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Phosphorus-cadmium interactions in paddy soils

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Abstract

Regular application of phosphate (P) fertilisers has been identified as the main source of heavy metal(loid) contamination including cadmium (Cd) in agricultural soils. Some of these P fertilisers that act as a source of Cd contamination of soils have also been found to act as a sink for the immobilisation of this metal(loid). In paddy soils, redox reactions play an important role in the (im)mobilisation of nutrients and heavy metal(loid)s, as a result of flooding of the rice plains. Although a number of studies have examined the potential value of P compounds in the immobilisation of metals in contaminated soils, there has been no comprehensive review on the mechanisms involved in the P-induced (im)mobilisation of Cd in paddy soils. There are a number of factors that influence P induced Cd (im)mobilisation in paddy soils that include pH, redox reactions, liming effect, rhizosphere acidification and root iron plaques. Following a brief overview of the reactions of Cd and common P compounds that are used as fertiliser in soils, the review focuses on the above mentioned mechanisms for the (im)mobilisation of Cd by P compounds in paddy soils. The role of iron plaques on Cd status in soil and rice plants is also discussed followed by a summary and future research needs.

Keywords:

Phosphorus, cadmium, (im)mobilisation, redox reactions, paddy soil, iron plaques.

1. Introduction

The impact of most human activities result in contaminating the environment with undesirable substances including heavy metal(loid)s added incrementally to soil and water. The industrial activities indiscriminately dump biologically essential [e.g., cobalt (Co), copper (Cu), chromium (Cr), manganese (Mn) and zinc (Zn)] and non-essential [e.g., cadmium (Cd), lead (Pb), nickel (Ni) and mercury (Hg)] elements. While the former are termed as ‘trace elements’ or ‘micronutrients’ due to their requirement in low concentration for plant, animal or human nutrition, the latter are phytotoxic and/or zootoxic and are widely known as ‘toxic elements’. At excessive concentrations, both these types of elements are toxic to plants, animals and/or humans.

The soil has become one of the major sources of heavy metal(loid)s due to increased human activities such as agriculture, mining and industrial activities. Most industries are progressively using land treatment as part of their waste management practices; as a result, soil accumulated metal(loid)s are reaching food chain through plant uptake and animal transfer. Most metal(loid)s in soils persists for a long time after their introduction as they do not undergo microbial or chemical degradation (Adriano et al., 2004). However, the mobilisation of metal(loid)s can be minimised through chemical and biological immobilisation, thereby limiting plant uptake and reducing metal(loid) leaching to groundwater (Harmsen and Naidu, 2013). There has been growing interest in the immobilisation of metal(loid)s using inorganic compounds (lime, phosphate compounds e.g. apatite rocks and alkaline waste materials) and organic compounds, such as ‘exceptional quality’ biosolid (Park et al., 2011; Zhou and Haynes, 2010).

Although phosphate compounds have the ability to immobilise metal(loid)s, regular application of phosphorus (P) fertilisers (mined and processed) has been identified as the main source of heavy metal(loid) contamination of soils (Loganathan et al., 2008; van Kauwenbergh, 2002; Table 1). Few researchers found that these P fertilisers not only act as a source of heavy metal(loid) contamination to agricultural soils but also as a sink for these metal(loid)s through immobilisation processes (Bolan et al., 2003a; Miretzky and Fernandez-Cirelli, 2008). Phosphate amendment has often been proposed as a practical remediation option for sites with Pb-contaminated soils (Freeman, 2012; Ma et al., 2009). However, in a recent study, Sanderson et al. (2014) observed that the nature of P compound, soil type and metal(loid) species influences the mobilisation and immobilisation of metal(loid)s.

Among the heavy metals, Cd is one of the major contaminants from phosphate fertilisers and Cd is more soluble compared to other metal(loid)s (Nordic Council of Ministers, 2003). Tirado and Allsop (2012) claimed that application of mineral phosphate fertilisers can contaminate the soil environment with 54–58% of Cd. Although more refined and slightly expensive P fertilisers (like diammonium phosphate (DAP) and triple superphosphate (TSP)) can minimise the Cd input to soils, most of the rice growers in some Asian countries prefer low cost P fertilisers (Katyal and Reddy, 2012) which are likely to contain high levels of Cd. Hence, the Cd contents in rice grains in some of the Asian countries are higher than countries like Australia, United States and Italy (Figure 1). The reason for this can be attributed to the accumulation of Cd over several years of P fertilisation (Table 2). Other sources of Cd contamination in soil include sewage sludge application, manure application, emissions from power stations, metal(loid) and cement industries (Bolan et al., 2013a; Grant, 2011; Ok et al., 2010; 2011). The bioavailability of Cd in soil is controlled by pH, soil structure, soil organic matter (SOM), and chemical speciation and the

uptake by plants occur mainly via Ca^{2+} , Fe^{2+} , Mn^{2+} , and Zn^{2+} transporters (Verbruggen et al., 2009). While most of the Cd accumulation occurs in roots, the capacity of translocation to shoots is a factor of tolerance mechanism by plants. Cadmium is one of the most mobile heavy metals and hence can be highly toxic to plants (Siebers et al., 2013).

Root iron plaques play an important role in rhizosphere accumulation of heavy metal(loid)s including Cd but the uptake by plants can be affected by the levels of Fe, Zn, Se and Mn in both plant and soil (Kovács et al., 2010; Liu et al. 2007; Saifullah et al., 2014; Sárvári et al., 2011; Sarwar et al., 2010). Microelements such as Zn, Fe, Se and Mn play a vital role in mitigating Cd stress to plants, by activating certain Cd avoidance and/or tolerance mechanisms in plants (Saifullah et al., 2014; Sarwar et al., 2010; Table 3). Choppala et al. (2014) listed the tolerance mechanisms as follows:

- synthesis of phytochelatin (PCs) and metallothioneins (MTs), especially Zn induced
- competition between micronutrients and Cd for the same membrane transporters
- alleviation of oxidative stress by antioxidant production
- restoration of chlorophyll structure damaged by Cd toxicity.

Since root iron plaques can both supply and restrain the above-mentioned microelements to plants, they can play a significant role in the competitive uptake of Cd by plants, which is dependent on the concentration of nutrients (e.g., P). For example, the root iron plaques in paddy crops not only help in the uptake and translocation of P but also act as a barrier to Zn uptake in rice plants (Zhang et al., 1998; 1999). In the presence of P fertilisers, Cd also possesses binding affinity similar to Zn and hence iron plaques play an important role in the uptake and accumulation of Cd in plants. Moreover, most natural P fertilisers are rich Mn and Zn (Table 1), which are competitors of Cd for adsorption sites in iron plaques and absorption to plants.

This review discusses the various sources of Cd in soils with a specific focus on P sources and emphasis on paddy soils, wherever appropriate. However, the chemistry of P and Cd interactions are not deemed only to paddy soils in the initial sections. Following a brief overview of the reactions of Cd and common P compounds that are used as fertiliser in soils, this paper focuses on the mechanisms for the (im)mobilisation of Cd by P compounds. The practical implications of P compounds on the transformation of Cd are discussed in relation to adsorption and precipitation of Cd in paddy soils. Both direct and indirect effects of P compounds on Cd (im)mobilisation are discussed where pH is one of the main influential factors (e.g., liming effect and rhizosphere acidification). The distinctive role of rhizosphere region in paddy soils in the presence of root iron plaques is explained with examples.

2. Sources of cadmium in soil environment

In terrestrial ecosystems, the soil is the chief repository of heavy metal(loid)s as a result of both pedogenic processes and anthropogenic activities. The bioavailability of trace elements is higher for those from anthropogenic than natural (pedogenic) sources (Lamb et al., 2009; Naidu and Bolan, 2008). In naturally occurring soil parent materials, the metal(loid)s are associated with ores and hence are not readily bioavailable for plant uptake. Cadmium is one such heavy metal(loid) which is being predominantly added to the environment through human activities, especially as P fertilisers and poses serious contamination issues in the food chain.

2.1 Geogenic

Naturally, Cd concentration in most terrestrial soil parent materials such as igneous rocks, sandstones and limestone is generally low compared to the rocks derived from their aquatic counterparts like lake sediments and marine black shales (Bolan et al., 2013a; Bramley, 1990; Loganathan et al., 2012; MacDonald et al., 2005). Although none of these rocks occur to any great extent in most agricultural soils, they can contribute to Cd accumulation especially in paddy soils derived from these rocks. Since Cd occurs mainly in association with Zn ores, sphalerite (zinc sulfide) forms the main commercial source of Cd. However, Parnell et al. (2014) observed Cd sulphide mineralisation in grey-black shales northwest of Scotland and observed that Cd is strongly redox-controlled under anoxic conditions and can mineralise in the presence of organic matter (OM). They also found that under fluctuated oxic and anoxic conditions, fractionation of Cd from Zn can lead to the formation of Cd sulphide rather than Cd-bearing sphalerite.

