



## Zinc solubility and fractionation in cultivated calcareous soils irrigated with wastewater



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### HIGHLIGHTS

- Isotopically exchangeable Zn in the calcareous soils of Peshawar is extremely low.
- There is no evidence of topsoil enrichment from the use of wastewater for irrigation.
- Solubility products for smithsonite and hydrozincite fail to describe Zn<sup>2+</sup> activity.
- A pH-dependent K<sub>d</sub> describing labile Zn = (Zn<sup>2+</sup>) also fails to describe Zn<sup>2+</sup> activity.
- DTPA extraction, SEP data and Zn E-values suggest labile Zn is adsorbed on carbonate.

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### ABSTRACT

The solubility, lability and fractionation of zinc in a range of calcareous soils from Peshawar, Pakistan were studied (18 topsoils and 18 subsoils). The lability (*E*-value) of Zn was assessed as the fraction isotopically exchangeable with <sup>70</sup>Zn<sup>2+</sup>; comparative extractions included 0.005 M DTPA, 0.43 M HNO<sub>3</sub> and a Tessier-style sequential extraction procedure (SEP). Because of the extremely low concentration of labile Zn the *E*-value was determined in soils suspended in 0.0001 M Na<sub>2</sub>-EDTA which provided reliable analytical conditions in which approximately 20% of the labile Zn was dissolved. On average, only 2.4% of soil Zn was isotopically exchangeable. This corresponded closely to Zn solubilised by extraction with 0.005 DTPA and by the carbonate extraction step (F1 + F2) of the Tessier-style SEP. Crucially, although the majority of the soil CaCO<sub>3</sub> was dissolved in F2 of the SEP, the DTPA dissolved only a very small proportion of the soil CaCO<sub>3</sub>. This suggests a superficial carbonate-bound form of labile Zn, accessible to extraction with DTPA and to isotopic exchange. Zinc solubility from soil suspended in 0.01 M Ca(NO<sub>3</sub>)<sub>2</sub> (PCO<sub>2</sub> controlled at 0.03) was measured over three days. Following solution speciation using WHAM(VII) two simple solubility models were parameterised: a pH dependent 'adsorption' model based on the labile (isotopically exchangeable) Zn distribution coefficient (K<sub>d</sub>) and an apparent solubility product (K<sub>s</sub>) for ZnCO<sub>3</sub>. The distribution coefficient showed no pH-dependence and the solubility model provided the best fit to the free ion activity (Zn<sup>2+</sup>) data, although the apparent value of log<sub>10</sub> K<sub>s</sub> (5.1) was 2.8 log units lower than that of the mineral smithsonite (ZnCO<sub>3</sub>).

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### 1. Introduction

Zinc deficiency is the most serious micronutrient problem affecting agricultural productivity in Pakistan (Rashid et al., 1994) and is particularly prevalent in Peshawar, Khyber Pakhtunkhwa Province. The deficiency in this region is characterised by very low available soil Zn measured as DTPA-extractable Zn (often <0.5 μg g<sup>-1</sup>) and AB-DTPA (ammonium bi-carbonate-DTPA) extractable Zn (below 1 μg g<sup>-1</sup>) (Khattak, 1991). Low availability of Zn is aggravated by the calcareous

nature of the soil, low organic matter content and coarse textured soils (Khattak, 1991). Agriculture in Peshawar mainly comprises small holdings (less than 5 ha land) used to grow vegetables because these are short duration crops that provide good economic returns in small scale production. Besides vegetables, the peri-urban agriculture in Peshawar mostly consists of fruit orchards (pear, apple peach, orange and plum). Water shortages have resulted from deficiencies in the irrigation distribution system, salinisation of ground water in some areas, recurrent droughts and increased demand from a rapidly growing population. In response, the use of untreated urban wastewater for agriculture has become a common and widespread practice, partly promoted to avoid contamination of the major surface water supply from

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the Kabul River (Ali et al., 2012). In the long term, the use of such wastewater may represent both a risk of toxicity and a potential benefit in terms of trace metal application to arable soils. Unfortunately, currently, there are no reliable estimates of Zn application to irrigated soils in the region arising from the use of wastewater.

