Clay minerals and metals in soils on mineralized limestone, western Thailand

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Introduction

Clay minerals, iron manganese and aluminum-oxides and organic matter are the most reactive solid constituents in soils and sediments, where they play a major role in the retention and transport of heavy metals (Stumm, 1992). The western part of Thailand is a traditional mining region with Pb, Zn, Au, Ag and Sn mines. Heavy metals including Pb, Cu, As, Ba, Fe and Zn have been released both naturally and by mining, and have been transported from mineralized sites to the adjacent landscape. In the mineralized area limestone is the dominant rock type and a typical karst topography has developed with steep sided limestone hills (Holdstock and Mlot, 2008). Lateral transport of heavy metals in solution, as rock fragments, in secondary minerals and adsorbed on to clay size constituents are likely to be an important processes. This research investigated the heavy metal concentrations and clay mineral composition of soils in this mineralized area.

Materials and Methods

Soil profiles at fifty seven sites were sampled at three depths (Ap, Ap-60 and 60-100 cm) at points along landscape traverses across geomorphologically contrasting sites in a mineralized area in Kanchanaburi Province, western Thailand. The physicochemical properties of soil samples were measured using standard methods. Heavy metal contents were determined by extraction with aqua regia followed by ICP-OES analysis, principal component analysis was used to interpret the dataset and to identify affinity groups of samples and properties.

For X-ray diffraction (XRD) analysis of the clay fraction, six representative geomorphologically contrasting soils were analyzed. Soil mineralogy was identified by X ray diffraction (XRD) analysis using monochromatized CuKα radiation with a Philips PW-3020 diffractometer (50 kV, 20 mA). Oriented clay was prepared on ceramic plates and XRD patterns were obtained from 4-45° 2θ with a step size of 0.02° 2θ. The clay was analysed by XRD when saturated with Mg^{2+} ions (Mg), solvated with glycerol (Mg+Gly), K^+ ions unheated (K) and heated at 550°C (K-heated 550 °C).

Results

Soil samples have silty clay loam, clay loam, silty clay and clay textures. The pH in water extracts varies between 4.4 and 7.4. There is a close association between As, Ba, Be, Ca, Cd, Mn, Ni, Pb, S, Sr and Zn (Fig. 1a). Crest soils had elevated concentrations of Cu, Cr, Mo, Ti and V, upper footslope soils had more As and Ni and lower footslope soils had more Co. Valley floor soils were associated with elevated Ca and Pb (Fig. 1b). The median concentrations of Pb and Zn in soils are sometimes higher than the limits listed in Thailand Soil Quality Standards for Habitat and Agriculture. Lead and Zn consistently showed higher median concentrations in soils at lower geomorphological settings (Fig. 2). Clearly some soils in the region can be regarded as contaminated and require special management.

X-ray diffraction analysis indicated that vermiculite, muscovite, illite, kaolinite, hematite and goethite are the dominant clay-size minerals in the soils (Fig. 3). Primary rock-forming minerals in the clay fraction of soils include quartz and feldspar. Clay mineral reflections for a representative sample are shown in Figure 3. Vermiculite is an abundant clay mineral in all geomorphological settings. Vermiculite is identified on the basis of strong 14 Å peak in XRD, which shifts to 10 Å after K-saturation and heating to 550°C (Fig. 3). Illite is identified on the basis of its strong basal reflection at 10 Å and a weaker one at 5 Å (Fig. 3). The illite resembles dioctahedral muscovite. Kaolinite is probably present but it is not easy to identify by XRD for this clay mineral assemblage because its most prominent peak at 7.2 Å overlaps with (002) vermiculite (Peuraniemi *et al*, 1997). Hematite, goethite and gibbsite are present in several samples. Iron oxides adsorb and incorporate trace metals in soils and sediments (Singh *et al*, 2002).