Black shales contain high concentrations of trace elements, including some toxic elements such as Cd. For example, Okchon black shale present in the central part of the southern Korean peninsula (about 5,100 km² of area constitutes around 5.5% of South Korea's total territory), contains rich concentration of toxic elements (Kim, 1989). Soils derived from these parent materials tend to reflect their extreme geochemical composition (Bowie and Thornton, 1985) and may influence human health by affecting the elemental composition of crop plants (Foth, 1978). This Okchon black shale is particularly rich in barium (Ba), Cd, molybdenum (Mo), vanadium (V), and uranium (U), where their mean concentrations are significantly higher than those in black slates (Chon et al., 1996; Kim and Thornton, 1993). In these soils, Cd uptake of crop plants is high because of its predominant presence as an exchangeable phase.

Black shales act as a source of these elements including Cd, in the rock–soil–plant–human system. In the black shale areas, high Cd concentrations are found in residual soils developed from

bedrock with high Cd concentrations. Rice grown near black shale areas show higher Cd concentrations compared to those grown in black slate or grey chlorite schist areas. Average Cd concentrations of rice cultivated in these areas were significantly higher than those in normal rice grown on uncontaminated soils (Masironi et al., 1977; Watanabe et al., 1989; Yoo et al., 1992). Lee et al. (2006) examined six areas in Duk-Pyung (South Korea) and found the highest average concentrations of 0.61 and 1.74 mg kg⁻¹ Cd in rice grains and stalks, respectively.

2.2 Anthropogenic

The Cd concentration in agricultural systems was low in pre-industrial revolution era as the main inputs from the weathering of rocks and volcanic activity. Industrial revolution have not only opened up more sources of Cd contamination but also created rapid accumulation of heavy metal(loid)s including Cd in soil through agricultural activity and other industrial processes such as smelting of metals, combustion of coal, oil and wood, and incineration of wastes. As mentioned earlier, the bioavailability of Cd from these anthropogenic sources are also high. Human activities such as the use of P fertilisers and the disposal of sewage sludges and mine tailings directly add Cd to the soil.

Most P compounds (both mined and processed) contain a group of trace elements, generally with high concentrations of Zn, Mn and Cd (Adriano, 2001; Bolan et al., 2003a; Loganathan et al., 2008; McLaughlin et al., 1996; Mortvedt, 1996; Syers et al., 1986; Table 1). In the process of adding P and also supplying some of the essential trace elements (e.g. Zn) to plants, these P compounds also introduce toxic elements such as Cd (Loganathan et al., 2008; McLaughlin et al., 1996; Naidu et al., 1997). Hence, the contamination of agricultural soils with Cd is of particular concern as this trace element reaches the food chain through regular and frequent use of

Cd-containing P fertiliser materials, such as single superphosphate (SSP), triple superphosphate (TSP), and phosphate rocks (PRs) (Loganathan et al., 2008). Moreover, the presence of Cd in amounts exceeding food guidelines has implications to both local and international trade.

Regular fertiliser applications not only improves crop production but also results in the accumulation of heavy metal(loid)s including Cd, in many countries. For instance, in Australia and New Zealand, most of the Cd accumulation in pasture soils has been attributed to the use of P fertilisers containing these trace elements, which originates from the PRs used (Bolan et al., 2003a; Loganathan et al., 2008; Table 1). Thus, manufactured P fertilisers also vary accordingly in their Cd content. The Cd in superphosphates is water soluble and P fertilisers, such as TSP and ammonium phosphates, generally contain lower Cd content relative to P (Loganathan et al., 2003). However, calcium (Ca) contents of P fertilisers play an important role in the bioavailability of Cd, because of its competition to sorption sites with Cd and also its ability to reduce the surface negative charge density of soil colloid particles (Naidu et al., 1997).

Loganathan et al. (1996) showed a positive relationship between total P and total Cd in soils that received accumulative P fertilisers. Comparison between unfertilised native and fertilised agricultural soils has often been employed to scrutinise the link between soil contamination and agricultural practices. For instance, few other researchers obtained significant positive correlations between total P and total Cd in pasture soils in New Zealand receiving long-term inputs of superphosphates (Gray et al., 1999; Roberts et al., 1994). McLaughlin et al. (1996) observed similar results for a range of Australian soils. This is not surprising considering the long history of superphosphates usage in both New Zealand and Australia, manufactured from PRs containing high levels of Cd (Rothbaum et al., 1986; Schipper et al., 2011). Interestingly, rice grains in Australia showed low Cd concentrations compared to their Asian counterparts such as India,

China and Japan (Figure 1; Rahman et al, 2014). In paddy soils, the redox reactions under flooding conditions play a role in fluctuating Cd concentrations at various growth stages (initial, vegetative, panicle and maturity). Siebers et al. (2013) observed a significant negative correlation ($R^2=0.8367$) between Total P and Total Cd concentrations at panicle stage and less significant positive correlation ($R^2=0.8005$) at maturity stage of paddy cultivation, under different rates of P application (Figure 2).

In paddy soils, where Cd is a serious health issue, some studies have reported that Cd is derived primarily from P fertilisers. Ramachandran et al. (1998) reported that the application of Mussoorie PR to cultivated paddy areas in India caused an increase in Cd content of the rice grains. Similarly, Khairiah et al. (2009) found that small amounts of Cd were found in the bioavailable form in soils amended with P fertilisers in Malaysia. However, Iretskaya et al. (1998) found that Cd in PR was not readily available to rice in limed soils, within few months of its addition. They observed that the availability increased markedly in the second year and presumed that there may be an increased dissolution of PR, particularly in the acidic soil environments.

Apart from fertilisers, other major anthropogenic sources (Table 4) include biosolids (Bolan et al., 2003b; Haynes et al., 2009; Park et al., 2011), mining and smelting (Bhattacharya et al., 2006; Concas et al., 2006) and industrial activities (Arao et al., 2010; Lin et al, 2002). Traditionally, biosolids are viewed as one of the major sources of metal(loid) accumulation in soils, and a large volume of work has been carried to examine the mobilisation and bioavailability of biosolids-borne metals in soil (Bolan et al., 2003b; Haynes et al., 2009; Park et al., 2011). Nowadays, biosolids composted from heavy metal-rich sewage sludge are stabilised with alkaline products to immobilise the heavy metals thereby limiting their bioavailability (Basta et al., 2001; Bolan et al., 2003b). However, in most developing countries biosolids is still considered as a major source of

heavy metal(loid) input to soils (Haynes et al., 2009). Kikuchi et al. (2007) conducted an experiment on the input-output balance of Cd under two different fertilisation regimes (chemical fertiliser and cow manure compost) at 20 t ha⁻¹ application rate. They observed that the cow manure compost loaded more Cd in the paddy soil compared to the chemical fertiliser although the inorganic counterpart contained 10 times more Cd than the compost. The output of Cd in the form of plant uptake and leaching was also higher in cow manure treatment compared to the chemical fertiliser (Figures 3 a and b). Similarly, Yada et al. (2006) studied the effects of P fertiliser and precipitation on a non-polluted paddy soil, and found that Cd accumulation in soil is more than the total of leaching, drainage water, irrigation water and uptake by rice grains (Figure 4).

Mining and allied activities such as mineral separation and processing (e.g. smelting of metal(loid) ores) are also responsible for the contamination of soil and water sources with heavy metal(loid)s including Cd. Bhattacharya et al. (2006) found that opencast mining activities have a serious environmental impact on soils and water streams and have generated millions of tons of sulfide-rich tailings. Agricultural activities around the dense mining area have been found vulnerable to high Cd concentrations, with high Cd uptake recorded in rice and some vegetables (Ok et al., 2011; Zhai et al., 2008). Long-term Cd exposure by regular consumption of rice and vegetables posed potential health problems to residents in the vicinity of mines. Kim et al. (2001) identified over 1000 abandoned metal(loid) mines in South Korea, which even after restoration schemes remains a potential risk to humans and to the ecosystems. In the absence of proper environmental treatment or restoration efforts, large amounts of mine wastes including tailings are becoming an important point source of toxic elements such as arsenic (As), Cd, Cu, Pb, and Zn in the environment. These materials are dispersed down slope by surface erosion, wind action, and effluent draining from the mine wastes contaminating the low-lying arable lands.

