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Assessment of trace element concentrations in soil and plants from cropland irrigated with wastewater

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ABSTRACT

Samples of soil and food plants were collected from wastewater-irrigated fields in the vicinity of Gaziantep, in southeast Turkey, and analyzed for several trace elements (TEs). The concentrations of Co, Mo and Zn in edible portions of corn, mint and vegetables (eggplant, pepper and tomato) were 0.03–0.66, 0.1–3.2 and 8–148 mg kg^{-1}, respectively. In the edible portions of corn and mint, Cd, Cr, Cu, Ni and Pb concentrations in all samples were <0.01–0.05, 2.0–5.5, 6–47, 0.6–6.7 and 0.2–3.5 mg kg^{-1}, respectively. No single plant species had consistently high concentrations of all metals. For example, corn had the highest concentration of Zn (89 mg kg^{-1}), but the lowest concentration of Cd (<0.01 mg kg^{-1}). The maximum concentrations of some TEs in some crop samples, as well as soil samples, exceeded certain threshold values set in Turkey and other countries. For some TEs there was little difference between wastewater-irrigated and control soil concentrations. Transfer factors (TFs; plant concentration/soil concentration) were high for Cu, Zn and Mo, in comparison with the other TEs (Cd, Co, Cr, Ni and Pb). Higher uptake of certain metals may be associated with the dominant form of the element in the soil matrix. The uptake of chemicals to plant tissues is influenced by the chemical and physical characteristics of the soil and species-specific factors. Although the geochemistry of the region plays a significant role in the levels of TEs in soil and plants, bioaccumulation of metals and subsequent toxicity to plants and animals can be exacerbated by higher environmental concentrations caused by wastewater irrigation and other anthropogenic factors.

1. Introduction

Several trace elements (TEs) have been identified as being essential for plant growth, including Cu, Zn, Mn, Fe and Mo. Though these micronutrients are essential for plant metabolic health, they can be phytotoxic in higher concentrations. Some TEs such as Co and Se are not essential to plant growth but are required by animals. There are also some TEs which have not been identified as essential elements for plants or animals, including Cd, Pb, Cr (VI), Ni, Hg and As. Heavy metals such as these can be highly toxic to living organisms, even at very low concentrations. TEs in an agroecosystem originate either from the parent soil materials or human activities (Adriano, 2001; Yaman, 2006; Fairbrother et al., 2007).

Sources of terrestrial TE contamination include atmospheric deposition from industrial air emissions (e.g., metal smelters), vehicle exhaust and degradation, mining and smelter wastes, and agricultural amendments such as various fertilizers and pesticides. Municipal refuse and sewage sludge can also be significant sources of soil TEs on a local scale (Senesi et al., 1999; Obbard, 2001; Smith, 2009). The ecological and human health impacts of elevated environmental metal concentrations have been known for several decades, and focused research efforts on adverse effects and mitigation strategies have gained momentum over this same time period.

A significant portion of observed contamination of field soil and crops results from irrigation using municipal and industrial wastewater. Using wastewater as an irrigation resource is common in many countries, including Turkey, which has one of the lowest per capita wastewater treatment plant rates in Europe. The widespread use of industrial and municipal wastewater for irrigation, often in peri-urban ecosystems, is due to its availability, scarcity of clean, fresh water and challenges associated with disposing of wastewater (Arslan-Alaton et al., 2007; Avci, 2013). Although this practice may be convenient and cost-effective, TEs in wastewater can find their way into the human food supply and pose significant adverse health effects, especially to those who are more

Abbreviations: DW, dry weight; ICP-MS, inductively coupled plasma mass spectroscopy; MAC, maximum allowable concentrations; OM, organic matter; SRM, standard reference materials; TE, trace element; TF, transfer factor from soil to crop; UWWTP, urban waste water treatment plant; w/v, the ratio of weight/volume

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vulnerable because of higher dietary proportions of certain foods and/or their age and pre-existing health issues.

Many studies have demonstrated that plants grown on wastewater-irrigated soils accumulate elevated levels of TEs (Demirezen and Aksoy, 2006; Chary et al., 2008; Tiwari et al., 2011).

However, TE concentrations in plant tissue from wastewater-irrigated fields are often in exceedance of maximum allowable concentrations (MACs), suggesting the possibility of risk to human health risk. Because bioaccumulation of inorganic chemical stressors from wastewater-irrigated soil into crop plants will raise the dietary exposure to those stressors as well as diminish crop yield and food quality, it may be necessary to abandon certain croplands as they become unsuitable for food production (Obbard, 2001; Smith, 2009).

The goal of this study was to determine the concentrations of Cd, Co, Cr, Cu, Mo, Ni, Pb and Zn in soils impacted by industrial and municipal wastewaters for decades, and in food crops which were irrigated with those wastewaters. TE concentration data collected during this research were compared to the MACs proposed by the FAO/WHO, WHO/EU and Turkish Regulations for food crops. Samples of corn (*Zea mays*), mint (*Mentha*) and vegetables from the Solanaceae family, eggplant (*Solanum melongena* L.), pepper (*Capsicum annuum* L.) and tomato (*Solanum lycopersicum* L.), were collected from 17 locations where crops have been irrigated with municipal and industrial wastewaters for several years. Co-located soil samples were also collected, as well as control samples from 25 unaffected sites.

2. Materials and methods

2.1. Study area

The study area was situated between 36°43′ E, 37°11′ N and 37°59′ E, 36°56′ N, near southeastern Gaziantep City (Fig. 1). The transitive climate (Mediterranean and Continental) in Gaziantep is marked by sharp seasonal variations in both temperature and precipitation. Temperatures in the study area range from −16.8 °C (January) to 42.0 °C (July) (Turkish State Meteorological Organization 1960–2006).

