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Effects of mining wastewater discharges on heavy metal pollution and soil enzyme activity of the paddy fields

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ABSTRACT

To study the effects of mining activities on the agricultural environmental quality, four representative paddy fields distributed at different towns (HSG, SNJ, NT and THJ) of Y County, northern Hunan Province, were investigated. It was found that the paddy fields at HSG, SNJ and NT were heavily polluted by heavy metals, especially Cu, Zn and Cd, due to long-term irrigation with the nearby stream water contaminated by mining wastewater. In contrast, the paddy field at THJ, far away from mining sites, was not polluted by heavy metals and regarded as a control. The rice grain produced at the fields of HSG, SNJ and NT had a high risk of Cd contamination. Soil enzyme activities and microbial biomass were significantly inhibited by the heavy metal pollution. Microbial biomass carbon and microbial biomass nitrogen at a severely polluted site of the field at HSG were only 31.6% and 64.4% of the controls, respectively. The activities of dehydrogenase, urease, catalase, acid and neutral phosphatase and sucrase were only 25.2%, 49.3%, 52.4%, 94.7%, 53.2% and 87.8% of the controls, respectively. The microbial parameters were mostly negatively significantly correlated with the contents of Cu, Zn, Cd and Ni in the paddy fields, fully suggesting that the heavy metals had toxic effects on microbial processes. Furthermore, the principal component analysis and cluster analysis indicated that the activities of dehydrogenase and microbial biomass carbon were the most sensitive to the toxicity of heavy metals and could be used as eco-indicators of soil pollution in the study areas.

1. Introduction

Incidents of heavy metal pollution in agricultural soils are often associated with mining activities (Sheoran and Sheoran, 2006). When a mine is exploited, the raw ore once deeply buried is uncovered and piled anywhere on the ground, and even occupies farming land. Moreover, the procedures of ore dressing and smelting release huge amounts of mining tail and wastewater. The mining wastes are highly enriched in heavy metals and will pose threat to nearby groundwater, streams and farming land if it is mismanaged. A cultivated site once covered by mining tailing due to the collapse of the tailing dam of a Pb/Zn mine in Chenzhou, Hunan Province, Central South China, still shows unusual high contents of heavy metals, with As and Cd in the soil exceeding the thresholds specified by the Chinese criteria (GB15618, 1995) by 24 and 13 times and those in the vegetables exceeding by 6.6 and 8.5 times (Liu et al., 2005). The soil-rice system seems more vulnerable to mining activities (Bai et al., 2011). A paddy field and its rice grain in Lechang, Guangdong Province, South China, are heavily contaminated by Cd due to the irrigation with untreated mining wastewater (Yang et al., 2006a). Likewise, paddy fields nearby a Pb/Zn mine at a karst area in Guangxi Province, South China, are severely polluted by Cd, Zn, Pb and Cu (Li et al., 2009). After an open mine and some smelting factories were established at Dabaoshan in Shaoguan, Guangdong Province, in 1960, the paddy fields in the lower reach of a stream nearby have suffered from the contamination of Cd, Zn, Pb and Cu due to long-term irrigation with acid mining wastewater (Li et al., 2004a; Xu et al., 2007; Zhou et al., 2007). In addition, the contamination of soil by heavy metals could also be caused by the emission of coal dust produced from coalmine exploitation (Bhuiyan et al., 2010; Dang et al., 2002). The contents of Cu, Zn, Cd and Pb and their availability in the soil of a coal mine in Tongchuan, Shanxi Province, are significantly enhanced, among which, Cd is most severely polluted (Guo et al., 2012).

