cd treatment. At the application rate of 11.43 Cd g ha⁻¹, an increase in total Cd concentration was observed throughout the experimental period. However, at the rate 2.7 g Cd ha⁻¹, total Cd decreased in 1995 but increased in 2006, while in the control treatment (0.03 g ha⁻¹) total Cd increased consistently despite at a much lower rate (Figure 1). Cadmium enrichment in soils through mineral fertilizers is reported in the literature. Loganathan et al. [29] and Gray et al. [30] reported that the long-term (10-47 years) application of phosphate fertilization to pasture systems in New Zealand caused a significant increase in total Cd in soils. Similarly, Czarnecki and During [28] found that pseudo total and mobile concentration of metals (Cd, Cu, Pb and Zn) increased in soils due to application of 14 years of mineral fertilizer application as compared to control plots.

Input Cd (g ha ⁻¹ y ⁻¹)	Plant Cd (mg kg ⁻¹)				
	1992	1995	1997	2002	2006
0.03	0.12 (± 0.015)	0.04 (± 0.014)	0.06 (± 0.016)	0.03 (± 0.013)	0.03 (± 0.009)
2.7	0.09 (± 0.032)	0.03 (± 0.007)	0.05 (± 0.02)	0.03 (± 0.014)	0.02 (± 0.009)
11.43	0.09 (± 0.026)	0.03 (± 0.011)	0.07 (± 0.02)	0.03 (± 0.018)	0.03 (± 0.011)

Table 4: Relationship between Cd in oat grain and Cd input in different years (Std.dv. are shown, n=6).

A slight increase in extractable Cd was observed in 1995 as compared to 1992 for the Cd input rates of 2.7 and 11.34 but the concentration decreased in all Cd treatment in 2006. Availability of the applied Cd may be attenuated over time by various aging processes. In a growth chamber study, Hamon et al. [55] reported that in the soils, where Cd application was terminated after 27 years of mineral fertilizer application, 40% of the added Cd over time was in plant available form, while in the soil where Cd application was still continuing (47 years after) about 72% of the Cd was in plant available form. The decrease in availability between the continuous and rundown plots indicates that stabilization processes occurring overtime decreased the availability of Cd added to the soil. This stabilization may provide a partial explanation for the lack of consistent trend in increasing Cd availability over time with repeated application of Cd in mineral fertilizer.

Change in Plant Cd concentration and uptake

Cadmium concentration in oat crop decreased during the period of 1992-1995 and then increases from 1995-1997, being highest in 1997 and then it decreases until 2006 (Figure 2). The differences in Cd among the years were significant ($p < 0.05$). There were minor changes in plant Cd concentration with increased Cd input. Although year to year variability in plant Cd concentration could be associated with dilution/ concentration effect as observed by Grant et al. [8] where the highest annual Cd concentration in the control treatments was associated with the lowest annual grain yield. This seems not to be the case in the present study because control plots with generally lower yield (Table 3) showed higher Cd concentration. In addition, the year 1992 with lowest yield in all the years showed much higher plant Cd concentration. However, as stated above, attenuation in Cd availability with time may be partly responsible for this variability.

Increase in soil pH decreased plant Cd concentration significantly in all the years. Such relationship between soil pH and plant Cd has been widely reported in the literature [19,31-33,56]. Wang et al. [31] reported that the extractable Cd increased with lowering of soil pH and resulted in enhancing phytoextraction. Reiser et al. [56] also showed that soil pH, soil Fe and soil Cd provided an excellent predictor of the $\text{Ca}(\text{NO}_3)_2$ -extractable soil Cd fraction, but they explained just 38% of the variation of Cd concentration in pasture grasses.

Conclusion

Long-term use of phosphorus fertilizers containing Cd is of greater concern because of danger associated with its build up in soils and further transfer to food chain. Thus, the major objective of this experiment was to assess the effect of Cd input and soil pH on the availability of Cd to plant. Cd input through fertilizers showed no significant effect on either plant Cd or soil Cd. Hence, we can conclude that plant Cd as well as soil Cd did not change over time at the rates of Cd added within the range used in this experiment. However, soil pH generally showed negative effect on Cd uptake and its availability to oat plant throughout the experimental period. Due to occasional (every 4th or 5th year) liming, soil pH was increased over 14 years leading to decreased plant Cd uptake and soil Cd concentration. Beside soil pH, grain yield also affected Cd uptake by oat plant as higher yield resulted in higher Cd uptake.

Model (WHAM) prediction of Cd uptake by plants showed that crop yield, pH and DOC in combination explained about 57% of the variation in Cd uptake and DOC ($r^2 = 0.47$, $p < 0.0001$) was the most important factor. However, in individual years (e.g. 2006) the combination of FA-Cd and yield did in fact explain 92% of the Cd-

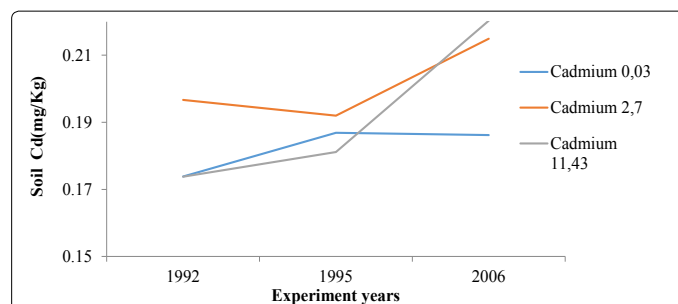


Figure 1: Long-term effect of Cd input through fertilizers on total Cd concentration in soil.

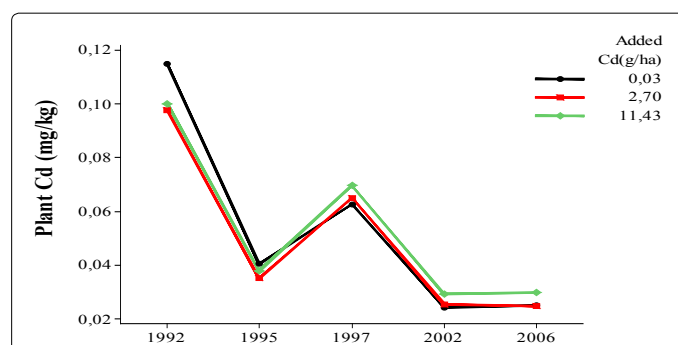


Figure 2: Long-term effect of Cd input through fertilizers on plant Cd.

uptake. A slight increase in extractable Cd in soil was observed after continuous fertilization. Since there was no significant effect of the rate of soil Cd application on the yield and plant Cd uptake, the long-term use of Cd enriched P-fertilizers increased the total concentration of soil Cd slightly. Even though soil Cd concentration increased with increase in Cd enriched phosphorus fertilizer, its bioavailability depended more on soil pH rather than Cd input through fertilizers.

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