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# Sorption–bioavailability nexus of arsenic and cadmium in variable-charge soils

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## HIGHLIGHTS

- Demonstrates the nexus between sorption and bioavailability of As and Cd in variable-charge soils.
- Liming variable-charge soils increase negative charge, thereby decreasing Cd bioavailability.
- Ageing of As and Cd increases their immobilization, thereby decreasing bioavailability.
- Phosphate enhances desorption and phytoavailability of As from sheep dip soil.
- Metal(loid)s transfer to food chain can be managed by controlling sorption reactions.

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## ABSTRACT

In this work, the nexus between sorption and bioavailability of arsenic (As) and cadmium (Cd) as affected by soil type, soil pH, ageing, and mobilizing agents were examined. The adsorption of As and Cd was examined using a number of allophanic and non-allophanic soils which vary in their charge components. The effect of pH and ageing on the bioavailability of As and Cd was examined using spiked soils in a plant growth experiment. The effect of phosphate (P)-induced mobility of As on its bioavailability was examined using a naturally contaminated sheep dip soil. The results indicated that the adsorption of both As and Cd varied amongst the soils, and the difference in Cd adsorption is attributed to the difference in surface charge. An increase in soil pH increased net negative charge by an average of 45.7 mmol/kg/pH thereby increasing cation (Cd) adsorption; whereas, the effect of pH on anion (As) adsorption was inconsistent. The bioavailability of As and Cd decreased by 3.31- and 2.30-fold, respectively, with ageing which may be attributed to increased immobilization. Phosphate addition increased the mobility and bioavailability of As by 4.34- and 3.35-fold, respectively, in the sheep dip soil. However, the net effect of P on As phytoavailability depends on the extent of P-induced As mobilization in soils and P-induced competition for As uptake by roots. The results demonstrate the nexus between sorption and bioavailability of As and Cd in soils, indicating that the effects of various factors on bioavailability are mediated through their effects on sorption reactions.

## 1. Introduction

The demand for safe disposal of wastes generated from agricultural and industrial activities is ever increasing, and soil is considered as a sink for the most of the waste-borne contaminants [1,2]. As land treatment is considered as an important waste management practice, soil becomes a major source of heavy metal(loid)s reaching the food chain, mainly through plant uptake and animal transfer [3,4]. Indiscriminate waste disposals have led to significant build up in soils of a wide range of metal(loid)s including arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), lead (Pb), selenium (Se), and zinc (Zn) [5]. Entry of soil-borne metal(loid)s into the food chain depends on the source and speciation of metal(loid) input, the properties of the soil, bioavailability of metal(loid), the rate and magnitude of uptake by plants, and the extent of absorption by birds and animals used for egg, milk, and meat production [5].

The general population may be exposed to As and Cd from air, food, and water [5], and soil plays a significant role in the transfer pathways of these two metal(loid)s. Increasing incidents of human and animal toxicity resulting from the accumulation of heavy metal(loid)s in soils have been reported in a number

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**Table 1**
Characteristics of soils used for adsorption and plant growth experiments [19].

| Soil locations | Soil classification | Organic carbon (g/kg) | pH | P retention (%) | Dominant clay minerals |
|---|---|---|---|---|---|
| Ballantrae | Typic Dystrandept | 58.5 | 5.62 | 42 | Mica/illite, chlorite, kaolinite, smectite, vermiculite |
| Egmont | Typic Dystrandept | 78.5 | 5.85 | 83 | Allophane, volcanic glass, chlorite, kaolinite, halloysite |
| Foxton | Dystric Fluventic Eutrochrept | 23.1 | 5.85 | 23 | Mica/illite, chlorite |
| Manawatu | Dystric Fluventic Eutrochrept | 29.1 | 6.01 | 33 | Mica/illite, chlorite, smectite, kandite |
| Patua | Typic Dystrandept | 89.7 | 6.12 | 95 | Allophane, volcanic glass, kandite |
| Tokomaru | Typic Fragiaqualf | 34.3 | 5.67 | 51 | Mica/illite, chlorite, kandite, kaolinite, smectite, vermiculite |
| Ramiha | Typic Dystrandept | 56.2 | 5.75 | 77 | Allophane, volcanic glass, chlorite, kandite, halloysite |
| Hamilton[a] | Typic Dystrandept | 39.7 | 5.89 | 78 | Allophane, volcanic glass, kandite |

[a] Sheep-dip soil (naturally As contaminated soil).

of countries. For example, significant adverse impacts of As on human health have been recorded in Bangladesh, India, and China, and it is claimed that millions of people are potentially at risk from As poisoning [6]. Similarly, Cd accumulation in the offal (mainly kidney and liver) of grazing animals in New Zealand and Australia made it unsuitable for human consumption and affected access of meat products to overseas markets [7]. Furthermore, bioaccumulation of Cd in potato (*Solanum tuberosum*), wheat (*Triticum* sp.), and rice (*Oryza sativa*) crops has serious implications to both human health and commodity marketing [8]. Recently, there has been concern about urban development of horticultural sites which contained toxic levels of Cu in soils resulting from excessive use of Cu-containing fungicides [9].