Discharge of chemical wastes into irrigation channels (used for flooding paddy fields) is a common practice in some urban and semi-urban areas throughout Asia, where paddy fields for rice production are often close to industrial sites (Arao et al., 2010; Lin, 2002). Wastewater discharged from metal(loid) plating factories (Higurashi et al., 1976), coating and paint factories (Masui et al., 1971), and electronics and home appliance manufacturing plants (Matsuzaki et al., 1987) is also an important source of Cd contamination. This wastewater often becomes mixed with irrigation water and thus contaminates paddy fields.

3. Reactions of cadmium in soils

The common retention reactions in soils involving heavy metal(loid) ions include sorption, precipitation, and complexation reactions, where the removal processes are through plant uptake, leaching, and volatilisation (Figure 5). The only metal(loid)s undergo volatilisation losses are As, Hg, and Se as they tend to form gaseous compounds (Bolan et al., 2013a; Mahimairaja et al., 2005). In paddy soils, the most important process which affects the soil chemistry is water-logging, which under continuous cultivation, can shift soil pH to neutrality and increase organic C and soluble P (Kim et al., 1991). However, pH is not the sole factor in paddy soils that controls movement of metallic ions within the soil. Redox potential (Eh) also plays an important role in the bioavailability and solubility of heavy metal(loid)s, which have been linearly correlated (Masscheleyn et al., 1991). Yaron et al. (1996) showed that a decrease in Eh increased solubility of some metals, under identical pH.

Understanding the factors controlling Cd speciation and bioavailability in flooded, drained, and alternately flooded/drained paddy soil will be crucial to developing and implementing best management practices needed for productive agricultural areas. Unlike upland soil, lowland rice

paddy soil undergoes a flooding and draining cycle, which can change soil conditions into anaerobic and aerobic states and modify the biological and chemical properties of the soil, especially pH and redox potential (Eh) (Kögel-Knabner et al., 2010). These modifications of soil properties are likely to impact Cd speciation present in the Cd-contaminated paddy soils.

3.1 Sorption/Desorption Process

Waterlogging of paddy soils contributes to an increased pH in acid soils and a decrease in pH of alkaline soils (Fageria et al., 2011; Patrick and Reddy, 1978; Ponnampereuma, 1972). Therefore, the pH tends to become neutral, whether the initial soil was acidic or alkaline. Increased pH in acid soils may result in more negative charges on soil clay colloids and OM surfaces, and, therefore, decreases the exchangeable heavy metals by immobilisation (Bolan et al., 2003c; Yuan and Lavkulich, 1997). Lim et al. (2002) investigated the changes of speciation of Cd in a tropical coastal clay soil at various pH values at different times and found that the changes of Cd in the exchangeable fraction were pH-dependent. Generally, the change was small under acidic conditions and larger decreases occurred at pH 7. By monitoring the process of heavy metals on iron oxide (α -FeOOH), Martínez and McBride (2001) found that either adsorption or coprecipitation of heavy metals with ferrihydrite was pH-dependent. They also found that an increasing pH and incubation time resulted in an increase of adsorption and coprecipitation of heavy metals. Zheng and Zhang (2011) suggested that increased concentrations of an OM-bound Cd fraction in flooded soil was probably due to metal–organic complex formation, which has a higher magnitude in waterlogged soils, because lower values of Eh and higher pH favored the formation of metal–organic complexes (Gambrell, 1994; Hettiarachchi et al., 2000; Sauve et al., 2000).

There is a dynamic equilibrium between metal(loid)s in solution and the soil solid phase, which is controlled by soil solution composition and properties of the soil. The nature of ligand ions (both organic and inorganic) and soil's pH induced metal(loid) sorption processes influence the concentration of metal(loid)s in soil solution (Bolan et al. 2003c; Harter and Naidu 1995). There are two main reasons for the effect of inorganic anions on the sorption of metal(loid) cations such as Pb and Cd: (i) Inorganic anions form ion pair complexes with metal(loid)s, thereby reducing their sorption (Hong et al., 2008); (ii) Specific sorption of ligand anions is likely to increase the negative charge on soil particles, thereby increasing the sorption of Cd (Naidu et al., 1994). Soils with pH>6.5 (common in paddy soils) may reduce the free metal(loid) ion activities under three different processes, (i) increase in pH-dependent surface charge on oxides of Fe, Al, and Mn; (ii) chelation by organic matter; (iii) precipitation of metal(loid) hydroxides (e.g., Cd(OH)₃) (Mouta et al. 2008; Stahl and James 1991). Lim et al. (2002) observed that pH influenced the changes in exchangeable fractions of Pb and Cd, where the change was minimal under acidic condition but observed larger decrease in the exchangeable fraction at pH 7.

Other chemical interactions that contribute to metal(loid) retention by colloid particles include complexation reaction between metal(loid)s and the inorganic and organic ligand ions. In paddy soils, the presence of a wide variety of anions supplied from various sources such as irrigation water, fertilisers and soil amendments, can easily form complexes with Cd extracted from soil adsorption sites (Traina, 1999). The organic component of soil constituents also has a high affinity for heavy metal(loid) cations such as Cu, Cd, and Pb because of the presence of ligands or groups that can form chelates with metal(loid)s (Harter and Naidu 1995; Bolan et al. 2011). As mentioned earlier, the pH and Eh conditions present in paddy soils are favorable for metal-organic complexes.

304

305 3.2 Precipitation/Dissolution

306 Under alkaline soil conditions ($\text{pH} > 7$), precipitation of heavy metal(loid)s occurs if the
 307 concentration of those ions are high, coupled with the presence of anions such as SO_4^{2-} , CO_3^{2-} ,
 308 OH^- , and HPO_4^{2-} (Naidu et al., 1997; Hong et al., 2007; Ok et al., 2010). Precipitation as metal(loid)
 309 phosphates/carbonates is considered to be one of the mechanisms for the immobilisation of heavy
 310 metal(loid)s such as Cu and Pb, especially in substrates containing high concentration of these
 311 metal(loid)s. Similarly, Cd forms precipitates with sulphides (e.g. CdS) and phosphates (e.g.
 312 $\text{Cd}_3(\text{PO}_4)_2$), where Cd phosphates starts precipitating even from neutral pH range as in paddy soils
 313 (Matusik et al., 2008; Makino et al., 2010). Hence, liming can also typically enhance the retention
 314 of metal(loid)s because of the pH effect (Adriano, 2001; Karalić et al., 2013).

315 Under submerged condition in paddy soils, Cd solubility decreases due to the formation of
 316 Cd sulphides as a result of reduced conditions with a sharp decrease in Eh, where sulphate ion can
 317 be reduced to sulphide ion (Iimura, 1978). The sulphide ion produced thus reacts with Cd to
 318 precipitate out of soil solution as cadmium sulphide. The precipitation of cadmium sulphide (CdS),
 319 in turn, lowers the Cd concentration in the soil solution, lowering the amount of the Cd
 320 bioavailable to rice plants. Makino (2002) found that sulphur species in soil solution plays an
 321 important role in Cd solubility, but the ratio of H_2S and total sulphur is more important. Also, CdS
 322 formation depends on the redox equilibrium between sulphate and sulphide (Makino et al., 2010).

323 Co-precipitation of metal(loid)s especially in the presence of iron oxyhydroxides has also
 324 been reported and often such interactions lead to significant changes in the surface chemical
 325 properties of the substrate. For example, Violante et al. (2007) noticed that As(V) was desorbed by
 326 P from a ferrihydrite on which As(V) was added than from a Fe- As(V) co-precipitate. In the case

of Cd, most P fertilisers have been tested for Cd removal from contaminated soils (Raicevic et al., 2005; McGrellis et al., 2001; Marchat et al., 2007; Bolan et al., 1999a; Lundager Madsen et al., 2004). Formation of cadmium phosphates is the general mechanism at neutral to alkaline conditions. However, under rice cultivation, the aqueous medium plays an important role in the formation of cadmium-phosphate precipitate, which will be explained under section 5.2.3.

3.3 Oxidation/Reduction

Metal(loid)s, including As, Cr, Cd, Hg and Se, are most commonly subjected to microbial oxidation/reduction reactions, thereby influencing their speciation and mobility. In paddy soils, oxidation reaction takes place during pre-harvest drainage of the flooded crops, making Cd available to rice plants (Inahara et al., 2007). Sulphide minerals, Fe and Zn are known to play important roles in the solubility of Cd. Oxidation of sulphide minerals can alter the Cd:Fe and Cd:Zn ratios (Chaney et al., 1996). But de Livera et al. (2008) claimed that differential oxidation of sulphide minerals may not increase the ratios when all the three metals are present in natural conditions. Instead, reactions involved in Fe redox (oxidation-reduction) reactions can influence Cd solubility under alternate oxidising and reducing conditions (Zhang et al., 2012). In another study, Jamil et al. (2013) evaluated the heavy metal(loid) contamination including Cd in slightly acidic cultivated paddy areas, exposed to fluctuating redox conditions. Their results revealed that high amounts of bioavailable Cd in paddy soils might be attributed to the soil type, redox conditions, and repeated application of fertilisers in the study areas.

