Preliminary results on heavy metals content in soils and water in an area with unexplored ephithermal porphyry occurences

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Abstract: The findings of studies on deposits of volcanic origin have led to a revival of interest in porphyry and epithermal mineral bodies in Sardinia. The Oligo-Miocene calc-alkaline volcanism outcrops throughout the western part of the island. Field surveys have indicated the widespread presence of metal bearing hydrothermal alterations in the subvolcanic rocks. A Cu-Au-Mo porphyry-type system recognisable as the "diorite model" has been discovered in the Siliqua area in the south and an exploration programme is being prepared. Recently an epithermal auriferous mineralisation, rich in iron sulphides, has been discovered in a nearby area. Their weathering generates acid mine and rock drainage (AMD-ARD) which can produce potentially large volumes of low-pH sulphate bearing waters during oxidation and leaching of the mine materials. These solutions can cause numerous geo-chemical problems especially in regard to metals mobility and precipitation outside the mine sites.

However the minerals of the propylitic halos act as a buffer against weathering under acidic conditions.

The study area comprises very evolved terrain under intense cultivation. The soils are typically poorly developed differing only slightly from the simply disintegrated rocks. Environmental issues related with open-pit mining, or the removal of material and accumulation in waste dumps in a semiarid climate concern largely the possible contamination of soils, surface water bodies and the consequences on deeper groundwater. But there are also risks involved in the geological and geochemical surveying of the area to delimit the ore bodies, and in opening up exploratory trenches and excavations. Current monitoring of surface waters and soils has already indicated high heavy metals concentrations.

1 INTRODUCTION

Most Tertiary metallogenic phenomena in Sardinia are related to hydrothermal activity associated with Oligocene-Miocene calc-alkaline volcanism (Figure1) In addition to long-known Mn occurrences, porphyry-type and epithermal occurrences have been discovered in the last decade.

During the eastward drift of the Palaeozoic-Mesozoic block formed by Sardinia and Corsica in the Oligocene-Miocene, calc-alkaline volcanism developed mostly in the western part of Sardinia. The significant phases of this volcanism, which took place between 29 and 13 Ma ago (Savelli et al., 1978) reflect the crustal movements between the African and European plates

