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# Fractionation of metals in cadmium contaminated soil: Relation and effect on bioavailable cadmium

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ABSTRACT

The effect of five metals (Cu, Fe, Mn, Pb and Zn) and soil pH, organic matter (OM) and oxidation–reduction potential (ORP) on bioavailable Cd in contaminated areas downstream of the Padaeng Zn mine in Mae Sot, Tak Province, Thailand was investigated. Soil samples were collected to characterize the bioavailable fractions of Cd, Cu, Fe, Mn, Pb and Zn by comparing weakly bound fractions with total metal concentrations using ICP-OES Spectroscopy. Acid digestion (US EPA, Method 3052) and the first two steps of the BCR sequential extraction method proposed by the Standards, Measurements and Testing Programme (SM&M) were adopted for the determination of total metals and bioavailable metals, respectively. Studied soil samples showed a wide range of physicochemical properties: pH (5.79 to 8.07); OM (0.52 to 4.16 g $kg^{-1}$ soil); ORP (−291.1 to 347.9 mV). Of the elements studied, Cd has the highest mobility since it presents the highest content in the first fraction BCR1 (exchangeable fraction) followed by Mn, Zn, Pb, Cu and Fe, respectively. Principal Component Analysis (PCA) together with correlation analysis showed supporting results, implying that some interactions and/or relations existed among these metals (Cd, Pb and Zn) in both bioavailable and total forms. Spearman correlation coefficients ($r$) all showed significant positive correlations: bioavailable Cd–bioavailable Pb; bioavailable Cd–bioavailable Zn; bioavailable Cd–total Cd; bioavailable Cd–total Pb, and bioavailable Cd–total Zn ($r$ = 0.296*, 0.946*, 0.554*, 0.321*, and 0.468*, respectively).



## 1. Introduction

Zinc (Zn) ore has been exploited from the Padaeng deposit located in the southeast region of Mae Sot District in Tak Province, Thailand for over three decades (see the location in Fig. 1). Paddy fields receiving irrigation water which has flowed through the Zn mineralized area associated with the Padaeng deposit have become contaminated with cadmium (Cd) and Zn (Simmons et al., 2005). This contamination has been an environmental issue since 2003 after the International Water Management Institute revealed their study on Cd contamination in rice and soil from this area. Cadmium was determined to be present in some paddy soils at considerable amounts resulting in above-normal uptake by rice plants grown in these areas (Simmons et al., 2003). This led the Royal Thai government to request farmers to suspend their rice cultivation since 2004 and promoted other non-edible crops. Later on several research papers related to potential risk of Cd on public health have been published on this issue (Swaddiwudhipong et al., 2007; Teeyakasem et al., 2007; and Apinan et al., 2009). In 2006, sugarcane cultivation for ethanol production was proposed as an economically viable option for contaminated land (Chantana et al., 2007). Cadmium (Cd) is a particularly interesting heavy metal. It can be accumulated by plants to levels that can be toxic to humans and animals when consumed even in minor amounts (Pinto et al., 2004). In soil, metals can be present in a number of chemical forms, and generally exhibit different physical and chemical behaviors in terms of chemical interaction, mobility, biological availability and potential toxicity. The mobility and bioavailability of individual trace metals are metal-specific (Lee, 2006). The most important factors influencing the form of bioavailable metal species in soil are soil pH, redox potential (ORP) and soil organic matter content (OM) (Manz et al., 1999; He and Singh, 1993; Kashem and Singh, 2001) which in turn determines the bioavailability of metals and uptake to the plants. These factors are interrelated as changing one factor may affect others (John and Leventhal, 1995).

Knowledge of the soil properties and interactions between other metals is important to assess the bioavailability of Cd and uptake by sugarcane in order to reduce potential food chain contamination (Pinto et al., 2004). For this purpose, various chemical extractions have been developed to determine element behavior including single and sequential extraction. Sequential extraction was selected in this study to fractionate the metals by using a series of extractions of increasing solvating power which are operationally defined. In order

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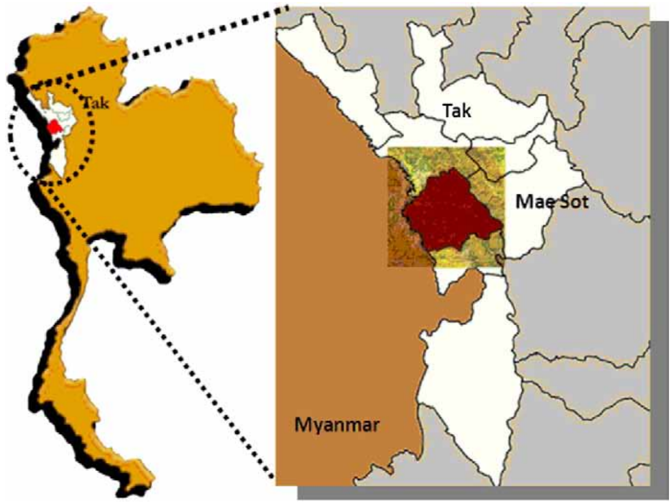


Fig. 1. Location of the study area, Mae Sot District, Tak Province, Thailand.

to evaluate the potential risks induced by the pollution of soil, it is necessary to define and quantify the form in which metals are present in the soil (sequential), not only the total concentration of the pollutants (single) but also the predictable impact of environmental changes (pH, ORP, OM, and the presence of other metals) on its mobilization. Thus, the main objectives of this study were (a) to determine concentrations of Cd and other associated metals (Cu, Fe, Mn, Pb and Zn) in soils from the contaminated area at Mae Sot District, Tak Province, Thailand; and (b) to investigate the relationship between soil properties (pH, OM and ORP) and other metals (Cu, Fe, Mn, Pb and Zn) on bioavailable Cd concentration.

