

Chemical forms of cadmium in a calcareous soil treated with different levels of phosphorus-containing acidifying agents

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Abstract. Calcareous soils with high background cadmium (Cd) levels are widely distributed in south-west China and soil acidity is a major environmental problem. However, little effort has been made to study the changes in chemical speciation as affected by soil acidification other than by acidic rain. In the present study, we investigated the impact of mono-ammonium phosphate (MAP) and phosphoric acid on soil pH and chemical transformation of Cd in calcareous soils. Calcareous soils collected from south-west China were treated with three concentrations (0.1, 0.2 and 0.4 mol kg⁻¹ soil) of MAP and phosphoric acid, and without the addition of acidifying agent, before being incubated at 25 ± 2°C near field capacity moisture content for 60 days. The chemical forms of Cd in the soils were determined by the Tessier sequential extraction scheme. The concentration of Cd in the form bound to iron and manganese oxides (Cd_{FeOx+MnOy}) decreased significantly with increasing levels of the two acidifying agents, but the concentration of exchangeable Cd (Cd_{Ex}) exhibited a significant increase, indicating that the two acidifying agents can effectively promote the transformation of Cd_{FeOx+MnOy} to Cd_{Ex}. MAP may promote the same amount of Cd_{FeOx+MnOy} to Cd_{Ex} as phosphoric acid at the same rate of addition, but the soil pH clearly differed, implying that an increase in water-soluble P with addition of acidifying agent may be one major factor affecting the chemical transformation of Cd. MAP and phosphoric acid should be used carefully as sources of water-soluble phosphorus for calcareous soils with high background concentrations of Cd.

Additional keywords: chemical transformation, water-soluble phosphorus.

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Introduction

Cadmium (Cd) is a heavy metal with high toxicity at very low concentrations (John *et al.* 1972; Friberg *et al.* 1974) and it is one of the most common soil pollutants (Bloemen *et al.* 1995; Andreu and Gimeno-Garcia 1996; Udom *et al.* 2004). In general, the toxicity of Cd in soil increases as its mobility increases. Previous studies have shown that the mobility of potentially hazardous trace metals in agricultural soils is closely related to the chemical transformations of these elements in the soil environment (Sposito *et al.* 1982; Navarro-Pedreño *et al.* 2003; Lafuente *et al.* 2008). It is therefore necessary to know the chemical forms of Cd in soils and the factors influencing the conversion of its chemical forms in soil.

Calcareous soils have high levels of calcium and magnesium carbonates formed largely by the weathering of calcareous rocks and fossil shell beds. These soils belong to Ustic Isohumisols according to the Chinese soil classification system (CSTCRGISS-CAS 1995) or to Cumulic Haplustolls

based on the US system of soil classification (Soil Survey Staff 1996). Calcareous soils are widely distributed in Guangxi, Guizhou and Yunnan provinces in China, with very high background Cd concentrations in calcareous soils in some areas. In general, the mobility and bioavailability of Cd in calcareous soils are lower than in other soils (Agency for Toxic Substances and Disease Registry 2008). However, the mobility and bioavailability of Cd in calcareous soils will increase significantly with changes in some physical and chemical properties of the soil, such as decreasing soil pH. Therefore, it is necessary to consider the problem of Cd activation in calcareous soils with high environmental background values.

It is well known that many physical and chemical properties of soil affect the chemical forms of Cd, including soil pH, soil solution ionic composition, the chloride concentration in the soil solution, cation exchange capacity, clay mineral content and types, organic matter content, calcium carbonate equivalent

