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## Metal hyperaccumulating Brassicaceae from the ultramafic area of Yahyalı in Kayseri province, Turkey

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**Abstract** Many of the plants found in serpentine areas are endemics and they may accumulate Ni at high concentration. High accumulation of Cr is rare, or in some views, never properly demonstrated. Generally, a very small proportion of any serpentine flora shows high accumulation of Ni, in some serpentine areas Ni accumulators are completely absent. There are approximately 570 hyperaccumulator plant species found on earth, 450 of them are Ni hyperaccumulators. A few of the Ni accumulators have potential for phytoremediation or phytomining. In the present study, 19 different Brassicaceae members growing in serpentine habitats in the district of Yahyalı, Kayseri province, Turkey viz., members of genera *Aethionema*, *Alyssum*, *Arabis*, *Hel-dreichia*, *Hesperis*, *Iberis*, *Isatis*, *Microthlaspi*, *Odontar-rhena*, *Pseudosempervivum* and *Thlaspi* were investigated. Nickel concentrations in the soil and underground and aboveground parts of plants were determined by using ICP-OES. It was observed that Ni concentrations of seven taxa (*Odontarrhena muralis*, *O. oxycarpa*, *Isatis cappadocica* subsp. *cappadocica*, *Microthlaspi perfoliatum*, *Pseudosempervivum sempervivum*, *Thlaspi triangulare*, *Thlaspi rosulare*) reach the threshold criterion of 1,000 mg kg<sup>-1</sup> for Ni hyperaccumulation. In this study Ni concentrations in aboveground tissues of *I. cappadocica* subsp. *cappadocica* are determined as 5,587 mg kg<sup>-1</sup> (in dry weight). Accordingly, it is suggested that this taxon be added to the list of Ni hyperaccumulator plants.

**Keywords** Serpentine · Ni-hyperaccumulator · *Isatis cappadocica* · Kayseri

### Introduction

The soils derived from ultramafic rocks often have a unique biogeochemistry. Serpentine soils are found in many parts of the world e.g. California, New Caledonia, Cuba, central Brazil, parts of Mediterranean Europe and Turkey. These soils have some characteristic properties: (1) deficient in essential plant nutrients such as Ca, K, and P, (2) rich in trace metal concentrations like Ni, Cr and Fe, (3) a high magnesium/calcium (Mg/Ca) quotient (Proctor and Woodell 1975; Brooks 1987; Roberts and Proctor 1992; Reeves and Adıgüzel 2008). Therefore, the serpentine vegetation is different from the vegetation of the surrounding rocks and corresponding soils. In addition, the some ultramafic areas are very rich in terms of endemic (Proctor and Woodell 1971).

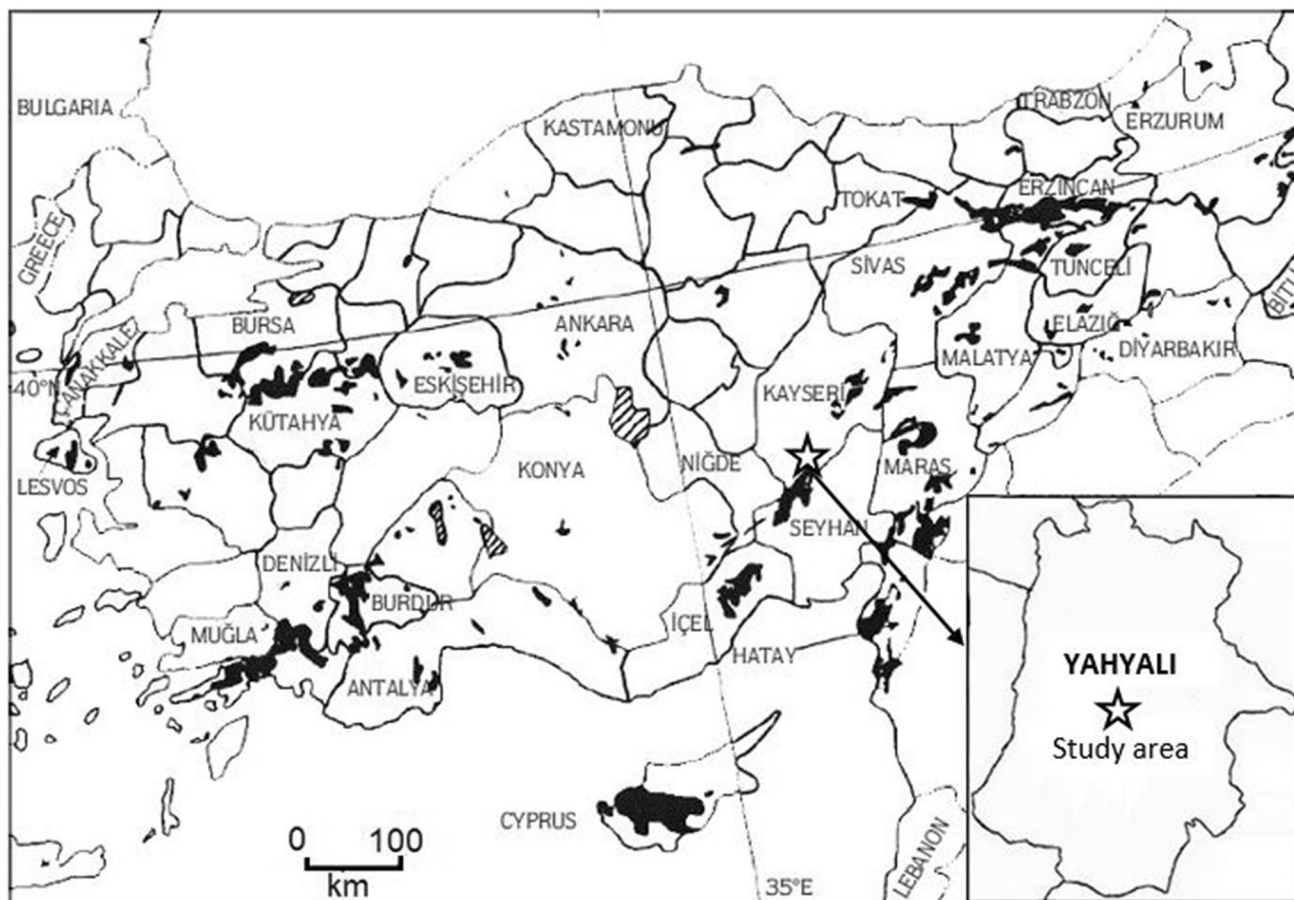
Serpentinophytes are model organisms that can be used in phytoremediation technology and in the resolution of environmental problems by removing toxic doses of trace metals (Brooks 1987; Chaney et al. 2005). These plants can accumulate trace metals in their roots and shoots, at a level greater than that in the soil (Raskin et al. 1994; Sheoran et al. 2013). In other words, plants that can tolerate high metal concentration by detoxifying metal collected in organs such as stem and leaf are known as hyperaccumulators. Some of the earlier dry matter concentration thresholds for hyperaccumulation of trace elements in the terrestrial plants have been revised more recently. Recommendations by Krämer (2010) and van der Ent et al. (2013) include: Cd > 100 mg kg<sup>-1</sup>; Co, Cu 300 mg kg<sup>-1</sup>; Ni 1,000 mg kg<sup>-1</sup>; Zn 3,000 mg kg<sup>-1</sup>; Mn 10,000 mg kg<sup>-1</sup>.

