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Abstract: One of the most important man-induced land transformations since many centuries is the terraced landform, an agricultural technique that characterizes many agroecosystems all over the world. In this study, our objectives were: i) to evaluate the background level of heavy metals in soils of a terraced ecosystem in the proximity of the Dolomites natural park, in northern Italy; ii) to ascertain the metal concentration range and spatial distribution; iii) to identify possible contamination of some sites, and the related environmental hazard.
Six different terraced landforms were selected; totally, 32 representative soil profiles were opened and sampled. Specific analyses of 15 potentially harmful trace elements (Sb, As, Be, Cd, Co, Cr, Hg, Ni, Pb, Cu, Se, Sn, Tl, V and Zn) were carried out in the laboratory by ICP-MS after digestion with HF and $HClO_4$.
Background levels of heavy metals in the soils investigated are consistent with currently recorded trace element concentrations of soils from Western Europe. A geological matrix effect may be accounted for metal release by parent material weathering. Nevertheless, metal accumulation in surface horizons at some sites has been recorded, and may be ascribed to atmospheric input. The extreme parts of the territory investigated, moreover, present significant concentrations of some metals. In particular, Cu, Pb and Zn contents in surface horizons suggest an anthropogenic enrichment. The human contribution could be due to past mine activities in the close vicinity, and metals have been probably vehicled southward through stream and/or wind transport. Moreover, Sn shows amounts overall above the allowed legislation threshold. In some cases it was not possible to assess if the presence, or the concentration level, of a metal could be related to natural sources or to recent, or past, human activities.

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***Highlights (for review)**

1. Evaluate the background level of heavy metals in soils of a terraced ecosystem in the proximity of the Dolomites natural park, in northern Italy;

2. Ascertain the metal concentration range and spatial distribution;

3. Identify possible contamination of some sites, and the related environmental hazard.

# Potentially harmful elements in terraced agroecosystems of NE Italy: geogenic vs anthropogenic enrichment

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## 1. Introduction

Soil is a limited resource, scarcely renewable, which plays several important functions, both biotic and abiotic, ecologic and socio-economic. Its genesis and evolution is strictly related to pedogenetic factors, both natural and anthropic, and its characteristics are related primarily to parent material and to biochemical processes it has undergone (Fontana et al., 2010).

One of the most important man-induced land transformations since many centuries is the terraced landform, an agricultural technique that characterizes many agroecosystems all over the world. In mountain regions with steep morphology, soil levelling enables to have nearly flat land, where soil and water are available for agriculture (Kribek et al., 2010). Land use change, therefore, may represent a significant impact and a threat to the environment, not only from the physical point of view, but also for possible consequences of using the land in an inappropriate manner (Zilioli et al., 2011). Knowledge of soil characteristic, therefore, is fundamental to understand its evolution, potential land use and management, protection and restoration.

A tool to evaluate soil contamination is monitoring trace elements concentration with reference to baseline levels (Salminen and Tarvainen, 1997). In current literature several reference values are available (Taylor, 1964; Kabata Pendias and Pendias, 2001; Steinnes, 2009); anomalies in comparison to those values may be related to particular chemical characteristics or may indicate contamination phenomena.

Significant differences in metal concentration may be recorded among various soil types: alluvial soils may record flooding episodes with metals convoyed by water along riverbeds (Zilioli et al., 2011); mountain soils may have lost most metals by erosion, wetland areas may act as a sink for metals linked to organic matter, in the proximity of mine areas soils may result enriched in trace elements released by ore minerals (Bini, 2012a). The natural background, therefore, may vary widely, and be much higher in comparison to data from literature. To define the pedo-geochemical background of a given area, several criteria have been proposed (Salminen and Tarvainen, 1997; Baize and Sterckeman, 2004; Ungaro et al., 2008; Kribek et al., 2010).

According to Baize and Sterckeman (2004), metal content in soil is generally consistent with that of the parent material. High metal contents in surface horizons, with a decreasing trend with depth, may indicate anthropogenic contamination (e.g. atmospheric input or discharge), unless local characteristics could explain such trend. Another possible background definition is the “typological approach” as defined in the system ISO 19258. 2005, i.e. to compare metal concentration in the same soil type (e.g. eutric cambisols), selecting not-contaminated sites, and sites that received anthropogenic inputs (e.g. industrial areas), or naturally enriched (e.g. mine areas, serpentine soils) (Bini et al., 2010).

Metal content comparison may be done also among soils with similar characteristics, for example determining metal contents of different textural classes (Baize and Sterckeman, 2004). In this case, the biochemical processes may be responsible for metal distribution in the various classes.

However, considering the multiplicity of factors and processes which contribute to soil genesis, background levels may vary extremely even within limited areas, and it may result somewhat difficult or impossible to ascertain if the presence (or the level) of a given chemical element could be related to natural sources or to past or recent human activities (Bini et al., 2010).

Quite recently, abandoned mine sites have been discovered to constitute a source of potentially toxic heavy metals and a threat to environment (Wahsha et al., 2012a).

The Val Belluna, in NE Italy, is an agricultural land close to the Dolomites National Park, and is nearly surrounded by mine areas (Imperina, Vallalta and Transacqua) which were intensely exploited in ancient times, until final closure in the ’60s of the last century.

Ore minerals in Valle Imperina are mainly copper pyrite ($CuS{\cdot}nFeS_2$) and chalcopyrite ($CuFeS_2$) with minor amounts of metal sulphides, as sphalerite (ZnS) and galena (PbS) with low Ag quantities. Vallalta, in XIX century, was the sixth European mine for mercury production, occurring as cinnabar (HgS), and partially as native Hg. Minerals occurring at Transacqua are siderite ($FeCO_3$), barite ($BaSO_4$), galena (PbS) and chalcopyrite ($CuFeS_2$), with discrete Ag quantities (Bini et al., 2012b).

Various metals (mainly Cu, Fe, Hg, Pb, Zn) were extracted from that areas (Fontana et al., 2010: Wahsha et al., 2012b), and it is supposed that the adjacent valley could be potentially enriched in those elements; both released from parent rocks and as wind-blown particles originated by mineral exploitation. Besides the geographical proximity (about 10 km) of Val Belluna from the historical mine centres, it is noteworthy to point out that the surrounding mine areas are crossed by streams (Imperina, Mis and Cismon), whose drainage waters may contribute to metal enrichment (Zilioli et al., 2011).

The objectives of the present study were:

i) to ascertain what is the natural level corresponding to the pedogeochemical background of PTEs in the study area;

ii) to contribute to the knowledge of heavy metal content and distribution in soils of the land, where typical crops are grown intensively, with reference to current regulatory levels;

iii) to distinguish between geogenic (glacial, fluvial, aeolian) and anthropogenic contribution to metal enrichment.

## 2. Materials and Methods

### *2.1. Description of the study area*

The study area (called Val Belluna) is located in northeast Italy, in the Veneto region. The altitude ranges between 520 and 580 meters, in the piedmont zone of the mountains that surround Belluno (Fig. 1). The Val Belluna extends for over 50km in NE-SW direction, and is crossed nearly completely by the river Piave. Both the river and the last glacial events contributed widely to model the landscape morphology, formed of shallow hills and a large alluvial plain. Urban settlements are located on the hills, while industrial plants are nearly absent, and agriculture is widespread on the bottom valley (Wahsha et al., 2012b).

The geological substratum is characterized by the prevalence of Quaternary colluvial deposits composed of marly limestone with abundant silty-clay matrix. Six different terraced landforms were selected; the terraces differed in land use, and presented different periods of abandonment (Fontana et al., 2010).

The soils of the investigated area have a moderately differentiated profile, with A-B-C horizonation, and are classified as Calcaric Cambisols or Leptic Luvisols (WRB, 2006). Our study concerned 32 soil profiles collected from six different ecosystems, mostly located in the hilly landscape north of the Piave river, outside of the Dolomites National Park (Fig.2).

### 2.2. Analytical procedure

For each ecosystem, representative soil profiles were opened, described and sampled According to the procedures described by Hood and Benton Jones (1997) and Margesin and Schinner (2005). Soil samples were air dried to a constant weight, and sieved through a 2mm stainless sieve to separate skeleton from fine earth. On the fine earth, routine analyses (pH, carbonate content, organic carbon, cation exchange capacity, texture, bulk density, porosity, water retention capacity) were carried out according to the manual of the Italian Ministry of Agriculture and Forestry (Violante, 2000),, in order to define basic soil characteristics.

An aliquot of earth fine was ground with a zircon mill (Retsh MM 200) to obtain soil material less than 100μm, for geochemical analyses of trace elements (As, Be, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Se, Sn, Tl, V, Zn).