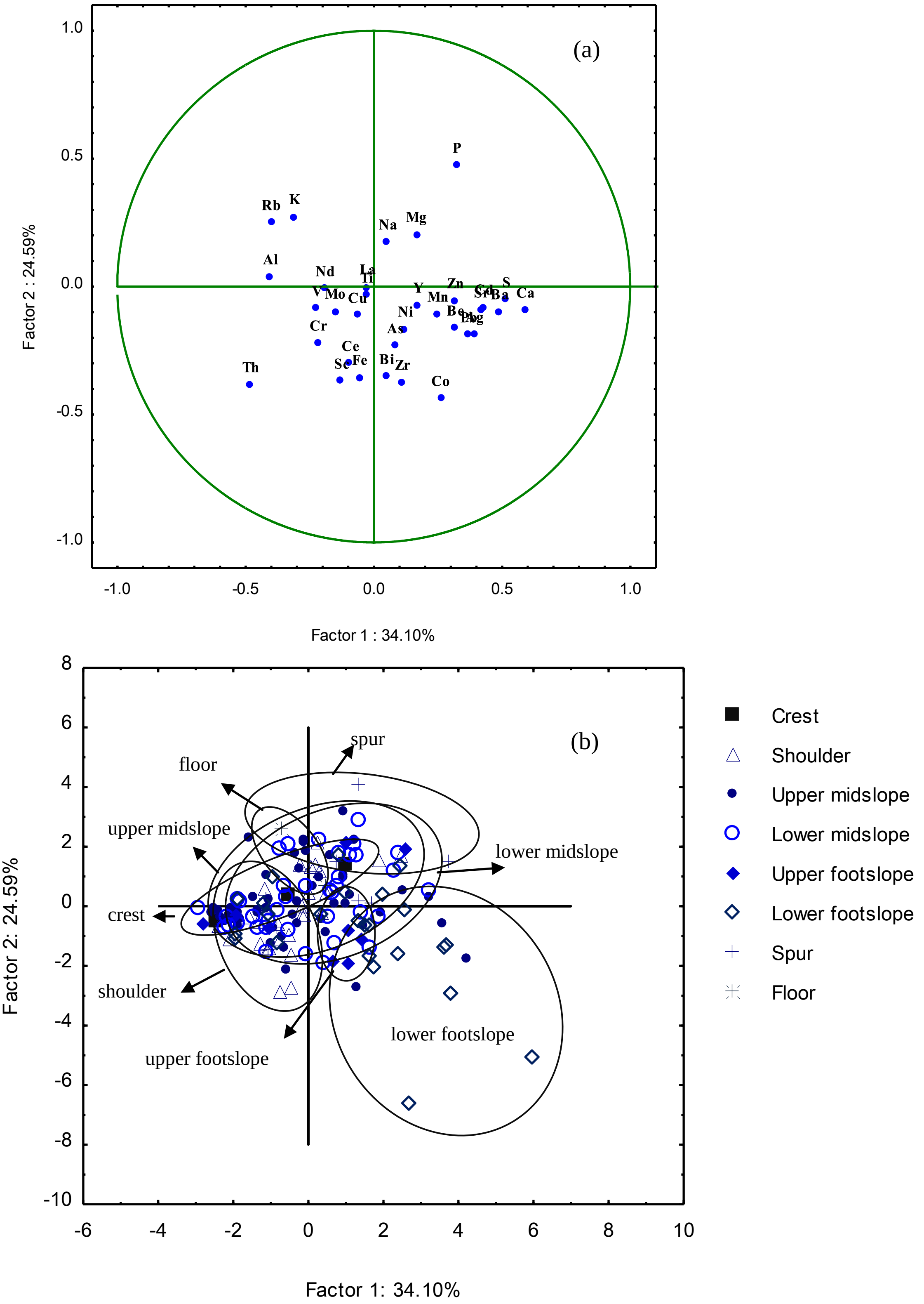

Figure 1. Factor analysis for the chemical composition and some additional properties of soil materials (a) distribution of chemical and other soil properties (variables) (b) distribution of soil samples (cases) for various geomorphic situations.