More than 570 plant species have been recorded as trace metal or metalloid hyperaccumulators worldwide. Of these, at least 450 are Ni hyperaccumulators (van der Ent et al. 2013). Brassicaceae is the one of the most important families in which Ni hyperaccumulators have

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**Fig. 1** Map of Turkey, showing areas of Ultramafic geology (in black) and the study area. The map is adopted from Reeves and Adıgüzel (2004)

been found (Reeves and Adıgüzel 2008). The Brassicaceae family is of particular interest, because it includes the largest numbers of species capable of accumulating exceptionally high content of compounds of Ni, Zn and Cd (Krämer 2010).

According to Flora of Turkey records, it is reported that there are 248 plants specific to serpentine, of which 119 are serpentinophytes and 129 are serpentinophages (Özdeniz et al. 2017). 55 serpentine areas in Turkey have been examined and 60 Ni-accumulators and more than 40 serpentine-endemics have been reported from these areas (Adıgüzel and Reeves 2012). The majority of these species belong to the genera *Alyssum*, *Bornmuellera*, *Cochlearia* and *Thlaspi* under the Brassicaceae family (Brooks et al. 1979; Reeves and Brooks 1983; Reeves et al. 1983; Reeves 1988; Reeves and Adıgüzel 2004, 2008). Also the Turkish species of *Cochlearia* that are Ni hyperaccumulators are now placed in the genus *Pseudosempervivum* as *P. aucheri* (Boiss.) Pobed. and *P. sempervivum* (Boiss. & Bal.) Pobed., and *Thlaspi* s.l. has been broken up into several genera, several of which (including *Noccaea*, *Microthlaspi* and some species still classified under *Thlaspi*) contain Ni hyperaccumulators (Reeves and Adıgüzel 2004, 2008). *Isatis pinmatiloba* and *Noc-*

*caea camlikensis* are the most recent recorded species of Ni hyperaccumulators from Turkey serpentine soils (Altınözlü et al. 2012; Aksoy et al. 2015).

In this study of some of the Brassicaceae of serpentine areas in the Aladağlar district of Yahyalı (Kayseri) we aimed to investigate trace metal concentrations in underground and aboveground tissues and soil of 19 taxa growing on ultramafic soils.

## Materials and methods

### Materials

The study site is quite extensive and not uniform in its topography and vegetation. 70% of the study area is mountainous and varies in terms of vegetation cover. The large areas to the south of the area are covered with forest, while in the north the steppe vegetation is dominant. The ultramafic area of Yahyalı in Kayseri province in Turkey has a large number of limestone-serpentine contacts. The most important ultramafic rocks in this area are located in the east and south side of Aladağ. The study area is lies between 37°46–55°N and 35°19–30°E and at altitude 700–2000 m (Fig. 1).

**Table 1** Study area and plant collection localities

| Sites   | GPS co-ordinates            | Altitude (m) | Collected species   |
|---|-----------------------------|--------------|---|
| Site 1<br>4 km from Çamlıca,<br>Koyuncu mines over                      | 37°54.827'N,<br>35°27.806'E | 1402         | <i>Aethionema armenum</i><br><i>Arabis nova</i><br><i>Isatis cappadocica</i> subsp. <i>cappadocica</i><br><i>Pseudosempervivum aucheri</i> *<br><i>Thlaspi oxyceras</i> |
| Site 2<br>Çamlıca—Ulupınar, Abbastepesi location                        | 37°53.793'N,<br>35°27.397'E | 1635         | <i>Aethionema speciosum</i> subsp. <i>speciosum</i><br><i>Odontarrhena oxycarpa</i> *   |
| Site 3<br>Taşoluk location-Değirmenocağı village,<br>Gökyar mining area | 37°52.175'N,<br>35°26.225'E | 1561         | <i>Odontarrhena muralis</i><br><i>Hesperis anatolica</i> *  |
| Site 4<br>Çamlıca-Ulupınar, summit of Kayapınar location                | 37°53.256'N,<br>35°26.844'E | 1765         | <i>Alyssum pseudomouradicum</i> *   |
| Site 5<br>2 km from Ulupınar village- Acısu location                    | 37°47.134'N,<br>35°19.233'E | 1085         | <i>Alyssum strigosum</i> subsp. <i>strigosum</i><br><i>Arabis aucheri</i>   |
| Site 6<br>Çamlıca-Ulupınar,<br>near the Ulupınar                        | 37°53.153'N,<br>35°23.604'E | 1387         | <i>Arabis alpina</i> subsp. <i>alpina</i><br><i>Microthlaspi perfoliatum</i>  |
| Site 7<br>near the Çubukharmanı   | 37°46.712'N,<br>35°25.827'E | 810          | <i>Thlaspi triangulare</i><br><i>Iberis simplex</i><br><i>Pseudosempervivum sempervivum</i> *   |
| Site 8<br>Çubukharmanı-Balçıcakırı                                      | 37°47.753'N,<br>35°29.115'E | 1754         | <i>Heldreichia bupleurifolia</i> subsp.<br><i>rotundifolia</i> var. <i>rotundifolia</i> *<br><i>Thlaspi rosulare</i> *  |