The fine powder was digested in Teflon tubes using a mixture of concentrated HF and $HClO_4$, following the procedure described by Margesin and Schinner (2005). All the measures of metal concentration were performed in conformity with technical guidelines EPA 6020A.2007, using an inductively coupled plasma – mass spectrometer (ICP-MS 7500 series Agilent) equipped with automatic sampler. The quality control procedures consisted of measuring soil double replicates and certified reference materials (CRM), assessing correspondence of obtained measures with declared values.

**3. Results and Discussion**

A typical geochemical association of mixed sulphide mine areas, which comprehends metals such as Cd, Co, Cr, Cu, Hg, Ni, Pb, Se, Zn (De Vivo, 2002), resulted from the soils surveyed. Moreover, As, Be, Sb, Sn, Tl, V were recorded.

Some of the investigated metals presented very low concentrations (e.g. Be, Cr, Ni, Sb, Se), in many cases (e.g. Hg, Tl) even below the detection limit as shown in tables 1-4.

In many of the analysed profiles, PTEs present concentrations decreasing with depth. However, only in the Municipalities of Sospirolo (Table 1) and Sovramonte (Table 4) trace elements (namely As, Be, Co, Cu, Zn) show contents above the limits of the Italian guidelines for residential areas. At some sites near Sedico (Table 2) high concentrations of Pb, Sn, and Zn are recorded. Concerning Sn, it is noteworthy to point out that nearly all the samples examined present concentrations above the legislation limit for green areas (1 mg $kg^{-1}$).

The fact that many elements are concentrated in the A horizon may be related to several factors. Surface horizons are generally enriched in organic matter, which could have a role in adsorbing trace elements (Adriano, 2001). On the other hand, it is possible that heavy metals be accumulated at surface since the past century, when mining activity was operating in a conterminous area (Fontana et al., 2010). Exploitation, grinding and roasting of minerals could have generated solid particulate added to soil. A third possibility is that metals could have a partial natural (geogenic) origin, and a partial anthropic origin, and the observed stratification could be a result of these two forms of diffused contamination (Baize and Sterckeman, 2004).

An outlook on the geographical characteristics of the studied area (Fig. 2) in relation to the recorded metal concentrations, allowed observing that:

- In the left side of the investigated area (Sovramonte) flows the Cismon river, after having crossed the mineralised area (Hg, As) of Transacqua;
- In the right side of the area (Sospirolo) flows the Mis Creek which comes from the Hg-mine area of Vallalta, a site known for flooding phenomena;
- The sampling sites in the municipality of Sedico are in close proximity of the confluence between the river Cordevole, and the Imperina Creek, after it drains the Imperina valley, that is mineralised with mixed sulphides (Cu, Pb, Zn);
- The municipalities that are located in the central parts of the Val Belluna (between Sovramonte and Sospirolo-Sedico) are not crossed by creeks or rivers coming from northern mineralised areas.

It is likely that higher concentrations of trace elements could be related to the migration of metals (e.g. Cu, Pb, Zn) released by the mineralised area north of Val Belluna, via water transport, in the extreme parts of the valley (Galan et al., 2008). Instead, in the central part such metal contamination does not occur, since geomorphological conditions do not enhance river flow through the valley. A second way of contamination could be related to former mine activities north of the Val Belluna, where atmospheric particulate from grinding and roasting of minerals could have been transported by dominant winds, and could have been deposited in the topsoil, contributing to the metal content enrichment in surface horizons. The mean values of total metal concentration are summarized in Table 5. All the elements, with the exception of Sn, present values generally below the National regulatory limits (D.L.152/06) for green and residential areas.

3.1 Antimony, chromium, nickel, selenium and thallium.

These elements are grouped in the discussion since they occur with concentrations below the regulatory limits for green and residential areas, and their amount, as it appears from Tables 1-4, is generally low.

Antimony concentrations in the examined area fall in the range 0.3 – 1.3 mgkg$^{-1}$, a little higher in comparison to crustal values (0,2 – 0,3 mgKg$^{-1}$) reported in literature (Alloway, 1995; Angelone and Bini, 1992). Data on Sb content in alluvial cambisols of the Piave watershed (Campana et al., 2007), instead, report mean Sb concentration in the range 0.69 - 1.06, which is consistent with our findings. However, six sites, located north-eastward (Sosp 2, Sosp 4, Sed 2) and south-westward (Sovr 3, Sovr 4, Sovr 8) of the investigated area, exceed the above range.

Chromium concentration in cambisols of the Piave fluvial system is up to 50mgkg$^{-1}$ (Bini, 2012a); in the investigated area, 9 sites, located at the extreme parts of the territory ( Sosp 2, Sosp 4, Sosp 9, Sovr 3, Sovr 4, Sovr 5, Sovr 7, Sovr 10, Sovr 12), present values exceeding the above threshold. All the samples, however, are largely below the regulatory guidelines.

Nickel concentration in the examined area is below the regulatory threshold, but at many sites is higher than the reported limit for cambisols of the Piave watershed (26 $mgkg^{-1}$: Bini, 2012a) The highest values were recorded at Sovramonte, in the SW part of the investigated area, Table 4.

The mean reference value for selenium in cambisols of the Piave fluvial system is 0.50 $mgkg^{-1}$ (Zilioli et al.,, 2011); in the examined area, Se concentration is in the range 0.1 - 0.7 $mgKg^{-1}$, which is consistent with reference data, with uniform distribution in the whole area, and well below the regulatory guidelines for green and residential areas (3 $mgkg^{-1}$).

Significant Tl concentrations, well below the regulatory guidelines (1 $mgkg^{-1}$) were observed only at three sites (Sosp 2 = 0,7 $mgKg^{-1}$; Sovr 4 = 0,5 $mgKg^{-1}$; Sovr 12 = 0,5 $mgKg^{-1}$); at the other sites, Tl concentration could not be detected, resulting below the detection limit by ICP-MS (0.1 $mgkg^{-1}$). Data from literature report Tl crustal concentration =0.45 $mgkg^{-1}$ and <0.14 $mgkg^{-1}$ in limestone (Bini, 2012a). Thallium concentration in soils is very little known, no data are available for soils of Italy, and therefore any comparison is possible.

### 3.2 Arsenic

The regulatory threshold (20 $mgkg^{-1}$) for As is exceeded at three sites of the Municipality of Sovramonte, (Table 4), and concentrations close to that limit were recorded at two sites in the same area. The reference value for As in cambisols of the Piave watershed is 13 $mgkg^{-1}$ (Bini et al., 2010); most sampling sites, however, currently exceed this value, possibly owing to As-sulphides (arsenopyrite FeAsS) occurring in the conterminous areas.

### 3.4 Beryllium

Beryllium concentrations close or slightly higher than the regulatory threshold (2 $mgkg^{-1}$) were found at Sospirolo (Sosp 1 and Sosp 2), NE of the investigated area, and at Sovramonte (Sovr 1, Sovr 3, Sovr 4, Sovr 5, Sovr 7, Sovr 10, Sovr 12), on the opposite side. The Be mean value in the Piave watershed cambisols is 1.02 mgkg$^{-1}$, slightly below the recorded Be concentrations at several sites in the area. Since no Beryllium ores occur in the proximity, the recorded Be concentrations may be considered as the natural Beryllium background of the investigated area.

3.5 Cobalt

Cobalt concentration in cambisols of the Piave fluvial system is 8.7 mgKg$^{-1}$ (Zilioli and Bini, 2009a), which is lower than the regulatory treshold (20 mgkg$^{-1}$); several soils exceed both these limits in the territory of Sovramonte (Sovr 3, Sovr 4, Sovr 5, Sovr 7, Sovr 10, Sovr 11, Sovr 12), and one at Sospirolo (P Sosp 9). The recorded cobalt concentrations may be related to the natural background of the investigated area, as happens for Beryllium.

3.6 Cadmium

Cadmium is geochemically associated to zinc, and may substitute for Zn in sphalerite (ZnS), which occurs in ore minerals of Valle Imperina, North of the investigated area. This element, owing to its known toxicity, has a very restrictive threshold (2 mgKg$^{-1}$) in the regulatory guidelines for green and residential areas; only three soils exceed slightly that threshold. The reference value for cambisols in the watershed, instead, is 0.33 mgKg$^{-1}$ (Zilioli and Bini, 2009b), which is lower than nearly all the recorded Cd concentrations in soils of the examined area, that could be related to mineralization and constitute the pedogeochemical background.

3.7 Vanadium

The mean level of vanadium in cambisols of the watershed is 57 mgkg$^{-1}$ (Campana et al., 2007), while in the regulatory guidelines it is 90 mgkg$^{-1}$. Only one soil exceeds such level, while 11 soils exceed the reference value for cambisols, at Sospirolo, NE (three soils), and Sovramonte, SW (eight soils), as for other metals. The recorded values could represent the pedogeochemical background for vanadium in the area.