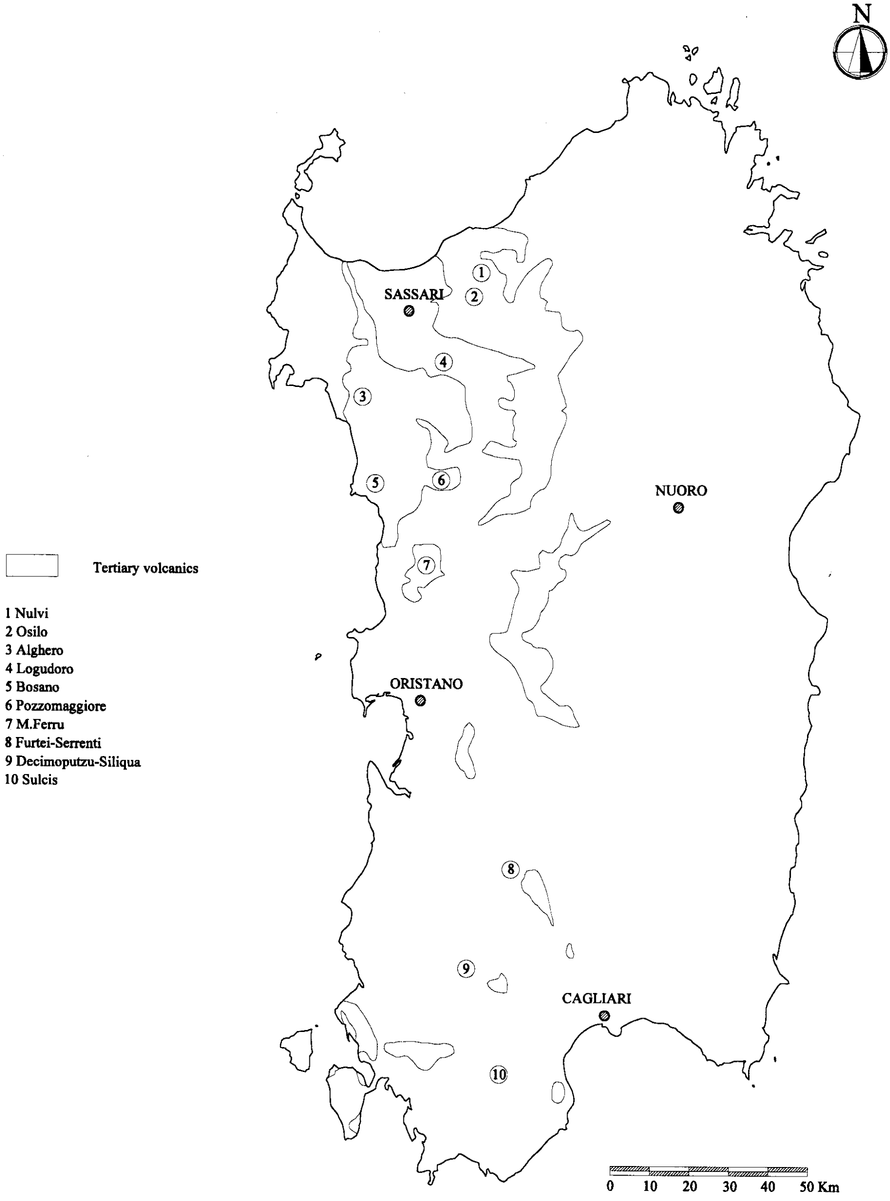


Figure1 Calc-alcaline volcanism in the western half of Sardinia. In the map are represented epithermal and porphyry mineralized bodies.

since the Mid-Oligocene. During the Middle to late Tertiary, the south-eastern European land-mass, to which the Sardinian-Corsican massif belonged, began to undergo rifting, with detachment and drift of the massif towards Italy (Cherchi et al. 1982). The first important calc-alkaline volcanic products, 29-Ma-old andesites and basalts, appear to be related to the consequent rift and graben structures that developed in Sardinia. Following this initial volcanism, ignimbritic products alternated with andesitic lavas in central and northern Sardinia. This volcanic cycle ended with andesitic, dacitic and rhyolitic products in the Miocene, about 14 to 13 Ma ago.

During the waning phases of this volcanism, hydrothermal activity produced local alteration and precious-base metal mineralisation occurring as epithermal, high- and low-sulphidation veins and stockworks containing pyrite, sphalerite, galena and minor chalcopyrite (Fiori et al.1996).

On the north west of the Island, a porphyrite body is known to occur at Calabona (Frezzotti et al. 1992). Another porphyry copper district (Maccioni et el.1992; Fiori et al.1998) has been discovered in the south-western part of the island with a major occurrence in the Siliqua-Decimoputzu area.

The object of this work is to establish a relationship between heavy metal distribution in the soils and their primary sources (sulphides and oxides) before exploration begins.

2 POLLUTION SOURCES

A Cu-Au-Mo porphyry-type system recognisable as the “diorite model” has been discovered in the Siliqua zone in the south and an exploration programme is being prepared (Fadda et al.1998). Recently an epithermal auriferous mineralisation, rich in iron sulphides, has been discovered in a nearby area (Figure2).

Field observations and geochemical surveys have pointed to the presence of some stock like structures of the andesite with a potassic alteration zone where amphibole has been replaced by biotite accompanied by abundant magnetite with minor pyrite and chalcopyrite. In the outer peripheral zone of the K-alteration, gold is present in concentrations far higher than the 2 ppm, that occurs in the classic mineralised shell of economic interest with pyrite, chalcopyrite and molybdenum. A propylitic halo with chlorite-epidote-calcite-albite-pyrite assemblage encloses the potassic zone. The epithermal (Mitza Purdia) system (Figure2), which outcrops to the east of the area exhibits different alteration features. Here in fact the alterations are typical of low temperature hydrothermalism. Alteration mineral assemblage consists chiefly of quartz-pyrite (marcassite)-kaolinite-baryte. The rock is brecciated and its textural and compositional characteristics suggest its origin is related to explosive phenomena of hydrothermal genesis. The metallic elements include gold in amounts of up to a few ppm.

