International Journal of Plant and Environment
Vol. 3, No. 2 (2017), 01-07

Studies on Trace Elements Distributed in *Glycyrrhiza* Taxa in Hatay-Turkey

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Publication Info

Article history:
Received : 28.05.2017
Accepted : 30.06.2017
DOI : https://doi.org/10.18811/ijpen.v3i02.10431

Key words:
Contamination
Glycyrrhiza taxa
Heavy metals
Plants
Soils

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Abstract

Glycyrrhiza is a widely distributed plant used as herbal medicine in Turkey and other parts of the world. The roots and stolons have been used in the traditional herbal treatments for over 4000 years. In this investigation we have tried to determine some trace elements (chromium, copper, iron, manganese, nickel and zinc) in the plant parts (root, stem and leaves) of *Glycyrrhiza glabra* var. *glandulifera*, *G. flavescens* ssp. *flavescens* and *G. echinata* as well as the soil samples supporting these taxa in Hatay region of Turkey. The results of analysis have revealed that the minimum and maximum concentrations measured in the plant parts are chromium (0.0000-0.0590 ppm), copper (0.0465-0.4495 ppm), iron (0.4200-9.2650 ppm), manganese (0.0000-0.6910 ppm), nickel (0.0050-0.8400 ppm), and zinc (0.0000-0.7200 ppm). In the soil the concentrations of chromium, copper, iron, manganese, nickle and zinc vary between 0.0000-0.0393, 0.0725-1.9745, 1.1500-13.5400, 0.6700-24.2250, 0.0350-57.1700 and 0.0000-0.9400 ppm respectively. The aim of this study was to draw attention to the use of *Glycyrrhiza* taxa in traditional medicine. The levels of accumulation of trace elements in different parts of *Glycyrrhiza taxa* are different and depend on the habitat. The results obtained indicate that the values in the natural liquorice populations in general are less than toxic levels.

1. Introduction

The origin of trace elements (TEs) in soil may be either natural (lithogenic, non-anthropogenic) or anthropogenic (human-induced). Natural procedures that introduce TEs to soil include mineral weathering, volcanic eruptions, and erosion (if non-accelerated or non-human-induced) (Ozturk *et al*., 2015; Antoniadis *et al*., 2017a). On a large scale, the lithogenic derivation of TEs is the most important factor affecting total TE content on topsoils (Tóth *et al*., 2016). Anthropogenic inputs are related mainly to industrial activities, such as mining, smelting, electroplating, wastewater discharge, and aerial deposition of industrial fumes, as well as agriculture, such as use of wastes, fertilizers, and human-induced erosion (Fleming *et al*., 2013; Ma *et al*., 2013; Rinklebe and Shaheen, 2014; Ozturk *et al*., 2015; Antoniadis *et al*., 2017a). Although natural TE inputs are not unlikely, anthropogenic activities are the major causes of TE accumulation (Deng *et al*., 2004; Ok *et al*., 2011a,b; Shaheen *et al*., 2017a,b), especially in the geographical vicinity of the polluting industrial activities (Li *et al*., 2015; Ozturk *et al*., 2015). Concerns have thus been raised over the fate of TEs accumulated in soil; this may then increase the risk of leaching of the mobile fractions of TEs down the soil profile that would result in the contamination of water bodies and sediments (Shaheen and Rinklebe, 2014; Shaheen *et al*., 2017a). Also these accumulated TEs increase the possibility of their transfer to the human food chain over time (Alloway, 1995; Gall *et al*., 2015; Antoniadis *et al*., 2017b,c).

The accumulation of TEs depends mainly on the intensity of industrial activities and its duration. Global fluxes vary greatly, but they may range from < 1 g ha^{-1} $year^{-1}$ for Cd to as high as 20 g ha^{-1} $year^{-1}$ for abundant and often used TEs in industry (such as Pb and Zn) (Antoniadis *et al*., 2017a). However, in intense cases of aerial deposition due to heavy industrial activity, fluxes may even be up to one order of magnitude higher. Developed countries usually have a long history of TE deposition, but due to tight legislations, the intensity of TE deposition has decreased in recent decades (Antoniadis *et al*., 2017a). On the other hand, in developing countries the trend is opposite. The history of TE deposition is rather short, but its intensity high, and thus the rate of yearly TE accumulation can be considerabley high (Cherfi *et al*., 2014; Zu *et al*., 2014; Antoniadis *et al*., 2017a).