## 2. Materials and methods

### 2.1. Study sites

Soil samples were collected in March, July and October 2007 from Cd and Zn contaminated areas in Mae Sot District, Tak Province. The geology of Zn mine deposit is grouped into the Upper Triassic–Jurassic Age which consisted of dark grey limestone and light grey bedded limestone with ammonite, brachiopods and coral reefs, inter-bedded with calcareous shale, sandstone and grey to brownish red lime-conglomerate (Department of Mineral Resources, 2002; Kaowichakorn, 2006). Ore minerals are mainly characterized by secondary zinc minerals, e.g. hemimorphite [$Zn_4Si_2O_7$ $(OH)_2$*$H_2O$], smithsonite ($ZnCO_3$), hydrozincite [$2ZnCO_3$*$Zn(OH)_2$] and loseyite [$(Mn, Zn)_7$ $(OH)_{10}(CO_3)_2$]. The Padaeng deposit was probably formed by the infiltration of Zn solution that was a result of oxidized primary Zn sulphide and subsequent groundwater transportation before being re-deposited along the fault plains, fractures and pore spaces of sandstone and dolomitic limestone (Kaowichakorn, 2006).

A total of 81 soil samples were randomly collected from within the Cd Zoning Map generated by the National Research Center for Environmental and Hazardous Waste Management (Zoning of Cd Levels in Flood Plains Area of Mae Tao and Mae Ku Subcatchments, Submitted to Padaeng Industry Ltd. (2005)) as shown in Fig. 2. Sampling was undertaken evenly throughout zones with high (>20 mg $kg^{-1}$), medium (3–20 mg $kg^{-1}$) and low (<3 mg $kg^{-1}$) soil Cd concentrations.

The following soil properties including: pH (1:2 soil/water suspensions) (Gleason et al., 2003) using a field-moist samples in the field, organic matter content (OM) by wet digestion according to the Walkley–Black procedure (Nelson and Sommers, 1996) and oxidation–reduction potential (ORP) using a field-moist samples in the field were determined (Gleason et al., 2003) to clarify their effects on the bioavailability of heavy metals in this study.

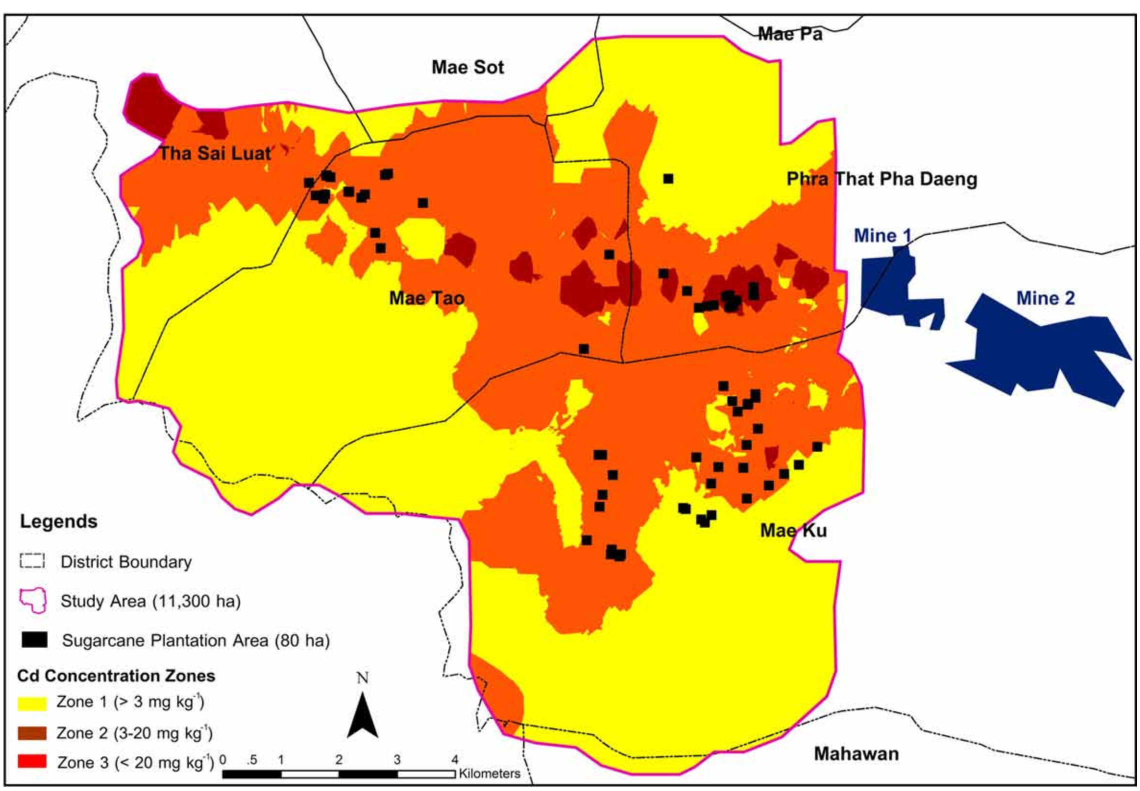


Fig. 2. Zoning of Cd contamination in the study area and soil sampling sites and the location of mines.