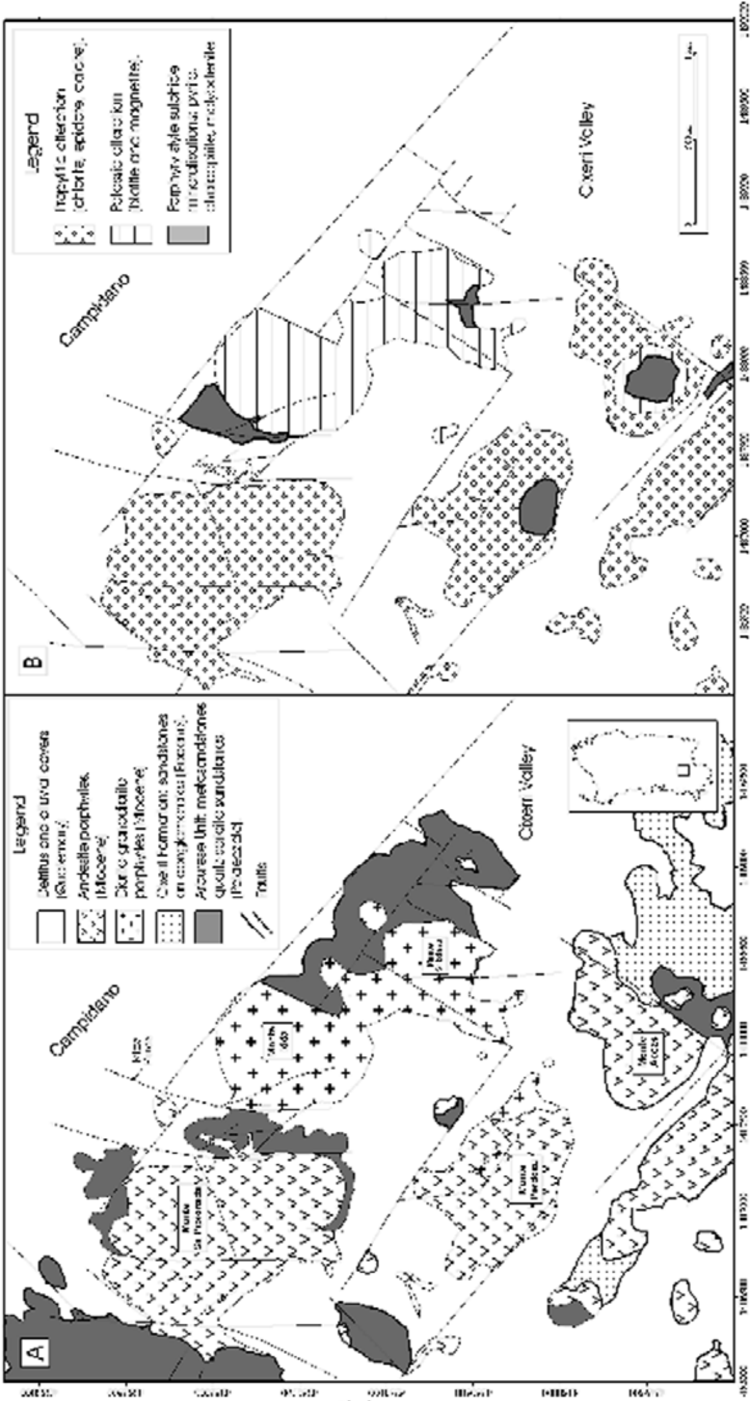


Figure 2 Sketch map showing the geology (A) and the alteration/mineralisation pattern (B) of the porphyry system of the Siliqua sector

3 ARD AND AMD GENERATION

The "porphyry type " and the "epithermal system" are characterised by abundant sulphide sulphur, often in amounts ten times higher that that of total metals content, including iron.

Because weathering-related reactions which generate acid mine drainage (AMD or ARD) are generally controlled by the metal-to-reduced sulphur ratio, porphyry and epithermal systems have the potential to produce very substantial volumes of low-pH, sulphate-bearing waters during oxidation and leaching, despite the relatively modest total sulphide contents of porphyry-hosted ore deposits (Jambor et al. 1994).

The abundance of pyrite, both in the ore-bodies and in the propylitic halos, means that active acid leaching is a major contributor to local weathering processes. For pyrite the oxidation reaction is:

$$FeS_2 + 7/2O_2 + H_2O= FeSO_4 + H_2SO_4$$

In turn, the ferrous iron of the sulphate is oxidised to ferric iron and a hydrolysis reaction follows, releasing additional sulphuric acid:

$$2FeSO_4 + 5H_2O + ½ O_2 = 2Fe(OH)_3 + 2H_2SO_4.$$

The effects of leaching are already evident in the unexploited ore outcrops. Mining and mineral processing operations will obviously enhance leaching by dramatically increasing the surface of the sulphide grains exposed to oxidation processes. However, the propylitic alteration commonly found in all the host rocks, provides an alkaline buffer that diminishes ARD and AMD of the system.

