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Coupling geochemical, mineralogical and microbiological approaches to assess the health of contaminated soil around the Almalyk mining and smelter complex, Uzbekistan

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HIGHLIGHTS

- Soil samples were collected along a transect downwind of an industrial and mining area.
- Smelter particles were found in the heavy mineral fraction with metal-bearing weathering rims.
- Dissolved and exchangeable metal concentrations decreased with distance.
- Significant correlations were found between metal contents and microbiological health parameters.

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ABSTRACT

This study describes the impact of airborne pollution resulting from mining and smelting activities on the soils of the Almalyk mining and industrial area (NE Uzbekistan). Samples were collected along a transect downwind of the industrial area. Enriched contents of some metals were found in the upper soil layers near the metallurgical complex ($Zn \leq 3010$ mg kg^{-1}, $Pb \leq 630$ mg kg^{-1}, $Cd \leq 30$ mg kg^{-1}) which suggests that these metals were derived from local stack emissions. The morphology and internal microstructure of metal-bearing spherical particles found in the heavy mineral fraction suggest that these particles were probably a result of inefficient flue gas cleaning technique of the smelter. The highest metal concentrations were found also in soil solutions and exchangeable solid fractions from the first three locations, and decreased with increasing distance from the pollution source along transect. Thermodynamic equilibrium calculations suggest that the mobile metal pool in the contaminated soil is mainly controlled by dissolution of metal carbonates formed as weathering product of the metalliferous particles. The health of the microbiological soil ecosystem was assessed by measurements of basal respiration, nematode abundance, biomass-related C and N content, and microbial metabolic quotient qCO_2. Significant correlations were found between the dissolved metal content and the microbiological health parameters, a negative one for C_{mic}/C_{org} ratio, and a positive one for qCO_2. A negative correlation was found between the amount of nematodes and the metal contents suggesting that the contaminated soil has significant impact on the functioning of the microbiological community. A better understanding of the spatial variations in the whole ecosystem functioning due to airborne impact could be very useful for establishing suitable land use and best management practices for the polluted areas.

1. Introduction

Soils around mining and smelting sites may act as an important sink for mobile metal(loid)s introduced to the environment via fly ash, dust and leachates from the mine quarries, dumps and tailings (Birkefeld et al., 2007; Martín et al., 2007; Cecchi et al., 2008; Ettler et al., 2012). Clearly, the bioavailability and ecotoxicity of metals depend on their speciation. Therefore, to understand the impact of contamination from fly ash and dust it is necessary to study not only the total concentrations

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of metals, but also their partition/distribution coefficients (K_d factors) and bioavailability (EPA, 1999; Weber and Karczewska, 2004). The bioavailability of metals is geochemically assessed by ion exchange (Peijnenburg et al., 2007). Single or sequential extraction schemes have primarily been developed to establish the mobility and availability of metal(loid)s and other toxic elements in soils and sediments contaminated by mine tailings (Fanfani et al., 1997; Cohen et al., 1998; Li and Thornton, 2001; Van Herck and Vandecasteele, 2001; Dold, 2003; Cappuyns et al., 2007; Pueyo et al., 2008; Favas et al., 2011). The extraction methods were also useful in screening waste from combustion and smelting (Kersten and Förstner, 1995; Vanek et al., 2008), and for evaluating potential remediation measures for smelter-ash contaminated soil (Nowack et al., 2010). However, metal ecotoxicity is not necessarily a simple function of the extractable metal present, but is controlled also by various physicochemical and biological co-factors, such as the pH of the soil, the organic matter and clay mineral content, the redox status, or the activity of the living biomass (Anderson and Domsch, 1990; Brookes, 1995; Neher, 2001; Van Gestel, 2008; Smolders et al., 2009). The complexity of these co-factors, and their considerable spatial and temporal variability in the field, make it difficult to predict metal ecotoxicity, and hence render environmental risk assessment more difficult. For this reason, chemical analyses alone are inadequate for the appropriate assessment of the health of soil and organisms (hereafter "soil health"), and should be corroborated by biological methods involving indicator organisms (Nahmani and Rossi, 2003; Jänsch et al., 2005; Yang et al., 2006; Yan et al., 2012).

The detrimental effects of metal(loid)s and other soil contaminants on soil health have been widely reported (Hattori, 1992; Bardgett et al., 1994; Kandeler et al., 1996; Klumpp et al., 2003). Measurements of the biomass of soil organisms, together with an understanding of their population dynamics, have been found to be a useful indicator of environmental pollution of various soil ecosystems (Ingham et al., 1986a, 1986b; Yeates et al., 2003). It is well known that metal contamination reduces soil respiration (Hattori, 1992), microbial biomass (Klumpp et al., 2003), invertebrate density and the resulting impact on trophic interactions (Vig et al., 2003; Caussy et al., 2003; Santorufo et al., 2012). In natural ecosystems, nematode abundance and community structure analyses were proved to be sensitive indicators of stress caused by soil pollutants and ecological disturbance (Sochova et al., 2006; Shao et al., 2008; Kapusta et al., 2011). The populations of omnivorous and predatory nematodes with a K-strategist type of life history appear to be sufficiently sensitive to metal pollution (Bongers and Bongers, 1998; Bakonyi et al., 2003), and the populations of several nematode taxa are significantly affected by the concentration of Cu, Ni, and Zn (Korthals et al., 1996a).

