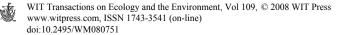
Effect of phosphorus in commercial fertilizers on phytoavailability cadmium and zinc uptake by sugarcane

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Abstract

The effects of phosphorus in commercial fertilizers on concentrations of total cadmium (Cd) and zinc (Zn), plant-available Cd and Zn and sugarcane uptake of Cd and Zn were studied. A single rate (312.5 kg/ ha) of 16-16-8 NPK fertilizer was applied on three levels (0-3, 3-20 and >20 mg) of Cd contaminated sugarcane cultivated field in Mae Sot district, Tak province. In order to investigate the effects of different rates of fertilizer application, 16-16-8 NPK fertilizer at the rate of 312.5, 625 and 1,250 kg fertilizer/ ha was applied to soils in a pot experiment and planted with a piece of mature cane stem. The pot experiment was conducted in a randomized block design with three replications. Repeat applications of fertilizer were made at the same rate in the fifth month of the cultivation for both field and pot experiments. Soil and sugarcane samples were collected at the end of the second and the sixth month respectively. After harvesting, sugarcanes were divided into five components: underground stems, roots, bagasses, juice and leaves. Chemical analysis of the field experiments showed that total Cd and Zn in sugarcane increased with Cd concentration in cultivated field and found that Cd and Zn mostly accumulated in roots. Longterm effects of fertilizer application was expected to be a concern although there was no higher Cd and Zn concentrations in soil after repeat fertilization in the fifth month of the cultivation. For the pot experiment, the results showed that higher P can make more Cd available and ease take up and accumulation in different parts of the sugarcane. Moderate P application rate reduced phytoavailability of Zn at the end of the second month because of the P-Zn mineral precipitation. However, the ability of sugarcane to uptake Zn increased again at the end of the sixth month of the cultivation at which time total P in the soil decreased. Total Cd and Zn in sugarcane were significantly increased with increasing 16-16-8 NPK fertilizer application rates and we found that Cd and Zn accumulated in sugarcane according to the following sequence: roots> underground stems (setts)> bagasses> leaves> juice.

Keywords: phosphorus, fertilizers, cadmium, zinc, phytoavailability, sugarcane.



1 Introduction

Natural geochemical processes and anthropogenic activities are two major means of releasing hazardous substances, such as heavy metals, into the environment. Among the various metals, cadmium (Cd) and zinc (Zn) are two widespread harmful heavy metals. Cd is closely related to Zn and will be found wherever Zn exists in nature. Department of Primary Industries and Mines [1] reported elevated levels of Cd in paddy soils and rice grain downstream of a Zn mining area in Pra Tad Padang, Mae Ku and Mae Tao sub-district, Tak province. Over 90% of rice grain samples collected contained Cd at concentrations exceeding the Codex Committee on Food Additive and Contaminants (CCFAC) draft Maximum Permissible Level for rice grain of 0.2 mg/kg. This level may cause health problems along the food chain. For this reason, it has become necessary to look economically efficient non-food crops to cultivate in Cd contaminated areas. Owing to the energy crisis in Thailand, sugarcane has been studied for use as a raw material for ethanol production. This led to the idea of sugarcane cultivation instead of rice farming in the affected areas. Meantime, the application of fertilizers has expanded rapidly in sugarcane cultivated fields in Tak province to promote sugarcane growth and improve the quality and quantity of sugarcane production.

Phosphorus (P) is one of the essential nutrients for plant growth. Plants need P for utilization of sugar and starch, photosynthesis, nucleus formation and cell division. However, a possible negative effect of P fertilizers is the contamination of cultivated lands by trace metals naturally present in the P rocks used to manufacture the fertilizers. Cd contaminate in phosphorus fertilizers is considered as one of the major sources of metal addition in agricultural soils. Moreover, contaminates could be taken up by plants and might accumulate in food chains. Many works have been done on the interaction between fertilizer application and the accumulation of Cd concentrations in soils and plants [2] and [3]. Tu et al. [4] examined the influence of nitrogen (N), P and potassium (K) fertilizers on the speciation distribution of lead (Pb) and Cd in red soil in China. Their findings suggest that applying chemical fertilizers may change the speciation and thus phytoavailability of heavy metals. However, there is still little information on the transport and accumulation of heavy metals in plants as related to the nutritional levels in the soil environment. Therefore, the phytoavailability of Cd and Zn after applying different levels of fertilizer was examined in this study.