4 SOILS AND STUDY METHODS

The soils typically found in this environment with semiarid climate, are poorly evolved, in fact they differ only slightly from the merely disintegrated rock, with weak argillification and oxidation (Maccioni et al.1992). The area sampled is situated at the foot of the Tertiary and Palaeozoic volcanic hills where the water draining from the mineralised outcrops collects, creating a potential source of pollution. The soils were sampled in 70 sites, over a fairly regular grid of about 40 m (Figure3). Because the soils were so thin, only the C horizon could be sampled. The samples were dried at ambient temperature, below 30°C, and Cu, Zn and Pb determinations were done on lots by means of atomic absorption spectrometry (A.A.S.).

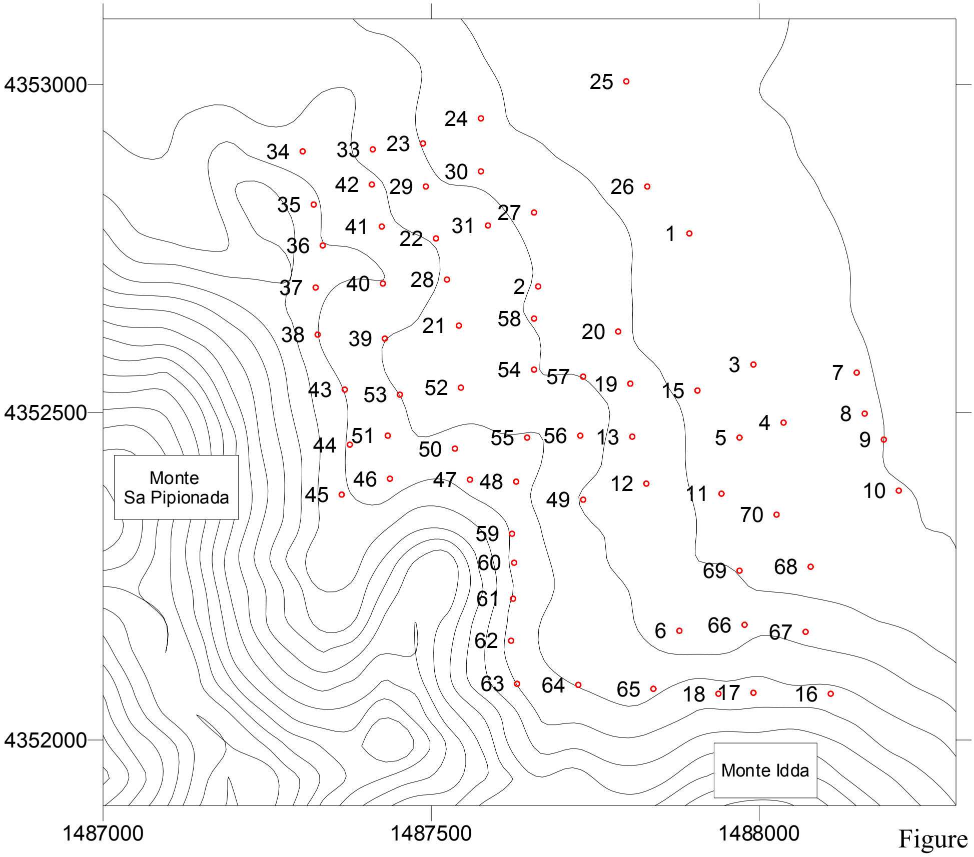


Figure 3 Schematic map showing the sampling pattern.

5 STATISTICAL DATA TREATMENT

Classical statistical treatments have been done on analytical data for all the soil samples for Zn, Pb and Cu to identify homogeneous populations. The distribution laws of these populations, their statistical parameters, and, consequently, their background values and anomaly thresholds (possible, probable and certain) have been determined. Henry's straight line and chi square tests were applied to verify the reliability of the inferred statistical laws. The statistical parameters obtained for the metals considered are given in Table1.

Table 1. Main statistical parameters for some of the metals. Anomaly thresholds are given respectively by: mean plus 1, 2 and 3 standard deviations (normal); mean by variation coefficient to the 1st, 2nd, and 3nd power.