## 3.8 Mercury

Mercury occurs in mine areas at Vallalta, north of Val Belluna, where it was exploited since 15th century as cinnabar (HgS) and partly as native Hg. In some of the analyzed samples, Hg traces have been detected; however, most samples exhibited Hg content below the detection limit (DL 0.1 $mgKg^{-1}$), and no sample exceeded the regulatory guidelines (1$mgkg^{-1}$).

## 3.9 Lead

The Dolomites area north of Val Belluna is known since Medieval Ages for mineral exploitation of lead sulphide (galena, PbS), particularly at Valle Imperina and Transacqua, where small quantities of Ag were found in galena crystals. The regulatory threshold for green and residential areas is 100 $mgKg^{-1}$. Only at one site (Sed 2) lead concentration (224 $mgkg^{-1}$) exceeded that threshold. The reference value for cambisols of the Piave watershed (36 $mgkg^{-1}$: Bini, 2007), however, is systematically exceeded in the investigated area.

## 3.10 Copper

In the investigated area copper occurs in large amounts as copper pyrite ($CuS.nFeS_2$) or chalcopyrite ($CuFeS_2$), whose alteration may mobilize copper to a great extent. Yet, at three sampling sites (Sovr 12, Peda 1, Peda 3) Cu concentrations exceeding the regulatory threshold (120 $mgkg^{-1}$) have been observed, while nearly all the sampling sites do not exceed the reference value for cambisols of the Piave fluvial system (64 $mgkg^{-1}$: Zilioli and Bini, 2009a). It is likely that both natural and anthropic contribution (from mining activity and agriculture) may concur to increase Cu content in the three sites.

## 3.11 Tin

The regulatory guidelines for green and residential areas indicate a tin concentration of 1 $mgkg^{-1}$; such threshold is systematically exceeded in soils analyzed, where mean concentrations ranged between 1,1 and nearly 3,0 $mgkg^{-1}$. The reference value for cambisols in the watershed is 2.27 $mgkg^{-1}$ (Zilioli and Bini, 2009b), which is consistent with the recorded values. At one site (Sed 2), the Sn concentration was 4,9 $mgkg^{-1}$, while at six sites it was below the detection limit (0,1 $mgkg^{-1}$). These results suggest that an anthropic origin of Sn is unlikely in the investigated area, since in the entire Veneto region the soil geochemical background for Tin falls in the range 2.7-7.8 $mgkg^{-1}$ (Zilioli and Bini, 2009a) The regulatory guidelines for Tin, therefore, are inconsistent with Sn concentrations recorded in the investigated area

3.12 Zinc

Zinc occurs in great amounts in the form of sphalerite (ZnS) at mining sites surrounding the Val Belluna; therefore, it is diffused also in conterminous land. Zn concentrations exceed the regulatory guidelines (150 $mgkg^{-1}$) at several sites in the area, particularly in the north-east and south-west parts (Sosp 2, Sosp 4, Sed 2, Giust 1, Sovr 5, Sovr 11, Sovr 12). Moreover, at sites where Zn concentration does not exceed the regulatory threshold, it is the most abundant among the metals examined. Consistently with Cu and Pb, Zn exceeds the mean level for cambisols of the Piave watershed (73 $mgkg^{-1}$: Zilioli and Bini, 2009b) at nearly all the sampling sites.

Metal distribution in the whole valley, besides the geogenic contribution due to parent rock weathering, was caused both by wind-born soil particles detached and suspended in the atmosphere, and by fluvial transport operated by streams crossing the mine area north of the valley. The vertical distribution of metals along the soil profile is generally decreasing with depth, with the exception of As at some sites. Surface enrichment may be related to metal dispersion models, which determined re-deposition of soil particles. Organic matter may have bond metals in the form of chelates, thus impeding migration towards bottomsoil. With oxidative conditions and pH values in the range 5-8, consistent with those recorded in Val

Belluna, elements such as As and V present moderate mobility (Bini, 2007). Conversely, with reducing conditions and high organic matter content, most elements, as Pb, Cu, Zn are relatively immobile.

The spatial distribution of metals in the study area may be explained by the action of glacial and stream deposits which affected the whole area since the last glacial period, creating a natural pedogeochemical background higher than expected for cambisols. The areas with major metal concentrations were Sospirolo-Sedico in the NE and Sovramonte in the SW, where they exceeded the regulatory guidelines. In the remaining land, instead, metal levels were below the regulatory limits, with the exception of Zn at site Giust 1 and Cu at Pedavena. The metal geographical distribution is consistent with the drainage network of the valley. Yet, the river Cismon flows at Sovramonte after having crossed the mine area of Transacqua, while Sospirolo lies close to the riverbed of the stream Mis descending from the mine of Vallalta, and the sampling sites near Sedico are affected by the stream coming from the Imperina mine. The central part of the valley, instead, presents the least metal concentrations, being not crossed by contaminated stream waters coming from adjacent mine areas (Fig. 2).

Prevailing winds in the area are rather strong, blowing in direction from north to south. Dust naturally originated during wind storms, or formed during mineral exploitation, may have been convoyed along the narrow valleys from the mine areas to the large Val Belluna, contributing to determine both the vertical and spatial variability of metal distribution.

### 3.14 Statistical analysis

The cluster analysis was applied to 7 representative profiles from the studied area in order to find similarities among groups of samples within a population of data described by a multivariate structure. The similarity dendrogram (Fig. 3) clearly shows that the soil horizons are grouped into 5 groups. Pedogenic (natural) horizons are located in the right side of the diagram, consistently with their origin (i.e. A horizons are grouped separately from B and BC/C horizons), while anthropogenic horizons (^A, ^B, ^C) are located in the left side. These results are consistent with our previous findings (Bini et al., 2010)**,** suggesting that the analysis of heavy metals could be useful for discriminating pedogenic and anthropogenic horizons, and enhance the identification of processes responsible for the formation of different soil types, and may be a useful tool to outline soil evolutionary trends.

Linear Correlation Coefficients

The univariate statistical analysis carried out on the whole data set of metal concentrations in soil horizons allowed identification of linear correlations between variables. The correlation matrix between the total heavy metal contents in 106 samples is reported in Table 5. Significant positive correlations ($p<0.05$, in bold) were observed between trace metal couples, consistently with their geochemical behaviour. The most significant correlations ($p <0.05$) were recorded for Be-Cr (0.817), Co-Cr (0.829), Co-Ni (0.869), Cr-V (0.805), Pb-Sn (0.881), Zn-Sn (0.837).

Antimony has significant correlations with Cd (0.733), Sn (0.684), V (0.648) and Zn (0.745), suggesting a mostly geogenic origin.

Be, Co and V are calcophilous elements linked primarily to calcareous parent material, while Cr and Ni are siderophilous elements, i.e. they are linked primarily to iron sulphides, mostly released by ore minerals. Conversely, Cd, Pb and Zn seem to be of mixed (geogenic/anthropogenic) origin, possibly wind-blown. Tin, which is strongly correlated to Pb (0.881), could be almost of geogenic origin. Elements such as Hg, As and Tl, instead, do not show any significant correlation; their concentrations, therefore, could represent the background level for the investigated area.

## 4. Conclusions

The soils of the Val Belluna are affected by heavy metal concentrations which are mainly related to the geological characteristics of the mine areas located north of the valley.

Element migration from north to south occurs as a consequence of both natural and anthropogenic factors, such as fluvial and wind transport, and mineral exploitation, which may produce synergic effects.

Surface soil horizons proved enriched in metals more than subsoil horizons, suggesting dust deflation to have occurred. The most metal-affected areas are those located in the proximity of streams flowing from mine areas in the north.

The whole area, therefore, presents a pedogeochemical background higher than expected in cambisols of the Piave watershed, and exceeding the regulatory guidelines for green and residential areas.

In the whole area, relatively high levels of As, Be, Cd, Co, Cr, Ni, Pb, Cu, Sn, V, Zn have been recorded. Tin shows amounts overall above the concentration limits for green and residential areas in Italy, and this may pose some problems in interpreting land use legislation acts. It is difficult, however, to distinguish natural (geogenic) from anthropogenic (mineral exploitation) PHEs contribution. Vertical variability could indicate surface enrichment from wind-blown soil particles entrapped in organic matter, while spatial variability could be related to fluvial transport and deposition downward from mine areas in the north.

The occurrence of rather high elemental concentrations in the investigated area, sometimes exceeding the regulatory guidelines, is not an actual anthropogenic contamination, but rather a direct consequence of mineral exploitation reflecting the environmental intrinsic characteristics, as orography and hydrological network.

The comparison of analytical data with regulatory guidelines would suggest that the Val Belluna is a contaminated site, and therefore should be restored; correlation with local geological and environmental conditions, instead, points to natural pedogeochemical background.