The accumulation of heavy metals in plants depends on various factors, such as distance from the pollution source, physical properties of heavy metals (e.g. mobility), emission intensity (e.g. traffic density), climatic factors (e.g. wind direction and force, precipitation and air circulation), soil and season types aerosol accumulation and topographical structures (Aksoy and Ozturk, 1996, 1997; Ozturk *et al*., 2015). Plants growing in contaminated areas mainly demonstrate visible symptoms on plant surfaces because of the heavy-metal accumulation in plant parts. However, some plants, or hyperaccumulators, are able to accumulate higher amounts of heavy metals in various plant tissues without toxicity symptoms; thereby, these plants cannot provide acceptable quantitative information on environmental pollution when compared with biomonitors (Prasad and Freitas, 2003; Ashraf *et al*., 2010; Ozturk *et al*., 2015). Thus, the selection of biomonitor plants is a very important initial step in research programmes aiming to decontaminate the polluted areas (Hakeem *et al*., 2015; Ozturk *et al*., 2015).

The aim of this study was to investigate the concentrations of elements like chromium, copper, iron, manganese, nickle and zinc in *Glycyrrhiza* taxa distributed in Hatay-Turkey.

2. Materials and Methods

2.1. Study area

The State of Antakya (Antiochia) in the upper Mesopotamian part of Turkey is located between 35°48' N and 37°00' N and between 35°46' E and 36°41' E in the most southern region of Turkey. The altitude varies from sea level to 2240 m. The Mediterranean Sea lies in its west, Syria in the south and east and Adana, Osmaniye and Gaziantep provinces in the North. The province is spread over an area of 5.559 km^2 and 46.1 percent of the land is mountain, 33.5 percent plain and 20.4 percent plateau and hillside (Altay *et al*., 2016; Karahan *et al*., 2016). The area is under the influence of the Mediterranean climate, annual average temperature varies between 15.1-20°C and average annual rainfall between 562.2-1216.3 mm, most of which falls in winter months (Anonymous, 1975-2008; Altay *et al*., 2016).

2.2. Sample collection, preparation and analytical techniques

Plant parts (root, stem and leaves) and soil samples were collected from 22 different localities in Hatay (Turkey). The number of samples per taxa was distributed as follows: *G. glabra* var. *glandulifera* (15), *G. flavescens* ssp. *flavescens* (5) and *G. echinata* (2). The location information of the collection sites is given below (Altay *et al*., 2016):

G. glabra* var. *glandulifera

G1: Samandağ-Çevlik Coast, roadside, 5 m, 36°03′02″N 35°57′56″E;

G2: Kırıkhan-Topboğazı Village, water channels, 96 m, 36°27′17.8″N 36°18′49.6″E;

G3: Kumlu-Uzunkavak Village, wheat field, 93 m, 36°28′34.5″N 36°27′38″E;

G4: Kırıkhan-Acarköy, water channels, 94 m, 36°31′49″N 36°25′ 03″E;

G5: Kırıkhan-Öz Soğuksu Village, hill slope, 127 m, 36°27′55.5″N 36°19′06.8″E;

G6: Reyhanlı-Konuklu Village, water channels, 80 m, 36°15′26.5″N 36°27′19.3″E;

G7: Reyhanlı-Alakuzu Village, roadside, 181 m, 36°17′14″N 36°38′23″E;

G8: Yayladağı-Üçırmak Village, olive field, 124 m, 35°58′40.2″N 36°11′37.4″E;

G9: Yayladağı-Karaköse Town, olive field, 370 m, 36°01′54.5″N 36°01′17.6″E;

