Cadmium and Zinc Concentrations in the Soils of the Oil Palm Plantations from Long Term Application of Phosphate Rock

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Abstract
Nowadays, there is an increasing concern about Cd and Zn accumulation in the soil caused by the continuous application of phosphate rock (PR) fertilizer. To investigate on this issue in Malaysia`s oil palm plantation, two well maintained oil palm plantations were selected. Six soils series with three different ages of oil palm (<10, >15, >20 years) that undergo scheduled fertilizer program was collected. Jawa, Selangor and Sedu series were selected from coastal areas. Munchong, Rengam and Segamat series were collected to represent inland areas. To support the findings of the field study, Zn and Cd adsorption isotherms were investigated using the same soil series. Also, studies on pH effect on Zn adsorption and competitive adsorption between Zn and Cd were conducted. Soil heavy metals mean concentrations were compared between three different ages of oil palm for each soil series. Results indicated no accumulation of Cd in all soil series but there are accumulations of Zn for Selangor and Segamat series. Of all the soil series studied, the Segamat series exhibited the highest amount of Cd and Zn adsorption. For Selangor and Segamat series, Cd adsorption was severely depressed by the presence of Zn. The increasing soil pH of the Selangor series as the age of the oil palm trees increased, led to the accumulation of Zn.

Key Words
Cadmium and Zn accumulation; adsorption isotherm; competitive adsorption; adsorption envelope

Introduction
Many studies from temperate regions show that long term application of phosphate rock (PR) fertilizer leads to the accumulation of Cd in agricultural soils due to the presence of this metal as an impurity in all phosphate rocks(Nziguheba and Smolders 2008). Phosphate rock (PR) is the main phosphorus fertilizer (PF) which is effectively and extensively used in the oil palm plantation. The amount added in a single fertilizer application may be insignificant compared with the volume of receiving soil but repeated application may lead to an increase in availability of these elements in agricultural soils over time (Camelo *et al.* 1997). Zinc is also found in PR as an impurity. In nature, there is high Zn to Cd ratio in PR. Two plantations, one located in the coastal area and the other in inland area were selected to represent oil palm plantations in Peninsular Malaysia that undergo scheduled fertilizer program. Different phosphorus fertilizer (PF) programs were practiced by these two plantations. Oil palm in the coastal area was annually applied with 0.34 kg-0.51 kg P_2O_5/tree using Christmas Island phosphate rock (CIRP) which ended when the age of the oil palm was 20 years. For inland soil, 0.23-0.58 kg P_2O_5/tree was applied using PR fertilizer until the oil palm trees were cut down. Generally, an oil palm tree will be cut down when the age exceeded 25 years because of the poor productivity. During the productive period, the PF program was carried out annually and there is a speculation that continuous application of PRs may lead to a gradual buildup of Cd in the oil palm soil system over time. However, there is lack of study on Cd accumulation in acid tropical soil due to PRs application. Adsorption is the process that may actively bind Cd and Zn to the solid phases of soils. Competitive adsorption between Cd and Zn to occupy adsorption sites in soil. Adsorption envelope measurement is necessary since pH is one of the most important parameters that affect metal adsorption in soil. Hence, this study was conducted to determine Cd and Zn in soil of different ages of oil palm grown on the same soil series and also to determine Cd and Zn adsorptive capacity potential and competitive adsorption between Cd and Zn soil grown used to grown oil palm. An Adsorption envelope was determined may occur to study Zn adsorption as a function of equilibrium solution pH.

Methods
To conduct this study, three dominant soil series each were selected from the two oil palm plantations. Soils of the coastal area consist of Jawa, Selangor and Sedu series. Munchong, Rengam and Segamat seires were collected as the inland soil series. For each soil series, three categories of oil palm age (<10, >15 and >20 years) were selected. For each categories, six soil points were randomly collected whereby for every sample

soil was collected at fronds heap and planting circle of oil palm at two depths (0-15 cm and 15-30 cm). Then the soils were composited together by depth. Total Cd and Zn were determined by the aqua- regia extractant. Cadmium and Zn adsorption capacity potential and competitive adsorption were determined by batch experiment on the same soil series grown with oil palm but the soils were collected from an undisturbed, unfertilized area. Initial concentration for adsorption isotherm: 0, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mg/L of Cd/Zn. The adsorption isotherm was fitted to both Freundlich and Langmuir equation. Selangor and Segamat series were selected for competitive adsorption and adsorption envelope measurement. For competitive adsorption, 100 mg/L of Zn was selected and Cd concentrations were varied (1, 5, 10, 20, 40, 50, 100 mg/L) to give Zn:Cd ratio 1:100, 1:20, 1:10, 1:5, 1:2.5, 1:2 and 1:1. The adsorption envelope study was carried out at 50 mg'L of Zn. The mixture was adjusted to pH 3, 4, 5, 6, 7, 8, 9 and 10 with 0.001 M NaOH or HCl. After 24 hours of shaking, pH equilibrium of the mixture was recorded. Cadmium and Zn were analyzed using the flame atomic absorption spectrophotometry (Perkin Elmer 5100).