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**Table 1**
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| *Profile* | *PTEs* | *Sb* | *As* | *Be* | *Cd* | *Co* | *Cr* | *Hg* | *Ni* | *Pb* | *Cu* | *Se* | *Sn* | *Tl* | *V* | *Zn* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Legislation Limits | 10 | 20 | 2 | 2 | 20 | 150 | 1 | 120 | 100 | 120 | 3 | 1 | 1 | 90 | 150 |
| **P Sosp 1** | A | 0.7 | 4.7 | 1.2 | 1.3 | 9.4 | 35.9 | 0.1 | 10.8 | 38.4 | 9.4 | 0.4 | 1.4 | < 0.1 | 50.0 | 107.0 |
| | BC | 0.6 | 4.4 | 1.0 | 1.2 | 8.5 | 32.0 | 0.1 | 10.2 | 30.4 | 8.5 | 0.3 | 1.1 | < 0.1 | 47.5 | 86.6 |
| | C | 0.3 | 3.1 | 0.5 | 0.7 | 5.6 | 21.4 | < 0.1 | 8.4 | 16.8 | 7.4 | 0.3 | 0.7 | < 0.1 | 33.1 | 46.2 |
| | 2Bw | 0.3 | 2.9 | < 0.1 | 0.4 | 5.2 | 17.0 | < 0.1 | 9.6 | 9.1 | 7.7 | 0.2 | 0.6 | < 0.1 | 26.1 | 32.1 |
| **P Sosp 2** | A | 1.3 | 7.7 | 2.2 | 3.0 | 13.0 | 58.6 | 0.2 | 15.5 | 74.0 | 9.5 | 0.4 | 2.8 | 0.6 | 89.8 | 193.1 |
| | Bw | 1.5 | 7.5 | 2.9 | 3.0 | 15.1 | 67.9 | 0.1 | 16.7 | 69.7 | 7.6 | 0.3 | 3.1 | 0.7 | 103.0 | 215.0 |
| | BC | 1.2 | 6.9 | 2.5 | 2.6 | 14.0 | 61.0 | 0.1 | 15.9 | 51.0 | 6.9 | 0.3 | 2.5 | 0.6 | 95.0 | 188.0 |
| **P Sosp 3** | A1 | 0.7 | 3.6 | 1.3 | 1.0 | 14.0 | 38.0 | 0.1 | 16.0 | 49.0 | 9.3 | 0.2 | 2.7 | < 0.1 | 44.0 | 118.0 |
| | A2 | 0.7 | 3.7 | 1.4 | 1.0 | 14.8 | 42.0 | 0.1 | 17.6 | 40.0 | 9.4 | 0.3 | 1.6 | < 0.1 | 48.7 | 93.0 |
| | C | 0.3 | 2.7 | 0.6 | 0.6 | 9.4 | 21.2 | < 0.1 | 18.7 | 12.3 | 9.2 | 0.2 | 0.6 | < 0.1 | 24.0 | 47.0 |
| **P Sosp 4** | A | 1.1 | 4.4 | 2.0 | 1.9 | 16.9 | 53.0 | 0.2 | 13.3 | 64.8 | 11.0 | 0.2 | 3.0 | < 0.1 | 78.7 | 156.0 |
| | C | 1.1 | 4.3 | 2.0 | 2.0 | 16.8 | 52.0 | 0.2 | 13.4 | 50.9 | 9.4 | 0.2 | 2.3 | < 0.1 | 76.0 | 132.0 |
| **P Sosp 5** | A | 0.6 | 7.1 | 0.7 | 0.5 | 6.9 | 26.9 | < 0.1 | 15.0 | 25.8 | 20.6 | 0.3 | 1.1 | < 0.1 | 37.4 | 69.3 |
| | C | 0.5 | 6.7 | 0.7 | 0.4 | 7.2 | 27.0 | < 0.1 | 15.3 | 22.0 | 15.4 | 0.3 | 1.0 | < 0.1 | 39.4 | 61.0 |
| **P Sosp 6** | A | 0.7 | 6.2 | 0.9 | 0.4 | 8.8 | 29.0 | < 0.1 | 18.9 | 28.9 | 21.2 | 0.3 | 1.6 | < 0.1 | 44.2 | 78.6 |
| | Bw1 | 0.5 | 5.2 | 0.7 | 0.3 | 8.2 | 26.0 | < 0.1 | 18.5 | 18.0 | 17.4 | 0.3 | 1.2 | < 0.1 | 41.9 | 58.0 |
| | Bw2 | 0.5 | 5.1 | 0.8 | 0.3 | 9.2 | 29.0 | < 0.1 | 24.0 | 16.4 | 16.9 | 0.3 | 0.9 | < 0.1 | 43.0 | 58.0 |
| | BC | 0.4 | 4.8 | 0.8 | 0.2 | 8.9 | 28.1 | < 0.1 | 24.5 | 13.9 | 15.7 | 0.3 | 0.8 | < 0.1 | 39.2 | 53.6 |
| **P Sosp 7** | A1 | 0.5 | 4.8 | 0.5 | 0.4 | 10.4 | 15.5 | < 0.1 | 17.9 | 30.0 | 21.7 | 0.3 | 1.1 | < 0.1 | 24.3 | 85.7 |
| | A2 | 0.5 | 4.8 | 0.5 | 0.4 | 10.6 | 15.5 | < 0.1 | 17.5 | 31.7 | 20.0 | 0.3 | 1.2 | < 0.1 | 24.6 | 77.6 |
| | AC | 0.7 | 4.6 | 0.7 | 0.3 | 17.9 | 20.1 | < 0.1 | 20.2 | 25.3 | 12.0 | 0.2 | 1.0 | < 0.1 | 29.8 | 67.0 |
| **P Sosp 8** | A | 0.8 | 9.2 | 1.5 | 0.9 | 10.9 | 10.3 | 0.1 | 16.2 | 54.4 | 13.4 | 0.3 | 2.3 | < 0.1 | 74.0 | 96.0 |
| | A2 | 0.9 | 8.7 | 1.4 | 0.8 | 11.9 | 38.6 | 0.1 | 17.2 | 41.0 | 18.5 | 0.3 | 1.7 | < 0.1 | 69.0 | 80.0 |
| **P Sosp 9** | A | 0.6 | 8.3 | 1.3 | 0.5 | 17.0 | 44.2 | < 0.1 | 53.8 | 25.9 | 28.3 | 0.4 | 1.1 | < 0.1 | 66.6 | 78.2 |
| | A2 | 0.7 | 10.5 | 1.8 | 0.6 | 22.0 | 60.0 | < 0.1 | 70.0 | 30.0 | 36.0 | 0.5 | 1.5 | < 0.1 | 88.0 | 99.0 |
| | C | 0.7 | 10.2 | 1.8 | 0.8 | 21.0 | 56.7 | < 0.1 | 70.5 | 26.0 | 34.0 | 0.5 | 1.3 | < 0.1 | 81.2 | 94.5 |
| **P Sosp 10** | A | 0.6 | 7.5 | 0.5 | 0.3 | 3.3 | 20.0 | < 0.1 | 12.0 | 30.0 | 6.0 | 0.4 | 0.9 | < 0.1 | 25.0 | 48.0 |
| | Bw1 | 0.4 | 5.2 | 0.8 | < 0.1 | 4.5 | 24.6 | < 0.1 | 15.6 | 10.5 | 4.0 | 0.4 | 0.6 | < 0.1 | 27.0 | 50.0 |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Bw2 | 0.4 | 5.5 | 1.4 | < 0.1 | 6.3 | 30.0 | < 0.1 | 20.0 | 8.3 | 5.0 | 0.5 | 0.6 | < 0.1 | 30.0 | 64.0 |
| | Bw3 | 0.3 | 4.1 | 0.9 | < 0.1 | 4.6 | 23.0 | < 0.1 | 16.0 | 5.1 | 4.1 | 0.3 | 0.5 | < 0.1 | 24.0 | 50.0 |

Table 1: Concentration of metals in soils of Val Belluna (Municipality of Sospirolo). Sb, As, Be, Cd, Co, Cr, Hg, Ni, Pb, Cu, Se, Sn, Tl, V and Zn are expressed as mg kg-1.