Metal	**Distribution**	**Median** (ppm)	**Background** (ppm)	**St. dev./ Var.coeff.**	**Anomaly thresholds (ppm)** **Possible**	**Probable**	**Sure**
Zn	Normal	110	110.6	37.6	148.2	185.8	223.4
Pb	Normal	70	69.7	16.3	85.9	102.3	118.6
Cu	Lognormal	140	114.3	2.58	294.4	758.6	1954.3

6 DISCUSSION AND CONCLUSIONS

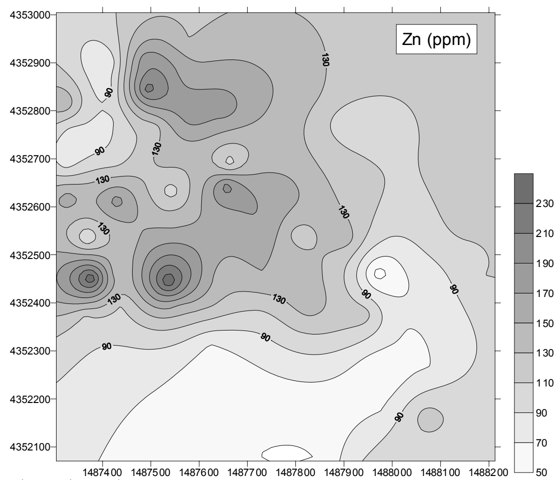
Based on the above data, anomaly contour maps have been compiled for each metal on the basis of the anomaly thresholds calculated for the total population. From examination of these maps the following observations can be made (Figure 4).

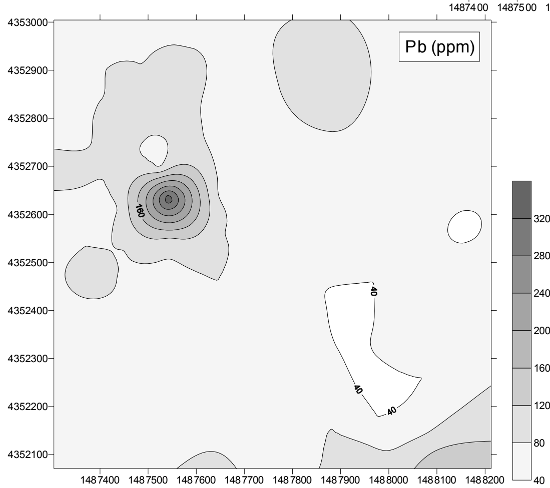
The copper, lead and zinc anomalies in the soils are strongly related to the parent rock and to the metals content in the bedrock. In fact, the soils concerned have formed simply by disintegration of the rock with argillification and oxidation. As the soils become deeper north-eastwards, the anomalies gradually diminish until they finally disappear. In the latter case, the soils are affected by the allochthonous material whose thickness progressively increases as the bedrock level descends near to the faults .

As far as the zinc is concerned, certain and probable anomalies are observed in the Palaeozoic terrain and this metal would appear to be closely associated with their formation. The copper, and to some extent the lead, are on the other hand closely related to the volcanic terrain and the anomalies for these two elements define the edges of the Tertiary volcanic rocks, in particular where the partly outcropping mineralisation occurs at M.te Idda. This is normal in the presence of hydrothermal systems which are the primary source of lead, and copper in particular.

By contrast, in the area where the epithermal gold-bearing mineralisation outcrops at “Mitza Purdia", the metals did not yield high values, precisely on account of the fact that the soils here are fairly deep and did not form in situ but were transported from neighbouring areas not yet, or only partly, exposed to supergenic alteration.

Thus, the findings suggest that the soils in the area concerned already contain anomalous heavy metals in nature even before mineral exploration. Analyses of the spring waters also revealed some metal anomalies (Table2).