The objectives of this study were to (i) determine the effect of P in fertilizers on total cadmium (TCd) and total zinc (TZn) in soil at different application rates and (ii) determine the association between the concentration of Cd and Zn in sugarcane(TCd, TZn) and the available Cd and Zn in soils.



2 Methodology

2.1 Field experiment

The field experiment was conducted in three sugarcane cultivation plots, located in Mae Ku and Mae Tao sub-district, Mae Sot, Tak province, which contained different levels of cadmium concentrations. The three locations include Mae Ku (0-3 mg Cd/kg dry soil), Mae Tao 1 (3-20 mg Cd/kg dry soil), and Mae Tao 2 (>20 mg Cd/kg dry soil). Soils were collected to determine basic physical and chemical properties. Background Cd and Zn in soil were determined by USEPA method 3052 and found to contain 2.58, 36.66, 174.51 and 2.35 mg Cd/kg dry soil and 35.12, 74.86, 2,098.67 and 28.00 mg Zn/kg dry soil for Mae Ku, Mae Tao 1, Mae Tao 2 and soil used in pot experiment, respectively.

All of these areas received an initial application of granular commercial NPK fertilizer (16-16-8) at the rate of 312.5 kg/ ha and a repeat application after five months. The fertilizer was analysed for heavy metal content and found to contain 0.39 mgCd/kg fertilizer and 26.82 mgZn/kg fertilizer. Three replicates of soil and sugarcane samples were collected at the end of the second and sixth month of the cultivation. Sugarcane samples were taken from the same area used in soil sample collection.

2.2 Pot experiment

2.2.1 Soil preparation

Soils collected from Mae Ku district, Mae Sot, Tak province were used in the pot experiment. The Soil was collected from 0-30 cm below surface horizon and allowed to air dry before being crushed to pass through a 2-mm sieve.

2.2.2 Plant preparation

Cut pieces of mature sugarcane stems (setts), LK 92-11 ecotype, were obtained from Kampangpetch province. The USEPA method 3052 was used for the analysis of background Cd and Zn in plant (setts) samples. Levels were non-detectable.

2.2.3 Experimental design and procedure

The experiment was conducted in a randomized block design with three replications with 20 kg of soil per pot. Each pot was planted with a sett. A month later, the first application of fertilizer was conducted. A granular commercial NPK fertilizer formulation (16-16-8) was applied to each pot at the rate of 0 (control group), 312.5, 625 and 1,250 kg fertilizer/ha. The control group did not receive any fertilizer addition, but was subjected to all other manipulation steps. Repeat applications of fertilizer were conducted at the same rate after four months (the fifth month of cultivation). Soil and sugarcane samples were collected at the end of the second and sixth month of the cultivation.



2.3 Sample preparation

Soils were dried at 105° C for 24 hr to constant weight and then they were crushed to pass through a 2-mm sieve and thoroughly mixed to homogenize. For the analysis of available Cd and Zn in soil, soil samples were air-dried for 72 hr and then crushed to pass through a 2-mm sieve and mixed to homogenize before analysis. Sugarcane samples were cleaned and washed with tap water twice and rinsed with deionized water and then they were divided into five parts: underground stems (setts), roots, bagasses, sugarcane juice and leaves. Samples were dried at 105° C for 24 hr to constant weight and dry matter yields were determined. After that, they were ground with electric mill and thoroughly mixed to homogenize.

2.4 Sample analysis

TCd and TZn in soil and sugarcane (underground stems, roots, bagasses and leaves) were determined by the USEPA method 3052 [5]. Sugarcane juice was analyzed by digestion in a mixture of 10: 1: 4 (v/v/v) of HNO₃ (14 M), H₂SO₄ (36.8 M) and HClO₄ (15.3 M) [6]. The digested solution was analyzed by graphite furnace atomic absorption spectroscopy. Total P in soil was determined by vanadomolybdate method [7]. Available Cd and Zn in soil were estimated by DTPA extraction method (0.005M DTPA+ 0.01M CaCl₂) [8].