\*Endemic species

Soils and specimens of the following plant taxa were collected from this serpentine habitat in 2012 and 2013: *Aethionema armenum* Boiss. (J. Çelik 1060), *Aethionema speciosum* Boiss. & A. Huet subsp. *speciosum* (J. Çelik 1063), *Alyssum pseudomouradicum* Hausskn. & Bornm. ex Baumg. (J. Çelik 1078), *Alyssum strigosum* Banks & Sol. subsp. *strigosum* (J. Çelik 1018), *Arabis alpina* L. subsp. *alpina* (J. Çelik 1005), *Arabis aucheri* Boiss. (J. Çelik 1017), *Arabis nova* Vill. (J. Çelik 1042), *Heldreichia bupleurifolia* Boiss. subsp. *rotundifolia* (Boiss.) Parolly, Nordt & Mumm var. *rotundifolia* (J. Çelik 1114), *Hesperis anatolica* A. Duran (J. Çelik 1052), *Iberis simplex* DC. (J. Çelik 1029), *Isatis cappadocica* Desv. subsp. *cappadocica* (J. Çelik 1044), *Microthlaspi perfoliatum* (L.) F. K. Mey (J. Çelik 1006), *Odontarrhena muralis* (Waldst. & Kit) Endl. (= *Alyssum murale*) (J. Çelik 1093), *Odontarrhena oxycarpa* (Boiss. & Balansa) Španiel, Al-Shehbaz, D. A. German & Marhold (= *Alyssum oxycarpum*) (J. Çelik 1068), *Pseudosempervivum aucheri* (Boiss.) Pobed. (J. Çelik 1045), *Pseudosempervivum sempervivum* (Boiss. & Balansa) Pobed. (J. Çelik 1036), *Thlaspi triangulare* (F. K. Meyer) Greuter & Burdet. (J. Çelik 1034), *Thlaspi oxyceras* (Boiss.) Hedge (J. Çelik 1043) and *Thlaspi rosulare* Boiss. & Balansa (J. Çelik 1112) (Table 1). The specimens collected were deposited in the Herbarium of Akdeniz University.

### Sampling

Soils were taken from the 0–5 cm zone, returned to the laboratory, sieved with a standard 4 mm sieve and air-dried. At least 15–30 adult plants were randomly se-

lected and collected from each site. Five plants were retained as herbarium specimens. Other plants from each site were divided into above- and below-ground parts. These were transferred to the laboratory in plastic bags. Plant samples were washed with tap water, followed by deionized water. They were dried in an oven (80 °C) until constant weight and brittleness. The samples were subsequently ground with a pestle and mortar. Homogenized plant materials and soil samples were then stored in clean paper bags before heavy-metal analysis.

### Chemical and statistical analyses

Soil samples (0.5 g dry weight) were digested with 10 mL of pure HNO<sub>3</sub> (65%), using a CEM–MARS 5 (CEM Corporation, Matthews, NC, USA) microwave digestion system (digestion conditions were the following: maximum power 1200 W; power 100%; ramp time 20 min, pressure 180 psi; temperature 180 °C; and hold time 10 min). After digestion, the volume of each sample was adjusted to 25 mL by using double-deionized water. Homogenized plant samples (0.5 g dry weight) were also prepared using the same procedure as for heavy-metal analysis. The soil and plant samples were analyzed for Ni, Cr, Cu, Zn and Fe by inductively coupled plasma–optical emission spectroscopy (ICP–OES; Varian-Liberty II Varian Australia Pty Ltd, Mulgrave, Vic., Australia). All chemicals were of analytical reagent grade. Standard peach leaves (NIST, SRM-1547) were used as a reference material. All analytical procedures were also performed using this reference material. Soil and plant samples were digested in triplicate and analyzed. The

means and standard deviation (SD) of the data were calculated by using the SPSS 15.00 version package (SPSS Inc., Chicago, IL, USA).

## Results

The concentrations of trace metals (Ni, Co, Cr, Cu, Fe, Pb, Zn) in soil, aboveground and underground parts of the plants are given in Tables 2 and 3.

