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Research article

The interactions of metal concentrations and soil properties on toxic metal accumulation of native plants in vanadium mining area

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ABSTRACT

High demand of Vanadium (V) in high-strength steel and battery manufacturing industry led to extensive V mining activity in China, and caused multi-metal pollution of soil around V mining area. To understand the phytoremediation potentials of native plants grown in V mining area, and the effect of soil properties and soil metal concentrations on toxic metal accumulations of native plants. *Setaria viridis*, *Kochia scoparia* and *Chenopodium album* were sampled from different sites in V mining area, soil properties, soil metal concentrations and metal accumulation amount of investigated plants were measured, bioaccumulation (BAF) and translocation (TF) efficiencies were calculated. Soil pH, cation exchange capacity (CEC) and available phosphorous (P) can significantly affect V and copper (Cu) uptake in the shoots of *Setaria viridis* while soil metal contents were lower than the permissible limits. Soil pH can significantly affect V accumulations in the roots and shoots of *Kochia scoparia* grown in slightly V polluted soils. *Setaria viridis* exhibited TF > 1 for moderately V and slightly chromium (Cr) polluted soils, and BAF > 1 for slightly Cu contaminated soils respectively. *Kochia scoparia* and *Chenopodium album* showed TF > 1 and BAF > 1 for slightly V polluted soils, respectively. *Setaria viridis* was practical for *in situ* phytoextractions of moderately V and slightly Cr polluted soils, and phytostabilization of slightly Cu contaminated soils. *Kochia scoparia* and *Chenopodium album* could be used as phytoextractor and phytostablizer in slightly V polluted soils in V mining area. Metal uptake of native plants grown in slightly multi-metal contaminated sites in V mining area can be manipulated by altering soil properties.

1. Introduction

Vanadium (V) is widely distributed in nature with an average concentration of 110 mg kg^{-1} (Anke, 2004) in the earth's crust (ranking 20th in abundance), and the average concentrations of Vanadium (V) in soil around the world established at 90 mg kg^{-1} (Reimann and Caritat, 1998). Mining, fossil fuel combustion and using V-containing phosphate fertilizers are the main anthropogenic sources of V, in fossil fuel (contains 0.1–1% V) combustion V is mainly concentrated in ash (Vachirapatama et al., 2002; Smith et al., 2013; Tissot and Welte, 1984). V has been mined extensively in China, South Africa, Russia and the U.S. A (Heinemann et al., 2000), because of its high utilization in high-strength steel and battery manufacturing and about 80% of the world produced V is used in steel industry as additives (Imtiaz et al., 2015a; b). Since high amount of vanadium is released in the environment by fossil fuel combustion, and it could stay in the environment for long period of time, V is ranked 3rd in the list of contaminants in Europe Community (Miramand and Fowler, 1998; Sabbioni et al., 1984).

V showed both essentiality (at trace amount) and toxicity (at excess amount) to organisms, V presence in soil at concentration lower than 2 mg kg^{-1} enhances chlorophyll synthesis, potassium consumption or nitrogen assimilation (Mandiwana and Panichev, 2009). In animals, V deficiency causes metabolic disturbance or inhibition, growth retardation and reduced reproductive capacity in chickens and rats (Frank et al., 1996; McCrindle et al., 2001). For humans, trace amount of V or V based nanomaterials were used to treat diabetes, cardiac disorders and Parkinson's disease (Vernekar et al., 2014). Moreover, V is an essential element for nitrogen fixing bacteria, tunicate and some fungi (Rehder, 2003; Kumar, 2011). The threshold levels for V toxicity were highly varied, greater than 30 mg kg^{-1} (Wang and Liu, 1999a,b), 40 mg kg^{-1} (Vachirapatama et al., 2011) and 300 mg kg^{-1} (Tian et al., 2015) soil V levels caused toxicity in soybean seedlings, green mustard and tomato, and rape, respectively, while no obvious toxic effect had

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been found in mustard and spinach grown in soil with 170 and 250 mg kg^{-1} V, respectively (Smith et al., 2013). For humans, higher than 3 mg/day can induce diarrhea, green tongue and hematological changes (Anke, 2004). In U.S, 0.33 mg L^{-1} is the accepted safe limit for vanadium in drinking water (US Department of Energy 1999). Despite the toxicity of excess soil V content, some plants and fungi can accumulate high amount of V in its tissues, the retention of V in cabbage roots at levels up to 2500 mg kg^{-1} dry weight (Hara et al., 1976) and mushrooms can accumulate 400 times more vanadium than plants (Berry et al., 1999; Hubregtse et al., 2005), showing good phytoremediation potentials to treat V contaminated sites. The remediation of large volumes of soils contaminated by mining activities using conventional physicochemical technologies would be very expensive and environmentally disruptive (Golubev, 2011). Plants grown in metal-rich soils or mining areas exhibit innate tolerance and may accumulate large amounts of toxic metals (Chamba et al., 2016). Furthermore, native plant species do not disrupt the ecosystem and environmentally friendly, preferable for *in situ* phytoremediation of various toxic metals (Rascio and Navari-Izzo, 2011; Willy, 2007). Plant with a BAF > 1 have the ability to phytostabilize, and those with a TF > 1 can phytoextract metals from contaminated soils, comprising the two branches of phytoremediation. There have been reports of phytoremediation of Cr, Cu and Zn (Bala and Thukral, 2011; Yllano, 2007; Gautam et al., 2016), but studies of V tolerance and accumulations in native plants grew in V mining area were lacking.