Results and discussion

For total Cd, Sedu, Rengam and Segamat series show significant differences ($p<0.05$) between three different ages of oil palm. However, for Segamat series, soil total Cd for oil palm age >20 years was less than soil total Cd for oil palm age >15 years. Meanwhile for Rengam series, soil total Cd for oil palm age >20 years shows a lower mean value than soil total Cd for oil palm age < 10 years. Soil total Cd for Sedu series decreased with the increase in oil palm age (Figure 1). For total Zn, only Selangor and Segamat series show significant differences ($p<0.05$) and an increment of soil total Zn with the increase in oil palm age (Figure 1).

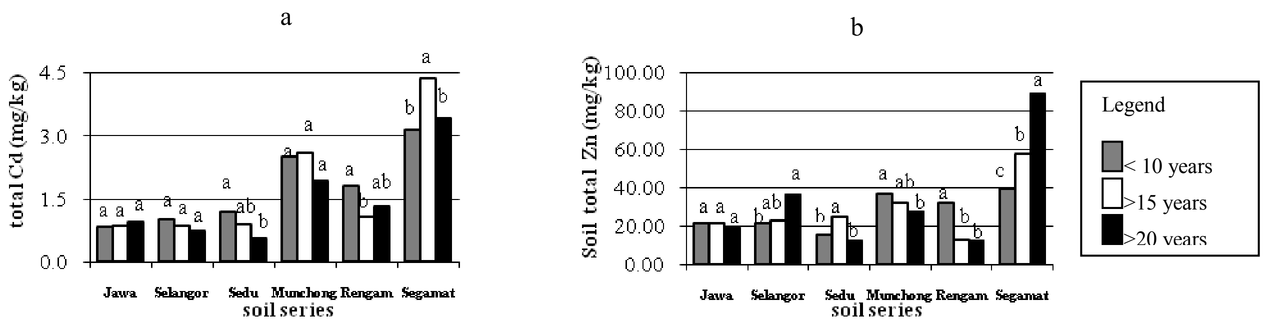

Figure 1. Total Cd (a) and total Zn (b) in soils for all soil series at three different categories of oil palm age.

From the adsorption isotherm studied, Cd and Zn adsorption data was better described by Freundlich equation. Values of Freundlich and Langmuir equation parameters as shown in Table 1. Segamat series gives the highest value of maximum adsorption (b) and can retain the largest amounts of Zn and Cd based on Kf values. Furthermore, Zn was adsorbed (range 250 to 1000 m3 /kg) about one double the amount of Cd (range 143 to 500 m3 /kg) for most of the soils series. This may possibly be the reason for the higher total Zn in oil palm plantations compared to the total Cd aside from naturally higher Zn than Cd in soils. The b and k values for Munchong series are not stated in the table because of the negative slope given by the linear form of the equation.

For both soil series, Zn adsorption is low at low equilibrium pH but, increased with increasing pH (Figure. 2). Increasing pH led to the increased number of negatively charged surface sites that consequently increased the number of sites available for Zn sorption. This might be the reason for the increase in soil total Zn for the Selangor series (field study) as the age of the oil palm trees increased. For the Segamat series, maximum

Table 1. Value of K_f (capacity adsorption), 1/n (rate of adsorption) of Freundlich equation and b (maximum adsorption), k (energy bonding) of Langmuir equation.