Ni concentration in the studied plants ranged from 8 to 8,100 mg kg<sup>-1</sup> in the above ground (AG) parts and 10–17,000 mg kg<sup>-1</sup> in the underground (UG) parts. The Ni concentrations in the dry weight of the aboveground parts of plants were found as follows: 2,497 mg kg<sup>-1</sup> in *Odontarrhena muralis*, 1,873 mg kg<sup>-1</sup> in *O. oxycarpa*, 8,085 mg kg<sup>-1</sup> in *Thlaspi triangulare*, 5,587 mg kg<sup>-1</sup> in *Isatis cappadocica* subsp. *cappadocica*, 2,270 mg kg<sup>-1</sup> in *Microthlaspi perfoliatum* (= *Thlaspi perfoliatum*), 8,100 mg kg<sup>-1</sup> in *Pseudosempervivum sempervivum*

(= *Cochlearia sempervivum*) and 4,563 mg kg<sup>-1</sup> in *Thlaspi rosulare*. Ni concentrations in the aboveground parts of these seven taxa are higher than both normal values and other taxa (Table 2). Mean concentration of Ni in the dry weight of the underground (roots) parts of plants was up to 6,390 mg kg<sup>-1</sup> in *Odontarrhena muralis*, 3,408 mg kg<sup>-1</sup> in *O. oxycarpa*, 17,000 mg kg<sup>-1</sup> in *Thlaspi triangulare*, 1,010 mg kg<sup>-1</sup> in *Microthlaspi perfoliatum*, 8,173 mg kg<sup>-1</sup> in *Pseudosempervivum aucheri*, 12,600 mg kg<sup>-1</sup> in *P. sempervivum*, 12,200 mg kg<sup>-1</sup> in *Thlaspi oxyceras* and 5,813 mg kg<sup>-1</sup> in *T. rosulare* (Table 2).

The concentrations of Ni in the aboveground and underground parts of *T. rosulare* and *T. oxyceras* collected from Yahyalı are 4,563–5,813 mg kg<sup>-1</sup> and 33–12,000 mg kg<sup>-1</sup> respectively (Table 2). The highest Ni concentration in a *Thlaspi* species was 8,085 mg kg<sup>-1</sup> in *T. triangulare* from Yahyalı. Also in dry of matter aboveground parts of *Microthlaspi perfoliatum* (= *Thlaspi perfoliatum*) a concentration of 2,270 mg kg<sup>-1</sup> was

**Table 2** Mean concentration of trace metals in underground and aboveground parts of plants collected from serpentine in Yahyalı (mg kg<sup>-1</sup> dry weight ± SD)

| Species                               | Plant parts | Ni                | Cr         | Cu         | Fe           | Zn         |
|---------------------------------------|-------------|-------------------|------------|------------|--------------|------------|
| <i>Aethionema armenum</i>             | AG          | 26 ± 0.2          | 5 ± 0.2    | 5.5 ± 0.05 | 867 ± 5      | 19 ± 0.4   |
|                                       | UG          | 98 ± 2            | 9 ± 0.1    | 4.4 ± 0.2  | 2,720 ± 41   | 15 ± 0.2   |
| <i>Aethionema speciosum</i>           | AG          | 593 ± 4           | 3.5 ± 0.02 | 1.7 ± 0.1  | 181 ± 3      | 16 ± 0.3   |
|                                       | UG          | 481 ± 8           | 6.4 ± 0.6  | 5.5 ± 0.1  | 1,198 ± 24   | 32 ± 0.1   |
| <i>Alyssum pseudomouradicum*</i>      | AG          | 12 ± 0.1          | 4 ± 0.02   | 1.4 ± 0.05 | 461 ± 1.1    | 10 ± 0.02  |
|                                       | UG          | 69 ± 1.1          | 5.8 ± 0.1  | 5.8 ± 0.1  | 4,014 ± 15   | 13 ± 0.02  |
| <i>Alyssum strigosum</i>              | AG          | 8 ± 0.1           | 5.4 ± 0.0  | 5.2 ± 0.02 | 902 ± 8      | 15 ± 0.3   |
|                                       | UG          | 10 ± 0.1          | 6.8 ± 0.05 | 5.9 ± 0.0  | 906 ± 16     | 11 ± 0.2   |
| <i>Arabis alpina</i>                  | AG          | 52 ± 0.2          | 10 ± 0.5   | 3 ± 0.1    | 1,765 ± 22   | 19 ± 0.3   |
|                                       | UG          | 212 ± 2.1         | 27 ± 0.6   | 4.2 ± 0.05 | 6,061 ± 20   | 21 ± 0.2   |
| <i>Arabis aucheri</i>                 | AG          | 19 ± 0.2          | 8.2 ± 0.2  | 7.7 ± 0.1  | 2,100 ± 70   | 21 ± 0.3   |
|                                       | UG          | 12 ± 0.1          | 5.6 ± 0.1  | 2.1 ± 0.02 | 504 ± 6      | 6.2 ± 0.05 |
| <i>Arabis nova</i>                    | AG          | 28 ± 0.3          | 5 ± 0.02   | 3 ± 0.02   | 573 ± 4      | 10.2 ± 0.1 |
|                                       | UG          | 89 ± 0.6          | 16 ± 0.5   | 9.4 ± 0.02 | 8,864 ± 26   | 16.3 ± 0.2 |
| <i>Heldreichia bupleurifolia*</i>     | AG          | 12 ± 0.1          | 4.3 ± 0.07 | 1.7 ± 0    | 315 ± 2.5    | 14.3 ± 0.1 |
|                                       | UG          | 84 ± 1            | 15.4 ± 0.2 | 4.7 ± 0.1  | 2,363 ± 36   | 29 ± 0.1   |
| <i>Hesperis anatolica*</i>            | AG          | 133 ± 0.4         | 13.2 ± 0.1 | 4 ± 0.05   | 3,035 ± 9.4  | 30 ± 0.3   |
|                                       | UG          | 175 ± 1           | 6.6 ± 1    | 11 ± 0.2   | 3,132 ± 66   | 5 ± 0.4    |
| <i>Iberis simplex</i>                 | AG          | 51 ± 1            | 9 ± 0.1    | 3 ± 0.05   | 1,680 ± 0.8  | 20 ± 0.3   |
|                                       | UG          | 59 ± 1            | 10.6 ± 0.2 | 2.2 ± 0.02 | 1,716 ± 12.7 | 33 ± 0.3   |
| <i>Isatis cappadocica</i>             | AG          | <b>5,587</b> ± 21 | 5.4 ± 0.1  | 3.7 ± 0.05 | 838 ± 8.5    | 50 ± 1     |
|                                       | UG          | 267 ± 2           | 27 ± 0.1   | 9 ± 0.2    | 9,646 ± 54   | 35 ± 0.6   |
| <i>Microthlaspi perfoliatum</i>       | AG          | <b>2,270</b> ± 38 | 10 ± 0.4   | 4 ± 0.1    | 1,709 ± 34   | 30 ± 0.2   |
|                                       | UG          | 1,010 ± 11        | 17 ± 0.2   | 4 ± 0.05   | 3,690 ± 39   | 31 ± 0.4   |
| <i>Odontarrhena muralis</i>           | AG          | <b>2,497</b> ± 12 | 4.7 ± 0.1  | 2.6 ± 0.02 | 1,035 ± 5    | 45 ± 0.4   |
|                                       | UG          | 6,390 ± 9         | 9 ± 0.3    | 8.2 ± 0.2  | 4,714 ± 15   | 77 ± 1.2   |
| <i>Odontarrhena oxycarpa*</i>         | AG          | <b>1,873</b> ± 25 | 4 ± 0.02   | 2 ± 0.0    | 864 ± 12     | 28 ± 0.7   |
|                                       | UG          | 3,408 ± 41        | 8 ± 0.1    | 7.4 ± 0.02 | 7,837 ± 69   | 77 ± 1.4   |
| <i>Pseudosempervivum aucheri*</i>     | AG          | 101 ± 2           | 4.8 ± 0.0  | 2.4 ± 0.02 | 1,246 ± 6.5  | 14 ± 0.1   |
|                                       | UG          | 8,173 ± 106       | 7 ± 0.07   | 8.1 ± 0.15 | 1,924 ± 23   | 63 ± 0.4   |
| <i>Pseudosempervivum sempervivum*</i> | AG          | <b>8,100</b> ± 4  | 3 ± 0.0    | 4 ± 0.02   | 159 ± 1.1    | 68 ± 1     |
|                                       | UG          | 12,600 ± 156      | 12 ± 0.1   | 12.4 ± 0.2 | 2,940 ± 38   | 90 ± 0.4   |
| <i>Thlaspi oxyceras</i>               | AG          | 33 ± 1.2          | 4 ± 0.17   | 2.8 ± 0.05 | 268 ± 5      | 14 ± 0.4   |
|                                       | UG          | 12,200 ± 236      | 23 ± 0.4   | 9 ± 0.07   | 7,053 ± 28   | 80 ± 1.2   |
| <i>Thlaspi rosulare*</i>              | AG          | <b>4,563</b> ± 21 | 9 ± 0.02   | 1.6 ± 0.02 | 127 ± 6      | 30 ± 0.3   |
|                                       | UG          | 5,813 ± 117       | 29 ± 0.3   | 6.2 ± 0.05 | 6,500 ± 71   | 74.3 ± 0.3 |
| <i>Thlaspi triangulare</i>            | AG          | <b>8,085</b> ± 3  | 5.1 ± 0.02 | 3.7 ± 0.07 | 742 ± 5      | 109 ± 2.3  |
|                                       | UG          | 17,000 ± 72       | 16 ± 0.4   | 11.4 ± 0.2 | 4,394 ± 52   | 159 ± 0.3  |