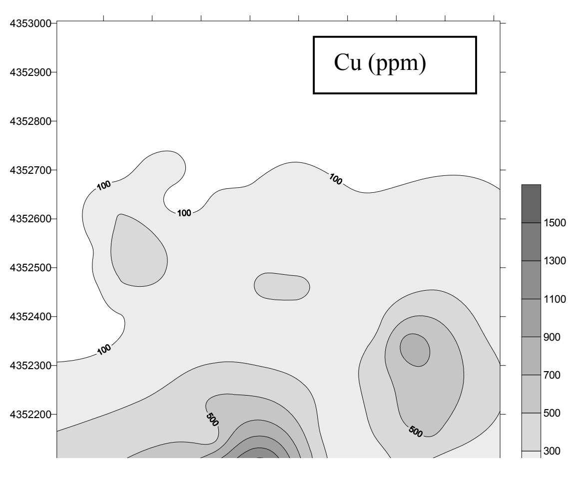


Figure 4 Distribution of Zn, Pb and Cu according to the anomaly thresholds given in Table 1

Table 2 Cu, Zn and Ba concentrations (mg/l) in the spring waters shown in Figure ph and temperature are also shown

	1	2	4	5	6	7	
Cu	**0.02**	**0.02**	**0.02**	**0.02**	**0.6**	**0.02**	**0.006**
Zn	**-**	**0.01**	**0.01**	**0.04**	**0.3**	**0.02**	**0.03**
Ba	**0.05**	**0.04**	**0.1**	**0.01**	**-**	**-**	**0.04**
pH	**8.6**	**8.5**	**7.1**	**-**	**7.6**	**7.5**	**9.7**
T°C	**14.7**	**17.8**	**23.1**	**-**	**10.4**	**14.2**	**16.0**

In this context, worthy of mention is the presence of copper oxides at the outlet of the spring situated near the mineralisation cropping out at M.te Idda. In any event, environmental protection measures need to be implemented to prevent serious water and soil pollution before undertaking any form of mining activity. This is an important issue as the area concerned is densely populated and the land is under cultivation. In fact, mining activity, including mineral exploration, could raise the metal concentrations, at least of Cu, Mo, Co, Pb and Zn, in surface waters and groundwater and consequently in the soils too as the result of natural drainage and irrigation. This process may be further enhanced by the semi-arid climate of Sardinia, where dry seasons alternate with wet ones triggering a series of reactions that condition the possibility of having reduced or oxidised mineral phases.

Another vehicle for metal dispersion is the dust produced by mining operations, especially as Sardinia is a windy island. In this context, the greatest environmental hazard is the atmospheric exposure of the sulphides. These minerals tend to oxidise relatively quickly producing acid drainage that can only be neutralised in part by the host rock, capable of fixing metals released by primary sulphides oxidation in stable supergenic conditions. Thus the soils, as well as surface- and ground-waters, should be monitored in order to control the environmental conditions in this area.

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Wstępne wyniki badań zawartości metali ciężkich w glebie i wodach na obszarze nieeksploatowanego występowania porfiru epitermalnego

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Streszczenie: Wyniki badań nad złożami pochodzenia wulkanicznego doprowadziły do ponownego zainteresowania się porfirami i mineralnymi ciałami epitermalnymi na Sardynii. Wapniowo-alkaliczny wulkanizm oligomioceński występuje w zachodniej części wyspy. Badania terenowe wykazały szerokie występowanie w skałach sub-wulkanicznych hydrotermalnych ciał metalonośnych. System typu porfirowego Cu-Au-Mo określany jako „model diorytowy" odkryto w rejonie Siliqua na południu i obecnie przygotowywany jest program badań w tamtym terenie. Niedawno w pobliżu odkryto epitermalną mineralizację złotonośną, bogatą w siarczki żelaza. Ich wietrzenie powoduje kwaśny drenaż skał (AMD-ARD), co może prowadzić do tworzenia potencjalnie dużych objętości wód siarczanowych o niskim pH, wskutek utleniania i ługowania wydobywanych surowców. Roztwory takie mogą stwarzać liczne problemy natury geochemicznej, szczególnie biorąc pod uwagę mobilność metali. Jednakże minerały aureoli propilitycznej mają działanie buforowe wobec wietrzenia w kwaśnym środowisku. Obszar badań obejmuje teren poddany intensywnej uprawie. Gleby są tu typowo słabo rozwinięte różniąc się nieznacznie od wietrzejących skał. Kwestie środowiskowe związane z górnictwem odkrywkowym bądź też usuwaniem materiału i jego gromadzeniem na składowiskach odpadów w klimacie półsuchym dotyczą głównie możliwego zanieczyszczenia gleby, wód powierzchniowych i wpływu tych zanieczyszczeń na głębsze wody podziemne. Obecny monitoring wód powierzchniowych i gleb wykazał wysokie stężenie metali ciężkich.