During soil oxidation at the pre-harvest drainage, the Fe concentration in soil solution decreases due to precipitation as Fe oxyhydroxides. Although the Eh does not affect the solubility of Cd directly in alkaline and neutral soils, Fe induced Cd adsorption can be observed in acidic soils

(Chuan et al., 1996). They observed that the pH played more significant role in metal(loid) solubilisation than redox potential because dissolution of Fe oxyhydroxides during low pH and reducing conditions control the release of Cd from soil. However, paddy soils usually maintain neutral pH under flooded conditions where Fe oxyhydroxides precipitate and can provide adsorbent surface for Zn and Cd, thereby reducing Cd:Zn ratio in soil solution.

In an experiment on Cd contaminated soils (spiked and field contaminated), de Livera et al. (2011) tested the effects of soil redox processes and the presence of added SO_4^{2-} or Zn on soil ageing and the resultant Cd solubility in Cd contaminated soils, under simulated paddy cultivation conditions. They observed that higher concentrations of SO_4^{2-} and/or Zn in the soil resulted in lower ratios of Cd:Fe and Cd:Zn in soil solutions, which can decrease the bioavailability of Cd under paddy cultivation. The addition of SO_4^{2-} (at high concentration) resulted in insoluble metal(loid) sulphides and they observed that the SO_4^{2-} reduction was more obvious in field contaminated soil compared to laboratory spiked soil, which can be attributed to the ageing of metals in soil.

4. Reactions of phosphate compounds in soils

With abundant usage of a range of P compounds for agricultural applications, their reactions in soil based on the form of P compounds play an important role in the (im)mobilisation of metal(loid)s. As agricultural fertilisers, P compounds are broadly grouped into water-soluble (fast-release) and water-insoluble (slow-release) fertilisers (Bolan et al., 1993). The important water-soluble P fertilisers include: single superphosphate (SSP), triple superphosphate (TSP), monoammonium phosphate (MAP) and diammonium phosphate (DAP). The important water-insoluble P fertilisers are phosphate rocks (PRs) and basic slag. Monocalcium phosphate (MCP) and ammonium

phosphate (AMP) are the principal P components present in superphosphates (SSP and TSP) and ammonium phosphates (MAP and DAP), respectively.

4.1 Water-soluble compounds

When superphosphate fertilisers are added to soils, the dissolution of MCP results in the formation of slowly soluble dicalcium phosphate (DCP) with a release of phosphoric acid close to the fertiliser granules (Eq.1). Phosphoric acid subsequently dissociates into H_2PO_4^- and hydrogen ions (protons – H^+). The protons reduce the pH around the fertiliser granules to a very low level (< 2 pH). When AMP fertilisers are added to soil, they dissociate into ammonium (NH_4^+) and H_2PO_4^- ions. The subsequent oxidation of NH_4^+ to NO_3^- results in the release of protons (Eq. 2).

The acidic solution around the fertiliser granules dissolves the Fe and Al compounds in the soil, resulting in the adsorption and precipitation of P. The retention of P by soils decreases the amount of P available for both plant uptake and leaching to groundwater. The acidity generated can also have important implications to the mobilisation of metal(loid)s. However, in the case of paddy soils, flooding influences pH of the soil, where P availability increases in acidic soil due to the reduction of ferric phosphate to more soluble ferrous form and the resultant hydrolysis of P compounds. In a similar way, P availability also increases in alkaline soils, where P from Ca and calcium carbonate liberates as a result of decrease in pH to near neutral conditions (Fageria et al., 2011).

4.2 Water-insoluble compounds

When insoluble P fertilisers, such as PRs are added to soil they need to be dissolved in soils for the P to become plant available. In soils, PRs dissolve by using the acid produced in the soils (Eq. 3). This is a major reason why PRs are very effective as a nutrient source mainly in acid soils (pH < 6.5) (Bolan et al., 1990; Danso et al., 2010) and as a metal(loid) immobilising agent in acid mine drainage (Evangelou and Zhang, 1995; Oliva et al., 2012). Similarly, in the case of paddy soils, flooding induces reducing conditions in the rhizosphere region, thereby inducing the dissolution of P from PRs. Once the PR is dissolved, the P released undergoes similar adsorption and precipitation reactions as in the case of soluble P fertilisers.

5. Mechanisms for (im)mobilisation of cadmium by phosphate compounds

Phosphate compounds affect the (im)mobilisation of Cd in the paddy soil-water-plant system through various processes (Figure 6). These include: phosphate compounds as a Cd source; P-micronutrient imbalance in plant nutrition; direct Cd adsorption by P compounds; direct precipitation of Cd with solution P as Cd phosphates; precipitation through the liming action of PRs; and rhizosphere modification through acidification. Both mobilisation and immobilisation of Cd in soils treated with a range of P compounds have been reported, and the probable mechanisms for the P-induced (im)mobilisation of Cd reported in the literature are given in Tables 5 and 6.

5.1 Phosphate compounds as a metal(loid) source

Many researchers reported a range of metal(loid)s including Cd, present in P based compounds

(McLaughlin et al., 1996; McBride and Spiers, 2001; Molina et al., 2009). Addition of P compounds to soils not only helps to overcome the deficiency of some of the essential trace elements, such as Zn, but also introduces toxic metal(loid)s, such as Cd (McLaughlin et al., 1996; Loganathan et al., 2012; Bolan et al., 2013b). In this regard, Cd contamination of paddy soils is of particular concern because this toxic element reaches the food chain through regular use of Cd containing fertiliser materials, such as SSP and TSP.

Accumulation of Cd in soils through regular fertiliser use has been observed in many countries (Table 7). For example, in New Zealand and Australia, most of the Cd accumulation in pasture soils has been derived from the use of P fertilisers containing high Cd concentration. The Cd in most P fertilisers originates mainly from the PRs used for manufacturing P fertilisers. It is important to stress that PR deposits vary in their Cd contents and hence manufactured P fertilisers also vary accordingly in their Cd content. For example, Roberts et al. (1994) obtained evidence for the enrichment of Cd in pastoral soils and there was a highly significant correlation between total soil P and total soil Cd across all sites, confirming the role of P fertilisers in soil Cd enrichment. This is not surprising considering the long use history in both New Zealand and Australia of superphosphates, manufactured from Nauru Island PR. Nauru superphosphates typically contain 34-69 mg Cd kg⁻¹ (Rothbaum et al., 1986; Schipper et al., 2011).

Similarly, Loganathan et al. (1996) examined the movement and distribution of Cd and P in a pastoral soil amended annually for 10 years with four forms of P fertilisers (SSP, DAP, North Carolina phosphate rock (NCPR) and Jordan PR (JPR)) which varied in their total Cd content. Both total and plant available Cd concentrations decreased with soil depth. Single superphosphate and NCPR which had higher Cd contents produced higher Cd concentration than DAP, JPR and

control treatments. Approximately 93% of the applied Cd was recovered in the top 120 mm soil and plant recovery of applied Cd ranged from 1.5 to 4.5%.

In the case of paddy soils, there are many studies on P fertiliser as a source of Cd (Arao and Ae, 2003; Malidareh et al., 2014; Mousavi et al., 2010; Sriprachote et al., 2012). A study by Jamil et al. (2013) found that the fertilisers commonly used for rice cultivation contained a certain amount of Cd. Although present in small quantities, the investigators warned that Cd could accumulate in soils after several years of application of fertilisers. Another study by Lavres et al. (2011) investigated the P uptake by upland rice and subsequent accumulation in grains from superphosphate fertilisers produced with sulphuric acid treatments of Brazilian PRs. The other objective of their study was to determine the translocation of Cd from P fertilisers to rice grains. Their results revealed that, although the grain Cd concentration was significantly affected by P rates, it did not exceed the permissible concentration for human consumption, according to Brazilian food legislation.