AG aboveground, UG underground

\*Endemic species

Bold values are represented the hyperaccumulator plants

**Table 3** Mean concentration of trace metal in serpentine soil of Yahyalı (mg kg<sup>-1</sup> dry weight)

| Species                               | Ni    | Cr    | Cu  | Fe     | Zn  |
|---------------------------------------|-------|-------|-----|--------|-----|
| <i>Aethionema armenum</i>             | 2,806 | 166   | 11  | 28,500 | 44  |
| <i>Aethionema speciosum</i>           | 2,387 | 214   | 17  | 28,400 | 69  |
| <i>Alyssum pseudomouradicum*</i>      | 2,387 | 214   | 17  | 28,400 | 69  |
| <i>Alyssum strigosum</i>              | 772   | 347   | 107 | 28,500 | 101 |
| <i>Arabis alpina</i>                  | 3,092 | 623   | 24  | 28,500 | 87  |
| <i>Arabis aucheri</i>                 | 772   | 347   | 107 | 28,500 | 101 |
| <i>Arabis nova</i>                    | 2,806 | 166   | 11  | 28,500 | 44  |
| <i>Heldreichia bupleurifolia*</i>     | 3,985 | 716   | 20  | 28,400 | 95  |
| <i>Hesperis anatolica*</i>            | 2,860 | 175   | 25  | 28,400 | 69  |
| <i>Iberis simplex</i>                 | 4,209 | 1,110 | 37  | 28,300 | 124 |
| <i>Isatis cappadocica</i>             | 2,806 | 166   | 11  | 28,500 | 44  |
| <i>Microthlaspi perfoliatum</i>       | 3,092 | 623   | 24  | 28,500 | 87  |
| <i>Odontarrhena muralis</i>           | 2,860 | 175   | 25  | 28,400 | 69  |
| <i>Odontarrhena oxycarpa*</i>         | 2,387 | 214   | 17  | 28,400 | 69  |
| <i>Pseudosempervivum aucheri*</i>     | 2,806 | 166   | 11  | 28,500 | 44  |
| <i>Pseudosempervivum sempervivum*</i> | 4,209 | 1,110 | 37  | 28,300 | 124 |
| <i>Thlaspi oxyceras</i>               | 2,806 | 166   | 11  | 28,500 | 44  |
| <i>Thlaspi rosulare*</i>              | 3,986 | 716   | 20  | 28,400 | 95  |
| <i>Thlaspi triangulare</i>            | 4,209 | 1,110 | 37  | 28,300 | 124 |

\*Endemic species

detected (Table 2). Ni concentrations in two *Pseudosempervivum* species collected from Yahyalı district are found to be 8,100 mg kg<sup>-1</sup> in *P. sempervivum* and 101 mg kg<sup>-1</sup> in *P. aucheri* (Table 2).

