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Potentially toxic elements in serpentine soils and plants from Tuscany (Central Italy). A proxy for soil remediation

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A B S T R A C T

Serpentine soils have relatively high concentrations of potentially toxic elements (PTEs) (Co, Cr, Cu, Fe, Ni) but generally low amounts of major nutrients. They often bear a distinctive vegetation, with specific tolerance to PTEs, and a frequently-used approach to understanding serpentine ecology and related environmental hazard has been the chemical analysis of soils and plants. In this paper we report the results of a study on serpentine soils and serpentinophytes from different outcrops in central Italy.
In this study, serpentine soils have neutral to sub-alkaline pH (range 6.05–8.15), sandy loam to clay loam textural class, paucity of essential nutrients. PTEs are more abundant in subsoil than in topsoil, consistently with the nature of parent material. Average content of Ni is 2342, Cr = 3502, Co = 149, Cu = 28, Mn = 1754, Zn = 91 mg kg^{-1}, respectively.
Trace elements in serpentine vegetation (both obligate and facultative serpentinophytes) are generally accumulated in roots, but some species (e.g. *Alyssum bertolonii*) are able to (hyper)accumulate metals (up to 2118 mg Ni kg^{-1}) in the aerial parts, without showing toxic features, owing to a tolerance mechanism to very high metal concentrations.
Serpentinophytes, therefore, could represent proxies for plants used in remediation of metal-contaminated soils with both phytoextraction and phytostabilization, and in phytomining as well.

1. Introduction

Soil and environmental contamination is a concern whose importance has been perceived only in recent years, and constitutes one of the greatest emergencies of XXI century, also because modern society is paying increasing attention to its effects on the human health (Bini and Wahsha, 2014), and is acquiring more and more consciousness of the disease risk connected to exposition to chemicals and toxic products such as metals, radionuclides, asbestos, and organic substances (Wahsha et al., 2015).

Soil contamination is not only a social and sanitary issue, but has also an economic concern, since it implies major costs related to decreasing productivity and monetary evaluation of the contaminated sites. Costs related to technologies of remediating contaminated sites (particularly with metals), moreover, are very high (Bini, 2010). In recent years, therefore, the interest of both public Authorities and private Companies focused towards innovative methodologies for decontamination and restoration of contaminated sites (Maleci et al., 2013; Wahsha et al., 2012a, 2012b; Chaney et al., 1997). Phytoremediation is an effective technology that holds great potential in cleaning up contaminants that: 1) are near the surface; 2) are relatively non-leachable; 3) cover large surface areas, and 4) pose little imminent risk to human health or to the environment. Moreover, it is cost-effective in comparison to other technologies and environmental friendly (Bech et al., 2014; Wahsha et al., 2012a). A crucial aspect in phytoremediation is to find out plants with ability to accumulate toxic elements in their tissues (Baker, 1981; Bech et al., 2014; Cunningham and Berti, 1993; Rascio and Navari-Izzo, 2011). In current literature (Brooks, 1987; Angelone et al., 1993; Brady et al., 2005; Barzanti et al., 2011; Harrison and Rajakaruna, 2011; Bonifacio et al., 2013; Van der Ent et al., 2013; D'Amico et al., 2014) there is evidence that plants growing on serpentine soils (serpentinophytes) are particularly tolerant to high heavy metal concentrations, since no toxicity symptoms are visible, out of the “serpentine syndrome” (Jenny, 1980).

Serpentine soils occupy only a very small part of the land surface of the earth (<1% according to Brooks, 1987); they are naturally metal-enriched, and are so infertile that few areas can be used for agriculture. The suggested causes of poor plant growth have been identified so far as trace metal toxicity, low Ca/Mg quotient, high pH values and poor nutrient balance (Proctor, 1971; Proctor and Woodell, 1975; Johnston and Proctor, 1981). In addition, they have relatively high concentrations of Potentially Toxic Elements (PTEs; e.g. Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn). Early and current studies on serpentine soils and their vegetation

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provide results on total soil metal concentrations, or on available fractions, and their translocation from soil to plants.

The plant adaption to high concentrations of metals in serpentine soils can be summarized in the capacity of the plant either to limit metal uptake and translocation or to accumulate the metal in non-toxic forms (Baker, 1981; Rascio and Navari-Izzo, 2011). The majority of serpentinophytes, both facultative and obligate, tend to limit metal absorption to roots so that leaf concentration is generally low (Vergnano Gambi et al., 1982). Only a few species, which have reached a high degree of adaption to serpentine soils, are able to translocate metals from roots to their aerial parts, as occurs for Ni in *Alyssum bertolonii* (Gabbrielli et al., 1990), and are referred to as hyperaccumulator plants (Baker, 1981). Hyperaccumulator plants include species that accumulate >10,000 mg kg^{-1} (Mn or Zn), >1000 mg kg^{-1} (Cu, Co, Cr, Ni, Pb), 300 mg kg^{-1} for Cu (Van der Ent et al., 2013) or >50 mg kg^{-1} (Cd) in their shoots (Rascio and Navari-Izzo, 2011.