(CCE), oxides of iron (Fe), manganese (Mn) and aluminum and redox conditions (Haghiri 1974; Naidu *et al.* 1994; Yasrebi *et al.* 1994; Basta *et al.* 2001). Soil pH is one of the major physicochemical properties of soil and, to a great extent, controls the chemistry of Cd in the soil environment (Mann and Ritchie 1993). Increasing soil acidity is a major environmental problem in China and the use of acidifying agents, including some acidifying fertilisers, can greatly accelerate the rate of acidification in addition to acid rain (Guo *et al.* 2010). The acidifying fertilisers include fertilisers containing the ammonium (NH₄) form of nitrogen, such as ammonium nitrate, urea, ammonium phosphate, mono-ammonium phosphate (MAP) and ammonium sulfate. There have been numerous studies on the effects of acid rain on the mobility of heavy metals in non-calcareous soils (Siepak *et al.* 1999; Guo *et al.* 2005; Kim *et al.* 2010). However, little attention has been paid to the effects of soil acidification in the absence of acid rain on the chemical transformation of heavy metals in calcareous soils.

Sequential extraction has been used to identify the chemical forms of trace elements and predict their mobility and bioavailability (Tessier *et al.* 1979; Ahnstrom and Parker 1999). In sequential extraction techniques, a sample is treated with a series of progressively harsher reagents to dissolve increasingly recalcitrant forms. In the case of heavy metals, these methods operationally estimate the amounts of metals in various solid pools that are commonly termed exchangeable, carbonate bound, Fe and Mn oxide bound, organic and residual. Although several sequential extraction techniques have been in use for four decades (Gibbs 1973; Tessier *et al.* 1979), there are no universally accepted procedures in terms of reagents and their order in the sequence (Sutherland *et al.* 2000). The Tessier scheme is a typically sequential extraction method that can provide more information about Cd mobility and bioavailability for calcareous soils than other sequential extractions tested (Abbaspour *et al.* 2007; Jalali and Khanlari 2008; Khanmirzaei *et al.* 2013).

In the past three decades, the mobility of Cd has been studied in diverse soils, including acid (Simard *et al.* 1999; Cornu *et al.* 2001) and alkaline (Walter and Cuevas 1999; Navarro-Pedreño *et al.* 2003) soils. Nevertheless, there is limited information on the chemical transformation of Cd as a result of soil acidification caused by factors other than acid rain in calcareous soils with

high Cd background concentrations. Phosphorus (P) is an essential nutrient element for plants and P deficiency in calcareous soils is a widespread problem in the cultivation of agricultural crops. It is therefore necessary to enhance P availability in many calcareous soils. MAP is an acidifying fertiliser that is often used in the blending of dry agricultural fertilisers and it can supply the soil with N and P in plant-available forms. Phosphoric acid is increasingly used as a source of water-soluble P and is an acidifying agent that can enhance P availability in calcareous soils (Gharaibeh *et al.* 2010). The objectives of the present study were to evaluate the impact of the two P-containing acidifying agents (MAP and phosphoric acid) on soil pH and chemical transformations of Cd in calcareous soil and to study the potential factors affecting the chemical transformation of Cd in an incubation experiment.

Materials and methods

Soil material

The tested soil was collected from the surface horizon (0–20 cm) of an upland field under cultivation with agricultural crops. The sampling site was in Huanjiang County, Guangxi Zhuang Autonomous Region, China. The area is located at 25°5'N, 107°59'E and is situated in the subtropical monsoon climatic zone with a temperate and humid climate throughout the year. The average annual temperature is 15.7°C and the mean annual precipitation is approximately 1750 mm, with approximately 70% of the precipitation occurring from April to September. The soil collected was air dried and passed through a 2-mm sieve. The particle size distribution was determined by laser diffraction methods (Segal *et al.* 2009) and the textural class is clay loam (sand: 27.09%; silt: 39.64%; clay: 33.27%) according to the US Department of Agriculture soil textural triangle (Soil Survey Division Staff 1993). Soil pH was measured with a pH meter (Sartorius Basic pH meter PB-10, Goettingen, Germany) with a soil:water ratio of 1:2.5. Soil organic matter was determined by wet oxidation at 180°C with a mixture of potassium dichromate and sulfuric acid (Agricultural Chemistry Committee of China 1983) and CCE was determined by neutralisation with HCl (Allison and Moodie 1965). Total concentrations of Cd, Fe and Mn were determined by