In our study, concentrations of Zn, Cu and Pb for three different *Arabis* species (*A. alpina* subsp. *alpina*, *A. aucheri* and *A. nova*) were determined to be normal, as serpentine soils are not normally enriched in these elements (Table 2). The highest Ni concentration in aboveground parts of *I. cappadocica* subsp. *cappadocica* is found to be 5,587 mg kg<sup>-1</sup> in our study (Table 2).

## Discussion

In this study Ni, Co, Cr, Cu, Fe, Pb and Zn concentrations of the Yahyalı Aladağlar serpentine soils and above-ground and underground parts of 19 species of Brassicaceae were studied to find possible relationships between soil and plant concentrations, and to seek potential accumulator plants. The concentrations of Ni, Cr and Fe in the soil of the study area exceeded the limit values stated by the Ministry of Environment and Urban Planning of Republic of Turkey (2017). Such high concentrations are one of the most prominent features of ultramafic rocks (Brooks 1987; Roberts and Proctor 1992). The following comments can be made on the accumulation of Ni and other elements in the species studied here.

### *Alyssum* and *Odontarrhena*

The genus *Alyssum* contains the largest number of Ni hyperaccumulators known worldwide at the present time. All are in sect. *Odontarrhena* which has been regarded as a separate genus at various times since 1830.

From about 200 currently recognised taxa in *Alyssum* s.l., 110 are found in Turkey, including 38 from sect. *Odontarrhena*. Of these, 32 have been listed as Ni hyperaccumulators by Reeves and Adıgüzel (2008); some appear to be serpentine-obligate while others are found both on serpentine and on other substrates. In a recent taxonomic and phylogenetic study genus of the *Alyssum* are separated 3 genera (*Alyssum* L., *Odontarrhena* C. A. Mey. ex Ledeb. and *Meniocus* Desv. by Şpaniel et al. (2015). After separation of the genus *Alyssum* in Turkey, there are 42 taxa in *Odontarrhena*, 7 species in *Meniocus* and remain taxa in *Alyssum*. All hyperaccumulator species of former genus *Alyssum* are now included in genus *Odontarrhena*. *O. muralis* is a polymorphic species that has been much studied over the whole of its very wide range in southeastern Europe, Turkey and further east. It is consistently found with high Ni concentrations when occurring on ultramafic soils (Doksopulo 1961; Brooks and Radford 1978). However, it is a facultative hyperaccumulator in the sense described by Pollard et al. (2014). Several sub-specific taxa from non-metalliferous soils have been found to have low Ni concentrations (Reeves et al. 1983), whereas in some regions such as central and northern Greece the species is a reliable indicator of ultramafics and always has high Ni concentrations (Kelepertsis et al. 1990). In Turkey two of the three varieties of *A. murale* subsp. *murale* recognised by Dudley (1965), var. *murale* (now *Odontarrhena muralis*) and var. *haradjianii* (Rech.) Dudley (now *Odontarrhena haradjianii*) have been collected from serpentine soils and are Ni hyperaccumulators; the highest values for specimens collected in Turkey are given as 21,340 mg kg<sup>-1</sup> for *O. muralis* and 16,220 mg kg<sup>-1</sup> for *O. haradjianii* (Reeves and Adıgüzel 2008). In the present work the mean Ni concentration in above ground parts of *O. muralis* was 2,497 mg kg<sup>-1</sup>. *Odontarrhena muralis* spec-

imens with up to 34,700 mg kg<sup>-1</sup> Ni have been found in the Balkans (Bani et al. 2010), leading to extensive studies on the use of this species for phytoremediation and phytomining (Chaney et al. 2005; Bani et al. 2015).

Of the other *Odontarrhena* species collected, *O. oxycarpa* is a known Ni hyperaccumulator with up to 7,290 mg kg<sup>-1</sup> being recorded for the specimen Kühne 1418 from the Amanus Mts. near Erzincan (Hatay province) (Brooks et al. 1979; Reeves 2017, unpublished data). It is a widely scattered Turkish endemic. Other collections with 7,286–16,250 mg kg<sup>-1</sup> Ni (Reeves and Adıgüzel 2008; Reeves 2017, unpublished data) were made from (1) the valley of Ecemiş Çayı SE of Hamidiye (Adana province); (2) 2 km SSW of Yelatan (Niğde province, on the W side of the Aladağ massif), and (3) 25 km E of Refahiye (Erzincan province). Because Brooks et al. (1979) also recorded two Ni values below 10 mg kg<sup>-1</sup> it seems likely that this species should also be regarded as a facultative hyperaccumulator. In the present study, *O. oxycarpa* was found at the location given in Table 1 with a mean Ni concentration of 1,873 mg kg<sup>-1</sup>.

The two *Alyssum* species collected in this study are *A. pseudomouradicum* Hausskn. & Bornm. and *A. strigosum* Banks & Sol. subsp. *strigosum*, both in sect. *Alyssum* (Dudley 1965). These have the expected low Ni concentrations (no more than 12 mg kg<sup>-1</sup>), as recorded by Brooks et al. (1979). Underground parts of the plants collected in this study were: *O. muralis*, 6,390 mg kg<sup>-1</sup>; *O. oxycarpa* 3,408 mg kg<sup>-1</sup>; *A. pseudomouradicum* 69 mg kg<sup>-1</sup>; *A. strigosum* 10 mg kg<sup>-1</sup>. Again, the distinction between the hyperaccumulators and the non-accumulators is clearly seen. Close to the present study area, near Büyükcakır village (Kayseri province), Altınözlü et al. (2012) found *Odontarrhena peltarioidea* (Boiss.) Španiel, Al-Shehbaz, D. A. German & Marhold subsp. *peltarioidea* (formerly *A. peltarioides* Boiss. subsp. *peltarioides*) with 4,411 mg kg<sup>-1</sup> Ni.