3 Results and discussions

3.1 Concentration of phosphorus in soils

Under the field conditions, total P in the three locations with different Cd contaminated levels were examined. Concentration of total P in Mae Ku area (< 3 mg Cd/kg) is lower at the end of the sixth month when compared to the second month even though a repeat application of fertilizer was conducted. For Mae Tao 1 (3-20 mg Cd/kg) and Mae Tao 2 (> 20 mg Cd/kg), total P in soils at the end of the sixth month of the cultivation increased and was higher than in the second month. Total P in 625 and 1,250 kg fertilizers/ha treatment increased at the end of the sixth month by an average of 13.57% and 31.71%, respectively.

For the pot experiment, at the end of the second month of the cultivation, total P in all treatments of fertilized soil increased with increasing fertilizer application rates and total P in 1,250 kg fertilizers/ha treatment was increased by an average of 9.4% above the control group (0 kg fertilizer/ ha). Concentration of total P in all treatments in the sixth month also gradually increased with fertilizer application rates. However, they were lower when compared to the second month's group even though a repeat application of fertilizer was conducted. This may be due to increased crop uptake of P during the peak rate of sugarcane growth. This result indicated that further additions of fertilizer are often required in order to maintain high crop yields. McLaughlin and Singh [9] mentioned that one of the reasons that P must be repeatedly applied to soils is to overcome the slow P fixation reactions.



3.2 TCd and TZn in soil

As figure 1 shows, Cd concentration in the soil from the three areas with Cd contamination of 0-3, 3-20 and > 20 mg Cd/ kg were 2.34, 34.03 and 172.77 mgCd/ kg respectively and Zn concentrations were 33.44, 71.48 and 2,091.54 mgZn/kg respectively, at the end of the second month. Cd and Zn concentration in field experiment soil decreased about 25% and 30%, respectively at the end of the sixth month. The results indicated no effect from 312.5 kg/ha NPK fertilizer application and repeat application which may be due to a low concentration of Cd and Zn in the fertilizer.

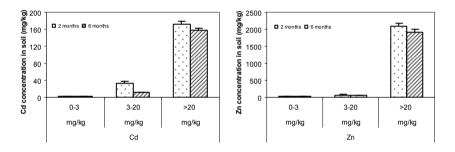


Figure 1: Effect of different fertilizer application rates on TCd and TZn in field experiment soil.

The results showed in the pot experiment that the concentrations of TCd in soil were gradually lowered in all three levels of fertilized soil at the end of the second and sixth months of the cultivation (table 1). The results tend to suggest that fertilization is not increasing levels of total Cd in soils, but may instead to be decreasing Cd concentrations because of effect of P addition in increasing ability of Cd to taken up by plant tissues. The reduction of Cd adsorption in the presence of phosphate in soils was reported by Krishnamurti et al. [10]. Because of the presence of Zn as an impurity in the fertilizer used in this study, the results do not show any clear relationship between TZn accumulated in soils and the 16-16-8 NPK fertilizer application rate in either the end of the second or sixth

Table 1:Effect of different fertilizer application rates on TCd and TZn in
pot experiment soil.

Fertilizer application rates (kg/ha)	Total Cd (mg/pot)		Total Zn (mg/pot)	
	2 months	6 months	2 months	6 months
0 (control group)	47.132±1.509 ^a	46.991±1.611	559.710±32.007	558.772±33.007
312.5	47.134±1.111	47.002±2.018	559.676±24.004	558.652±41.004
625	47.061±2.027	46.972±1.115	559.650±22.009	558.726±50.009
1,250	47.011±1.614	46.963±1.215	559.728±41.018	558.934±20.018

^{*a*} Mean ± Standard deviation.



month as presented in table 1. Concentrations of TZn in soil were lower in the 312.5 and 625 kg fertilizer/ha as compared to the non-fertilized soil (0 kg fertilizer/ha). However, total Zn accumulated in soil at 1,250 kg fertilizer/ha treatment was higher than in non-fertilized soil. This could result from the application of fertilizer containing Zn in amounts exceeding crop uptake which will inevitably result in an accumulation of Zn in soil. In addition, a higher soil Zn can then enhance more Cd desorption, and hence, increase Cd concentration in the soil solution which might then increase Cd phytoavailability [11]. Thus, this may affect lower of Cd concentration in soil in the 1,250 kg fertilizer/ha treatment.

