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Background levels of some trace elements in calcareous soils of the Hamedan Province, Iran

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ABSTRACT

Natural concentrations of trace elements are necessary for assessing trace elements contamination affected by anthropogenic activities in soils. This study was conducted to establish background concentrations of cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb) and zinc (Zn) in 50 unpolluted native soils with a total of 100 soil samples (surface and subsurface soil layers) in Hamedan province of Iran. Different methods have been used for the evaluation of background limits, and the relationships between soil properties and trace elements concentrations and among trace element concentrations have been analyzed. Values from Geometric Mean (GM) procedure had the lowest background limit, while the GM $\times$ GSD^2 (geometric standard deviation) method produces the highest background limits. The percentage of outliers in Median + 2MAD (median absolute deviation) ranged from 4.0 to 16.0% for natural data and from 0.0 to 12% for log-transformed data. The smallest outlier percentage was for Cd and Cr, and it was higher for Co, Cu, and Zn. The obtained geochemical baseline concentrations (mg kg^{-1}) based on Median + 2MAD were (log-transformed data) Cd 1.36, Co 15.42, Cr (natural data) 36.69, Cu 29.99, Fe 25.79 (g kg^{-1}), Mn 368.68, Ni (natural data) 53.59, Pb 39.60, Zn 103.80. Carbonate calcium had significant negative correlations with Co, Cr, Cu, Fe, and Mn, indicating that trace elements are not included in the crystal structure of secondary carbonate minerals; consequently, accumulation of $CaCO_3$ causes a dilution effect in the soils. The content of clay, silt and organic matter had significant role in the accumulation of Mn, Ni, and Pb in the soils of the studied area. Significant correlation was found among Co, Cr, Cu, Fe, Mn, and Ni and between Zn with Cd, Cr, Cu, Mn, and Ni. Factor analysis of trace elements explored six factors attributing 64.1% of the total variability. According to the results found by upper whisker method, correlation analysis and factor analysis, studied trace elements contaminated none of the soil samples, natural accumulation processes influenced their contents in soils and origin of trace elements may be lithogenic, but their sources may be different.

1. Introduction

In the past years, considerable growth in agriculture, urban life and industry has been increased the concentration of trace elements in soil and water that endangers ecosystems and human health (Buccolieri et al., 2010; Rekasi and Filep, 2012; Oliveira et al., 2014). Studying of soil pollution requires comparing the contents of trace elements of a soil to those occurring in natural conditions (Birani et al., 2015). Metal background concentration or natural concentrations of trace elements is important for deciding contamination level, risk assessment of contaminants and understanding effects of past land use practices on the levels of inorganic compounds in soils (Breckenridge and Crockett, 1998; Roca-Perez et al., 2010; Sanjeevani et al., 2015). Different approaches have been used to establish the background levels of trace elements in soils (Tobias et al., 1997). Empirical (geochemical), theoretical (statistical) and integrated methods (combining both empirical and theoretical methods) are the main approaches described in literature for estimating geochemical background concentrations (Dung et al., 2013).

Baseline concentrations are expected range of trace element concentrations around a mean in a normal sample medium and are defined as 95% of the expected range of background concentration (Bech et al., 2005; Tume et al., 2006a; Kabata-Pendias and Pendias, 2011). Geochemical baseline concentration (GBC) and background level (BL) concepts have been used to establish the natural concentrations of trace elements in soil. They also can be used to estimate the degree of soil pollution (Tume et al., 2006b; Roca-Perez et al., 2010; Alfaro et al., 2015). The BL measurement represents the natural concentration of an element in soil without human influence. The term GBC is often used to express an expected range of element concentrations in soils. It is not

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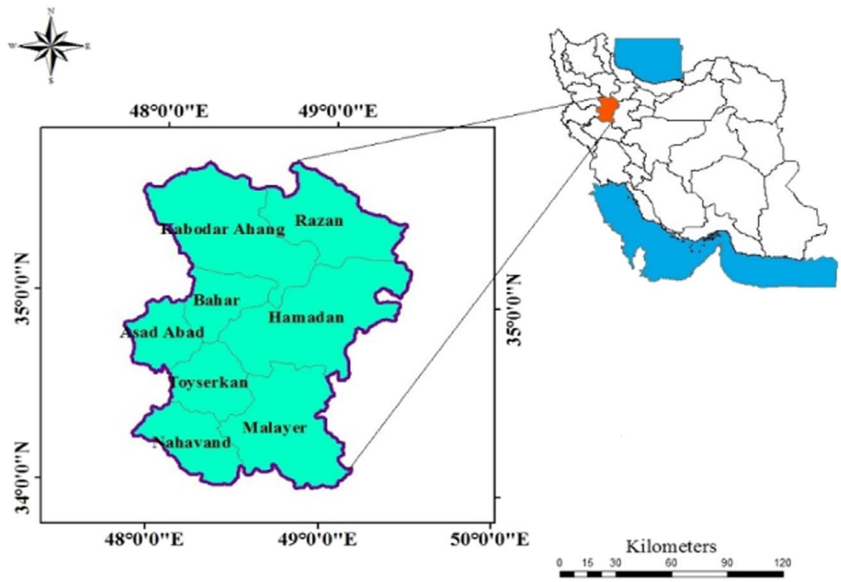