### *Thlaspi*

Many species of *Thlaspi* have been well established as zinc and/or nickel hyperaccumulators, as discussed in publications involving comprehensive surveys of *Thlaspi* s.l. (Reeves and Brooks 1983; Reeves 1988). Nomenclature in this genus has been controversial. The revision of Meyer (1973) which recognized more than 100 species subdivided into 12 smaller genera, was rejected in the publication of Flora of Turkey (Davis et al. 1988), but has received some support from more recent molecular work (e.g. Mummenhoff and Koch 1994; Mummenhoff et al. 1997; Koch and Mummenhoff 2001; Al-Shehbaz et al. 2007; Al-Shehbaz 2014). Many *Thlaspi* species (including many of the Ni hyperaccumulators) have been transferred to the resurrected genus *Noccaea*, but hyperaccumulation is also seen in species classified in Meyer's genera *Masmenia*, *Microthlaspi* and *Thlaspiceras*. Using the nomenclature of *Thlaspi* s.l. Reeves

(1988) recorded Ni hyperaccumulation in *Thlaspi cypricum*, *T. elegans*, *T. jaubertii*, *T. ochroleucum*, *T. oxyceras* and *T. rosulare*. The listing under *T. oxyceras* included 11 specimens of taxa described by Meyer as species of *Thlaspiceras*, using small samples sent by Meyer (e.g. *T. bovis*, *T. crassifolium*, *T. eigii*, *T. rechingeri*, *T. triangulare*), finding very high Ni in each one. Because of the uncertainty about the status of these taxa, the results were summarized under *Thlaspi oxyceras*, showing 14 samples with 3,080–35,600 mg kg<sup>-1</sup> Ni. Extreme values included 35,600 mg kg<sup>-1</sup> in Meyer's *Thlaspiceras crassifolium*, 34,700 mg kg<sup>-1</sup> in *T. dolichocarpum*, 30,000 mg kg<sup>-1</sup> in *T. rechingeri* and 25,000 mg kg<sup>-1</sup> in *T. triangulare*. Full details of the Ni analyses and specimens of Meyer's *Thlaspiceras* taxa are given in Reeves and Adıgüzel (2008). Their publication also included Ni concentrations as high as 56,020 mg kg<sup>-1</sup> for *Thlaspi oxyceras* in specimens collected near Yarpuz (Osmaniye province) in the Amanus Mts.; this is one of the highest Ni concentrations recorded in plant leaves.

Analyses of 11 specimens of *Thlaspi perfoliatum* L. (= *Microthlaspi perfoliatum* (L.) F. K. Meyer) were also reported by Reeves and Adıgüzel (2008); five were found with high Ni, extreme values being 8,120 mg kg<sup>-1</sup> for a sample from Hazar (Elazığ province) and 7,370 mg kg<sup>-1</sup> for a sample from Kabaktepe, SW of Elbistan (Maraş province) (Reeves 2017, unpublished data).

In the present work, specimens identified as *Thlaspi oxyceras*, *T. rosulare*, *T. triangulare* and *Microthlaspi perfoliatum* have been obtained and analyzed (Table 2). The values found here for samples of above-ground material of *T. rosulare* (4,563 mg kg<sup>-1</sup>), *T. triangulare* (8,085 mg kg<sup>-1</sup>) and *Microthlaspi perfoliatum* (2,270 mg kg<sup>-1</sup>) confirm the earlier observations of Ni hyperaccumulation by these species, noted above. Underground parts of *T. rosulare* and *T. triangulare* had even higher Ni concentrations than the above-ground parts. The low value (33 mg kg<sup>-1</sup>) recorded here for *T. oxyceras* is very surprising, in the light of the consistently high values, always > 500 mg kg<sup>-1</sup> and often > 10,000 mg kg<sup>-1</sup>, recorded for leaves of this species in Reeves and Adıgüzel (2008). In the present case, the high Ni seems confined to the underground parts.

### *Pseudosempervivum*

Two Turkish endemic species of interest here were formerly included in *Cochlearia*, but were transferred to the genus *Pseudosempervivum* by Pobedimova as *P. aucheri* (Boiss.) Pobed. and *P. sempervivum* (Boiss. & Bal.) Pobed. These species were established as Ni hyperaccumulators under their *Cochlearia* names (Reeves 1988); further specimens were obtained and analyzed in the work reported by Reeves and Adıgüzel (2008) who recorded 3,130–21,550 mg kg<sup>-1</sup> Ni in 11 specimens of *P. aucheri* and 2,210–34,130 mg kg<sup>-1</sup> Ni in 10 specimens of *P. sempervivum*. In the present work, both species have

been found in the study area; high Ni ( $8,100 \text{ mg kg}^{-1}$ ) was measured in above-ground parts of *P. sempervivum*, but surprisingly, there was a much lower concentration ( $101 \text{ mg kg}^{-1}$ ) in *P. aucheri*, although both species had very high Ni in underground parts.

### *Isatis*

It has been stated (Reeves 2017, unpublished data) that analysis of 24 specimens of 17 different *Isatis* taxa from Turkey showed that all but two had Ni concentrations below  $20 \text{ mg kg}^{-1}$ . Some of these were definitely from serpentine soils, some were possibly from serpentine (because of their collection locations) and others were from other substrates. The samples were from both herbarium and field collections. The two exceptions were serpentine specimens: *I. huber-morathii* Davis with  $34 \text{ mg kg}^{-1}$  from Sapan dağ, Kayseri, 15 km S of Pınarbaşı (Hüber–Morath 11017) and *I. pinnatiloba* Davis with  $33 \text{ mg kg}^{-1}$  from Marmaris–Enecik, Muğla (Davis 25334). A specimen of *I. glauca* ssp. *exauriculata* collected in 2001 from serpentine soil on the road from Kurutilek–Karataş, Erzincan was found to have  $14.7 \text{ mg kg}^{-1}$  Ni (Reeves 2017, unpublished data). All these values are normal for plants on serpentine.