Table 1. Sequential extraction steps as described by Tessier *et al.* (1979)

Step	Chemical form	Symbol	Reagents	Time
1	Exchangeable	Ex	16 mL of 1.0 M MgCl ₂ (pH 7)	2 h (20 ± 2°C)
2	Bound to carbonates	Car	16 mL of 1.0 M NaOAc (pH adjusted to 5 with HOAc)	6 h (20 ± 2°C)
3	Bound to iron and manganese oxides	FeOx+MnOx	20 mL of 0.04 M NH ₂ OH·HCl in 25% (v/v) HOAc	6 h (96 ± 2°C)
4	Bound to organic matter	OC	6 mL of 0.02 M HNO ₃ and 10 mL of 30% H ₂ O ₂ (pH adjusted to 2 with HNO ₃), 6 mL aliquot of 30% H ₂ O ₂ (pH adjusted to 2 with HNO ₃), 10 mL of 3.2 M NH ₄ OAc in 20% (v/v) HNO ₃	2 h (85 ± 2°C), 3 h (85 ± 2°C), 0.5 h (20 ± 2°C)
5	Residual	Res	10 mL aqua regia, 5 mL 20% (v/v) HNO ₃	3 h (60°C), 2 h (125°C), 2 h (150°C), 0.5 h (80°C)

inductively coupled plasma mass spectrometry (ICP-MS) after digestion with aqua regia.

Incubation experiment

A 2×3 factorial experiment as a completely randomised design with three replicates was used to study the transformation of chemical forms of Cd in the calcareous soil with different levels of the two P-containing acidifying agents. Factors comprised the two P-containing acidifying agents (MAP and phosphoric acid) at three application rates (0.10, 0.20, and 0.40 mol kg^{-1} soil). In previous studies of heavy metal transformations, the incubation times ranged from several days to tens of weeks, but most were around 60 days (Mann and Ritchie 1994; Ma and Uren 1998; Lim *et al.* 2002; Lu *et al.* 2005; Rajaie *et al.* 2006). Therefore, an incubation period of 60 days was used in the present study. The experimental units were pots containing 100 g soil mixed with the P-containing acidifying agent. In addition, three pots of soil without acidifying agent were used as controls (CK). Enough distilled water was added to bring the soil moisture to near pot capacity. Pots were covered with Parafilm with a few holes to prevent rapid evaporation while allowing gaseous exchange. The pots were incubated at room temperature ($25 \pm 2^\circ\text{C}$). Soil moisture was maintained near field capacity by adding water to a constant weight once every 3 days. The soil in each pot was mixed well once every 7 days to maintain intimate contact with the acidifying agent. At the end of incubation, all the incubated soil samples were air dried and passed through a 2-mm sieve. The chemical forms of Cd were determined by sequential extraction as described by Tessier *et al.* (1979) and indicated in Table 1. The concentrations of Cd in the five chemical fractions were also determined by ICP-MS after they were extracted. Lake sediment for extractable trace elements (GBW07436) that was obtained from National Research Center for Certified Reference Material (Beijing, China) was used to compare recovery based on sequential extraction with certified values, and the mean recovery of total Cd (the sum of the five individual chemical fractions) was $92.6 \pm 12.7\%$. To evaluate the acidification effects of the

two P-containing acidifying agents on the calcareous soil, the pH values of all the incubated soil samples were also determined by a pH meter (Sartorius Basic pH meter PB-10) with a soil : water ratio of 1 : 2.5.

Statistical analysis

To characterise the relationship between chemical transformation of Cd and soil pH and the level of added P-containing acidifying agent, simple linear regression analysis and multiple stepwise regression were used. Descriptive statistics was used to compare the three observations of three replicates for each treatment. In the present study, both descriptive statistics and regression analysis were performed using SPSS for Windows version 13 (SPSS Inc., Chicago, IL, USA).