Fig. 1. Location of the study areas.

generally a true BL and is defined as 95% of the expected range of background concentration. The GBC has been shown to be the best approach to establish the concentrations of an element in natural soils (Kabata-Pendias et al., 1992; Dudka et al., 1995; Chen et al., 1999; Gil et al., 2004), thus BL is the GM, and the lower GBC was calculated as GM/GSD^2, while the upper GBC was calculated as the $GM \times GSD^2$ (GM: geometric mean, GSD: geometric standard deviation). The upper GBC was considered a reference value (RV). Reference value of a trace element can be obtained from either its BL or GBC (Gil et al., 2004, 2010; Ramos-Miras et al., 2011). Dudka et al. (1995) recommended the use of the upper limit of the GBC range as an RV to assess trace metal contamination in soils. These background measurements could represent natural concentrations in soils, a reference to determine local or regional variations in trace elements, or to anticipate potential hazards from polluting sources, or both (Kabata-Pendias et al., 1992; Alonso Rojo et al., 2004).

Natural background concentrations of trace elements in soils have been evaluated in several studies (Markert and Li, 1991; Yamasaki et al., 2001; Alonso Rojo et al., 2004; Bech et al., 2005; Horckmans et al., 2005; Tume et al., 2006a, 2006b; Roca-Perez et al., 2010; Papastergios et al., 2011; Ramos-Miras et al., 2011; Roca et al., 2012; McDowell et al., 2013; Oliveira et al., 2014; Gabos et al., 2014; Alfaro et al., 2015; Birani et al., 2015). Due to anthropogenic activities, it is often difficult to assess the natural background concentrations of trace elements in soils (Shah et al., 2012). Therefore, GBC has been determined in a given region within a certain time (Chen et al., 2001). In addition, BL of trace elements are dependent on the parent material, the weathering processes of soil, clay, and organic matter content. Therefore, BL of trace elements should be determined locally (Horckmans et al., 2005).

Studies on baseline concentrations and BL of trace elements in Iran are rare and very few works studied BL of trace elements such as Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in Iranian soils. Sayadi and Sayyed (2011) reported natural local background concentrations of Cd, Co, Cr, Cu, Ni, Pb and Zn in the soils of Tehran in Iran. Abbaslou et al. (2014) assessed trace element concentrations in soils of arid regions of southern Iran and background values were calculated in order to find soil contamination criteria and to estimate anthropogenic contributions. Esmaeili et al. (2014) calculated regional geochemical background and threshold value of trace elements in Esfahan province of Iran and indicated that Cu, Pb, Zn and Cd enrichment in agricultural soils.

This study aims to provide reference levels for trace elements in uncontaminated calcareous soils in Hamedan Province, western Iran. Therefore, the purposes of the present study were to: (1) determine the total concentrations of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in 100 natural soils (2) establish the BL of trace elements using different methods and (3) determine relationships between trace elements and soil properties, and among the various trace elements.

2. Materials and methods

2.1. Area description

Hamedan province is located in western Iran (longitudes 33° 59′ 11″ to 35° 44′ 27″ N and latitudes 47° 44′ 23″ to 49° 27′ 51″ E) with about 1.75 million inhabitants and an area of 19,368 km^2. The study area has a cold and semi-arid climate. The mean annual rainfall being approximately 300 mm which is occurred from October to May, with a maximum during November and February of each year. The mean monthly temperatures varying between − 4 and 25 °C, and the mean annual value is 11 °C. The annual potential evaporation far exceeds the annual rainfall with a mean annual amount of approximately estimated from 1975 to 2001, is 1505 mm for Hamedan city. Agriculture is a major industry and principal land use in Hamedan province. The soil of the area is mostly classified as Entisols and Inceptisols. Annual and perennial plants are the main plants in the studied area and some of the common plants are *Astragalus* spp., *Stipa barbata* Desf., *Euphorbia aellenii* Rech. F., *Lepidium latifolium* L., *Chenopodium botrys* L., *Chenopodium murale* L., *Acantholimon festucaceum* Boiss., *Phlomis orientalis* Mill., *Centaurea* spp., *Achillea setacea* Waldst, and Kit., and *Alhagi camelorum* Fich. (Jalali and Khanlari, 2008; Jalali and Sajadi Tabar, 2011).

The dominant and geological structure of area include alluvial terraces from the Quaternary period, orbitoline limestone, shale and marl from the late Cretaceous period, metamorphic sandstone from the Jurassic period and andesitic lava and reef limestone from late Paleogene and early Neogene periods (Soffianian et al., 2014).

2.2. Soil sampling

Soils were sampled from fifty sites under natural vegetation and without anthropogenic influence. Five different subsamples were collected at each sampling site from two depths: surface (0–0.2 m) and subsurface soil layers (0.21–0.40 m) using stainless steel augers and were mixed. Soil samples were stored in marked plastic bags and were transferred to a laboratory for analysis. Location of study areas was presented in Fig. 1.