5.2 Phosphate-induced (im)mobilisation of cadmium

5.2.1 Direct adsorption by phosphate compounds

Depending on the source, application of P compounds can cause direct adsorption of metal(loid)s onto these P compounds, enhance anion-induced metal(loid) adsorption through increased surface charge, decrease metal(loid) adsorption through metal(loid)-complex formation, and induce desorption of Cd, through competition (Table 5). Some P compounds such as apatite mineral have been effective in adsorption of Cd (Table 6) where the order of adsorption by apatite largely pH dependent (Chen et al., 1997). Hydroxyapatite is also shown to be adsorbing metal(loid)s such as

Zn and Cu (Wang and Zhang, 2014) and Cd (Middelburg and Comans, 1991; Barka et al., 2012). Metal(loid) adsorption onto apatite is facilitated through the exchange of Ca^{2+} from the apatite particle by the metal(loid) in the soil solution (Zhu et al., 2010). However, Xu et al. (1994) concluded that in the case of Zn and Cd, surface complexation and co-precipitation (Eq. 4) are the most important mechanisms contributing to the overall adsorption process by hydroxyapatite.

5.2.2 Phosphate-induced Cd adsorption

Bolan et al. (1999a) reported that anion-induced metal(loid) adsorption is one of the mechanisms for immobilisation of a number of cations, including Cd^{2+} . Some researchers have shown that low or moderate enrichment of oxides with P can enhance the adsorption of Zn^{2+} , Cd^{2+} or Cu^{2+} by variable charge components such as Al and Fe oxides (Wang and Xing, 2004; Ren et al., 2012; Tiberg et al., 2013; Stietiya and Wang, 2014), thereby causing increases in surface negative charge.

Several mechanisms can be advanced for H_2PO_4^- -induced metal(loid) adsorption by soils, including: (i) increase in negative charge (ii) co-sorption of H_2PO_4^- and metal(loid) as an ion pair; and (iii) surface complex formation of metal(loid) on the P compound. Bolan et al. (1999b) showed that the nature of anion adsorbed, pH and electrolyte concentration of the solute plays an important role on the surface charge acquired through specific adsorption of anions (Eq. 5). The most frequently offered causes for P-induced increase in negative charge include, (Hingston, 1981; Bolan et al., 2003a): (i) a shift in the zero point of charge to lower pH values; (ii) neutralisation of positive charge; and (iii) electrolyte inhibition.

Bolan et al. (1999b) obtained a good relationship between the increase in negative charge resulting from $\text{H}_2\text{PO}_4^{-}$ enrichment and the increase in Cd^{2+} adsorption. However, only a small fraction of the increased negative charge was occupied by Cd^{2+} . Similarly, Naidu et al. (1994) demonstrated that the effect of ionic strength on Cd^{2+} adsorption was induced through its effect on surface charge. Phosphate enriched minerals such as gibbsite and goethite can increase the adsorption of Ca^{2+} and Zn^{2+} through surface complex formation (Rietra et al., 2001; Helyar et al., 1976). In this case, specifically sorbed anions, such as $\text{H}_2\text{PO}_4^{-}$ form complexes with soil surface so that cations (including Cd^{2+}) are adsorbed onto the adsorbed anion. Hence, surface complexation is usually suggested as one of the mechanisms for the immobilisation of metal(loid)s, such as Cd and Zn by hydroxyapatite (Xu et al., 1994; Cao et al., 2004).

Siebers et al. (2013) studied the distribution of Cd among various fractions in paddy soils at different stages of rice cultivation (initial, vegetative, panicle and maturity stages), treated with four different levels of P (0, 50, 200 and 1000 mg kg^{-1}). They observed an increase in soil pH at all growth stages as the P addition increased (Figure 7a). The levels of soluble Cd in soil increased throughout the growth stages, however it was less significant in vegetative and panicle stages. At 1000 mg kg^{-1} P addition, there were significant differences in Cd solubility and the soluble Cd concentration in soil increased through the various growth stages of paddy cultivation (Figure 7b). However, the addition of P showed a significant decrease in soluble Cd fraction only at the highest treatment (1000 mg kg^{-1}), which can be attributed to phosphate induced Cd adsorption (Figure 7b).

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504 5.2.3 Precipitation as cadmium phosphate

The P radical can combine with over 30 elements to form P minerals (Clark, 1993). Because of its high reactivity, the precipitation as metal(loid) phosphates is one of the main mechanisms for the immobilisation of metal(loid)s, such as Cd, Pb and Zn. These new metal(loid)-P compounds have extremely low solubility over a wide pH range, which makes P application an attractive technology for managing metal-contaminated soils. Advanced studies using X-ray absorption fine structure spectroscopy (XAFS) indicate that formation of surface precipitates may occur even when solution concentration is undersaturated with respect to homogeneous precipitation of pure metal(loid) precipitate phase (Ford and Sparks, 2000).

There have been few studies on the effect of P addition on $\text{Cd}_3(\text{PO}_4)_2$ precipitate formation in Cd contaminated soils, but without direct evidence (Nriagu et al., 1984; Ma et al., 1993; Cotter-Howells and Caporn, 1996). Bolan et al. (2003a) proposed that precipitation as metal-phosphates and hydroxides is the main mechanism for the immobilisation of metals, including Cd. At the pH range of most paddy soils (6.5 to 7.5), metal(loid) phosphates and hydroxides are fairly insoluble. Many studies have also outlined the stability (chemical and thermodynamic) of metal(loid) phosphates over a broad range of pH and Eh. Matusik et al. (2008) studied the effect of three different P compounds (K_2HPO_4 , $\text{NH}_4\text{H}_2\text{PO}_4$ and a commercial P fertiliser) on Cd immobilisation from aqueous solutions, under a broad pH (4-9) range. Although P compounds reduced Cd solubility in soil, pH changes influenced the immobilisation/precipitation processes. The P compounds removed less Cd (80 %) at $\text{pH} \leq 5$ compared to 99 % at a pH range between 6.75 and 9. They observed crystalline phase of cadmium phosphate ($\text{Cd}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$) only under acidic conditions; however, at pH 7 (paddy soil pH range), formation of $\text{Cd}(\text{H}_2\text{PO}_4)_2$, $\text{Cd}_3(\text{PO}_4)_2$ and $\text{Cd}_5\text{H}_2(\text{PO}_4)_4 \cdot 4\text{H}_2\text{O}$ were also observed.

McGowen et al. (2001) have examined the immobilisation of As, Cd, Pb and Zn in a

smelter-contaminated soil using DAP. Application of high levels of DAP at a rate of 2300 mg P kg⁻¹ was very effective in immobilising Cd, Pb and Zn in the contaminated soil. Others have also shown that Cd₃(PO₄)₂ can control Cd solubility in P-sufficient soils or soils amended with P (Santillan-Medrano and Jurinak, 1975; Street et al., 1978; Hong et al., 2010). Because the solubility of Cd₃(PO₄)₂ is too high to control the concentration of Cd in suspensions involving Fe and Al oxides in soils, it is doubtful this solid phase can play a significant role in the immobilisation of Cd and possibly Zn (Soon, 1981; Xiong et al., 1995). In paddy soils, moisture management plays an important role in the (im)mobilisation of Cd and P, where P is available and Cd availability is limited (Li and Xu, 2014). They observed formation of P-Cd precipitate in continuously flooded paddy soil and attributed that highest soil available P could result in highest residual Cd, as observed by Bolan et al. (1999b).

5.2.4. Through liming action of phosphate rocks

In addition to the formation of new solid phases discussed above, metal(loid) immobilisation may also ensue from the formation of metal(loid) oxyhydroxides due to the buffering capacity (or liming action) of hydroxyapatite (Chen et al., 1997; Ma and Rao, 1997; Basta et al., 2001). Phosphate rocks neutralise acids during the dissolution reactions in soils and thus can also have some liming effect through two processes. Firstly, most PRs contain some free calcium carbonate (CaCO₃) which can act as a liming agent itself. Secondly, the dissolution of the apatite mineral in soils consumes acids, thereby reducing soil acidity. The equivalent liming values of various PRs range from 450 to 560 kg CaCO₃ per tonne of PR, with the most liming value coming from the dissolution of apatite mineral (Table 8). The potential value of PRs as a liming material in mitigating acid mine drainage has been documented both under laboratory and field conditions (Frazer, 2001; Mauric and Lottermoser,

2011). Treating acid mine drainage with PRs not only neutralises the acid through their buffering action but also reduces the solution concentration of metal(loid)s through precipitation and ion exchange reactions (Feng et al., 2000; Oliva et al., 2012).