Toxic metal bioavailability is the most important factor to be measured in the phytoremediation process of a contaminated soil. Such bioavailability depends on several factors as soil characteristics and plant species growing in this soil. Soil pH, redox potential, total organic matter content, cation exchange capacity (CEC), macronutrient contents were considered to be the main factors affecting toxic metal speciation and metal forms consequently affect metal accumulation in roots or root to shoot translocation (Pilon-Smits, 2005; Sposito, 2008; Violante et al., 2010). But there are a few reports of interactions between soil V, Cr, Cu contents and soil properties (Welch, 1973; Wang and Liu, 1999a,b; Larsson et al., 2015). Hence, in this study three dominant native plant species found on sites adjacent to V mine tailings without any obvious metal toxicities (chlorosis) were chosen and the effects of soil V, Cr and Cu levels and soil properties on bioaccumulation and metal uptake of native plants were investigated.

2. Material and methods

2.1. Site description

The sampling sites are located in southeastern Yunxi County, Shiyan City, Hubei Province, China (E 110.43, N 32.96, altitude 311.25 m), which has a mean annual temperature of 16 °C and an average precipitation of 820 mm. This area is classified as having a northern subtropical continental monsoon climate. This study was conducted in a V mine tailing field that consists of a flat area, containing powdered or ball-shaped roasted stone coal slag produced from roasting and leaching raw stone coal, that was discarded and flattened, hills and downhill contaminated by leachate from tailings (Fig. 1). No plants grow on the flat area because it lacks soil, but various plant species were found on the margins of the flat area, on hills and downhills. The sampling sites 1, 2, 3, 7, 9 and 11 were located on hills where mine tailing were piled up on the top of it; the sampling sites 4, 6 and 8 were distributed on the margins of flat area; the downhill contained site 5 and site 10 (Fig. 1). The soil texture of all sampling sites were sandy clay loam and main pollutants in soil such as V, Cr and Cu were derived from the leaching of these tailings by rain fall and dispersing by winds.

2.2. Soil analysis

Soil samples (0–20 cm depth) were collected from eleven sites in May 2016. At each site, five sub-samples were collected from approximately evenly distributed sampling points using a 30 × 30 cm^2 grid and combined into a composite sample; 1 kg of this composite sample was transported to the laboratory, air dried and passed through a 5-mm-mesh filter in preparation for analysis. The chemical characteristics of the soils from the eleven sampling sites are listed in Table 1. Total metal concentrations were determined using an inductively coupled plasma emission spectrometer (Thermo Scientific iCAP 7000 series) after 0.5 g of soil samples in triplicate was microwave digested (CEM MARs5, USA) using 9 ml of aqua regia (HCl: HNO_3, 3:1, v/v). V, Cr, Cu, zinc (Zn) and manganese (Mn) were detected in investigated samples. Certified standard reference materials (GBW08302) obtained from National Sharing Platform for Reference Materials of China (CNRM) were used for the evaluation of analytical results for the determination of total vanadium concentration. According to soil total metal concentrations and Chinese Soil Environmental Quality Standard for Agricultural Land and single factor pollution index (P_i) (Eq. (3)) the major toxic metal pollutants and pollution levels were assayed. Since the concentrations of Zn and Mn were lower than soil background levels in all investigated sites and $P_i < 1$, V, Cr and Cu were considered as the major toxic pollutants in this study.

Soil pH was measured in a soil–H_2O suspension (1:5, w/w) using a 716 DMS Titrino pH meter (Thermo Scientific, Origon Star A214, USA) fitted with a glass electrode. Organic matter (OM) was measured by the Walkley-Black titration method (Baker, 1936). The CEC was analysed by leaching with NH_4OAc at pH 7, followed by distillation (George and Higginson, 1992). Available phosphorus (AP) was extracted using $NaHCO_3$ solution and its content was determined using the Mo-Sb colorimetric method (Bray and Kurtz, 1945), and available K was extracted using a fresh sample-to-extractant ratio of 1:5 (w/v) in 1 M NH_4OAc at pH 7, which was shaken for 1 h on a reciprocating shaker at 250 rev min^{-1} (Helmeke and Sparks, 1996) and then analysed using a flame photometer. Total N was measured using the Kjeldhal method (George et al., 2013).

One-Way ANOVA was conducted to compare the difference among soil properties in three different studying areas and sampling sites in each group.

2.3. Plant analysis

Plant samples were collected in end of May, 2016 after about 50 days of growing. The most abundant native plant species grown in investigated sites were chosen. *S. viridis* was collected from sites 1,2,3 and 4, *K. scoparia* was sampled from sites 2, 5,6,7 and 8 and *C. album* was collected from sites 9,10 and 11, respectively, forming an *in-situ* concentration gradient experiment of toxic metal. The morphology such as physical structure, height, leaf width, leaf length, leaf area and root structure (Plant Photo Bank of China, PPBC) of these three plants was highly varied, for each sample, five individual plants were collected randomly from the same sites where soil sampled and after oven dried the biomass was calculated. All plants appeared healthy with root systems in good condition, with no leaf chlorosis and necrosis. Species identification was performed at the Institute of Botany, Chinese Academy of Sciences, according to the PPBC. Fresh plant material was washed thoroughly with tap water, cleaned with distilled water and then separated into roots and shoots. The roots were then soaked in 20 mmol L^{-1} Na_2-EDTA solution for 20 min to remove the heavy metal absorbed on root surface.

All plant parts were oven dried at 72 °C for 72 h and then ground into powder using a hammer mill. Plant samples (0.5 g) were accurately weighed in polyvinyl containers followed by the addition of nitric acid (3.3 ml), hydrogen peroxide (1.7 ml) and water (1 ml). The plant material was then treated in the same way as the soil samples.

Data obtained from triplicate observations are presented as means ± standard deviation (SD). The least significant difference (LSD) was used to assess differences among plants or treatments. The