Results and Discussion

Soil properties

The properties of the tested soil are given in Table 2, which shows that the soil was slightly alkaline and with a low CCE. The soil may have been slightly alkaline because of the low concentration of calcium carbonate (CaCO_3 ; 10.4%), with a large proportion of the carbonates washed out from the surface horizon. The concentration of total Cd in the soil was very high and was approximately 33 times as high as the guideline value of the Chinese Environmental Quality Standard for Soils (GB 15618-1995) (www.zhb.gov.cn/english/chanel-5/GB15618-1995.doc) for total Cd (0.30 mg kg^{-1}). The chemical form of Cd in the soil was also analysed and most of

Table 2. Selected chemical and physical properties of the test soil
SOM, soil organic matter; CCE, calcium carbonate equivalent

pH	SOM (%)	CCE (%)	Total metal concentration (mg kg^{-1})		
			Cd	Fe	Mn
7.29	2.61	1.55	9.86	50903	7611

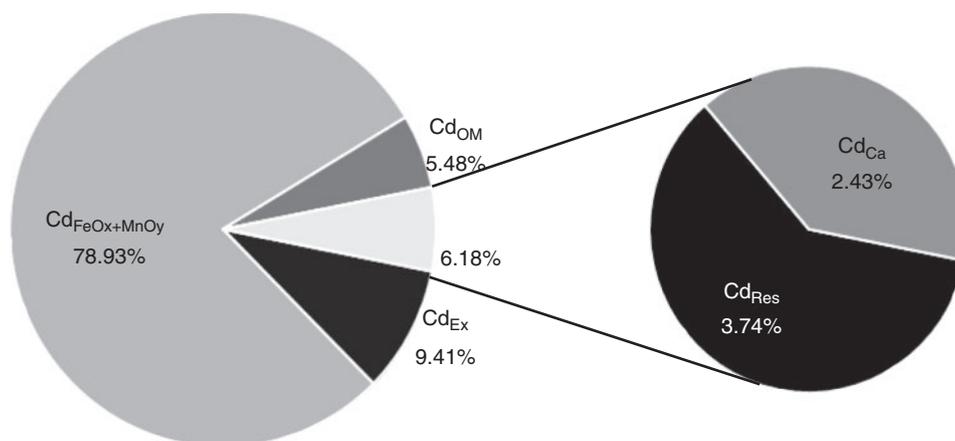


Fig. 1. Proportion of the five fractions of Cd in the untreated calcareous soil. Cd_{Ex} , exchangeable Cd; Cd_{Ca} , Cd bound to carbonates; $\text{Cd}_{\text{FeOx+MnOy}}$, Cd bound to iron and manganese oxides; Cd_{OM} , Cd bound to organic matter; Cd_{Res} , residual Cd.

the Cd was only slightly available, being mostly bound to Fe and Mn oxides and not carbonates (Fig. 1). This result is consistent with the result of heavy metal analysis showing that the soil had high concentrations of Fe and Mn oxides and a low concentration of CaCO_3 . Although the exchangeable Cd (Cd_{Ex}) in the soil accounted for only 9.41% of total Cd, the amount of Cd_{Ex} was greater than that in normal soil. Thus, the migration and toxicity of Cd in the test soil require further investigation.

Acidifying effects

Although both phosphoric acid and MAP are P-containing acidifying agents, the acidifying effects of the two agents on the calcareous soil were significantly different (Fig. 2). The acidifying effect of phosphoric acid was significantly stronger than that of MAP and the pH of the soil decreased sharply with increasing application rate of phosphoric acid. This indicates that phosphoric acid is a strong acidifying agent, whereas MAP is a weak acidifying agent because it had good acid buffering capacity. It is well known that phosphoric acid is a