G10: Altınözü-Tepehan Village, roadside, 430 m, 36°08′38″N 36°13′2.1″E;

G11: Altınözü-Akamber Village, wheat field, 282 m, 36°05′34.5″N 36°14′11.5″E;

G12: Erzin-Burnaz, sand dune, 7 m, 36°55′32″N 36°02′21.5″E;

G13: Harbiye-Sofular Village, wheat field, 461 m, 36°06′26″N 36°10′24.7″E;

G14: Antakya-I˙skenderun Highway, roadside, 95 m, 36°16′35.2″N 36°11′25″E;

G15: Antakya-Paşaköy, hill slope, 110 m, 36°22′09.6″N 36°14′09.7″E.

G. flavescens* ssp. *flavescens

F1: Samandağ-Çevlik coast, stony area, 23 m, 36°13′34.5″N 35°50′37″E;

F2: Antakya-Gülderen village, frigana, 578 m, 36°18′3.8″N 36°06′23.6″E;

F3: Kızıldag-near old radar, roadside, 1,087 m, 36°17′41″N 36°04′2.5″E;

F4: Antakya-Ballıöz village, roadside, 303 m, 36°14′44″N 36°04′12″E;

F5: Samandağ-Batıayaz village, *Pinus brutia* forest, 417 m, 36°11′14.5″N 35°59′05″E.

G. echinata

E1: Kırıkhan-I˙cada village, wheat field, 90 m, 36°28′0.7″N 36°23′52.9″E;

E2: Kırıkhan-Muratpas¸a village, water channels, 91 m, 36°28′34.5″N 36°27′38″E.

Soil samples were collected from 0-30 cm depth, brought to the laboratory, air dried and sieved using 2 mm mesh. Plant samples (root, stem and leaf) were dried in the oven at 80 °C for 24 h and milled (Altay *et al*., 2016). The chromium, copper, iron, manganese, nickle and zinc in both plant parts and soil samples were measured by Inductively Coupled Plasma Optical Emission Spectroscopy (Varian Liberty Series II).

3. Results and Discussion

The mean concentrations of chromium, copper, iron, manganese, nickle and zinc in plant parts and soil samples are presented in Tables 1-6.

The results of the analysis of *G. glabra* var. *glandulifera* (root, stem, leaf) collected during flowering season show that on dry weight basis the concentrations of chromium, copper, iron, manganese, nickle and zinc range between 0-0.0407, 0.0915-0.4495, 0.7850-3.9950, 0-0.1680, 0.0550-0.4300 and 0-0.2700 (ppm) in roots; 0-0.0105, 0.0804-0.2260, 0.4200-1.1700, 0-0.1835, 0.0100-0.0950 and 0-0.1650 (ppm) in stem; 0-0.0190, 0.0465-0.1605, 1.7600-5.8850, 0.1305-0.6190, 0.0050-0.3200 and 0.0500-0.4050 (ppm) in leaves, respectively. Moreover, chromium, copper, iron, manganese, nickle and zinc values in the soil samples measured at the same time ranged between 0-0.0393, 0.0955-1.9200, 1.1500-6.9200, 0.6700-9.6850, 0.3000-8.6650 and 0-0.6150 (ppm).

In the surface soil and in plants, contamination from various sources such as various industrial wastes and sewage sludges may increase the amount of chromium. The plant parts used here are from natural populations. In the light of the information obtained, *Glycyrrhiza* taxa in the study area are not exposed to any pollution by chromium.

Table 1: Chromium in plant parts and soil samples (ppm) (0 values mean that chromium is not detectable, material is clean).