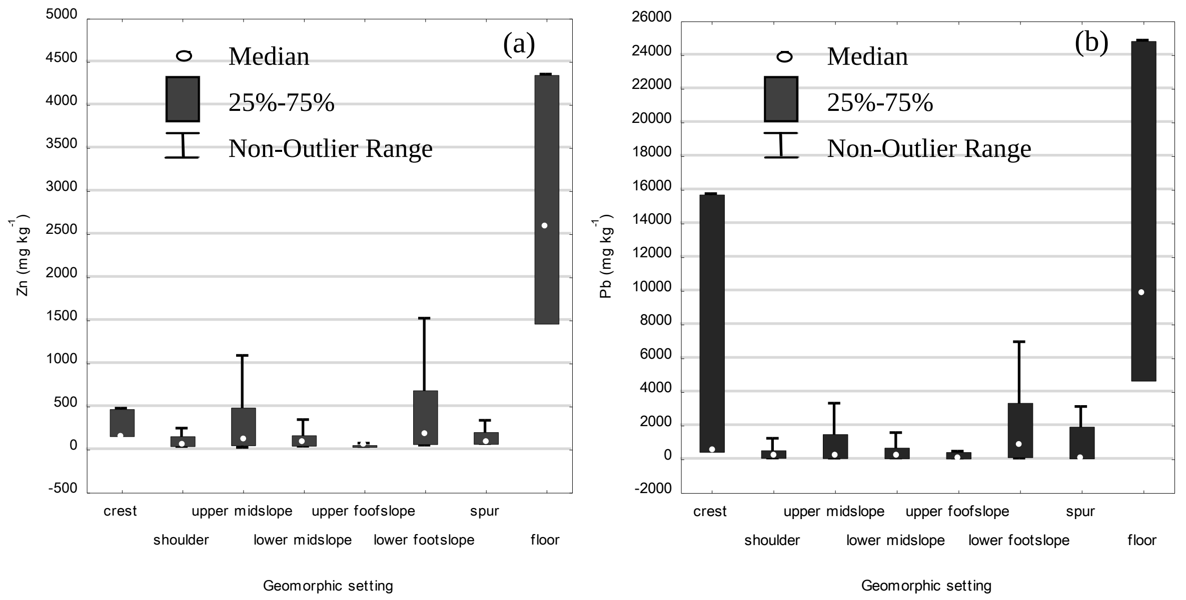

Figure 2. Range and median values of zinc (a) and lead (b) concentrations for each geomorphic setting.

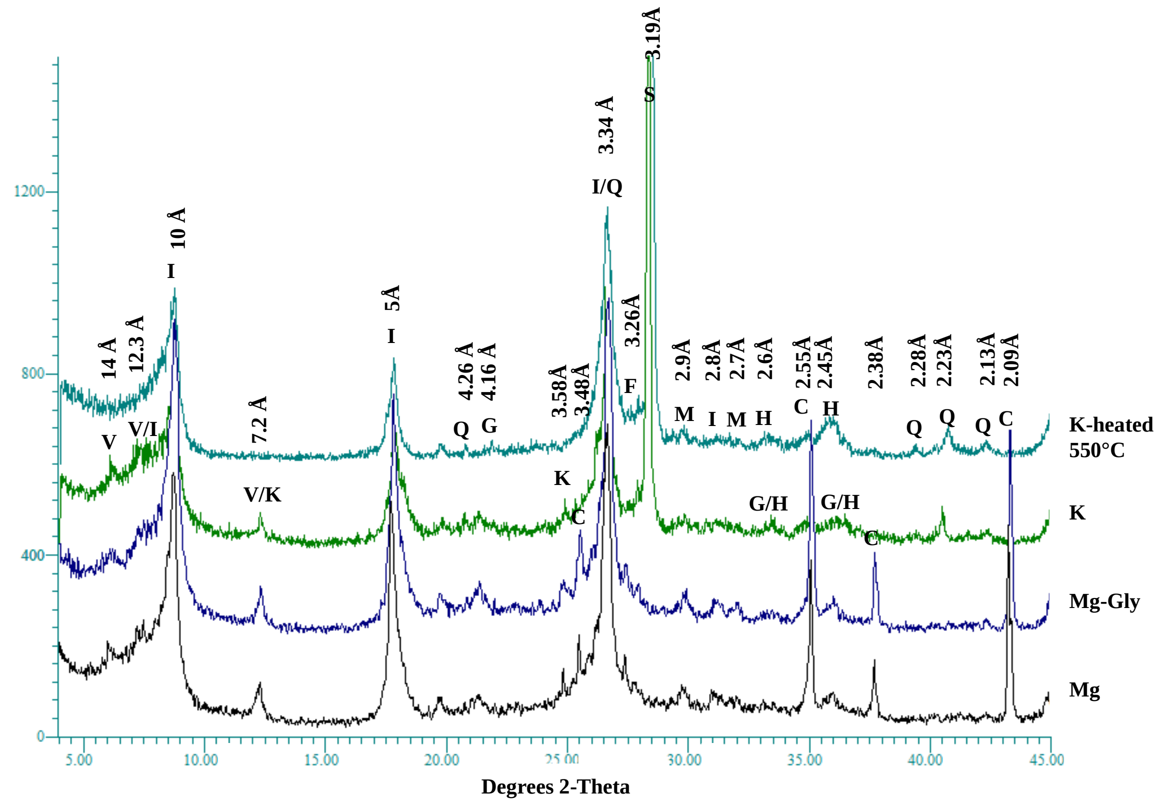

Figure 3. XRD patterns of the clay fraction of a soil developed from mineralized limestone. Vermiculite (V), interstratified vermiculite/illite (V/I), illite (I) kaolinite (K), muscovite (M), goethite (G), hematite (H), quartz (Q), feldspar (F), sylvite impurity due to K saturation (S) and supporting corundum plate (C).