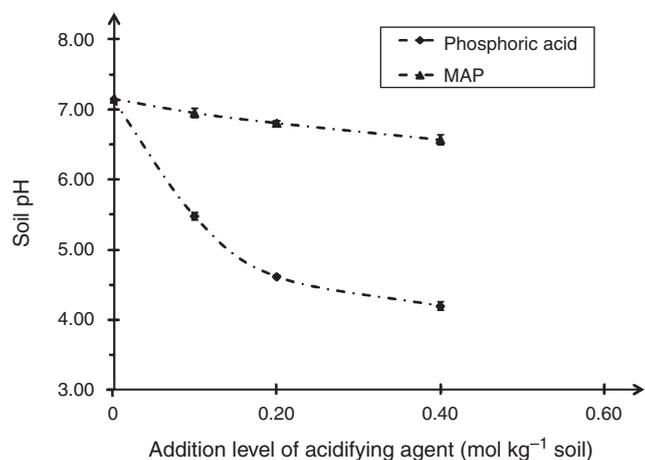


Fig. 2. Acidifying effects of phosphoric acid and mono-ammonium phosphate (MAP) on the calcareous soil. Data are the mean \pm s.d. of three observations.

triprotic acid with three ionisable hydrogen atoms. The hydrogen ions are lost sequentially and the anions, after successive dissociation, are H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} . Each successive dissociation step occurs with decreasing ease. Thus, H_2PO_4^- is a very weak acid and HPO_4^{2-} is an extremely weak acid. MAP in soil can simultaneously provide H_2PO_4^- and HPO_4^{2-} to the soil solution and this gives it a weak acidifying effect (Lu 2000).

Chemical transformation of Cd

The chemical forms of Cd in the calcareous soil treated with different levels of P-containing acidifying agents are presented in Table 3. Cadmium in the fractions bound to iron and manganese oxides ($\text{Cd}_{\text{FeOx+MnOy}}$) and Cd_{Ex} were the two dominant Cd fractions in the treated calcareous soil, whereas other fractions accounted for a small proportion. With increasing levels of acidifying agents, the concentration of $\text{Cd}_{\text{FeOx+MnOy}}$ decreased significant, whereas the concentration of Cd_{Ex} exhibited a significant increase with both acidifying agents (Fig. 3). This indicates that addition of both agents promoted the chemical transformation of $\text{Cd}_{\text{FeOx+MnOy}}$ to Cd_{Ex} in the calcareous soil. It was difficult to discriminate changes in the other three fractions (bound to carbonates, bound to organic matter and residual) among the treatments because of their low concentrations.

From Fig. 4 it can be seen that the concentration of Cd_{Ex} had a tendency to decrease with soil pH, whereas the concentration of $\text{Cd}_{\text{FeOx+MnOy}}$ exhibited the opposite tendency. Soil pH is one of the most important factors affecting the sorption of Cd (Naidu *et al.* 1994) and the impact of changes in soil pH on the sorption of Cd on Fe and Mn oxides may perhaps explain, in part, the conversion of Cd chemical forms in the calcareous soil treated with P-containing acidify agents. From Figs 2 and 3, MAP promoted about the same amount of $\text{Cd}_{\text{FeOx+MnOy}}$ to Cd_{Ex} as phosphoric acid at the same application rate (in mol kg^{-1} soil), whereas soil pH clearly differed between the two treatments. This indicates that soil pH is not the sole factor affecting the chemical transformation of Cd in the soil. Compared with MAP, phosphoric acid was more suitable for soil pH adjustment in the calcareous soil when considering the potential hazard of the Cd

Table 3. Characterisation of the chemical forms of Cd in a calcareous soil treated with different application rates of phosphoric acid (P1, 0.1 mol kg^{-1} soil; P2, 0.2 mol kg^{-1} soil; P3, 0.4 mol kg^{-1} soil) and mono-ammonium phosphate (N1, 0.1 mol kg^{-1} soil; N2, 0.2 mol kg^{-1} soil; N3, 0.4 mol kg^{-1} soil)