Measuring metal lability is important for the assessment of metal toxicity or deficiency in soils (Degryse et al., 2004; Marzouk et al., 2013a) and normally involves one of a range of single chemical extractions. Most single-step extractants for cationic metals fall into one of three broad classes: solutions of neutral salts (e.g.,  $MgCl_2$ ,  $CaCl_2$ ,  $NaNO_3$ , and  $NH_4NO_3$ ), weak and strong acids (especially acetic and nitric acids), and chelating agents such as DTPA and EDTA (Gupta and Aten, 1993; Lebourg et al., 1996). However, all chemical extraction procedures are intended to completely solubilise a particular metal fraction and yet leave other forms of metal in the solid phase. The difficulty in achieving this, as a universal objective for all soils, inevitably causes uncertainty in interpreting the results of chemical extraction procedures. Calcareous soils may be particularly problematic in this regard because of surficial metal precipitates on  $CaCO_3$  particles (Papadopoulos and Rowell, 1988; Rowell, 1997). Soil metal  $E$ -values determined by stable isotopic dilution may provide a more meaningful estimate of 'reactive' metal because, mechanistically, the method simply mimics the natural solid = solution equilibrium of the soil with a spiked isotope without disrupting the solid phase (Ahnstrom and Parker, 2001). Moreover,  $E$ -values have been shown to provide a better prediction of free  $Zn^{2+}$  activity in the soil solution when used as inputs to geochemical models in place of total soil metal content or popular single extractants such as 0.05 M EDTA and 0.43 M  $HNO_3$  (Marzouk et al., 2013a) – especially in calcareous soils. On the other hand, the addition of stable isotopic Zn to a calcareous soil suspension is not without potential methodological problems. Because of the higher Zn concentration needed, compared to the use of a radio-isotope (e.g.,  $^{65}Zn$ , Tye et al., 2003), there is the possibility of precipitation. In addition, the added complexity required for isotopic labelling and assay makes chemical extraction more attractive to laboratory managers.

The objectives of the current work were to:

- (i) investigate the chemical associations of selected trace elements (Co, Ni, Cu, Zn, Cd, Pb) and structural cations (Fe, Mn, Ca) using a range of single-step extractions and a sequential extraction method in soils irrigated with wastewater from Peshawar, Pakistan;
- (ii) develop a reliable method to measure isotopically exchangeable Zn in calcareous Peshawar soils and compare Zn  $E$ -values ( $Zn_E$ ) with the single and sequential extraction fractions;
- (iii) compare, under controlled conditions, a simple solubility model with an adsorption model based on a labile  $Zn^{2+}$  Kd value as alternative approaches to predicting free  $Zn^{2+}$  ion activity in the solution phase of calcareous soil suspensions.

The importance of the current study lies in (i) its application to the soils of Peshawar, an important agricultural region which suffers from endemic Zn deficiency, (ii) the direct comparison of multiple approaches to determining a capacity term for labile Zn as a predictor of Zn free ion activity (intensity) and (iii) the investigation of superficial mixed Zn deposits as the possible origin of labile Zn fractions in such soils.

## 2. Materials and methods

### 2.1. Site description

The Peshawar Valley is a kidney-shaped basin (5500 km<sup>2</sup>) located at the southern foothills of the Himalayas between longitude 71°, 15' and 72°, 50' E and latitude 33°, 15' and 33°, 40' N in the Khyber Pakhtunkhwa Province of Pakistan (Fig. 1). The west to south-east