Gaziantep is a vital commercial, economic and industrial center with a population of about 1.5 million people. The city is home to several large-scale industrial firms such as textile manufacturing, chemical production, cement construction, energy and machine manufacturing. There are also several other small- and medium-size businesses, the most important of which is leather processing and product manufacturing.

The majority of wastewater comes primarily from two different branches within the city (Fig. 1). The first branch originates from the Baspinar Industrial Zone which releases effluent from large-scale industries into the Nizip River. This River carries effluent to an urban wastewater treatment plant (UWWTP) recently constructed by the Gaziantep Chamber of Industry. The second branch consists of wastewater from domestic and small-scale industries that are pumped into the Bagirsak River, which carries effluent to a second UWWTP constructed by the Gaziantep City municipality, near the town of Oguzeli. Physical or biological treatment technologies are utilized in the UWWTPs (activated sludge, trickling filters); few of them are sufficiently advanced to provide effective removal of heavy metals and other ions (Arslan-Alaton et al., 2007; Avci, 2013). The inefficiency of processes at many UWWTPs yields little concentration reduction of key chemical stressors and general pass-through of many heavy metals and other ions (Senesi et al., 1999; Ziolko et al., 2011), leaving significant quantities in the final effluent, which can then be accumulated by plants from the soil receiving effluent irrigation water.

Soil in the study area is geologically limestone. The soil is rich in calcium and aluminum oxides, and contains high amounts of lime, in the range of 12–83 percent calcium carbonate. Not surprisingly, the soils are slightly alkaline to alkaline, with a pH range of 7.5–8.3. Calcium and magnesium are the dominant (~90 percent) exchangeable cations. The OM content of the regional soils ranges from 1.4 to 2.5 percent in the upper layers, which is relatively low (Tekin, 1990).

2.2. Sample collection and preparation

Samples were collected during September and October 2010. Edible portions of corn (seeds), mint (leaves), eggplant, pepper and tomato plants (fruits) (~2 kg fresh plant biomass) were obtained from 17 locations within the study area. Plant portions were removed by hand with the assistance of a clean scissors or knife, if needed. Each harvested plant sample was homogenized by turning the collected material over several times by hand in a mixing bowl. The mixed samples were placed in clean plastic bags, labeled and transported to the laboratory where they were washed with tap water, followed by a distilled water rinse to removed dirt, dust and external invertebrates. The samples were dried in an oven at 70 °C for 24 h. Each dried sample was crushed separately using a steel grinder; the crushed material was passed through a 1-mm sieve (100 mesh). The grinder was cleaned and decontaminated before use and between samples to ensure no cross-contamination occurred.

Co-located soil samples were collected on the same date as the plant samples. The soil samples were collected at a depth of about 10 cm below the surface. The upper 10 cm of soil were removed by hand or using a clean shovel, if needed. Approximately 500 g of soil were placed into a polyethylene container, labeled and transferred to the laboratory. The samples were dried in an oven at 70 °C for 24 h, ground in a porcelain mortar and passed through a 1-mm sieve (100 mesh). Control soil samples were also collected in the field from a location near the study area but unaffected by irrigation with wastewater.

2.3. Analysis

The samples were digested by wet ashing (Mitra, 2003). A 0.5 g aliquot of the edible portion of the plant sample was digested with concentrated HNO_3. The residue was further digested using aqua regia (1:3, conc. HNO_3:HCl solution, by volume). A 0.5 g portion of each soil sample was digested using aqua regia. After evaporation of the liquid portion, 2 percent (w/v) HNO_3 was added to both the plant and soil digested aliquots, followed by centrifugation. Metal concentrations in the clear solutions were determined by inductively coupled plasma mass spectrometry (ICP-MS) (PerkinElmer, SCIEX ELAN–9000; PerkinElmer SCIEX, Concord, ON, Canada).

Blank digests were conducted separately for soil and plant samples. In the digestion procedures, high-purity HNO_3 (65 percent, Merck) and HCl (37 percent, Merck) were used. Double distilled water was used for all analytical procedures, where appropriate.

To determine $CaCO_3$ content of the soil, a 0.5 g aliquot of the soil sample was treated with 10 mL of concentrated HCl. The volume of the carbon dioxide produced was measured using a calcimeter (Scheibler unit), and compared to with the volume of carbon dioxide produced by pure $CaCO_3$ (ISO, 1994). The soil pH value was determined according to the appropriate ISO (1994) method.

2.4. Statistical analysis

All the data were statistically analyzed using ANOVA SPSS version 11.5. Duncan′s multiple comparison test was used to detect the differences.

3. Results and discussion

3.1. Analytical quality control analyses

All reagent blank concentrations for both plant and soil analyses were below the analytical detection limit (Table 1). Percent recoveries of known standards were all 100 ± 10 percent.

3.2. Trace element concentrations in wastewater-irrigated and control soils

Several soil minerals incorporate TEs into their structure, including carbonates, oxides, sulfides or salts. The dominant TE minerals in any particular soil will vary depending upon the nature of that soil (Adriano, 2001; Yaman and Bakirdere, 2003; He et al., 2005). It is not surprising, therefore, that soils from around the world demonstrate a substantial range of TE concentrations (Table 2). An increase in TE concentrations in soil has been shown to occur in response to irrigation with industrial or municipal wastewater. Tiwari et al. (2011) reported a higher concentration of metals in order of Fe > Mn > Zn > Cd > Cu > Pb > Cr > As in soil irrigated with industrial effluent than soil irrigated with tube well water. Irrigation of soil by TE-containing wastewater may result not only in higher TE concentrations, but also in greater bioavailability to plants. Any given soil matrix has only a limited absorptive capacity, which can be exceeded by repeated wastewater application. In addition, the form of a particular element may render it less likely to be sorbed