Data are the mean \pm s.d. of three observations. The control group was treated with distilled water only. Cd_{Ex} , exchangeable Cd; Cd_{Ca} , Cd bound to carbonates; $\text{Cd}_{\text{FeOx+MnOy}}$, Cd bound to iron and manganese oxides; Cd_{OM} , Cd bound to organic matter; Cd_{Res} , residual Cd

Treatment	Cd_{Ex} (mg kg^{-1})	Cd_{Ca} (mg kg^{-1})	$\text{Cd}_{\text{FeOx+MnOy}}$ (mg kg^{-1})	Cd_{OM} (mg kg^{-1})	Cd_{Res} (mg kg^{-1})
Control	1.05 \pm 0.08	0.24 \pm 0.05	7.68 \pm 0.10	0.52 \pm 0.02	0.37 \pm 0.06
P1	1.93 \pm 0.13	0.27 \pm 0.08	6.84 \pm 0.13	0.42 \pm 0.05	0.40 \pm 0.03
P2	2.63 \pm 0.11	0.32 \pm 0.06	6.13 \pm 0.09	0.37 \pm 0.03	0.42 \pm 0.07
P3	3.66 \pm 0.04	0.39 \pm 0.04	5.01 \pm 0.12	0.31 \pm 0.07	0.47 \pm 0.02
N1	1.72 \pm 0.10	0.25 \pm 0.07	7.20 \pm 0.09	0.33 \pm 0.04	0.36 \pm 0.05
N2	2.42 \pm 0.09	0.21 \pm 0.04	6.58 \pm 0.15	0.28 \pm 0.05	0.37 \pm 0.04
N3	3.52 \pm 0.05	0.17 \pm 0.03	5.52 \pm 0.11	0.20 \pm 0.04	0.45 \pm 0.06

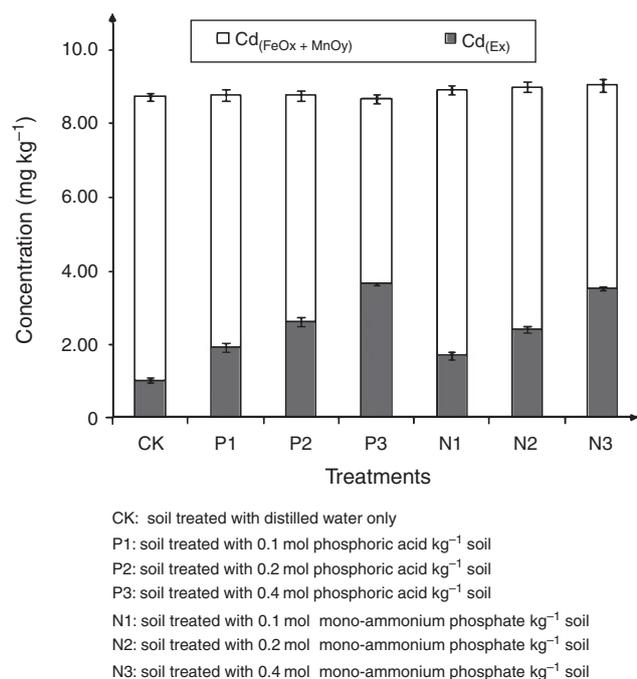


Fig. 3. Concentrations of Cd in the exchangeable (Cd_{Ex}) fraction and bound to iron and manganese oxides (Cd_{FeOx+MnOy}) with different application rates of phosphoric acid and mono-ammonium phosphate (MAP). P1–P3, 0.1, 0.2 and 0.4 mol phosphoric acid kg⁻¹ soil, respectively; N1–N3, 0.1, 0.2 and 0.4 mol MAP kg⁻¹ soil, respectively. Data are the mean ± s.d. of three observations.