Microbial communities are sensitive to soil micro-environments and easily vary with the alteration of soil chemical properties (Corstanje et al., 2007). Mining activities are likely to affect the structure and function of soil microbial communities through altering soil micro-environments, especially the accumulation of heavy metals (Castillo and Wright, 2008). Heavy metals have toxic effects on soil microorganisms (Begonia et al., 2004; Obbard, 2001). They inhibit microbial activities and change the diversity of microbial communities (Hinojosa et al., 2004). Soil microbial functioning can be indicated by microbial biomass

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carbon (MBC) and microbial biomass nitrogen (MBN), soil respiration, soil enzyme activity and microbial structure (Gil-Sotres et al., 2005; Kızılkaya et al., 2004; Liao and Xie, 2007; Wang et al., 2007a; Zhang et al., 2008).

Both soil enzyme activity and microbial biomass are important factors of soil quality as involved in nutrient cycling (Dick et al., 1996; Kaschuk et al., 2010). Soil enzymes are involved in C and N mineralization (Dick et al., 1996; Edwards, 2002), and almost all ecological reactions in soil are conducted by enzyme catalysis. Sucrase in soil, for example, breaks down sucrose into glucose and fructose for providing energy for soil organisms (Mikanova, 2006). Urease hydrolyzes urea to release ammonium into soil (Nannipieri et al., 1978). Acid and neutral phosphatases mainly participate in the hydrolysis of organic phosphorous compounds and transform them into inorganic phosphorous (Dick and Tabatabai, 1983; Pant and Warman, 2000; Pascual et al., 1998). Microbial biomass serves as a pool of nutrients and plays an irreplaceable role in the sustainability of soil ecosystem. Soils with high microbial biomass could stock and recycle more nutrients (Kaschuk et al., 2010), which are essential for plant growth.

Soil enzyme activity and microbial biomass are much sensitive to heavy metal pollution, hence regarded as sensors of soil environmental quality (Chaperon and Sauvé, 2007; Mikanova, 2006; Renella et al., 2003). In addition, compared with the structural flexibility of microbial communities, both are relatively more stable and easily determined. Therefore, they are widely used as eco-indicators of the soils surrounding mines (Gülser and Erdoğan, 2008; Kuperman and Carreiro, 1997).

However, the responses of soil enzymes to heavy metal stress are not always the same, and sometimes even vary greatly due to their different characteristics. Generally, intracellular enzymes are more sensitive to metal toxicity. Dehydrogenase is a typical intracellular enzyme, and exists only in the cells and catalyzes the dehydrogenation of substrate (Chu et al., 2003). Catalase also exists intracellularly and catalyzes the breakdown of hydrogen peroxide and prevents it from poisoning organisms (García-Gil et al., 2000). In comparison, urease is involved in hydrolyzing urea extracellularly and could be combined with humus to form stable compounds outside the cells (Nannipieri et al., 1978).

Hunan Province, Central South China, is a well-known nonferrous metal base in China. Situated in the northern part of the province, Y County is abundant in mineral resources, with many ore exploiting and processing factories. On the other hand, this county is near to the Dongting Lake and has a long history of rice cultivation. Our previous investigations in 2009 found the unusual accumulation of heavy metals in the soil-rice systems in Y County, especially a high rate of Cd-contaminated rice (Du et al., 2013). The anomaly of heavy metals in the paddy fields might be caused by the special parent materials in the county, or by the long-term excessive application of chemical fertilizers and fungicides (Carnelo et al., 1997; Marschner et al., 2003; Taylor, 1997). It might be also related to local mining activities (Bhuiyan et al., 2010; Ibaraki et al., 2009), which was frequently reported in China recently (Bai et al., 2011; Liu et al., 2005; Yang et al., 2006a). In this study, some heavily polluted paddy fields and nearby irrigation streams in Y County are intensively monitored to track the sources of metal pollutants in the rice-soil system, and the responses of soil enzyme activity and microbial biomass to the heavy metal pollution are also studied to find sensitive eco-indicators for the assessment of soil environment quality in the study areas.