flowing River Kabul and its tributaries irrigate the basin and join the Indus at the eastern end of the province at Khairabad (Tariq, 2001). The valley is surrounded by ridges of rocks ranging in age from Precambrian to Tertiary (Rafiq et al., 1983). Igneous rocks such as granites and seyenites and metamorphic rocks like gneiss and schists are common along the northern and northeastern boundary (Kemp and Jan, 1980). In the south and west, the rocks are consolidated sediments including sandstones, shales and limestone formed during the Mesozoic and Lower Tertiary. The consolidated basement rock of the Valley itself consists of Tertiary molasses deposits. According to Nizami (1973), the Peshawar area was transformed into a lake several times during the Middle Pleistocene, when the outflow of the Indus River was blocked. The lake deposits show alternating sandy and silty layer. The lake must have been quite extensive since its deposits are even encountered near Matanni, high up the southern piedmont. Several erosion cycles since the Middle Pleistocene have been recognised. During that time much of the loess cover was removed (Kruseman & Naqvi, 1988).

### 2.2. Soil Sampling procedures, sample preparation and analytical procedures

A total of 36 soil samples ( $n = 36$ ; 18 topsoils, 0–30 cm and 18 subsoils, 30–60 cm) were collected after a preliminary analysis of 201 representative soil samples taken from fields irrigated with wastewater within the project area (Peshawar, Pakistan). The soil samples were named after their location within Peshawar; the full list of locations is given in Perveen et al. (2010). Composite soil samples at 0–30 cm and 30–60 cm depth intervals were taken, using a W-transect approach, from a range of fields cultivated with vegetables, including cabbage, tomato, carrot, onion, beans, lettuce and spinach. Soil samples were air dried and sieved to <2 mm.

Soil pH was determined in soil:water suspensions (1:2.5 ratio). Soil texture was determined using the hydrometer method (Koehler et al., 1984). Total soil carbonate content was measured by the Collins' Calcimeter method (Piper, 1954). For multi-element analysis, soil subsamples were ground in an agate Planetary Ball Mill (Model PM400; Retch GmbH and Co., Germany). Approximately 200 mg of finely ground soil was digested using 2.5 mL hydrofluoric acid (HF; 40% AR), 2.0 mL  $HNO_3$  (TAG), 1.0 mL  $HClO_4$  (AR) and 2.5 mL  $H_2O$  in a 48-place Teflon-coated graphite block digester (Model A3, Analysco Ltd., UK) with PFA digestion vials; all acids were either analytical reagent (AR) or trace analysis grade (TAG) from Fisher Scientific, UK. Multi-element analysis was undertaken by ICP-MS (Model X-Series<sup>II</sup>, Thermo-Fisher Scientific, Bremen, Germany) in 'collision cell mode' (7% hydrogen in helium) to reduce polyatomic interferences. Internal standards included Sc ( $50 \mu g L^{-1}$ ), Rh ( $10 \mu g L^{-1}$ ) and Ir ( $5 \mu g L^{-1}$ ) in 2% TAG  $HNO_3$ . External multi-element calibration standards (Claritas-PPT grade CLMS-2, Certiprep) included a wide range of trace metals; the certified reference material NIST 2711 (Montana soil) was used for quality assurance (average recovery for all metals was  $95 \pm 4\%$ ).

#### 2.2.1. Single and sequential extraction procedures (SEPs)

Triplicate samples of 4.0, and 1.0 g soils (<2 mm sieved) were suspended in 8 mL of 0.005 M DTPA (Quevauviller et al., 1996), and 10 mL of 0.43 M  $HNO_3$  (Groenberg et al., 2010), respectively and shaken end-over-end in polypropylene centrifuge tubes, for 2 h. Suspensions were then centrifuged at 2500 rpm for 15 min and the supernatant was filtered (0.22  $\mu m$ , Millex® Millipore) and acidified to produce 2%  $HNO_3$  prior to multi-element analysis by ICP-MS.

Sequential chemical extraction followed the method described by Li and Thornton (2001), developed from that of Tessier et al. (1979). The extraction was carried out progressively on an initial soil weight of 1.0 g. The sequence of fractions is nominally designated as 'Exchangeable' (F1), 'Carbonate' (F2), 'Fe/Mn oxides' (F3), 'Organic matter and Sulphides' (F4) and 'Residual' (F5). After each successive extraction, the supernatant solution was separated by centrifugation and filtration.

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