Sø et al. (2011) stated that the CaCO_3 –water– CO_2 – PO_4 system is a complex system to study, because the parameters of the system are linked and Ca^{2+} activity is inversely correlated to the activity of CO_3^{2-} . The pH of the system not only affects the protonation of phosphate but also carbonate. Apart from the pH, Ca^{2+} activity as a result of Ca-complexation, also affects the speciation of phosphate. Thakur et al. (2011) has summed up the reactions (Eq. 6, Eq. 7 and Eq. 8) involving CaCO_3 and Cd as follows:

In paddy soils, addition of CaCO_3 along with commercial P fertilisers showed residual Cd associated with carbonate at the harvesting stage of rice thereby limiting Cd availability to soil (Kim et al., 2004). Cattani et al. (2008) also showed that the addition of CaCO_3 decreased the Cd concentration in rice by 25%.

5.2.5 Rhizosphere acidification

Phosphate compounds affect metal(loid) transformation in the rhizosphere primarily through their effects on soil pH (i.e., acidification). Superphosphates and AMPs are the most common soluble P fertilisers used in agriculture. The dissolution of MCP in soils results in the formation of DCP with a release of phosphoric acid close to the fertiliser granules. Nitrogen-containing P fertilisers, such as

MAP and DAP cause soil acidification mainly through the natural process of nitrification. Acidification caused by P fertilisers induces the mobilisation of metal(loid)s. For example, application of DAP has been shown to enhance metal(loid) solubilisation through acidification (Basta and McGowen, 2004; Khan and Jones, 2009). Acidification affects the transformation of metal(loid) ions through several ways, foremost of which include: (a) modification of surface charge in variable-charge soils; (b) altering the speciation of metal(loid)s; and (c) influencing the reduction and oxidation reactions of the metal(loid)s (Adriano 2001).

Shuman and Wang (1997) studied the difference in pH and P concentration between rhizosphere and non rhizosphere paddy soils and found that pH and P were lower in the former soil. They also linked the transformation of metals including Cd to the oxidising power of the rice cultivars which is controlled by the amounts of Fe and Mn oxides in the soil. Therefore, in paddy soils, higher the oxidising power of the rice varieties and the amount of Fe and Mn oxides present in the soil, the availability of heavy metal(loid)s including Cd will be lower. Hu et al. (2009) studied the rhizosphere effects of two rice cultivars and found low exchangeable Cd concentrations in the rhizosphere region. However, they were not able to find out the exact mechanism of this result as they did not study the effect of P. One possibility is the formation of Cd phosphates outside the rhizosphere region (Figure 6).

6. Influence of phosphorus and root iron plaque on Cd translocation in rice

Most wetland plants (including rice) form special zones called root plaques as a result of a reaction between released oxygen (from plants) and soluble Fe^{2+} in soil (Taylor et al., 1984; Otte et al., 1989; Ye et al., 1998; Li et al., 2011; Figure 6). Hence, iron plaques possess the chemical characteristics similar to iron oxides in soil and therefore can sequester both cations and anions.

Many studies have demonstrated that iron plaque can sequester metals on root surfaces and hence decrease metal(loid) uptake and tolerance by wetland plants (Ye et al., 1998; Batty et al., 2000; Hansel et al., 2001; Blute et al., 2004). Studies by Wang et al. (2011) showed that rice cultivars with higher oxygen release potential through roots highly limited the transfer of As and Cd to grains. Higher oxygen release potential is referred to radial oxygen loss (ROL) of a wetland plant, which affects the extent of iron plaque formation. Borch et al. (2007) stated that P has a strong impact on Fe reduction and transformation. In paddy soil, transformation of ferrihydrite was significantly reduced in the presence of P, suggesting that surface modification by P may stabilise ferrihydrite, thereby supporting the formation of iron plaques (Borch and Fendorf, 2007).

Also, several studies have shown that iron plaque on rice root surfaces facilitates sequestration of Al (Chen et al., 2006), As (Liu et al., 2003; 2005), and Se (Zhou et al., 2007), and limit toxicities of Cu, Cd, Ni and Zn to plants (Greipsson, 1995; Greipsson and Crowder, 1992). Research by Zhang et al. (1998 and 1999) showed enhanced Zn and P uptake, when $\text{Fe}(\text{OH})_3$ was added for inducing the iron plaque formation. Given the close association of Zn and P with Cd chemistry in soils, the influence of iron plaque on Cd uptake in rice can be synergistic. However, Liu et al. (2007) showed that iron plaque is not the main barrier to Cd uptake by rice. Studies by Kukier and Chaney (2002) showed co-existence of both Cd and Zn in the soil under rice cultivation. Although P fertilisers supply Cd to soil, Moral et al. (1994) observed synergistic interactions.

Liu et al. (2007) examined the effect of P addition in paddy soils under the presence and absence of root iron plaques. Although there was no influence of P supply on iron plaque-Cd interaction, root tissue was found to be the main barrier in Cd uptake by plants. They observed that addition of P increased shoot Cd concentrations, thereby underscoring the role of root iron

plaques. The translocation of Cd to the rice plants was found to be high under external P and Zn applications. There have been studies on iron plaque, both as a barrier (Greipsson, 1995; Batty et al., 2000) and a source (Zhang et al., 1998) of heavy metal(loid)s, thereby resulting in the uptake of toxic elements such as Cd in rice plants. Hence, there is no direct evidence on the influence of phosphorus compounds on the adsorption of heavy metal(loid)s in iron plaques. According to Zhang et al. (1998), uptake of toxic elements and nutrients by wetland plants depends on the extent of iron plaque formation. Since iron plaques are formed mostly under nutrient (P) limiting conditions and high concentrations of aluminium (Al), more studies need to be conducted to explore the role of iron plaques in limiting Cd uptake by rice plants.

7. Summary and Future Research Needs

Although P fertilisers act as an essential nutrient input for sustainable crop production, they can act both as a source and sink for a number of essential and harmful elements. Among the essential trace elements, reactive PRs are a major source of Zn to paddy crops in many countries. However, toxic metal(loid)s such as Cd added through P fertilisers in paddy soil can contaminate not only the soil but also result in the uptake of Cd, resulting in contaminated grains of this major staple food. Although there are several processes (including chemical remediation and phytoremediation) and practices (e.g. use of soil amendments), they end up either unsustainable or non-practicable in paddy soils due to the repeated flooding and draining cycles and the resultant redox reactions (Figure 8).

Legislatory measures have been adopted by regulatory agencies in many countries in recent years to minimise adverse environmental and human health impacts through fertiliser practices, including P based compounds. Although such stringent regulatory policies have led to new high

quality fertiliser products containing no or much reduced levels of metal(loid)s, the cost of such products discourage large-scale applications by the farming community, especially in developing countries. Strategies that minimise adverse impacts of long-term P-fertilisation are based on understanding the dynamics of P-metal(loid) interactions in soils. Phosphate-induced stabilisation of metal(loid)s in soils results from adsorption and precipitation reactions. A large number of studies have provided conclusive evidences for the potential value of both water-soluble (e.g., DAP) and water-insoluble (e.g., PRs) P compounds to immobilise Cd in soils, thereby reducing their mobility and bioavailability for plant uptake (Table 6). Similarly, the fact that P fertilisers can also mobilise Cd through rhizosphere acidification and microbial association has opened up debate on the role of P in Cd solubility in soils (Table 5). However, in the case of paddy soils, the flooding of the paddy fields influences the mobility of both P and Cd, and P influenced Cd solubility (Figure 6).

The addition of P fertilisers in paddy soil has both advantages and disadvantages over the status of Cd in both soil and plant. It is therefore, important that future research should aim to focus on the role of P fertilisers in paddy cultivation and also their role in Cd (im)mobilisation in paddy soils and uptake by rice plants.

Key areas that require further research include:

- An investigation of the effect of Cd additions through P fertilisers on soil microbial activity under field conditions.
- Influence of soil type on chemodynamics of phosphate-Cd interactions.
- The effect of continued application of acidifying P fertilisers on long-term efficacy of P sinks to immobilise Cd.

- 664 ➤ The impact of P-rich organic amendments on Cd biogeochemistry in soils and their role in
665 rhizosphere region of rice plants.
- 666 ➤ Application of advanced spectroscopic studies to examine the stability of Cd immobilisation.
- 667 ➤ Long-term stability of P-induced immobilisation of Cd, after repeated flooding-draining
668 cycles.
- 669 ➤ Molecular approaches to develop more understanding about the mode of action of P
670 solubilising bacteria in highly Cd contaminated paddy soils.

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Table 1 Heavy metal concentration in phosphate compounds from various sources
(Adriano, 2001; McLaughlin et al., 1996; Syers et al., 1986).