**Table 2**
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Table 2: Concentration of metals in soils of Val Belluna (Municipalitiy of Sedico). Sb, As, Be, Cd, Co, Cr, Hg, Ni, Pb, Cu, Se, Sn, Tl, V and Zn are expressed as mg kg-1.

| **Profile** | **PTEs** | **Sb** | **As** | **Be** | **Cd** | **Co** | **Cr** | **Hg** | **Ni** | **Pb** | **Cu** | **Se** | **Sn** | **Tl** | **V** | **Zn** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Legislation Limits | 10 | 20 | 2 | 2 | 20 | 150 | 1 | 120 | 100 | 120 | 3 | 1 | 1 | 90 | 150 |
| P Sed 1 | A | 0.3 | 4.7 | < 0.1 | 0.7 | 2.3 | 7.1 | < 0.1 | 6.4 | 26.0 | 9.0 | 0.2 | 1.1 | < 0.1 | 7.6 | 41.0 |
| | AC | 0.2 | 3.0 | < 0.1 | 0.5 | 2.1 | 6.3 | < 0.1 | 5.5 | 11.0 | 4.6 | 0.2 | 0.9 | < 0.1 | 6.1 | 17.6 |
| | C | 0.3 | 1.7 | < 0.1 | 0.4 | 1.5 | 4.8 | < 0.1 | 4.8 | 2.5 | 2.7 | 0.1 | 0.4 | < 0.1 | 4.8 | 11.5 |
| P Sed 2 | A | 1.1 | 9.4 | < 0.1 | 1.7 | 5.6 | 16.4 | 0.3 | 12.0 | 224.0 | 24.0 | 0.6 | 4.4 | < 0.1 | 18.3 | 244.0 |
| | AC | 1.0 | 12.9 | 0.6 | 1.4 | 9.8 | 22.0 | 0.2 | 12.8 | 189.9 | 21.5 | 0.5 | 5.3 | < 0.1 | 21.0 | 160.0 |
| P Sed 3 | A | 0.6 | 6.2 | < 0.1 | 1.0 | 4.8 | 17.8 | 0.1 | 8.1 | 56.0 | 57.0 | 0.3 | 2.3 | < 0.1 | 25.0 | 123.6 |
| | C | 0.3 | 6.6 | < 0.1 | 0.5 | 2.6 | 11.0 | < 0.1 | 5.2 | 23.9 | 14.0 | 0.2 | 0.9 | < 0.1 | 15.0 | 42.0 |

Table 3
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Table 3: Concentration of metals in soils of Val Belluna (Municipalities of San Gergorio, Santa Giustina, Pedavena, Feltre and Cesio Maggiore). Sb, As, Be, Cd, Co, Cr, Hg, Ni, Pb, Cu, Se, Sn, Tl, V and Zn are expressed as mg kg-1.

| Site | Profile | PTEs | Sb | As | Be | Cd | Co | Cr | Hg | Ni | Pb | Cu | Se | Sn | Tl | V | Zn |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Legislation Limits | 10 | 20 | 2 | 2 | 20 | 150 | 1 | 120 | 100 | 120 | 3 | 1 | 1 | 90 | 150 |
| San Gergorio | P Greg 1 | A | 0.5 | 3.0 | 1.2 | 0.8 | 15.5 | 39.0 | 0.1 | 19.2 | 40.0 | 14.4 | 0.2 | 1.5 | < 0.1 | 47.1 | 118.0 |
| | | AC | 0.5 | 3.2 | 1.5 | 1.0 | 16.8 | 45.0 | 0.1 | 23.6 | 28.3 | 18.2 | 0.2 | 1.4 | < 0.1 | 5.3 | 113.0 |
| | P Greg 2 | A | 0.7 | 4.3 | 1.1 | 1.2 | 17.1 | 39.7 | 0.2 | 25.0 | 65.0 | 21.5 | 0.3 | 1.8 | < 0.1 | 43.6 | 135.5 |
| | | AC | 0.6 | 3.9 | 1.1 | 1.0 | 17.7 | 40.0 | 0.1 | 25.5 | 39.6 | 20.6 | 0.3 | 1.6 | < 0.1 | 16.4 | 108.6 |
| | P Greg 3 | A | 0.8 | 5.1 | 0.7 | 0.7 | 7.5 | 22.5 | < 0.1 | 17.6 | 38.0 | 13.0 | 0.3 | 1.0 | < 0.1 | 30.9 | 95.3 |
| | | Bw | 0.5 | 4.5 | 1.1 | 0.4 | 10.8 | 35.0 | < 0.1 | 27.0 | 17.5 | 10.7 | 0.2 | 1.0 | < 0.1 | 36.0 | 81.0 |
| | | BC | 0.6 | 6.0 | 1.0 | 0.5 | 9.8 | 31.0 | < 0.1 | 21.0 | 25.0 | 11.1 | 0.3 | 0.9 | < 0.1 | 40.0 | 79.0 |
| | P Greg 4 | A | 0.8 | 6.3 | 0.9 | 0.6 | 11.0 | 27.6 | 0.1 | 23.7 | 31.5 | 13.9 | 0.3 | 1.0 | < 0.1 | 33.6 | 82.7 |
| | | Bw | 0.7 | 6.3 | 1.1 | 0.3 | 11.8 | 31.0 | < 0.1 | 25.0 | 26.0 | 12.0 | 0.3 | 0.9 | < 0.1 | 36.0 | 77.0 |
| | | BC | 0.6 | 4.0 | 0.8 | 0.3 | 9.4 | 25.0 | < 0.1 | 24.0 | 15.0 | 12.0 | 0.2 | 0.7 | < 0.1 | 27.3 | 66.0 |
| Santa Giustina | P Giust 1 | A1 | 0.8 | 3.5 | 1.3 | 1.8 | 13.7 | 33.0 | 0.2 | 13.6 | 59.3 | 13.9 | 0.3 | 2.3 | < 0.1 | 40.0 | 153.0 |
| | | A2 | 0.7 | 3.0 | 1.2 | 1.5 | 12.0 | 30.0 | 0.1 | 12.0 | 50.3 | 12.0 | 0.2 | 1.9 | < 0.1 | 36.2 | 130.5 |
| | | AC | 0.6 | 5.7 | 1.1 | 1.6 | 12.8 | 28.4 | 0.2 | 13.2 | 34.4 | 12.6 | 0.3 | 1.3 | < 0.1 | 34.0 | 106.0 |
| Pedavena | P Peda 1 | A | 0.5 | 7.6 | 0.9 | 0.7 | 11.0 | 30.0 | < 0.1 | 32.0 | 36.0 | 147.0 | 0.4 | 1.2 | < 0.1 | 50.0 | 135.0 |
| | | AC | 0.5 | 7.4 | 1.0 | 0.6 | 12.0 | 28.0 | < 0.1 | 33.0 | 30.0 | 95.0 | 0.3 | 1.1 | < 0.1 | 45.0 | 92.0 |
| | P Peda 2 | A | 0.7 | 8.4 | 0.9 | 0.6 | 13.0 | 30.0 | < 0.1 | 40.0 | 38.0 | 37.0 | 0.4 | 1.2 | < 0.1 | 39.0 | 100.0 |
| | | AC | 0.9 | 9.2 | 1.1 | 0.6 | 15.0 | 32.0 | < 0.1 | 45.0 | 32.0 | 44.0 | 0.4 | 0.8 | < 0.1 | 44.0 | 106.0 |
| | P Peda 3 | A | 0.8 | 9.0 | 1.3 | 0.6 | 17.0 | 37.0 | < 0.1 | 36.0 | 42.0 | 131.0 | 0.4 | 2.5 | < 0.1 | 77.0 | 142.0 |
| | | AC | 0.9 | 9.4 | 1.3 | 0.6 | 17.0 | 40.0 | < 0.1 | 38.0 | 39.0 | 122.0 | 0.3 | 2.5 | < 0.1 | 82.0 | 130.0 |
| | P Peda 4 | A | 0.6 | 8.4 | 1.1 | 0.6 | 14.0 | 28.0 | < 0.1 | 31.0 | 32.0 | 38.0 | 0.4 | 1.3 | < 0.1 | 61.0 | 86.0 |
| | | AC | 0.5 | 7.1 | 1.0 | 0.4 | 13.0 | 24.0 | < 0.1 | 26.0 | 18.0 | 32.0 | 0.3 | 0.9 | < 0.1 | 52.0 | 60.0 |
| Feltre | P Felt 1 | A | 0.8 | 11.8 | 0.7 | 0.6 | 8.8 | 24.0 | < 0.1 | 29.0 | 32.0 | 35.0 | 0.3 | 1.1 | < 0.1 | 33.0 | 104.0 |
| | | Bw1 | 0.7 | 10.0 | 0.7 | 0.6 | 8.8 | 23.0 | < 0.1 | 28.0 | 25.0 | 30.0 | 0.3 | 0.9 | < 0.1 | 33.0 | 80.0 |