Taxa	Soil	Root	Stem	Leaves
G1	0	0,0227	0,0105	0
G2	0	0,0160	0	0,0090
G3	0	0	0,0095	0
G4	0	0	0	0
G5	0	0,0361	0,0059	0
G6	0,0150	0,0105	0	0
G7	0,0040	0,0008	0	0,0045
G8	0,0120	0,0105	0	0
G9	0,0241	0,0013	0	0,0190
G10	0	0,0100	0,0053	0
G11	0,0393	0,0056	0	0
G12	0	0,0031	0,0095	0,0065
G13	0	0,0103	0	0
G14	0	0	0	0
G15	0,0035	0,0407	0	0
F1	0,0001	0	0	0,0182
F2	0,0150	0,0444	0,0141	0
F3	0	0,1352	0,0185	0,0085
F4	0,0205	0,0158	0,0115	0,0188
F5	0	0,0235	0,0201	0,0115
E1	0,0030	0,0590	0	0,0040
E2	0	0,0160	0,0017	0,0070

Table 2: Copper in plant parts and soil samples (ppm)

Taxa	Soil	Root	Stem	Leaves
G1	0,4895	0,1444	0,1480	0,0920
G2	0,6925	0,4112	0,1275	0,1270
G3	1,4275	0,1379	0,0996	0,0685
G4	0,8580	0,1388	0,1306	0,1175
G5	0,8525	0,1109	0,0865	0,0825
G6	1,9200	0,1540	0,1406	0,1080
G7	1,2485	0,2170	0,1977	0,1605
G8	1,1700	0,2125	0,1977	0,0920
G9	0,7875	0,1500	0,2260	0,1360
G10	0,6275	0,4495	0,1684	0,1000
G11	1,0450	0,2504	0,0811	0,0900
G12	0,0955	0,0953	0,0804	0,0835
G13	0,5835	0,0915	0,0867	0,0504
G14	0,6725	0,2075	0,1090	0,0765
G15	1,7310	0,1246	0,0835	0,0465
F1	0,5120	0,0894	0,0676	0,0915
F2	1,0342	0,1051	0,1202	0,1370
F3	0,1645	0,0877	0,1282	0,1345
F4	0,0725	0,0720	0,1188	0,0695
F5	0,8835	0,0867	0,1970	0,0860
E1	0,8705	0,2533	0,1030	0,0990
E2	1,9745	0,2712	0,1153	0,0925

Table 3: Iron in plant parts and soil samples (ppm)

Taxa	Soil	Root	Stem	Leaves
G1	4,3700	2,7500	0,4850	2,6250
G2	6,9200	3,0550	0,7300	5,8850
G3	1,3450	3,1500	0,6100	1,9900
G4	4,1550	3,9950	0,4950	5,1350
G5	1,1500	3,5500	0,5550	1,9950
G6	2,9735	3,2250	0,5250	3,2450
G7	4,3350	1,7800	0,4550	2,9500
G8	2,0750	1,2200	0,4550	2,3350
G9	3,7500	0,7850	0,6950	4,1800

Taxa	Soil	Root	Stem	Leaves
G10	4,9300	1,8350	0,5500	1,7600
G11	2,8150	2,5750	0,5050	3,0900
G12	1,3800	2,0900	0,6500	4,9000
G13	3,3700	1,8300	1,1700	2,4250
G14	4,7250	3,6550	0,7000	3,7250
G15	5,3700	3,2050	0,4200	3,1675
F1	12,8800	2,3900	0,6500	1,5550
F2	9,8200	9,2650	0,8950	1,9800
F3	13,5400	4,4700	3,1000	5,2500
F4	7,5800	3,8450	0,5650	2,8200
F5	6,6500	2,8250	0,8700	1,3700
E1	3,2000	3,9500	1,6950	3,1600
E2	1,5500	2,2950	0,7150	2,7100

Table 4: Manganese in plant parts and soil samples (ppm)