Phosphate compound ^a	Concentration (mg kg ⁻¹)								
	As	Cd	Co	Cu	Zn	Mn	Ni	Pb	Hg
GPR	4	38	3	15	393	7	-	-	-
NFPR	7	3	5	4	57	212	-	-	-
JPR	12	4	<1	8	235	5	-	-	-
NCPR	23	48	2	9	400	7	9-51	<1 – 51	0.4 – 2.1
SPR	5	11	3	6	178	91	-	-	-
MPR	3	8	6	4	90	151	-	-	-
NIPR	3	100	6	8	1010	122	-	-	-
APR	7	12	4	12	560	2	-	-	-
MIPR	2	10	<1	6	220	2	-	-	-
CRP	-	2	4	5	95	100	-	-	-
IRP	-	-	109	32	187	975	-	962	-
SSP	-	-	77	15	165	890	-	488	-
TSP	-	-	47	49	418	75	-	238	-
DAP	-	-	16	7.2	112	307	-	195	-

^aPhosphate rocks: GPR - Gafsa phosphate rock, NFPR - North Florida phosphate rock, JPR – Jordan phosphate rock, NCPR – North Carolina phosphate rock, SPR –Sechura phosphate rock, MPR- Mexican phosphate rock, NIPR – Nauru Island phosphate rock, ARP – Arad phosphate rock, MIPR – Makatea Island phosphate rock, CRP, Chatham Rise phosphorite, IRP – Indian phosphate rock; Phosphate fertilisers: SSP – Single super phosphate, TSP – Triple superphosphate, DAP – Diammonium phosphate.

Table 2 Phosphorus fertilisation and estimated cadmium concentration for selected countries

Country	Rice growing area (ha)	Total P input (Mg yr ⁻¹)	Total Cd input (kg yr ⁻¹)	Estimated Cd concentration (mg kg ⁻¹ soil)
China	30171500	1810.29	90514.5	0.006
India	44700000	1086.21	54310.5	0.00243
Bangladesh	10117000	151.755	7587.75	0.0015
Vietnam	7648000	344.16	17208	0.0045
Thailand	10048000	331.584	16579.2	0.0033
Philippines	4037000	60.555	3027.75	0.0015
Myanmar	6000000	72	3600	0.0012
Brazil	3169000	110.915	5545.75	0.0035
Japan	1801000	165.692	8284.6	0.0092
Pakistan	2114000	100.415	5020.75	0.00475
Cambodia	1873000	28.095	1404.75	0.0015
US	1318000	79.08	3954	0.006
S Korea	1050000	73.5	3675	0.007
Indonesia	11523000	253.506	12675.3	0.0022

Cd concentration = 5 mg kg⁻¹ fertiliser; Soil BD = 1000 kg m⁻³; Fertiliser application depth = 5 cm; Phosphorus application rate – FAO (2007)

Table 3 Effect of selected trace elements on cadmium uptake

Plant	Element	Effect	Reference
<i>Oryza sativa</i>	Iron	Iron plaques on rice roots act as a barrier in Cd uptake by rice plants by acting as a buffer or reservoir under low soil Cd concentration (10 mg kg ⁻¹).	Liu et al., 2007
<i>Oryza sativa</i>	Magnesium, iron and zinc	Chlorophyll destruction was higher in Mg-sufficient leaves than Mg-deficient seedlings that were treated with Cd, and Mg deficiency protected seedlings from Cd toxicity.	Chou et al., 2011
<i>Oryza sativa</i>	Copper	Cd accumulation in plant tissue increased in the presence of Cu in soil, thereby showing that Cu influences Cd mobilisation.	Huang et al., 2009
<i>Oryza sativa</i>	Selenium	Se application alleviated Cd toxicity by decreasing Cd uptake. Se activates protective mechanisms that can alleviate oxidative stress in both enzymatic and non-enzymatic ways.	Lin et al., 2012

Table 4 Selected references on cadmium contents in different land uses and their respective sources.

Land use	Source	Cd concentration in soil (values in mg kg ⁻¹)	Reference
Orchards	P fertiliser	0.07-3.62 ^a	Mann et al., 2002
Barley	P fertiliser	0.001-0.009 ^b , 0.02-0.07 ^c	Singh and Myhr, 1998
Potato	P fertiliser	0.084-0.122 ^d	Sparrow et al., 1993
Soybean, paddy	P fertiliser	0.31-13.9 ^a , 0.030 to 13.3 ^e	Sriprachote et al., 2012
Radish	Mining	6.03 ^a	Hong et al., 2005
Pasture	P fertiliser	0.149-0.435 ^a 0.112-0.561 ^a , 0.011-0.028 ^h , 0.047- 0.170 ⁱ , 0.067-0.493 ^j , 0.04-1.53 ^a	Loganathan et al., 1996 Andrews et al., 1996 Roberts et al., 1994
Paddy	Mining	0.9-1.7 ^a 0.006 ^a	Jung and Thornton, 1997 Rogan et al., 2009
Maize, paddy	Mining	0.83-4.29 ^a	Murakami et al., 2007
Wheat, clover, lettuce, ryegrass	P fertiliser	0.064-0.130 ^a	Gray et al., 1999
Sugar cane	P fertiliser	<0.01-2.17 ^a , 0.003-0.678 ^c , 0.003- 1.780 ^l , 0.005-1.667 ^m , 0.001-0.161 ⁿ	Rayment, 2005
Paddy	P fertiliser	0.045-0.052	Malidareh et al., 2014
Cabbage, carrot	P fertiliser	~0.4-1.5 ^b	Guttormsen et al., 1995
Paddy	Biosolids MSW, P fertiliser, VC	0.173 ^g	Mousavi et al., 2010
	P fertiliser	0.9-7.4 ^a , 0.5-5.1 ^e	Arao and Ae, 2003

MSW-Municipal Solid Waste, VC-Vermicompost, ^aTotal Cd, ^bNH₄NO₃ extractable, ^cDTPA extractable, ^dTuber Cd, ^eExtractable with 0.1 M HCl, ^f0.1 N HCl extractable, ^gAvailable, ^hDifferential pulse anodic stripping voltammetry analysis (H₂O DP-ASV) indicates the free Cd ions that associated with labile complexes, ⁱ0.05M CaCl₂ extraction, ^j0.05M EDTA DP-ASV, ^k1M NH₄OAc DP-ASV extraction, ^lEDTA extractable, ^mExtractable with 1M HCl, ⁿExtractable with 0.1M CaCl₂, ^o0.01M CaCl₂ extractable, ^p1M NH₄OAc extractable

Table 5 Selected references on the mobilisation of cadmium by water-soluble and water-insoluble phosphate compounds

Land use system/crops grown	P compound ^a	Method of investigation ^b	Proposed primary mechanism	Reference
Water-soluble phosphate compounds				
Maize, tomato	Tri Calcium Phosphate	PB, AAS	Rhizosphere modification	Jiang et al., 2008
Paddy	SSP	PB, ICP-MS	Competitive root absorption	Arao and Ae, 2003
Barley	NPK fertilisers	PB, CF, GF-AAS	Cd source-dissolution	Singh and Myhr, 1998
Paddy	K ₂ HPO ₄ ·3H ₂ O	PB, GF-AAS	Competitive root absorption	Liu et al., 2005
Soil ^d	NPK fertilisers	PB, CF	Cd source-dissolution	He and Singh, 1993
Potato	TSP	PB, CF, AAS	Cd source-dissolution	Sparrow et al., 1993
Paddy, Soybean	NPK fertiliser	PB, CF, AAS	Competitive root absorption	Sriprachote et al., 2012
Clover, lettuce, carrot, ryegrass, wheat	SSP	PB, GF-AAS	Cd source-dissolution	Gray et al., 1999
Pasture grass	(NH ₄) ₂ HPO ₄	PB, CF, AAS	Competitive root absorption	Loganathan et al., 1996
Durum wheat, flax	NH ₄ H ₂ PO ₄	PB, GF-AAS	Rhizosphere modification	Grant et al., 2010
Paddy	Calcium-Magnesium Phosphate	PB, CF, AAS	Competitive root absorption	Li et al., 2009
Paddy	Phospho-gypsum	PB, ICP-AES	Cd source dissolution	Lee et al., 2006
<i>Sedum alfredii</i>	KH ₂ PO ₄ , Ca(H ₂ PO ₄) ₂ ,	PB, ICP-OES	Competitive root absorption	Huang et al., 2012