However, Altınözlü et al. (2012) collected *I. pinnatiloba* from various serpentine localities in SW Turkey, and state that 7 specimens showed  $23\text{--}1,441 \text{ mg kg}^{-1}$  Ni, two of them having more than  $1,000 \text{ mg kg}^{-1}$  (1,441; 1,288). These authors show a strange and inexplicable variation of plant Ni with DTPA-extractable Ni in the soil (the highest foliar Ni was from soil with the lowest extractable Ni). The exact localities of the high-Ni specimens were not stated. They also recorded  $275 \text{ mg kg}^{-1}$  in this species in greenhouse experiments, and indicated that *I. pinnatiloba* should be considered as a new Ni hyperaccumulator. This species is endemic to SW Turkey (Muğla province) and is recorded as occurring on both limestone and serpentine (Davis 1965); it has been noted as a species at Kersele bay, L. Köyceğiz (Reeves 2017, unpublished data), possibly on serpentine. It may be a facultative hyperaccumulator of Ni in the sense of Pollard et al. (2014). However, the wide range of Ni concentrations for specimens all collected from serpentine probably puts this species in the category of ‘erratic’ hyperaccumulation as described by Reeves et al. (2015) for *Pimelea leptospermoides* in Queensland, Australia, where it was shown that pH variation, even for a serpentine endemic, could produce a wide variation in Ni uptake. Possibly this is also the explanation for the variable Ni concentrations in serpentine specimens of *I. pinnatiloba*.

*Isatis cappadocica* (with its several subspecific taxa) is a much more widespread species, occurring not only Turkey but in Armenia, Azerbaijan, Georgia, Iraq and Iran, on a wide variety of substrates. A specimen of subsp. *alyssifolia* (Davis 31671) collected from Keşiş dağ above Cimin (Üzümlü) may well have been from an

ultramafic substrate, but was found to have only  $10 \text{ mg kg}^{-1}$  Ni (Reeves 2017, unpublished data). The present observation of  $5,587 \text{ mg kg}^{-1}$  in *I. cappadocica* should stimulate further investigation of this genus in Turkey. This should include analyses of specimens from known ultramafic substrates and comparison with those from other soils, together with detailed analysis of the soils themselves (including pH measurements and total and extractable metal concentrations). This would help to ascertain the conditions under which Ni hyperaccumulation in this species can be expected. It is also of interest that this species has also been recorded as a hyperaccumulator of arsenic, with up to  $3,000 \text{ mg kg}^{-1}$  (Karimi et al. 2010).

Other *Isatis* species in Turkey may be suitable subjects for further work on possible Ni accumulation: (1) *I. spectabilis* may be a serpentine endemic, being found on ‘igneous slopes’ of the Tunceli–Pülümür region (Davis 1965); (2) several other species may be serpentine endemic or may occur sometimes on serpentine: *I. amani* Davis; *I. takhtajanii* (from Erzincan–Keşiş dağ); *I. huber-morathii* (but as noted above, the Type, from serpentine has only  $34 \text{ mg kg}^{-1}$  Ni); *I. davisiana* H. Misirdali.

### Other genera

Species analyzed from the sites studied in the present work in *Aethionema*, *Arabis*, *Heldreichia*, *Hesperis* and *Iberis* have not exhibited Ni hyperaccumulation, although *Aethionema speciosum* had  $593 \text{ mg kg}^{-1}$  Ni. It is noted that *Ae. spicatum* has been found with  $1,110 \text{ mg kg}^{-1}$  (Reeves et al. 2001).

Elements other than Ni. Strongly elevated Cu concentrations are only occasionally found in ultramafic soils: examples from Malaysia and Brazil (with soil Cu sometimes exceeding  $5,000 \text{ mg kg}^{-1}$ ) have been discussed by van der Ent and Reeves (2015). Even here, however, the foliar Cu concentrations are generally tightly controlled so that concentrations above  $75 \text{ mg kg}^{-1}$  are rarely found. In the present work, soil Cu concentrations are not abnormal and all foliar Cu concentrations lie in the range  $1\text{--}8 \text{ mg kg}^{-1}$ .

Where high Ni concentrations in plants from ultramafic soils are accompanied by unusually high concentrations of both Cr ( $> 15 \text{ mg kg}^{-1}$ ) and Fe ( $> 1,500 \text{ mg kg}^{-1}$ ), this suggests the possibility of soil contamination. However, in this study (Table 2) there is no evidence of such a problem in the analyses of the above-ground plant parts. High Fe concentrations in the underground parts, as seen in some analyses here, are not unusual, especially as insoluble coatings rich in Fe and some other elements can form on root surfaces and the Fe concentrations in ultramafic soils are naturally high. There is nothing abnormal about the Zn concentrations in either the soils or the plants analyzed in the present work.

## Conclusions

Hyperaccumulation of Ni has been observed in seven of the species from the ultramafic soils of the Aladağlar area near Yahyalı (Kayseri province), Turkey. Six of these were previously recorded as hyperaccumulators from studies in other ultramafic areas of Turkey. However, the record of 5,587 mg kg<sup>-1</sup> in *Isatis cappadocica* adds another species to the list of Turkish hyperaccumulators. As it occurs on other substrates with low Ni in both the soils and plants, it may be regarded as a facultative hyperaccumulator. Further studies are needed of about species of this genus on ultramafic soils. Of the species studied here *Odontarrhena muralis* is the one with the greatest potential for phytoremediation and phytomining.

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