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Bw2 | 0.7 | 11.0 | 0.8 | 0.4 | 9.4 | 24.0 | < 0.1 | 30.0 | 24.0 | 25.0 | 0.3 | 0.7 | < 0.1 | 34.0 | 76.0 |
| | | BC | 0.8 | 11.0 | 0.8 | 0.5 | 10.0 | 24.0 | < 0.1 | 32.0 | 35.0 | 27.0 | 0.3 | 0.8 | < 0.1 | 36.0 | 80.0 |
| | P Felt 2 | A | 0.7 | 12.0 | 1.2 | 1.0 | 15.0 | 35.0 | < 0.1 | 45.0 | 37.0 | 46.0 | 0.5 | 1.2 | < 0.1 | 47.0 | 101.4 |
| | | Bw | 0.7 | 11.0 | 1.0 | 0.7 | 12.4 | 32.0 | < 0.1 | 38.0 | 31.0 | 76.4 | 0.4 | 1.4 | < 0.1 | 41.0 | 95.0 |
| | | BC | 0.7 | 11.0 | 1.2 | 0.7 | 13.0 | 34.0 | < 0.1 | 41.0 | 27.0 | 38.7 | 0.4 | 0.9 | < 0.1 | 45.0 | 78.0 |
| | P Felt 3 | A | 1.0 | 15.2 | 1.1 | 0.6 | 12.0 | 30.0 | < 0.1 | 36.0 | 43.0 | 26.0 | 0.5 | 1.1 | < 0.1 | 44.0 | 97.2 |
| | | AC | 1.1 | 14.0 | 1.0 | 0.7 | 11.0 | 28.8 | < 0.1 | 34.0 | 33.0 | 26.0 | 0.5 | 0.9 | < 0.1 | 42.6 | 86.0 |
| | | C | 0.3 | 5.3 | < 0.1 | 0.2 | 4.4 | 11.1 | < 0.1 | 13.0 | 7.4 | 11.0 | < 0.1 | 0.2 | < 0.1 | 14.3 | 34.0 |
| Cesio Maggiore | P Cesio 1 | A1 | 0.7 | 8.5 | 1.0 | 0.9 | 13.0 | 31.0 | < 0.1 | 47.0 | 35.0 | 40.0 | 0.37 | 1.4 | < 0.1 | 37.0 | 122.0 |
| | | A2 | 0.5 | 7.3 | 0.8 | 0.7 | 11.5 | 27.0 | < 0.1 | 40.0 | 26.0 | 33.0 | 0.4 | 1.1 | < 0.1 | 33.0 | 97.0 |
| | | C | 0.4 | 4.4 | < 0.1 | 0.4 | 3.8 | 9.5 | < 0.1 | 15.5 | 7.6 | 11.0 | 0.2 | 0.3 | < 0.1 | 11.0 | 37.2 |
| | P Cesio 2 | A | 0.9 | 10.6 | 1.2 | 1.1 | 15.0 | 34.0 | 0.17 | 49.1 | 46.7 | 44.0 | 0.5 | 1.9 | < 0.1 | 45.2 | 147.5 |
| | | C | 0.8 | 10.0 | 1.3 | 1.1 | 16.2 | 33.0 | < 0.1 | 51.0 | 38.0 | 42.0 | 0.6 | 1.8 | < 0.1 | 41.0 | 129.0 |

**Table 4**

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| *Profile* | *PTEs* | *Sb* | *As* | *Be* | *Cd* | *Co* | *Cr* | *Hg* | *Ni* | *Pb* | *Cu* | *Se* | *Sn* | *Tl* | *V* | *Zn* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Legislation Limits | 10 | 20 | 2 | 2 | 20 | 150 | 1 | 120 | 100 | 120 | 3 | 1 | 1 | 90 | 150 |
| P Sovr 1 | A1 | 0.7 | 13.0 | 0.9 | 0.4 | 8.9 | 20.0 | < 0.1 | 17.7 | 42.1 | 22.0 | 0.3 | 1.9 | < 0.1 | 29.0 | 103.0 |
| | A2 | 0.6 | 14.0 | 1.1 | 0.3 | 10.0 | 23.0 | < 0.1 | 16.6 | 32.0 | 16.0 | 0.3 | 1.8 | < 0.1 | 34.0 | 82.0 |
| | C | 0.8 | 23.0 | 1.4 | 0.4 | 12.0 | 29.0 | < 0.1 | 28.0 | 35.0 | 24.0 | 0.5 | 2.1 | < 0.1 | 41.0 | 90.0 |
| P Sovr 2 | A | 0.7 | 16.0 | 1.1 | 0.3 | 11.0 | 24.0 | < 0.1 | 24.0 | 42.6 | 25.0 | 0.3 | 1.7 | < 0.1 | 38.0 | 89.0 |
| | Bw1 | 0.7 | 16.2 | 1.2 | 0.3 | 11.5 | 24.0 | < 0.1 | 25.0 | 31.0 | 27.0 | 0.3 | 1.5 | < 0.1 | 37.0 | 84.7 |
| | Bw2 | 0.6 | 17.2 | 1.2 | 0.3 | 12.0 | 25.0 | < 0.1 | 26.0 | 28.0 | 27.0 | 0.3 | 1.5 | < 0.1 | 39.0 | 83.0 |
| | BC | 0.7 | 19.0 | 1.4 | 0.4 | 14.0 | 28.0 | < 0.1 | 30.0 | 33.4 | 27.7 | 0.4 | 1.8 | < 0.1 | 45.0 | 95.0 |
| P Sovr 3 | OA | 1.0 | 12.3 | 1.0 | 0.8 | 15.2 | 32.0 | 0.1 | 4.0 | 43.0 | 30.0 | 0.4 | 1.8 | < 0.1 | 44.0 | 119.0 |
| | A | 1.4 | 21.0 | 2.1 | 1.7 | 29.0 | 58.0 | < 0.1 | 81.0 | 53.0 | 42.0 | 0.5 | 2.6 | < 0.1 | 76.0 | 130.0 |
| | AC | 1.4 | 22.0 | 2.2 | 1.5 | 29.0 | 58.0 | < 0.1 | 81.0 | 57.3 | 40.0 | 0.5 | 1.9 | < 0.1 | 76.0 | 123.0 |
| P Sovr 4 | A | 1.2 | 15.0 | 1.5 | 1.2 | 22.0 | 39.0 | 0.1 | 55.5 | 70.0 | 45.0 | 0.5 | 2.2 | < 0.1 | 53.5 | 130.0 |
| | AC | 1.3 | 25.8 | 2.7 | 2.3 | 34.9 | 64.4 | < 0.1 | 87.4 | 51.2 | 76.6 | 0.8 | 2.5 | 0.5 | 83.7 | 143.4 |
| P Sovr 5 | A1 | 1.1 | 11.0 | 1.8 | 1.6 | 28.7 | 48.3 | < 0.1 | 76.3 | 60.7 | 53.7 | 0.7 | 2.1 | < 0.1 | 63.7 | 198.0 |
| | A2 | 1.1 | 14.0 | 2.1 | 1.6 | 34.0 | 55.0 | < 0.1 | 89.0 | 50.0 | 60.0 | 0.6 | 1.8 | < 0.1 | 72.0 | 142.0 |
| | C | 1.1 | 14.0 | 2.2 | 1.6 | 37.0 | 60.0 | < 0.1 | 95.0 | 47.0 | 52.0 | 0.6 | 1.9 | < 0.1 | 80.0 | 140.0 |
| P Sovr 6 | A | 0.7 | 18.6 | 1.8 | 0.4 | 17.6 | 41.0 | < 0.1 | 46.8 | 41.6 | 70.0 | 0.4 | 1.7 | < 0.1 | 49.0 | 99.0 |
| | AC | 0.5 | 14.0 | 1.6 | 0.3 | 15.0 | 35.0 | < 0.1 | 41.0 | 28.0 | 40.0 | 0.4 | 1.3 | < 0.1 | 43.0 | 82.0 |
| P Sovr 7 | A | 0.7 | 13.0 | 2.2 | 0.7 | 31.0 | 56.0 | < 0.1 | 60.0 | 47.0 | 51.0 | 0.6 | 1.8 | < 0.1 | 64.0 | 122.5 |
| | AC | 0.6 | 13.0 | 2.5 | 0.8 | 36.0 | 62.0 | < 0.1 | 69.4 | 41.0 | 56.0 | 0.7 | 1.9 | < 0.1 | 71.0 | 133.0 |
| P Sovr 8 | A | 1.1 | 10.2 | 1.1 | 1.8 | 16.0 | 31.0 | 0.2 | 40.0 | 82.0 | 33.0 | 0.7 | 2.1 | < 0.1 | 41.0 | 118.0 |
| | AC | 0.9 | 10.5 | 1.2 | 1.6 | 18.0 | 30.0 | 0.2 | 43.0 | 44.0 | 35.0 | 0.6 | 1.4 | < 0.1 | 40.8 | 91.9 |
| | C | 0.7 | 8.8 | 1.0 | 1.3 | 16.7 | 23.0 | 0.1 | 38.0 | 27.0 | 30.0 | 0.5 | 0.9 | < 0.1 | 31.0 | 73.0 |
| P Sovr 9 | A1 | 0.5 | 5.7 | 0.7 | 0.9 | 12.0 | 16.0 | < 0.1 | 28.0 | 36.0 | 31.0 | 0.4 | 1.1 | < 0.1 | 22.0 | 101.0 |
| | A2 | 0.5 | 6.5 | 0.8 | 0.9 | 14.0 | 20.0 | < 0.1 | 34.0 | 36.0 | 35.0 | 0.4 | 1.1 | < 0.1 | 26.0 | 105.0 |
| | AC | 0.4 | 6.3 | 0.9 | 1.0 | 15.4 | 20.0 | < 0.1 | 35.0 | 26.0 | 34.0 | 0.4 | 0.8 | < 0.1 | 28.0 | 83.0 |
| P Sovr 10 | A | 0.8 | 11.2 | 2.4 | 1.6 | 30.0 | 86.0 | < 0.1 | 115.0 | 50.0 | 27.0 | 0.6 | 2.1 | < 0.1 | 77.0 | 130.0 |
| | AC | 0.8 | 11.3 | 2.4 | 1.6 | 29.0 | 88.0 | < 0.1 | 119.6 | 40.0 | 29.0 | 0.7 | 2.1 | < 0.1 | 77.0 | 126.0 |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| P Sovr 11 | A1 | 0.9 | 13.0 | 1.3 | 1.1 | 19.0 | 34.0 | 0.1 | 51.0 | 45.0 | 53.0 | 0.4 | 2.2 | < 0.1 | 44.0 | 274.0 |
| | A2 | 0.7 | 13.0 | 1.3 | 0.9 | 18.0 | 32.0 | < 0.1 | 50.0 | 32.0 | 47.0 | 0.3 | 1.5 | < 0.1 | 46.0 | 98.0 |
| | AC | 0.7 | 12.0 | 1.4 | 0.9 | 20.0 | 36.0 | < 0.1 | 56.0 | 30.0 | 42.0 | 0.3 | 1.8 | < 0.1 | 45.9 | 94.0 |
| P Sovr 12 | A1 | 1.0 | 12.9 | 2.1 | 1.4 | 32.0 | 63.9 | 0.3 | 97.2 | 66.9 | 185.0 | 0.6 | 3.7 | < 0.1 | 75.9 | 192.0 |
| | A2 | 1.0 | 12.0 | 2.2 | 1.4 | 35.0 | 66.2 | 0.3 | 102.6 | 58.0 | 163.0 | 0.6 | 2.9 | 0.5 | 78.9 | 179.0 |
| | AC | 0.8 | 11.0 | 1.7 | 1.1 | 28.0 | 55.0 | 0.1 | 83.0 | 40.0 | 91.9 | 0.5 | 2.2 | < 0.1 | 64.2 | 131.0 |