Taxa	Soil	Root	Stem	Leaves
G1	3,6750	0,0695	0	0,2010
G2	3,3350	0,0370	0,0410	0,3775
G3	7,2000	0,0785	0,0580	0,4140
G4	5,5500	0,0955	0,0540	0,4060
G5	5,4350	0,1680	0,1835	0,6190
G6	4,9450	0,1365	0,0340	0,3085
G7	6,9850	0,0300	0	0,4125
G8	4,5350	0	0	0,1305
G9	2,6700	0	0,0035	0,1935
G10	0,6700	0,0025	0,0015	0,3643
G11	3,2000	0,0190	0,0340	0,3680
G12	2,0500	0,1255	0,0805	0,6115
G13	5,4850	0,0140	0,0375	0,3535
G14	1,6430	0	0,0300	0,2405
G15	9,6850	0,1225	0,0645	0,4365
F1	24,2250	0,1170	0,0080	0,2400
F2	11,4800	0,3110	0,0625	0,2190
F3	9,8650	0,6910	0,1405	0,3110
F4	1,0550	0,1585	0,0445	0,3335
F5	4,7850	0,1490	0,0330	0,2620
E1	4,2350	0,1205	0,0155	0,2895
E2	2,6750	0,1165	0,0495	0,3360

Table 5: Nickle in plant parts and soil samples (ppm)

Taxa	Soil	Root	Stem	Leaves
G1	1,7000	0,1700	0,0350	0,0600
G2	1,2900	0,0600	0,0365	0,0700
G3	1,4650	0,4300	0,0300	0,0200
G4	3,9250	0,3650	0,0550	0,3200
G5	1,7000	0,3950	0,0250	0,0275
G6	1,0700	0,0700	0,0100	0,0650
G7	1,0500	0,0750	0,0950	0,0650
G8	1,8800	0,1700	0,0950	0,0650
G9	0,9200	0,0800	0,0900	0,0900
G10	2,8500	0,0650	0,0325	0,0820
G11	1,2550	0,0600	0,0195	0,0350
G12	0,3000	0,2050	0,0285	0,0350
G13	4,2050	0,0850	0,0600	0,0613
G14	1,4300	0,0550	0,0700	0,0050
G15	8,6650	0,2500	0,0400	0,0475
F1	57,1700	0,8400	0,0950	0,0700
F2	11,4400	0,2850	0,1100	0,1100
F3	36,6950	1,3800	0,3050	0,4400
F4	0,0350	0,0400	0,0350	0,0195
F5	2,7800	0,0250	0,0800	0,0350
E1	4,3550	0,2050	0,0300	0,0550
E2	1,1800	0,1000	0,0800	0,0900

Table 6: Zinc in plant parts and soil samples (ppm)

Taxa	Soil	Root	Stem	Leaves
G1	0,0300	0,0550	0,0550	0,2100
G2	0	0,2700	0,0950	0,1750
G3	0,2450	0,0002	0,0002	0,0850
G4	0,5250	0,0020	0,0750	0,1700
G5	0,1200	0	0,0010	0,2200
G6	0,0200	0,0350	0	0,0950
G7	0,2750	0,0550	0,0600	0,3650
G8	0,6150	0,0800	0,0600	0,1750
G9	0,1800	0,0300	0,1650	0,1000
G10	0,2300	0,0500	0,0750	0,1150
G11	0,2100	0,1050	0,0050	0,2200
G12	0,2300	0	0	0,1050
G13	0,1650	0	0	0,0500
G14	0,0110	0,0500	0,0130	0,1500
G15	0,4800	0	0	0,4050
F1	0,9400	0,1900	0,0750	0,0600
F2	0,0800	0,2450	0,1550	0,3250
F3	0,2150	0,1800	0,1300	0,2550
F4	0	0,0325	0,2650	0,3600
F5	0,0100	0,0750	0,7200	0,2000
E1	0,0700	0,0850	0	0,3550
E2	0,3500	0,1000	0,0040	0,1950

The results of the analysis of *G. flavescens* ssp. *flavescens* (root, stem, leaf) collected during flowering season show that on dry weight basis the values of chromium, copper, iron, manganese, nickle and zinc range between 0-0.1352, 0.0720-0.1051, 2.3900-9.2650, 0.1170-0.6910, 0.0250-1.3800 and 0.0325-0.2450 (ppm) in roots; 0-0.0201, 0.0676-0.1970, 0.5650-3.1000, 0.0080-0.1405, 0.0350-0.3050 and 0.0750-0.7200 (ppm) in stem; 0-0.0188, 0.0695-0.1370, 1.3700-5.2500, 0.2190-0.3335, 0.0195-0.4400 and 0.0600-0.3600 (ppm) in leaves, respectively. Their concentrations in the soil samples range between 0-0.0205, 0.0725-1.0342, 6.6500-13.5400, 1.0550-24.2250, 0.0350-57.1700 and 0-0.9400 (ppm) respectively.