	NaH ₂ PO ₄ , NH ₄ H ₂ PO ₄			
Soil ^d	NH ₄ H ₂ PO ₄	CF, ICP-AES	Rhizosphere modification	Lambert et al., 2007
<i>Thlaspi caerulescens</i>	K ₂ HPO ₄	PB, CF, ICP-AES	Rhizosphere modification	Xie et al., 2009
Bean	TSP	PB, AAS	Cd source dissolution	Mendes et al., 2006
Corn	SSP	PB, ICP-AES	Competitive root absorption	Prochnow et al., 2001
Pasture grass	Superphosphate	CF, GF-AAS	Cd source dissolution/desorption	Gray et al., 1999
Paddy	KH ₂ PO ₄	PB, AAS, ICP-MS	Physiological/rhizosphere modification	Sasaki et al., 2012
Paddy	P ^c	Soil Extraction ICP-OES	Physiological	de Livera et al., 2011
Paddy, soybean, maize	SSP	PB, ICP-OES	Competitive root absorption	Murakami et al., 2007
Pasture grass	SSP	TL, GF-AAS	Source dissolution	Gray et al., 2003
Paddy, soybean	SSP	PB	Competitive root absorption	Murakami et al., 2008
Paddy	P ^c	AD, ICP-AES, XAFS	Desorption	Khaokaew et al., 2011
Paddy	P ^c	PB, ICP-OES	Competitive root absorption	Murakami et al., 2009
Paddy	Fused superphosphate	PB, AAS	Competitive root absorption	Ok et al., 2011

Table 5 continued in next page

Water-insoluble phosphate compounds				
Clover, lettuce, carrot, ryegrass, wheat	PR	PB, GF-AAS	Cd source dissolution	Gray et al., 1999
Paddy soils in green house conditions	PR	PB, ICP	Cd Source dissolution	Iretskaya et al., 1998
Barely	PR	PB, CF, GF-AAS	Cd source dissolution	Singh and Myhr, 1998
Pasture grass	PR	PB, CF, AAS	Cd source dissolution	Loganathan et al., 1996
Soil ^d	PR	PB, CF	Cd source dissolution	He and Singh, 1993
Hydroxyapatite surfaces	Hydroxyapatite	AD	Sorption (Surface complexation, co-precipitation, ion exchange, solid dissolution)	Xu et al., 1994
Bean	PR	PB, AAS	Cd source dissolution	Mendes et al., 2006

^aSSP – Single super phosphate, TSP – Triple superphosphate; PR - Phosphate rock. ^bMethod of investigation: 1. Chemical – adsorption/desorption (AD); chemical fractionation (CF); solubility diagram (SD); transport/leaching (TL); 2. Biological – phytoavailability bioassay (PB). ^c Phosphate compound not specified; ^dlanduse type not specified.

Table 6 Selected references on the immobilisation of cadmium by phosphate compounds.

Land use system/crops grown	P compound	Method of investigation	Proposed primary mechanism	Reference
Contaminated soil/mine	Superphosphate	XRD, XRF	Precipitation as metal phosphate	Munksgaard et al., 2012
Paddy	$\text{Ca}(\text{H}_2\text{PO}_4)_2$	XRD, XRF	Precipitation as metal phosphate	de Livera et al., 2011
Wastewater	$(\text{NH}_4)_2 \text{HPO}_4$	XRD	Precipitation as metal phosphate	Mobasherpour et al., 2012
Radish	$\text{Ca}(\text{H}_2\text{PO}_4)_2$	PB	Phosphate-induced adsorption	Hong et al., 2009
Polluted soils	K_2HPO_4 , Na_2HPO_4	XRD / XRF	Phosphate-induced adsorption	Matusik et al., 2008
Tobacco	K_2HPO_4	XRF	Phosphate-induced adsorption	Keller et al., 2005
Soil ^a	K_2HPO_4	Fractionation	Phosphate-induced adsorption	Bolan et al., 2003a
Contaminated soil/lettuce	Rock phosphate/soil P	PB	Precipitation as metal phosphate	Basta et al., 2001
Legume based pasture	K_2HPO_4	AD, SD	Phosphate-induced adsorption	Bolan et al., 1999a
Soil ^a	K_2HPO_4	AD, SD	Phosphate-induced adsorption	Naidu et al., 1994
Soil ^a	Nano-hydroxyapatite	XRF	Precipitation as metal phosphate	Zhang et al., 1998
Contaminated sediments	Hydroxyapatite	XRF	Precipitation/adsorption	Seaman et al., 2001
Contaminated soil	PR	CF	Precipitation as metal phosphates	Basta et al., 2001
Maize	Hydroxyapatite	CF	Precipitation/adsorption/ion exchange	Boisson et al., 1999

Industrial effluent	Hydroxyapatite	AD	Adsorption, ion exchange, surface complexation, precipitation	Mandjiny et al., 1998
Contaminated soil	PR	CF	Precipitation/adsorption	Chen et al., 1997
Aqueous solutions	Hydroxyapatite	CF, PB	Cation exchange	Jeanjean et al., 1995
Soil ^a	Hydroxyapatite	AD, EXAPS	Surface complexation and precipitation	Xu et al., 1994

^alanduse type not specified

Table 7 Phosphorus (P) and cadmium (Cd) concentrations in various phosphate fertilisers and the calculated number of years required to exceed the threshold concentration of Cd (3 mg Cd kg⁻¹) in soils due to fertiliser application.

Phosphate fertiliser	Concentration		Years required to exceed the threshold limit ^a
	P (g kg ⁻¹)	Cd (mg kg ⁻¹)	
Single superphosphate	98	32	166
Triple superphosphate	190	70	152
Diammonium phosphate	200	10	1125
North Carolina phosphate rock	132	54	135
Sechura phosphate rock	131	12	614
Egyptian phosphate rock	130	10	732
Gafsa phosphate rock	134	70	107

^aAt an annual fertiliser application rate of 40 kg P ha⁻¹

Table 8 Theoretical liming value and acidity equivalent of phosphate compounds.

Phosphate compound	Total P (% w/w)	Free CaCO₃ (% w/w)	Liming value (kg CaCO₃ Mg⁻¹)	Acidity equivalent^a (kg CaCO₃ Mg⁻¹)
Diammonium phosphate	20	-	-	740
Monoammonium phosphate	21	-	-	550
Single superphosphate	10	-	-	80
Triple superphosphate	18	-	-	150
North Carolina Phosphate rock	13.1	11.7	536	-
Sechura phosphate rock	13.1	5.1	470	-
Gafsa phosphate rock	13.4	7.1	500	-
Chatham phosphorite	8.9	27.6	560	-
Arad phosphate rock	14.1	8.2	533	-
Youssafia phosphate rock	13.8	5.4	495	-
Khourigba phosphate rock	14.4	6.1	520	-
Egyptian phosphate rock	13.0	4.9	465	-
Jordan phosphate rock	13.4	7.7	505	-
Nauru phosphate rock	15.6	4.1	540	-
Christmas Island	16.4	2.1	545	-
Duchess phosphate rock	13.5	1.8	450	-

^aEquivalent acidity is kg calcium carbonate required to neutralise the acidity caused by 1000 kg (1 Mg) of the fertiliser.

Figure 1

Figure 1 Comparison of cadmium concentrations in rice grain for selected countries

Figure 2

Figure 2 Relationship between P applied and total Cd in paddy soils at panicle and maturity stages (Adapted from Siebers et al., 2013).

Figure 3

Figure 3a. Cd input-output flux in 2001 for cow manure application in paddy soil (Adapted from Kikuchi et al., 2007)

Figure 3b. Cd input-output flux in 2002 for commercial NPK application in paddy soil (Adapted from Kikuchi et al., 2007)

Figure 4

Figure 4. Cd input-output flux in a non-polluted paddy soil (Adapted from Yada et al., 2006)

Figure 5

Figure 5. Reactions of metals in soils (Cottenie and Verloo, 1984, Naidu et al., 1997, Gao et al., 2010, Loganathan et al., 2012)

Figure 6

Figure 6. Reactions of phosphorus and cadmium in paddy bulk soil and rhizosphere (Zheng and Zhang, 2011; Simmons et al., 2008; Ibaraki et al., 2009; Ponnamperuma, 1972; Khaokaew et al., 2011; Zhang et al., 2012; de Livera et al., 2011)

Figure 7

Figure 7a Effect of P addition (mg kg^{-1}) on pH in paddy soil, under different growth stages of cultivation (Adapted from Siebers et al., 2013).

Figure 7b Effect of P addition (mg kg^{-1}) on soluble Cd concentration in paddy soil, under different growth stages of cultivation (Adapted from Siebers et al., 2013).

Figure 8

Figure 8 Schematic representation of paddy cultivation stages with plausible reactions of heavy metal(loid)s as affected by flooding-draining cycle and phosphorus fertiliser.