The present study focuses on the Almalyk mining and smelting complex, a major source of air and soil pollution in Uzbekistan (Kodirov and Shukurov, 2009). In a previous study, significant metal contamination and its impact on nematode population have already been reported for soils collected in this area (Shukurov et al., 2005). To date, however, there have been no studies of metal bioavailability in the polluted soils. Here we report data of a more extended triad-like ecological risk assessment applying in parallel different analysis methods. In our triad procedure, we couple a geochemical approach, involving both metal geochemical equilibrium modeling and kinetic extraction data, with an evaluation of the soil microbiological ecosystem. The triad-like ecotoxicity assessment approach has not yet been widely reported in the literature. The aims of our study are to (i) use microspectroscopic analysis and geochemical equilibrium modeling to assess the mechanisms controlling the bioavailability of the metals in the soils along a transect downwind the industrial complex, (ii) evaluate the impact of the metals on soil health using microbiological indicators such as the soil free-living nematode abundance, basal respiration, the C and N content of the microbial biomass, as well as microbial health indices such as the metabolic quotient, and (iii) examine the analytical data for any correlations between the chemical and biological parameters of the soil, with the ultimate aim of assessing the extent of the soil pollution in the area of interest.

2. Materials and methods

2.1. Sampling sites

The study site is located 65 km from Tashkent, the capital city of Uzbekistan, in the Akhangaran river valley between the Chatkal and Qurama mountain ranges (Western Himalayan Tien-Shan orogen). The industrial area lies in the floodplains of the Akhangaran river near the city of Almalyk (40°50′N–69°34′E). The Qurama Mountain ridge is rich in nonferrous metal resources, and in this area metal mines were founded in the early 50's. The Almalyk mining and smelting complex (AMSC) is the largest nonferrous mining company in Uzbekistan, producing refined copper, gold, silver, lead, metallic zinc, and other products. It has a mining capacity of about 25 Mio. metric tons of ore per year, and an annual metal production of 130,000 t Cu, 40,000 t Zn, and 80,000 t Pb (Levine and Wallace, 2010). However, AMSC started with no efficient flue gas cleaning facility, and the complex has become a major source of air pollution in the region. It is reported to emit about 100,000 t per year of harmful substances (including sulfur dioxide, black carbons, nitrogen oxides, sulfuric acid, metal(oid)s, etc.), which represents approximately 13% of all airborne emissions of these pollutants from point sources in Uzbekistan (UNECE, 2001).

The study area lies in a mountain valley with large variations in both seasonal and daily air temperature due to a continental climate with hot and dry summers and short, cold winters. The prevailing winds are westerly and south-westerly along the river valley. The average annual rainfall is between 100 and 200 mm, which is less than the rate of evaporation (UNECE, 2001). The study area is surrounded by a chain of mountains, which limits air circulation and exchange, thereby increasing the airborne pollution impact on soils and vegetation. Since 1994, the State Committee for Geology and Mineral Resources is carrying out routinely environmental monitoring in the Almalyk industrial area. This has revealed severe contamination of surface and groundwater, soil and vegetation (UNECE, 2001). The vegetation in the study area is mainly composed of annual and perennial plants, most notably *Astragalus*, *Stipa*, *Medicago*, and *Artemisia* genera, which prosper in the alkaline lithosols (FAO, 2003) with high levels of $CaCO_3$.

2.2. Soil sampling

Soil samples were collected in June 2005, when rainy weather softened the soil, in duplicate from two topsoil layers: 0–10 and 10–20 cm, at 11 equidistant (2 km apart) sampling plots (in total 44 soil samples 200 g each). The plots were aligned on a 20 km E–W transect along the Akhangaran river valley downwind of the AMSC pollution source which starts at the copper refinery and smelting factory, and ends in a rural grassland area near the town of Pskent (Fig. 1). The transect passes the Almalyk mineral fertilizer factory, industrial landfills (phosphogypsum, metallurgical slags), and agricultural lands (Fig. 1). The land use and characteristics of each sampling plot are as follows: L_1 (0 km, 40°51′40″N/69°33′18″E) grassland at the border of the Cu processing factory, L_2 (2 km, 40°51′41″N/69°32′4″E) grassland nearby the Cu smelter slag wastes and chemical factory, L_3 (4 km, 40°51′45″N/69°30′41″E) grassland nearby the phosphogypsum landfills of chemical factory, L_4 (6 km, 40°51′47″N/69°29′21″E) grassland in rural area, L_5 (8 km, 40°51′43″N/69°28′10″E) grassland in agricultural area, L_6 (10 km, 40°51′42″N/69°26′39″E) grassland in agricultural area, L_7 (12 km, 40°51′52″N/69°25′23″E) grassland in agricultural area, L_8 (14 km, 40°51′58″N/69°24′0″E) grassland in agricultural area, L_9 (16 km, 40°52′2″N/69°22′37″E) grassland in agricultural area, L_{10} (18 km, 40°52′10″N/69°21′18″E) grassland in rural area, and L_{11} (20 km, 40°52′12″N/69°19′52″E) grassland in rural area. Two samples were collected at each plot from each of the two soil layers (44 samples