The results of analysis of *G. echinata* (root, stem, leaf) collected during flowering season depict that on dry weight basis the values of chromium, copper, iron, manganese, nickle and zinc range between 0.0160-0.0590, 0.2533-0.2712, 2.2950-3.9500, 0.1165-0.1205, 0.1000-0.2050 and 0.0850-0.1000 (ppm) in roots; 0-0.0017, 0.1030-0.1153, 0.7150-1.6950, 0.0155-0.0495, 0.0300-0.0800 and 0-0.0040 (ppm) in stem; 0.0040-0.0070, 0.0925-0.0990, 2.7100-3.1600, 0.2895-0.3360, 0.0550-0.0900 and 0.1950-0.3350 (ppm) in leaves, respectively. In the soil samples the values of chromium, copper, iron, manganese, nickle and zinc were measured as 0-0.0030, 0.8705-1.9745, 1.5500-3.2000, 2.6750-4.2350, 1.1800-4.3550 and 0.0700-0.3500 (ppm) respectively.

Chromium compounds are highly toxic to plants and are detrimental for their growth and development (Shanker *et al*., 2005). Although low concentrations are not affective, it is toxic to higher plants at 100 ppm dw (Davies *et al*., 2002). The concentration of chromium in plants in the environment vary between 0.1-0.5 ppm (Blum *et al*., 2012). The normal limits of copper in plant tissues should lie in the range of 3-12 ppm (Blum *et al*., 2012). The normal limits of iron, manganes, nickle and zinc in plants should lie between 220-1200, 20-400, 0.2-2 and 20-100 ppm (Prasad, 2008; Blum *et al*., 2012).

The normal concentrations in soils are reported to range between chromium10-50 ppm, copper 10-40 ppm, iron 30-500 ppm, manganese 300-1000 ppm, nickle 10-50 ppm, and zinc 10-300 ppm (Kabata-Pendias and Mukherjee, 2007; Prasad, 2008; Blum *et al*., 2012).

These findings enlighten the fact that the values of chromium, copper, iron, manganese, nickle and zinc in the plant samples (root, stem, leaves) of *Glycyrrhiza* taxa (*G. glabra* var. *glandulifera*, *G. flavescens* ssp. *flavescens*, *G. echinata*) and the soils supporting these plants are lower than normal range. Only in *G. flavescens* ssp. *flavescens* soils the values for nickle are higher than others, the reason being these plants flourish on serpentine soils.

4. Conclusion

Trace elements play an important role in the environmental pollution (Prasad, 2008). Phytoremediation can be employed for removing excessive toxic elements from the soil (Blaylock and Huang, 2000; Ashraf *et al*., 2010; Dağhan and Ozturk, 2015; Hakeem *et al*., 2015; Ozturk *et al*., 2015; Sabir *et al*., 2015). One of the practices in this connection is to undertake measurements via biomonitoring. This can be done by analyzing soils and plant samples at regular intervals. Monitoring of heavy metals in the ecosystems surrounding us with the help of soils and plants gives positive results due to their immobility. Some species are accumulators or even hyperaccumulators, while others are excluders. The disadvantage with the plant biomonitors is that their reaction not only depends on the quantity of the substance to be monitored but also other morphological features of plant species as well as soil type, nutrient status and moisture, nutrient status of the soil and climatic parameters.

Our results clearly depict that no heavy metal pollution in plant and soil specimens collected from the research area has been observed. The plant material collected is safe to use for herbal preparations.

Acknowledgments

This study was supported by Scientific Research Commission of Mustafa Kemal University, Hatay, Turkey (Project No: 1204 Y 0130).

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