3.3 Available Cd and Zn

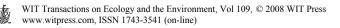
Under the field conditions, an increase of available Cd and Zn in field experiment soils was proportional to the level of Cd contaminate in the sugarcane cultivated areas. Available Cd and Zn increased in the sixth month of the cultivation (table 2). This can be a result of high Cd contaminate in sugarcane cultivated areas and not an effect of the phosphorus nutrient contained in the fertilizer.

Location	Available Cd (mg/kg)		Available Zn (mg/kg)	
Location	2 months	6 months	2 months	6 months
Mae Ku	$0.055{\pm}0.017^{a}$	0.247±0.012	1.079 ± 0.010	1.991±0.012
Mae Tao 1	0.189 ± 0.004	0.327±0.006	3.258±0.004	4.489±0.004
Mae Tao 2	18.521±0.015	30.457±0.007	154.774±0.009	216.563±0.016

Table 2:	Available Cd and Zn in different levels of Cd contaminated areas.
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^{*a*} Mean \pm Standard deviation.

For the pot experiment, the results showed that an increasing of the 16-16-8 NPK fertilizer application rates also increased availability of Cd at the end of the second and sixth months of the cultivation (figure 2). Higher P contained in the fertilizer would be likely to enhance the Cd uptake by the plant or phytoavailability of Cd in soil. Phytoavailability of Zn, at the end of the second month, was lower in all rates of fertilized soil as compared to non-fertilized soil (0 kg fertilizer/ha). The decrease in Zn with fertilizer addition strongly suggests enhanced Zn adsorption on the surface due to P inputs or P-Zn mineral precipitation. Mench et al. [12], McGowen et al. [13] and Cotter-Howells and Caporn [14] proposed precipitation of P-Zn minerals as the mechanism reducing solution concentrations of Zn in soils. This is consistent with Choudhary et al. [15] and Grant and Bailey [16], they reported that Zn in soils would occupy most of the newly-formed adsorption sites created by the P addition; or consume phosphate for precipitation and would allow available Cd to increase with the fertilizer applications. However, the lower solution Zn (available Zn) with the fertilizer addition does not show any clear relationships between Zn in soil extracts and fertilizer addition, especially when one considers that a fair amount



of Zn was added as a contaminant in the fertilizer [17]. At the end of the sixth month, P in soil in all treatments appears to be lower than in the second month because of using P in plant growth. Thus, the P-Zn mineral precipitation is decreased and it can induce higher phytoavailability of Zn.

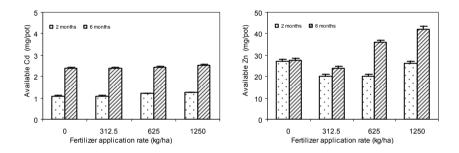


Figure 2: Effect of different fertilizer application rates on available Cd and Zn in pot experiment.

3.4 TCd and TZn accumulation in sugarcane

Cd and Zn taken up in sugarcane also increased with the proportion present in sugarcane cultivated areas. The decreases of Cd and Zn accumulation in sugarcane at the end of the sixth month are the result of increasing sugarcane growth and dry matter yield (figure 3). The accumulation of Cd and Zn in different parts of the sugarcane had the following sequence: roots> underground stems (setts)> bagasses> leaves> juice (figure 4).

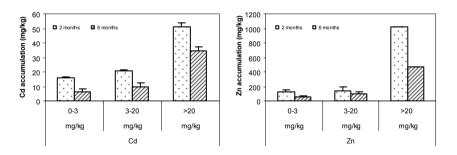


Figure 3: Cd and Zn accumulated in field experiment sugarcane.