Unlike organic contaminants, metal(loid)s do not undergo microbial or chemical degradation and the total concentration in soils persists for a long time after their introduction [10]. With greater public awareness of the implications of contaminated soils on human and animal health, there has been increasing interest amongst the scientific community in the development of technologies to remediate metal(loid) contaminated sites. For diffuse distribution of metal(loid)s such as fertilizer-derived Cd input in soils, remediation options generally include amelioration of soils to minimize their bioavailability. Bioavailability can be minimized through chemical and biological immobilization of metal(loid)s using a range of inorganic compounds, such as lime and phosphate (P) compounds, and organic compounds, such as 'exceptional quality' biosolids [11,12]. The more localized metal(loid)s contamination found in urban environments such as Cr contamination in timber treatment sites, is remediated by their mobilization processes that include phytoremediation and chemical washing. Removal of metal(loid)s through phytoremediation techniques and their subsequent recovery (i.e. phytomining) or their safe disposal are attracting research and commercial interests [13,14].

Physico-chemical interaction of metal(loid)s with soil is the primary factor which controls their bioavailability. Metal(loid)s in the solid or sorbed phase are usually unavailable, and the uptake by organisms including higher plants usually occurs when these metal(loid)s become soluble and reach the solution phase or pore water. Thus, processes influencing the equilibrium between soluble and solid or bound phases for heavy metal(loid)s (i.e. sorption reactions) impact their overall bioavailability. Metal(loid)s may undergo a time-dependent sequestration in soil that results in a decline in their bioavailability [15]. This process, known as ageing, is attributed to the sequestration of contaminants into solid phase either in mineral nanopores or partitioning to specific and non-specific sites of organic matter [16–18]. The hypothesis of this research work is that the sorption of metal(loid)s controls their bioavailability in soils, and therefore, the effects of various factors on bioavailability are mediated through their effects on sorption. In this paper, the link between sorption and bioavailability of a metalloid (As) and a metal (Cd) as affected by soil type, soil pH, ageing, and mobilizing agents was examined.

## 2. Materials and methods

### 2.1. Soil samples

Seven surface (0–15 cm) soils from New Zealand which vary in their variable-charge characteristics were used to examine the effect of soil type on adsorption of As and Cd (Table 1). The soils contain varying amounts of a number of variable-charge components, such as organic matter, allophane, kaolinite, and iron (Fe) and aluminium (Al) hydrous oxides. Based on the amount of variable-charge components, these soils are grouped into two broad categories: (i) allophanic soils (Patua, Egmont, and Ramiha soils), and (ii) non-allophanic soils (Ballantrae, Foxton, Manawatu, and Tokomaru). The former group generally contains significant amounts of allophanic clays, such as imogolite, and higher amounts of other variable-charge components (Table 1) [19].

The Egmont and Tokomaru soils which vary in their variable-charge characteristics were used to examine the effects of pH on surface charge and subsequent adsorption of As and Cd. The soils were treated with four levels of calcium hydroxide ($Ca(OH)_2$) (~250–850 kg/ha) to achieve a pH range of 5.65/5.85–8.25 (control). These samples were incubated in a glasshouse for 4 weeks and subsequently used for surface charge, and As and Cd adsorption measurements. The Egmont soil was also used to examine the effect of pH and ageing on the phytoavailability of As and Cd in a glasshouse experiment.

A naturally As-contaminated soil collected from an abandoned sheep dip site in Hamilton, New Zealand was also used to examine the effect of P on the mobility and bioavailability of As. About 1500 g of air-dried soil was placed into heavy-grade polyethylene bags and P solution as $KH_2PO_4$ was added at a rate equivalent to 0, 50, 100, 250, or 500 mg P/kg (~15–150 kg/ha). The moisture content was adjusted to field capacity with distilled water. Soil and P solutions were mixed thoroughly and incubated at 25 °C for 4 weeks. The incubated soil samples were used for monitoring mobility and phytoavailability of As.

### 2.2. Surface charge and As and Cd adsorption

The surface charge was measured using 0.1 M NaCl following the ion-retention method of Schofield [20]. Briefly, a 2 g portion of soil was shaken with 30 mL of 0.1 M NaCl solution in a centrifuge tube for 30 min, centrifuged, the supernatant solutions decanted, and the soil retained for additional four washings with the electrolyte. The sorbed Na and Cl were then extracted by shaking for 20 min with 5 lots of 20 mL of 1 M $NH_4NO_3$ solution. Chloride was measured using the spectrophotometric method of Florence and Farrer [21] and Na by atomic emission at 589 nm in the presence of 0.2% $KNO_3$.

Adsorption of As and Cd was measured at various concentrations (0–500 mg/L) of As and Cd using $K_2HAsO_4$ and $Cd(NO_3)_2$, respectively, prepared in 0.01 M $KNO_3$ as the background electrolyte. Soil samples were mixed with As and Cd solutions at a soil:solution ratio of 1:10 by shaking on an end-over-end shaker for 16 h at