



# Residual effects of monoammonium phosphate, gypsum and elemental sulfur on cadmium phytoavailability and translocation from soil to wheat in an effluent irrigated field



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## H I G H L I G H T S

- Residual monoammonium phosphate (MAP) and gypsum reduced the Cd uptake in wheat.
- Amendment of residual elemental sulfur (S) increased Cd uptake in plants.
- Gypsum had the highest cost-benefit ratio compared with MAP and elemental S.
- Gypsum may be used to enhance crop production in Cd-contaminated soils.

## A R T I C L E I N F O

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## A B S T R A C T

Cadmium (Cd) accumulation in agricultural soils is one of the major threats to food security. The application of inorganic amendments such as mono-ammonium phosphate (MAP), gypsum and elemental sulfur (S) could alleviate the negative effects of Cd in crops. However, their long-term residual effects on decreasing Cd uptake in latter crops remain unclear. A field that had previously been applied with treatments including control and 0.2, 0.4 and 0.8% by weight of each MAP, gypsum and S, and grown with wheat and rice and thereafter wheat in the rotation was selected for this study. Wheat (*Triticum aestivum* L.) was grown in the same field as the third crop without further application of amendments to evaluate the residual effects of the amendments on Cd uptake by wheat. Plants were harvested at maturity and grain, and straw yield along with Cd concentration in soil, straw, and grains was determined. The addition of MAP and gypsum significantly increased wheat growth and yield and decreased Cd accumulation in straw and grains compared to control while the reverse was found in S application. Both MAP and gypsum decreased AB-DTPA extractable Cd in soil while S increased the bioavailable Cd in soil. Both MAP and gypsum increased the Cd immobilization in the soil and S decreased Cd immobilization in a dose-additive manner. We conclude that MAP and gypsum had a significant residual effect on decreasing Cd uptake in wheat. The cost-benefit ratio revealed that gypsum is an effective amendment for decreasing Cd concentration in plants.

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## 1. Introduction

Soil is both a sink for contaminants including toxic heavy metals

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such as cadmium (Cd), and a source of nutrients for supporting plant growth and development (Rehman et al., 2015; Mohiuddin et al., 2016; Rizwan et al., 2016a). In numerous plant growth trials, it is evident that heavy metals significantly influence the plant growth as well as cause health hazards (Rizwan et al., 2012; Adrees et al., 2015a; Tauqeer et al., 2016; Wang et al., 2016). Compared to other toxic heavy metals, Cd is readily mobile and active metal and is toxic even at lower concentration (He et al., 2015; Rizwan et al., 2016a; Ran et al., 2016). Recent studies revealed that Cd could be the key factor behind unavailability of safe food on a sustainable basis (Ran et al., 2016; Yang et al., 2016). Cadmium toxicity is also harmful to plant growth and development, as it hinders plant's physiological and metabolic processes (Li and Xu, 2015; Lopez-Luna et al., 2016).

The agricultural sector is a vital component of the Pakistani economy, and water scarcity is a continuing concern for overall productivity due to higher dependency on single river system (Rehman et al., 2015; Ngigi, 2016). Thus, unavailability of fresh water forces the farmers to use raw city effluents and sewage water as an alternate source of irrigation (Khan et al., 2016a; Rehman et al., 2015). Soils irrigated with raw city effluents might be a potential source of Cd which may be taken up by plants causing toxicities at different levels. Thus, there is an urgent need to employ remediation techniques aiming to reduce Cd availability and uptake by plants.

Different remediation techniques may be used for the reduction of Cd availability and uptake by plants (Adrees et al., 2015b; Sabir et al., 2015). The use of inorganic amendments for Cd decontamination is more feasible and economic strategy when compared with other remediation strategies especially dealing with large areas (Rizwan et al., 2016b). Complexation and precipitation of Cd by the use of organic or inorganic amendments are documented methods for reducing Cd uptake by plants (Li et al., 2016; Rizwan et al., 2016b). Inorganic amendments like gypsum, phosphate fertilizers, limestone, elemental sulfur, and iron oxides have proved to be suitable amendments for immobilization of Cd in the soil and reducing its uptake by plants (Cui et al., 2016; Zhao et al., 2016). In contrast, there is also a chance that Cd availability may increase by the application of certain inorganic material like sulfur (Asgher et al., 2014; Khan et al., 2015). In a previous study, we reported that the application of gypsum and mono-ammonium phosphate decreased the Cd uptake by wheat and rice crops while elemental sulfur increased the Cd uptake in these crops grown under field conditions (Rehman et al., 2015). However, little is known about the residual effects of these amendments on Cd uptake by plants. Therefore, studying the residual effects of these amendments on subsequent crops may provide a better understanding of the suitability of these amendments for in situ Cd immobilization in the soil. Our objective was to investigate the residual effects of gypsum, mono-ammonium phosphate (MAP) and elemental sulfur for in situ Cd immobilization in the soil and uptake by wheat plants grown in an aged-contaminated soil receiving raw city effluents for 30 years.