Serpentinophytes, therefore, have attracted great interest for the study of resistant mechanisms to PTEs penetration, and could constitute a useful tool in the development of phytotechnologies for remediation (mainly phytostabilization) of contaminated sites (Hill et al., 2014; O'Dell and Claassen, 2011).

The objectives of this study were:

- To determine the heavy metal (Co, Cr, Cu, Ni, Pb, Zn) concentrations in serpentine soils in central Italy;
- To assess the PTEs concentration in plants, both obligate and facultative serpentinophytes;
- To evaluate the feasibility of contaminated sites remediation with plants growing on serpentine soils.

2. Materials and methods

2.1. Site location and field sampling

Representative soil profiles (totally 22) were selected at different historical sites of serpentinite outcrops in central Italy (Fig. 1). The selected sites were at variable topographic position (elevation ranges between 200 and 850 m a.s.l.), located on steep slopes (20–30%), at midslope linear position. Soils were at an early stage of pedogenesis, shallow (depth varied between 40 and 100 cm), rocky, with no formation of diagnostic horizons (unless a Bw at some sites), i.e. they are mostly Entisols (Udorthents and Xerorthents according to the pedoclimate conditions), with some Inceptisols (Eutrudepts) in areas with more gentle morphology (Soil Survey Staff, 2014).

The soil profile was described and sampled from the whole thickness of the genetic horizons (A, AC, B when present and C) and the parent rock. The soil samples were air dried and sieved at 2 mm for routine analyses, according to recommendations of the Soil Survey Staff (2004).

Samples (both roots and leaves) of obligate serpentinophytes (e.g. *Stachys recta* spp. *serpentini*; *Thymus striatus* spp. *ophioliticus*; *Minuartia laricifolia* spp. *ophiolitica*; *A. bertolonii*) and facultative serpentinophytes growing on serpentine soils (*Silene armeria*, *Biscutella* gr. *laevigata*, *Cistus salvifolius*) were gathered at the same site than soils.

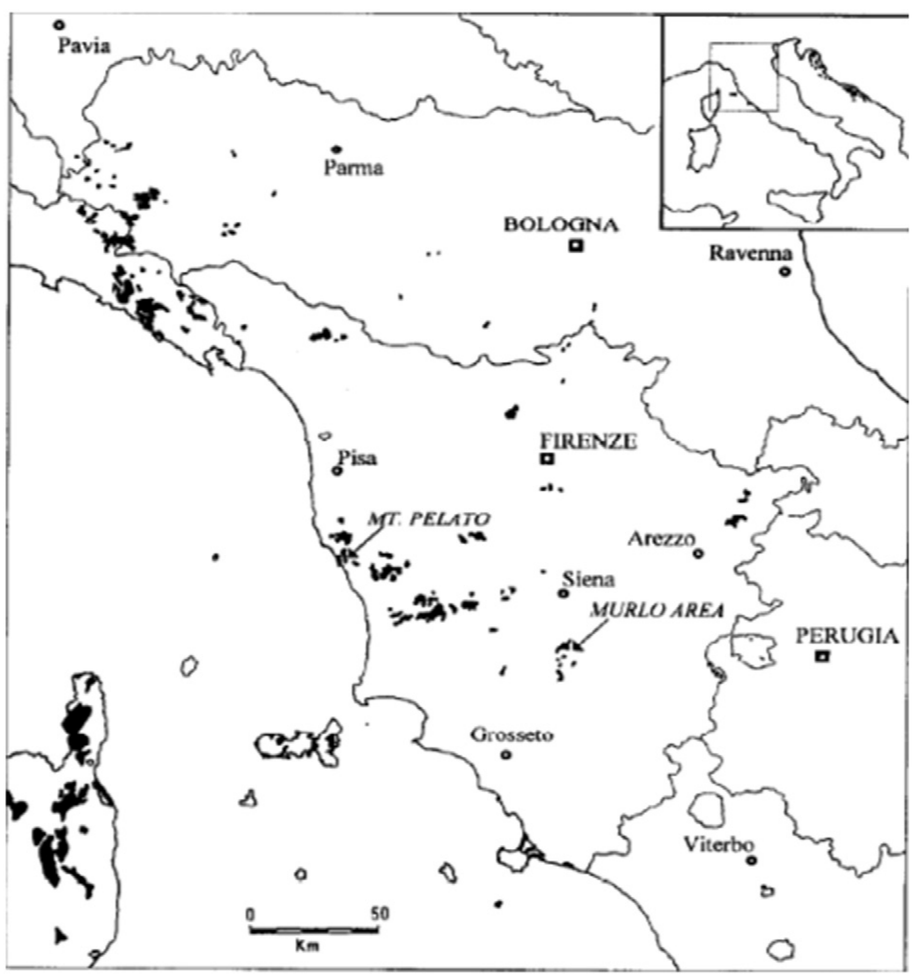

Fig. 1. Outcrops of serpentine rocks (black areas) in Northern Apennines (adapted from Robinson et al., 1997).