Hydroxy-interlayered vermiculite (HIV) clay mineral occurs in the subsoils and is typical of moderately acidic soil pH (pH 4.7-5.3) in lower midslope and lower footslope situations (Fig. 4). HIV is stable in moderately acidic and oxidizing conditions in soil horizons with low organic matter content and with frequent wetting and drying cycles (Rich, 1968).

A mixed-layer clay mineral of the vermiculite/illite type gives a broad peak between 14 and 10 Å (Fig. 5) and collapse to 10Å for K^+/ 550 °C treatment. This occurs in all subsoils and dominates in the lower footslope, spur and valley floor soils. Mixed-layer clays can form by weathering involving the removal of some interlayer cations (K), hydrothermal alteration or removal of interlayer hydroxide interlayers. In some cases it may represent an intermediate stage in the formation of a swelling mineral from a non-swelling mineral (Meunier, 2007).

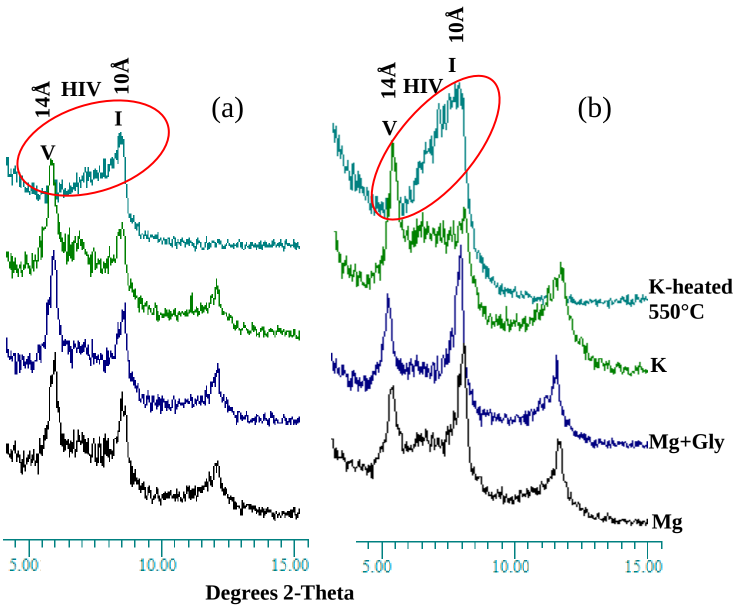

Figure 4. XRD patterns of the clay fraction showing a hydroxy-interlayered vermiculite (HIV) clay mineral in lower midslope (a) and lower footslope (b) soils. The 14Å reflection collapses to an asymmetrical broad 10Å reflection on K^+sat/heating at 550°C due to the interlayer Al-OH complex.

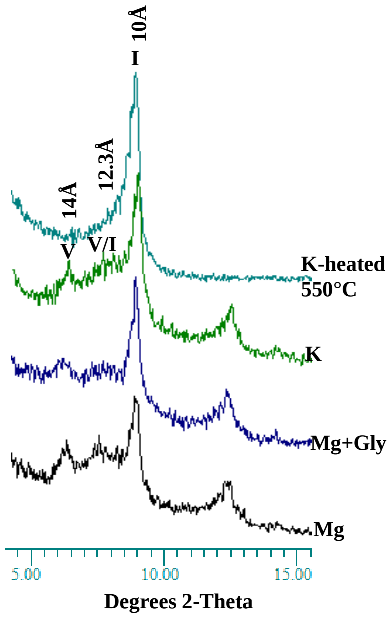

Figure 5. XRD patterns of the clay fraction of a valley floor soil showing the mixed-layer mineral vermiculite/illite (V/I) which collapses to a sharp 10Å reflection on K^+sat/heating at 550°C.

Conclusions

Illite and vermiculite are common clay minerals in these soils. In lower geomorphological sites interstratified vermiculite/illite and hydroxy-interlayered vermiculite occur in the clay fraction. Iron oxides are quite abundant in the soil and may retain heavy metals. Soils in the valley floor have the highest accumulations of Pb and Zn and as valley floors soils are the prime agricultural and habitat zone this indicates a potential environmental hazard. These results support the hypothesis that the accumulations of Pb and Zn are associated with iron oxides and clay minerals. This study provides a basis for the recognition of potential hazards from heavy metal in soils and for remediation actions to safeguard public health in mineralized areas in Thailand.

Acknowledgments

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