## 2. Materials and methods

### 2.1. Site selection and characteristics

A field was selected in the suburbs of Multan city (30° 12' N, 71° 28' E and 215 m above sea level) of Punjab, Pakistan. The selected field had been previously irrigated with raw city effluents and sewage water for last 30 years. The field used was from our earlier experiment (Rehman et al., 2015) where amendments were applied in ten treatments viz: control (T<sub>1</sub>), MAP @ 0.2% (T<sub>2</sub>), MAP @ 0.4% (T<sub>3</sub>), MAP @ 0.8% (T<sub>4</sub>), gypsum @ 0.2% (T<sub>5</sub>), gypsum @ 0.4% (T<sub>6</sub>),

gypsum @ 0.8% (T<sub>7</sub>), elemental sulfur @ 0.2% (T<sub>8</sub>), elemental sulfur @ 0.4% (T<sub>9</sub>) and elemental sulfur @ 0.8% (T<sub>10</sub>) with four replicates. No further amendments were applied in the present study. Prior to the sowing of wheat, a representative soil sample was collected from control plots and analyzed for various physicochemical properties as follows:

Jenway pH meter (Model 671P) was used for pH determination of saturated soil paste (pH) by directly pushing the electrode into the saturated soil paste. The ammonium bicarbonate diethylene-triamine-penta-acetic acid (AB-DTPA) extraction method was exploited for determination of bioavailable heavy metals (Soltanpour, 1985). For this, air-dried soil (10.0 g) was added in 20 ml of freshly prepared AB-DTPA solution and the mixture was horizontally shaken for about 30 min and then filtered for the determination of bioavailable heavy metals by using an atomic absorption spectrometer (Solar S-100; Thermo Electron, Massachusetts, USA). Amacher (1996) procedure was followed for the determination of total metal concentration in soil. In brief, 10 ml of concentrated HNO<sub>3</sub> were added in air-dried soil (1.0 g) and kept overnight and then the mixture was heated at 200 °C. After cooling the mixture, 1 ml of HNO<sub>3</sub> and 4 ml of HClO<sub>4</sub> were added and again heated to 200 °C until fumes of HClO<sub>4</sub> appeared, cooled and added 1:10 HCl and heated at 70 °C for 1 h and finally 50 ml volume was made with 1% HCl and filtered (Whatman filter paper No. 42) the mixture for further analysis. Soil texture was determined following the protocol of Bouyoucos (1962). Soluble ions including Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Cl<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> were determined by the titration method (Richards, 1954). Electrical conductivity of the saturation extract (EC<sub>e</sub>), sodium adsorption ratio (SAR) and cation exchange capacity (CEC) were also determined following the methods described by Richards (1954). Calcium carbonate contents were determined by calcimeter method (Moodie et al., 1959) while soil organic matter (OM) was determined following Walkley-Black method (Jackson, 1962).

The soil was a sandy clay loam and physicochemical properties of the soil are given in Table 1. Available Cd values vary in the pots with the amendments applied (Rehman et al., 2015). Raw city effluent that was used for irrigation was analyzed before each irrigation and the average properties of the water along with permissible limits are also given in Table 1.

### 2.2. Sowing of wheat

Wheat variety Inqalab-91 was sown by a broadcast method using a seed rate 125 kg ha<sup>-1</sup> in rotation after rice of the previous experiment (Rehman et al., 2015) which had been followed by first wheat crop grown with amendment application and the rice without application of amendments. Fertilizers NPK @ 30-75-20 kg ha<sup>-1</sup>, were applied as urea, diammonium phosphate and sulfate of Potash at the time of sowing, respectively. Five irrigations (each of 4 inch depth) with raw city effluents were applied to mature the crop, while 67.3 mm rainfall was recorded during the growth period (Agricultural Metrology Cell, CCRI, Multan, Pakistan). The experimental design was a completely randomized block design (RCBD).

### 2.3. Plant sampling and analysis

The wheat was harvested at maturity, after 145 days of sowing, and plant samples were collected after the separation of grain and straw. Plant samples were washed with tap water and then gently rinsed in 1% HCl and then with distilled water. Samples were oven dried at 70 °C till constant weight. Willey mill having stainless steel blades was used for grinding of samples. For digestion, 1.0 g straw/grain sample was taken in 10 ml di-acid mixture (concentrated

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