Table 4: Concentration of metals in soils of Val Belluna (Municipalitiy of Sovramonte). Sb, As, Be, Cd, Co, Cr, Hg, Ni, Pb, Cu, Se, Sn, Tl, V and Zn are expressed as mg kg-1.

**Table 5**
**Click here to download Table: table 5.doc**

Table 5: Linear correlation coefficient calculated on the concentrations of metals in soils. Indicates correlation is significant at the 0.05 level (2-tailed).

| | *Sb* | *As* | *Be* | *Cd* | *Co* | *Cr* | *Hg* | *Ni* | *Pb* | *Cu* | *Se* | *Sn* | *Tl* | *V* | *Zn* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sb | 1 | | | | | | | | | | | | | | |
| As | 0.549 | 1 | | | | | | | | | | | | | |
| Be | 0.506 | 0.372 | 1 | | | | | | | | | | | | |
| Cd | 0.733 | 0.099 | 0.564 | 1 | | | | | | | | | | | |
| Co | 0.539 | 0.509 | 0.731 | 0.439 | 1 | | | | | | | | | | |
| Cr | 0.533 | 0.317 | 0.817 | 0.571 | 0.829 | 1 | | | | | | | | | |
| Hg | 0.09 | 0.019 | -0.129 | 0.077 | 0.025 | -0.024 | 1 | | | | | | | | |
| Ni | 0.376 | 0.555 | 0.587 | 0.249 | 0.869 | 0.757 | 0.011 | 1 | | | | | | | |
| Pb | 0.551 | 0.224 | 0.029 | 0.526 | 0.138 | 0.121 | 0.362 | 0.031 | 1 | | | | | | |
| Cu | 0.181 | 0.368 | 0.235 | 0.022 | 0.48 | 0.289 | 0.06 | 0.523 | 0.061 | 1 | | | | | |
| Se | 0.456 | 0.609 | 0.419 | 0.306 | 0.699 | 0.527 | 0.125 | 0.772 | 0.384 | 0.443 | 1 | | | | |
| Sn | 0.684 | 0.321 | 0.357 | 0.655 | 0.365 | 0.395 | 0.264 | 0.198 | 0.881 | 0.252 | 0.415 | 1 | | | |
| Tl | 0.034 | -0.046 | 0.025 | 0.075 | -0.063 | 0.007 | -0.032 | -0.084 | 0.008 | -0.105 | -0.066 | 0.002 | 1 | | |
| V | 0.648 | 0.363 | 0.756 | 0.521 | 0.676 | 0.805 | -0.087 | 0.559 | 0.077 | 0.384 | 0.406 | 0.402 | 0.034 | 1 | |
| Zn | 0.745 | 0.314 | 0.475 | 0.722 | 0.571 | 0.586 | 0.183 | 0.396 | 0.698 | 0.369 | 0.448 | 0.837 | 0.031 | 0.532 | 1 |

Caption to figures

Fig 1. – Location of the studied area and sampling sites of Val Belluna.

Fig 2. – The geographical characteristics of Val Belluna

Fig 3. – The similarity dendrogram calculated for the investigated PHEs Vs soil horizons

fig 1
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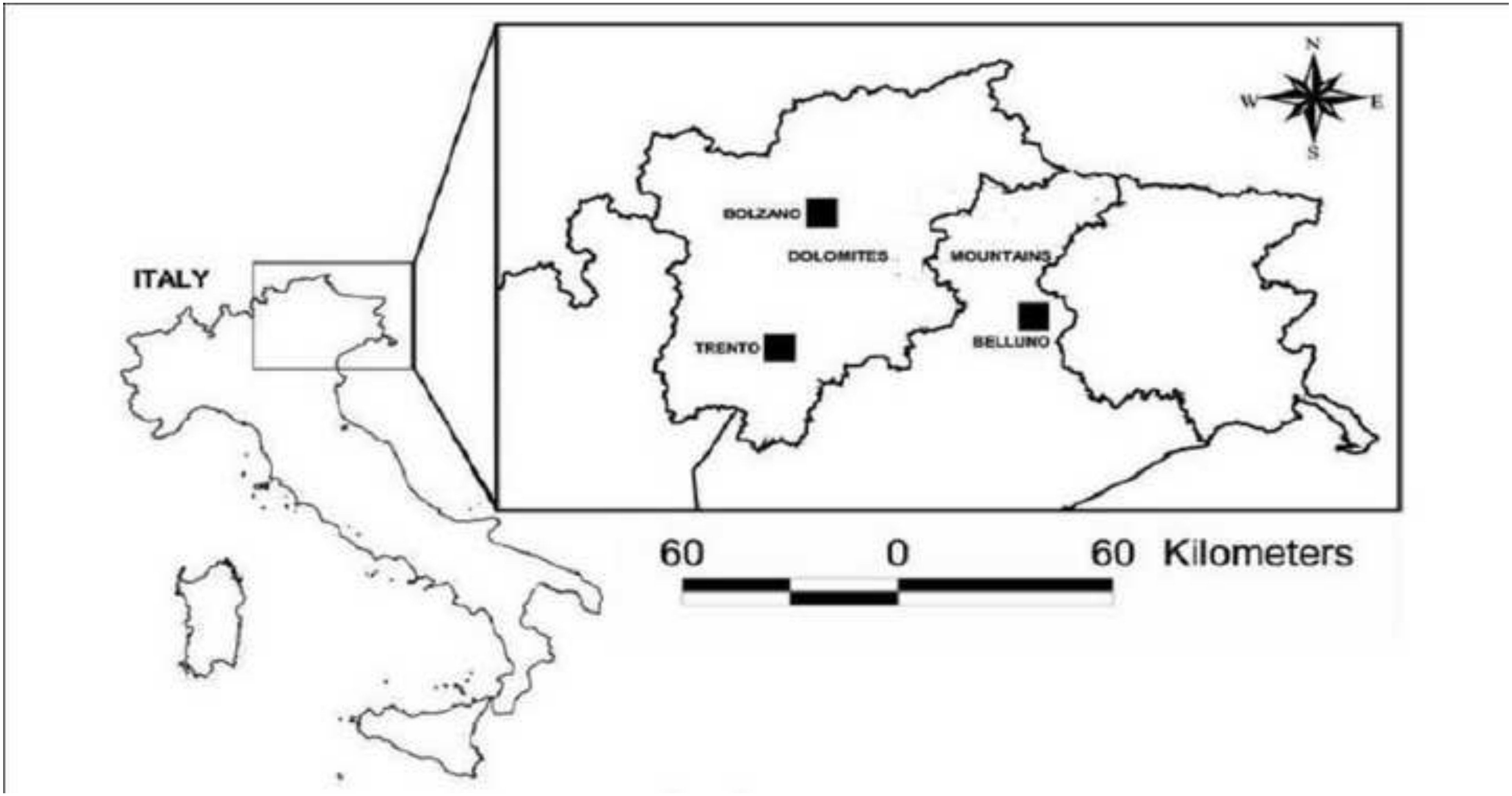