In the pot experiment, the results illustrated in figure 5 shows that the concentration of TCd in sugarcane was gradually promoted with increasing of 16-16-8 NPK fertilizer application rates and found that Cd and Zn are mostly accumulated in the 1,250 kg fertilizers/ha treatment. Cd accumulation in sugarcane at the end of the second and sixth months of the cultivation were 161.91 and 288.30 µg Cd/ plant, respectively and Zn accumulations were 561.85

and 1,645.86 μ g Zn/ plant, respectively. The results strongly indicated that TCd and TZn in sugarcane at the end of the sixth months were higher than in the end of second month of the cultivation. This could result from the greater growth of plants with application of P fertilizers which increased the capacity of plant to accumulate Cd and Zn.

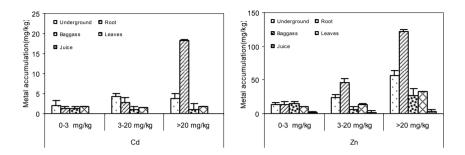


Figure 4: Cd and Zn accumulation in different parts of sugarcane in field experiment at the end of the sixth month.

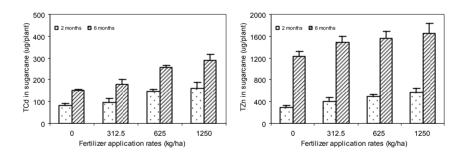
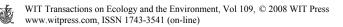


Figure 5: Cd and Zn accumulation in pot experiment sugarcane under different rates of fertilizer.

For the chemical analysis of TCd and TZn accumulation in different parts of sugarcane at the end of the second month, sugarcane was botanically separated into only four parts (underground stems (setts), root, bagasses and leaf). Because of incomplete maturity of sugarcane juice was not available. The results show that most accumulation of Cd and Zn occurred in the roots followed by underground stems (setts), bagasses and leaves, respectively. The results show the same trend at the end of the sixth months of the cultivation. TCd and TZn accumulated in five parts of mature sugarcane had the following sequence: roots> underground stems (setts)> bagasses> leaves> juice (figure 6). The result shows low Cd contaminate in juice. Thus, it can be assumed safe to use as a raw material in ethanol production.



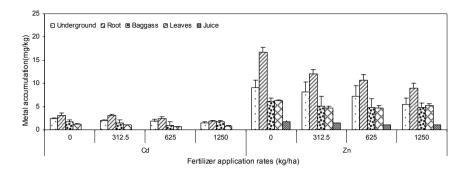


Figure 6: Cd and Zn accumulation in different parts of field experiment sugarcane at the end of the sixth month.

4 Conclusions

The addition of 312.5 kg fertilizer/ ha to sugarcane cultivated areas showed no effect on increasing Cd and Zn concentration in soils even with a repeat application of fertilizer in the fifth month of the cultivation. However, long-term effects of fertilization should be considered and need additional study. The phytoavailability of Cd and Zn to be taken up into sugarcane are proportional to the levels of Cd contaminate in sugarcane cultivated areas. The results showed no effect of fertilization on available Cd and Zn. This could have resulted from already high Cd contamination in the sugarcane cultivated areas.

For the pot experiment, total P in all treatments of fertilized soil increased with increasing fertilizers application rates both at the end of the second and sixth months. However, they were lower in the sixth month when compared to the second month group. Increasing P as fertilizer is applied to soils can induce more Cd in an available form and promote take up and accumulation in different parts of the sugarcane. Therefore, TCd in soil would decrease. For Zn, at the end of the second month, phytoavailable Zn was lower in all rates of fertilized soil as compared to non-fertilized soil (0 kg fertilizer/ha). The decrease in Zn with fertilizer addition strongly suggests enhanced Zn adsorption on the surface due to P inputs or P-Zn mineral precipitation. Also, Zn could be taken up more easily by sugarcane at the end of the sixth month because of decreasing P in the soil. TCd and TZn accumulation in different parts of sugarcane had the following sequence: roots> underground stems (setts)> bagasses> leaves> juice.

Acknowledgements

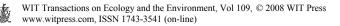
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