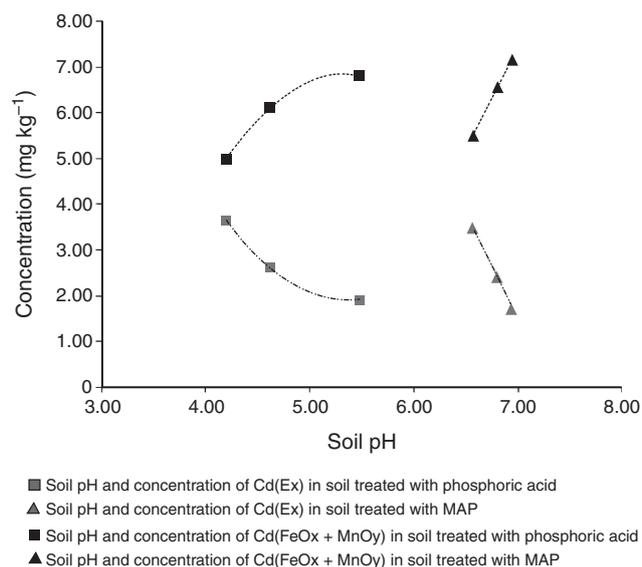


Fig. 4. Relationship between soil pH (mean of three observations) and concentrations of Cd in the fractions bound to iron and manganese oxides (Cd_{FeOx+MnOy}) and exchangeable (Cd_{Ex}) in calcareous soil treated with different levels of phosphoric acid or mono-ammonium phosphate (MAP). Data are the mean ± s.d. of three observations.

present. However, the problem of Cd activation in calcareous soil with high environmental background values should not be overlooked.

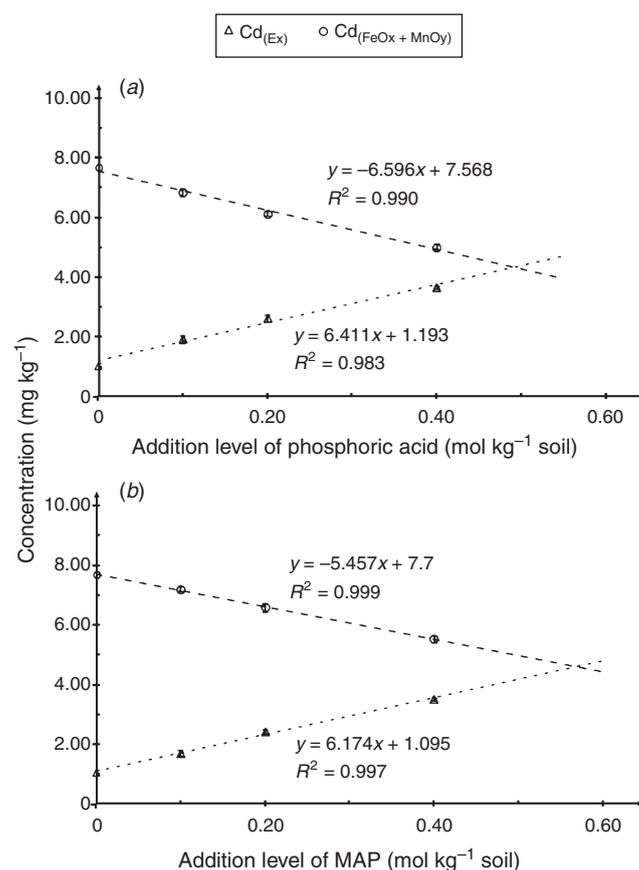


Fig. 5. Relationship between application rate (mol kg⁻¹ soil) of the two P-containing acidifying agents, namely (a) phosphoric acid and (b) mono-ammonium phosphate (MAP), and concentrations of Cd in the fractions bound to iron and manganese oxides (Cd_{FeOx+MnOy}) and exchangeable (Cd_{Ex}) in the calcareous soil. Data are the mean ± s.d. of three observations.