2. Materials and methods

2.1. Study areas

Situated in the northern part of Hunan Province, Y County adjoins the Xuefeng Mountains on the east, faces the Dongting Lake on the north, and is about 80 km northwest from Changsha, the provincial capital of Hunan Province (Fig. 1). The county has a subtropical monsoonal climate, with mean annual temperature 16.5 °C and mean annual precipitation 1465 mm. Affected by the extension of the mountains, the county shows undulating hills and is abundant in mineral resources, including Sb and Mn ores, coal, pyrite and navajoite. However, as Y County is close to the Dongting Lake Valley, it has a long history of rice cultivation. The area of paddy fields in the county, mainly distributed in small plains and valleys among hills, reaches 5.51×10^4 ha, making up 84.5% of the total farming land in the county. Currently, Y County mostly grows single-crop rice a year, which is sowed in middle April and harvested in late September.

The contents of heavy metals in the paddy fields in all the fifteen towns of Y County, northern Hunan Province, were grid-sampled and monitored in 2009 (Du et al., 2013). The results indicated that the contents of heavy metals in some paddy fields of the county are far beyond the thresholds specified by the Chinese criteria (GB15618, 1995). Especially, Cd contamination of the soil and rice grain seems common and serious. In this work, four representative paddy fields at HSG, SNJ, NT and THJ Towns of Y County were selected based on our previous work and coded as the HSG, SNJ, NT and THJ, respectively (Fig. 1). The samples of soil, rice grain and water were collected from the fields and nearby streams (Table 1). The fields at the HSG were intensively sampled on the two sides of the contaminated stream (Fig. 1).

2.2. Sampling and pre-treatment

Water samples in streams were collected and put into clean polythene bottles, and then acidified without filtering and stored in refrigerator (4 °C) for measuring total content of heavy metals including both water-soluble and particle-adsorbed forms. A cultivated layer (0–10 cm) of soil at each monitoring point was collected in middle September, when the rice was ripe, and late November, 2012, after harvesting, using a clean plastic spade. Each soil sample was divided into two parts. One was air-dried in room, ground and then passed through 2 mm and 0.149 mm sieves successively for physical–chemical analyses and heavy metal determination, and the other was kept fresh at 4 °C in a refrigerator for soil microbial analyses in a week. Rice grain samples were collected at each monitoring point shortly before harvesting in middle September and carried to laboratory for heavy metal determination.

2.3. Chemical analyses

2.3.1. Physical–chemical properties

Soil pH was measured by a pH meter with the soil/water ratio being 1:5. The grain-size composition of soil was by the pipette method. Soil organic matter content was by the $K_2Cr_2O_7$-$FeSO_4$ method. Soil cation exchange capacity (CEC) was by the NH_4OAc (pH 7.0) exchanging method. Total nitrogen (TN) content of soil was by the Kjeldahl method. NH_4^+ content of soil was by the alkali-diffusion method. Total phosphorus (TP) of soil was by the mixed acids ($HF + HClO_4$) digestion-colorimetric method. Available P of soil was by the $NaHCO_3$ (pH 8.5) extraction-colorimetric method. Total potassium (TK) of soil was by the mixed acids digestion-flame photometer method. Available K of soil was by NH_4OAc extraction-flame photometer method (Zhang and Gong, 2012).

2.3.2. Total heavy metals

Water sample of 200 ml was evaporated in water bath and then digested using mixed acids (68% HNO_3 + 60% $HClO_4$) in a beaker. Soil sample (<0.149 mm) of 0.2 mg was digested using mixed acids (68% HNO_3 + 60% $HClO_4$ + 40% HF) in a Teflon crucible. Fine rice powder was weighed (2.0 g) in a beaker and immersed in 30 ml 68% HNO_3 overnight, and digested after adding 2 ml 60% $HClO_4$.

Heavy metal concentrations in the three digested solutions were determined by the inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Prodigy, Leeman, U.S.) and the graphite furnace atomic absorption spectrophotometry (GF-AAS, ZEEnit 600/650, Analytik Jena, Germany). The detection limits for heavy metals in the