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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 influences 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.

## 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 persist 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.

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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 | – | – | – |
| IPR | – | – | 109 | 32 | 187 | 975 | – | 962 | – |
| SSP | – | – | 77 | 15 | 165 | 890 | – | 488 | – |
| TSP | – | – | 47 | 49 | 418 | 75 | – | 238 | – |
| DAP | – | – | 16 | 7.2 | 112 | 307 | – | 195 | – |

[a] Phosphate 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, IPR — Indian phosphate rock; Phosphate fertilisers: SSP — single superphosphate, 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 | 30,171,500 | 1810.29 | 90,514.5 | 0.006 |
| India | 44,700,000 | 1086.21 | 54,310.5 | 0.00243 |
| Bangladesh | 10,117,000 | 151.755 | 7587.75 | 0.0015 |
| Vietnam | 7,648,000 | 344.16 | 17,208 | 0.0045 |
| Thailand | 10,048,000 | 331.584 | 16,579.2 | 0.0033 |
| Philippines | 4,037,000 | 60.555 | 3027.75 | 0.0015 |
| Myanmar | 6,000,000 | 72 | 3600 | 0.0012 |
| Brazil | 3,169,000 | 110.915 | 5545.75 | 0.0035 |
| Japan | 1,801,000 | 165.692 | 8284.6 | 0.0092 |
| Pakistan | 2,114,000 | 100.415 | 5020.75 | 0.00475 |
| Cambodia | 1,873,000 | 28.095 | 1404.75 | 0.0015 |
| US | 1,318,000 | 79.08 | 3954 | 0.006 |
| S Korea | 1,050,000 | 73.5 | 3675 | 0.007 |
| Indonesia | 11,523,000 | 253.506 | 12,675.3 | 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).

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 Allsopp (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 (Fig. 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).

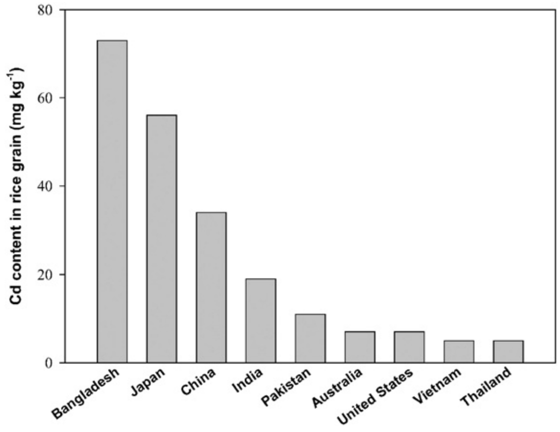

**Fig. 1.** Comparison of cadmium concentrations in rice grain for selected countries.

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 Sarwar 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 Sarwar et al., 2014; Sarwar et al., 2010; Table 3). Choppala et al. (2014) listed the tolerance mechanisms as follows:

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