Both MAP and phosphoric acid are used as sources of water-soluble P. From Fig. 5 it can be seen that there was a significant linear correlation between concentrations of Cd_{Ex} and Cd_{FeOx+MnOy} and the addition rate of the two P-containing acidifying agents, and that the two acidifying agents at the same level of addition provided the same amount of P in water-soluble form to the calcareous soil. This indicates that the application rate of water-soluble P may be an important factor affecting the chemical transformation of Cd in calcareous soil. The increase in water-soluble P in calcareous soils with addition of the two P-containing acidifying agents induced the absorption of Cd on Fe oxides and the conversion of P in water-soluble form to the Fe-bound form (Jalali and Ranjbar 2010). This may explain the chemical transformation of Cd in calcareous soil treated with the two P-containing acidify agents.

To study the main factors affecting the chemical transformation of Cd in calcareous soil treated with the two P-containing acidify agents, two independent variables (soil pH and the addition level of P in water-soluble form ($P_{addition}$)) were used in a multiple stepwise regression analysis. The results (see Eqns 1 and 2) indicated that only $P_{addition}$ remained as a statistically significant predictor variable ($P < 0.05$):

$$\text{Cd}_{\text{Ex}} = 6.206 \times P_{\text{addition}} + 1.254 \quad (1)$$

$$(R^2 = 0.983; \text{SE} = 0.137)$$

$$\text{Cd}_{\text{FeOx+MnOy}} = -6.437 \times P_{\text{addition}} + 7.520 \quad (2)$$

$$(R^2 = 0.990; \text{SE} = 0.107)$$

where Cd_{Ex} is the concentration of exchangeable Cd in mg kg^{-1} , $\text{Cd}_{\text{FeOx+MnOy}}$ is the concentration of Cd in the form of bound to iron and manganese oxides in mg kg^{-1} and P_{addition} is the addition level of P in water-soluble form in mol kg^{-1} soil. From Eqns 1 and 2 it can be seen that the two models had a high coefficient of determination (R^2) and a small standard error of the estimate (SE), which means the chemical transformation of Cd in calcareous soil treated with the two P-containing acidify agents was mainly associated with the addition level of P in water-soluble form and not soil pH. However, several studies have reported that water-soluble phosphate compounds can immobilise Cd through various mechanisms, such as surface complexation, ion exchange, precipitation and adsorption (Levi-Minzi and Petruzzelli 1984; Pearson *et al.* 2000; McGowen *et al.* 2001; Bolan *et al.* 2003; Thawornchaisit and Polprasert 2009). Further research is needed to investigate the mechanism of chemical transformation of Cd in calcareous soil treated with the two P-containing acidify agents.

Numerous studies have shown that the use of phosphate fertilisers can control plant accumulation of Cd (Takijima and Katsumi 1973; MacLean 1976; Williams and David 1976; Street *et al.* 1978). However, the present study suggests that MAP applied as a phosphate fertiliser cannot reduce the availability of Cd in calcareous soil and should therefore be used carefully in the study area and in other regions with similar conditions.

Conclusions

The concentration of total Cd in the calcareous soil of the study area was very high and most of the Cd in the soil was only slightly available, being primarily bound to Fe and Mn oxides. Phosphoric acid is a strong P-containing acidifying agent that can significantly decrease the pH of the calcareous soil at a low application rate, whereas MAP is a weak P-containing acidifying agent and acidifying fertiliser that can slightly decrease the pH of the soil at normal application rates with its higher acid buffering capacity. However, both P-containing acidifying agents can markedly and effectively promote the conversion of $\text{Cd}_{\text{FeOx+MnOy}}$ to Cd_{Ex} . The amount of $\text{Cd}_{\text{FeOx+MnOy}}$ converted to Cd_{Ex} was significantly correlated with the addition rate of the two acidifying agents, and the increase in water-soluble P in the calcareous soil with the addition of acidifying agent induced the adsorption of Cd on Fe oxides. Considerable attention should be paid to the problem of Cd activation in calcareous soils with application of the two acidifying agents.

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