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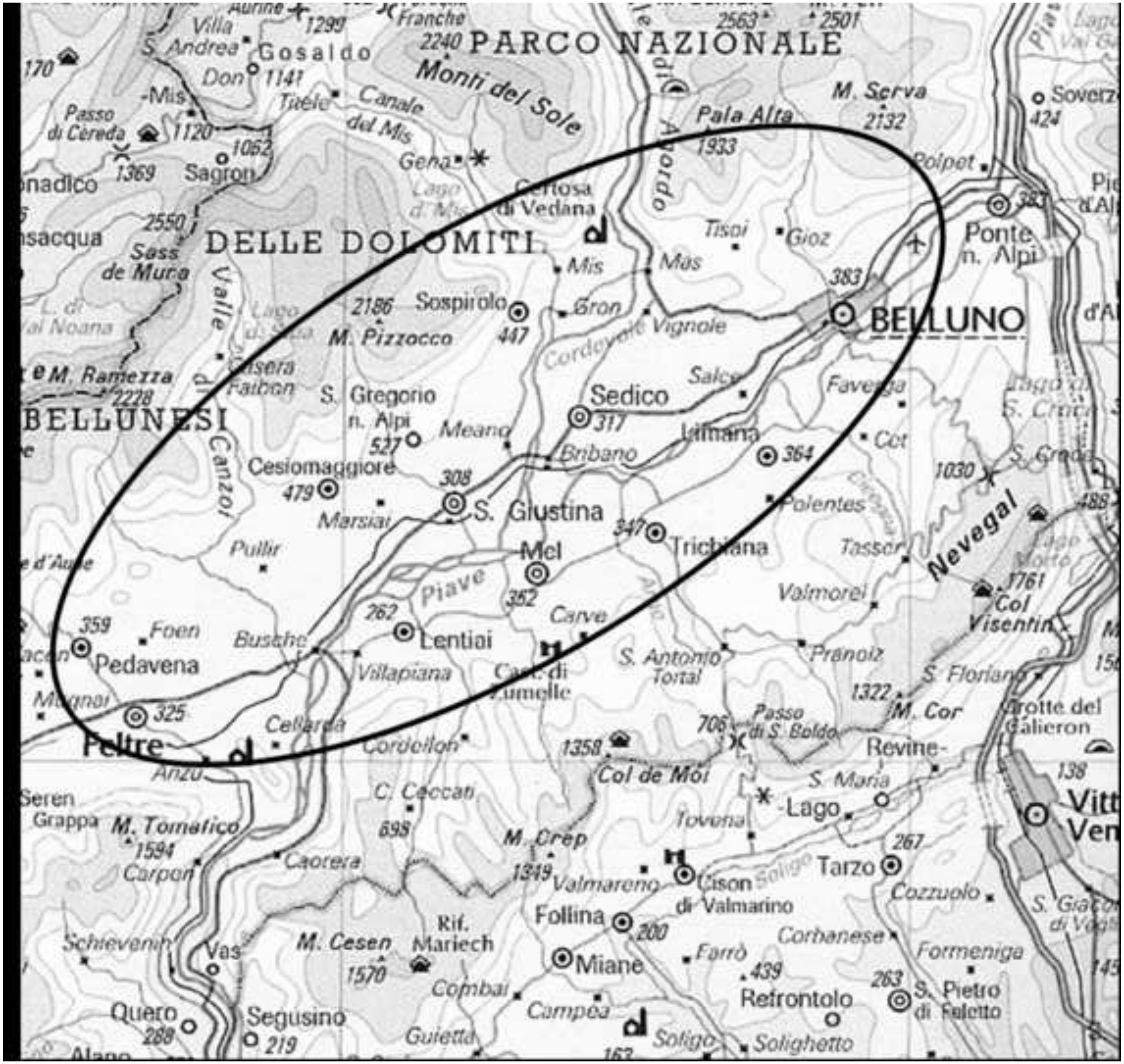

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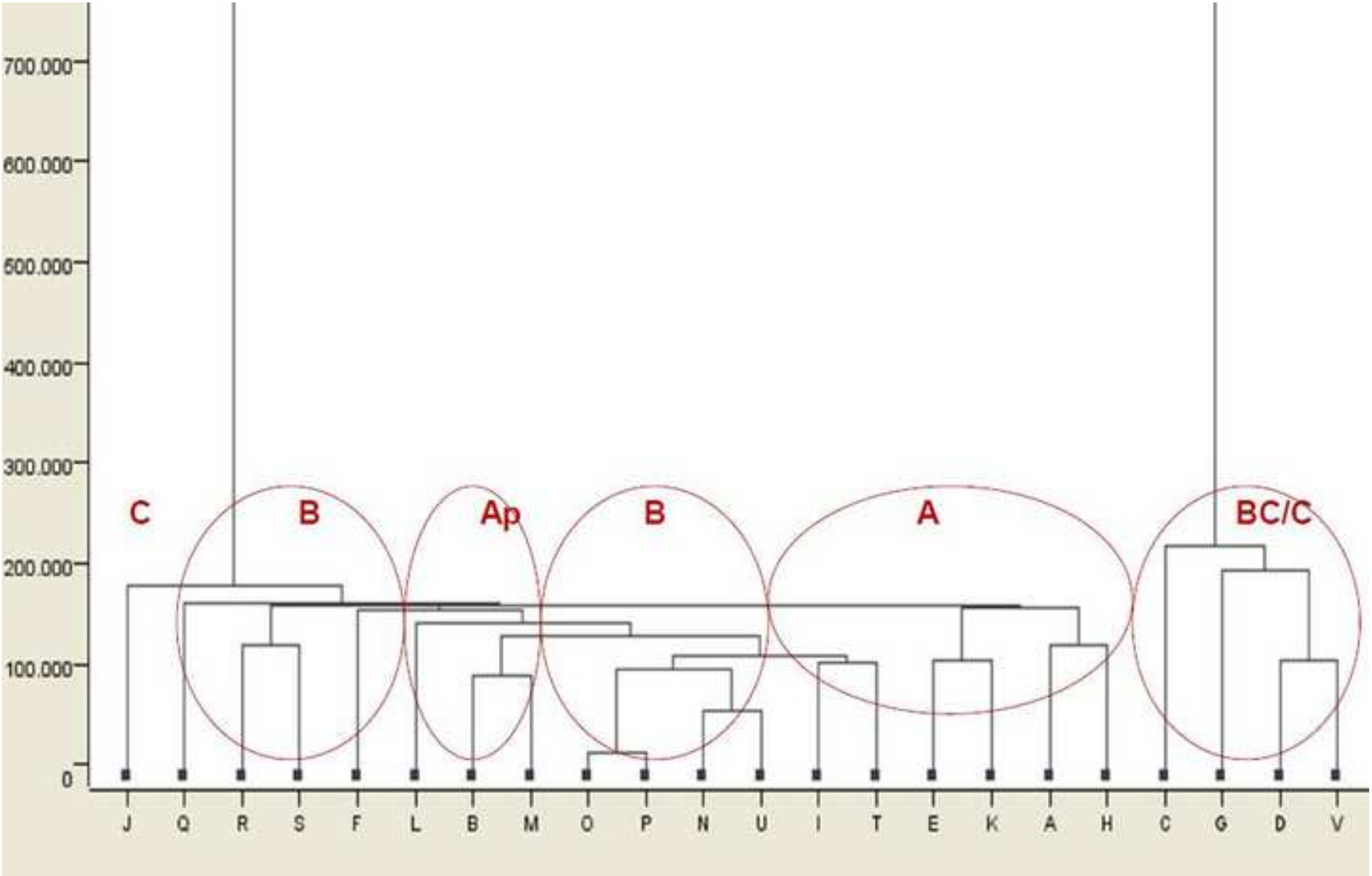

***Authorship Confirmation**

**Dear Editors-in-Chief (Journal of Geochemical Exploration):**

**On behalf of myself and our research group we would like to submit the attached manuscript, "*Potentially harmful elements in terraced agroecosystems of NE Italy: geogenic vs anthropogenic enrichment*" for consideration for possible publication in the Special Issue of Potentially Harmful Elements in Soils: Concentration, Distribution, Risk Assessment and Remediation, Prof. Jaume Bech.**

**This paper has not been published or accepted for publication. It is not under consideration at another journal. An earlier version of this work was presented in the EUROSOIL 2012 which was held in Bari 2012. That paper was modified to reflect the comments received at EUROSOIL.**

**Kind regards,**

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