Soil series	Freundlich				Langmuir			
	K_f (m^3/kg)		1/n		b (mg/kg)		k	
	Cd	Zn	Cd	Zn	Cd	Zn	Cd	Zn
Jawa	4.05	8.83	0.791	0.783	250	500	0.012	0.013
Selangor	4.90	1.10	0.658	0.962	143	500	0.018	0.002
Sedu	2.74	8.17	0.917	0.723	333	333	0.010	0.016
Munchong	17.18	1.43	1.543	1.191	-	-	-	-
Rengam	1.62	1.15	0.847	0.892	167	250	0.008	0.003
Segamat	55.98	56.36	0.451	0.513	500	1000	0.051	0.028

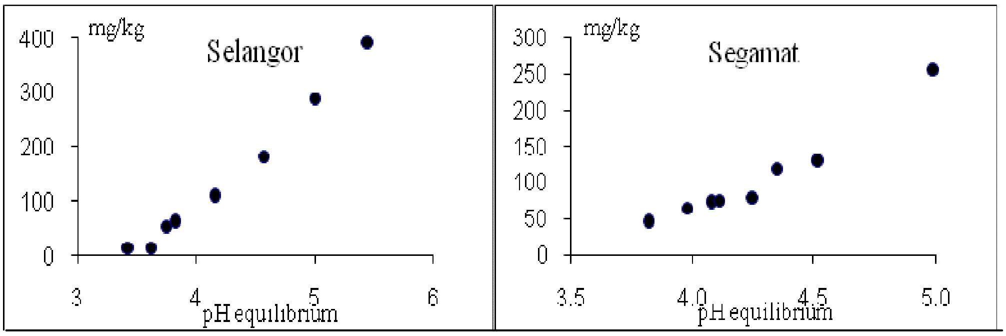

Figure 2. Adsorption envelope of Zn for Selangor series (coastal) and Segamat series (inland).

adsorption accurs at pH 5. This may be due to the deprotonation of the most active surface of goethite as a result of surface hydrolysis with an increase in pH from 5 to 6 (Mustafa *et al.* 2004).This explains the increased accumulation of soil total Zn for the Segamat series with increasing age of the oil palm trees.

The trend of competitive adsorption for Segamat series is the same as when the Cd was added individually but the amount adsorbed was much lower than the single adsorption. For Selangor series, increasing the initial concentration of Cd from 1, 5, 10, 20, 40, 50 and 100 mg/L while maintaining the initial Zn concentration at a constant 100 mg/L resulted in no Cd adsorption except for Zn:Cd ratio 1:1, though the amount adsorbed was much less than single adsorption. Figure 3 shows clearly that the presence of Zn significantly reduced Cd adsorption due to the competition for adsorption sites. Also, Zn exhibits a higher affinity for soil surface, thus more Zn was adsorbed compared to Cd. This could be the reason for the low retention of Cd for all soil series in oil palm plantation.

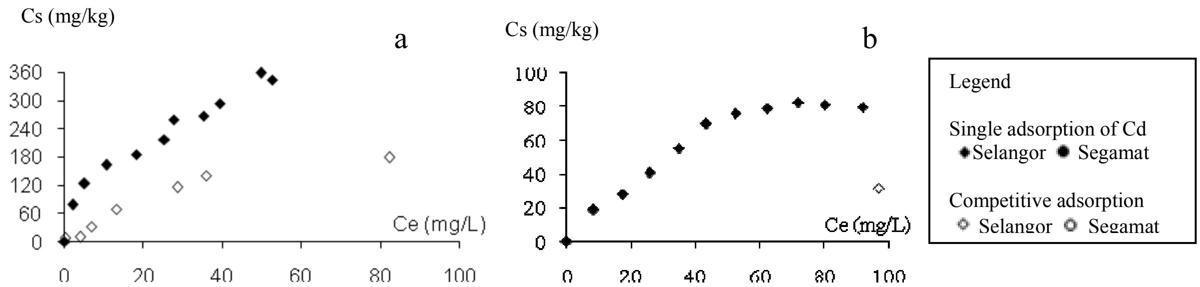

Figure 3. Single adsorption (adsorption isotherm) of Cd and competitive adsorption between Cd and Zn in the a) Segamat series b) Selangor series.

Data in Table 1 and Fig 3 shows that Segamat series has the highest capacity to adsorb cations. This might be the reason that Segamat series can adsorb Cd for all Zn:Cd ratios. For other soil series, Zn competes strongly in soils with a lower capacity to hold metal cations (Fontes and Gomes 2003; Lu and Xu 2009) where Cd site was occupied by Zn and may possibly result in the zero adsorption of Cd for all Cd concentrations except for Zn:Cd ratio1:1.

Conclusion

There was no clear trend of accumulation of Cd in the soil between different ages of oil palm grown on the same soil series, but there were accumulations of Zn in Selangor and Segamat series. Zinc accumulation in Segamat and Selangor series is consistent with results of the adsorption study. Cadmium adsorption was significantly reduced by the presence of Zn.

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