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LICHEN BIOMONITORING OF TRACE ELEMENTS IN THE MT. AMIATA GEOTHERMAL AREA (CENTRAL ITALY)

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The possible contribution of Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Pb, Sb, Sr, Ti, V and Zn from geothermal exploitation to the environmental contamination of Mt. Amiata was evaluated by assaying the epiphytic lichen *Parmelia sulcata* from two sampling areas: Piancastagnaio, where there are geothermal power plants, and a remote site distant from geothermal power plants. The results showed that the geothermal power plants at Piancastagnaio do not represent a macroscopic source of atmospheric contamination by most elements. On the other hand, there are indications that for Co, Mo and Sb emissions from the geothermal power plants are a source of air pollution.

Key words: trace elements, heavy metals, contamination, air pollution, geothermal energy, power plants, bioaccumulation, epiphytic lichens

Introduction

The exponentially increasing energy requirement and the need for alternative and renewable energy resources have drawn a great deal of attention to geothermal energy. Italy was the first country in the world to produce electricity from geothermal sources in 1904, and currently is the fourth country for geothermoelectric production, with an installed power of about 700 MW which provide a yearly generation of 3.5 billion kWh, accounting for 1.5 % of total national energy production. The vapor-dominated fields of Larderello, Travale-Radicondoli and Mt. Amiata, in Tuscany, account for almost all of Italy's geothermoelectric production, and the regional input of energy from this source increased from 4.3 % in 1976 to 22 % in 1994. (ALLEGRINI et al. 1995).

The geothermal area of Mt. Amiata seems very promising for the further exploitation of deep reservoirs (>3000 m) and the number of wells and power plants will probably increase in the near future. This however causes growing concern among the inhabitants about possible health and environmental effects due to this increasing exploitation. A study of lichen biodiversity in this area revealed poor air quality in the surroundings of geothermal power plants, probably caused by the noxious gaseous pollutant H_2S (LOPPI and NASCIMBENE 1997), and analysis of As, B and Hg concentrations in lichen thalli showed that the geothermal power plants are an important source of Hg contamination in the area (LOPPI 1997).

For several geothermal fields there is evidence that, besides those of As, B and Hg, concentrations of other trace elements, such as Al, Ba, Cd, Cu, Fe, Mn, Pb, Sb and Zn, are higher in the vicinity of geothermal installations (CONNOR 1979; LOPPI 1995; LOPPI and BARGAGLI 1996).

The aim of the present study was to evaluate the possible contribution of Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Pb, Sb, Sr, Ti, V and Zn from geothermal exploitation to the environmental contamination of Mt. Amiata, by assaying epiphytic lichens. To achieve this goal, two sampling areas were selected: 1) Piancastagnaio, where there are geothermal power plants; 2) a control site distant from geothermal power plants.

Study Area

The geothermal field of Piancastagnaio (Figure 1) lies on the south-eastern slope of Mt. Amiata (1738 m) and extends over an area of about 80 km^2, with an elevation ranging from 350 to 1000 m. The geological setting consists of sedimentary (up to 700–800 m) and volcanic (above 800 m) rocks. The climate is humid sub-Mediterranean, with mean annual rainfall in the range of 1000–1555 mm and mean annual temperatures ranging from 9.7 to 11.3 °C.

Four power plants are in operation in the area. Three of them have a nominal power of 20 MW with a condensing turbine, and use fluids from the deep reservoir (about 3500 m). The other power plant is non-condensing with a nominal power of 8 MW; the fluids exploited are from the shallow reservoir (about 800 m). All of them re-inject the exploited fluids for waste disposal.

Materials and Methods

In May 1995, in each of the two areas selected (Figure 1), 10 whole thalli of the foliose lichen *Parmelia sulcata* were collected from the trunks of free-standing oak trees, at a height of 1.5–2 m above the ground. In the laboratory, composite lichen samples from each site were air-dried and sorted to remove as much extraneous material as possible. Since certain elements accumulate in foliose lichens in zones according to age, i.e. exposure time (LOPPI et al. 1997), only the outermost 3 mm of the thallus were detached and analyzed. This part is physiologically the most active and has an age of about one year (FISHER and PROCTOR 1978).

The samples were powdered and homogenized and about 150 mg were mineralized in a pressurized digestion system (Teflon bomb) with concentrated HNO_3 for

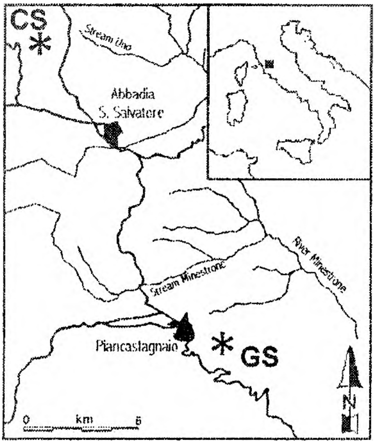

Fig. 1. Study area with location of sampling sites.
GS = geothermal site, CS = control site

10 h at 130 °C. Trace element concentrations, expressed on a dry weight basis, were determined by: 1) atomic absorption spectrophotometry, using a graphite furnace for Cd, Co, Mo and Pb, and a hydride generator for Sb; 2) inductively coupled plasma emission spectrometry for Al, Ba, Cr, Cu, Fe, Mn, Sr, Ti, V and Zn. Analytical quality was checked by analyzing the Standard Reference Materials No. 1572 'citrus leaves' and No. 1573 'tomato leaves'.

Results and Discussion

Table 1 summarizes the results of analytical determinations of lichen samples at the two locations examined. Levels of Ba, Cd, Cu, Mn, Pb, Sr and V gave results in line with the values normally found in unpolluted areas of Tuscany (LOPPI and DE DOMINICIS 1996; LOPPI et al. 1998), indicating that the Mt. Amiata area is not affected by atmospheric deposition of these elements. On the other hand, the concentrations of some elements (Al, Cr, Fe, Ti, Zn) were higher in the Mt. Amiata area (both at the geothermal and the control site) than in other, unpolluted, areas of Tuscany. Aluminium, Cr, Fe and Ti are lithogene elements which in lichens are generally strongly correlated, owing to soil contamination of thalli (LOPPI et al. 1999). High Zn concentrations in *P. sulcata* thalli from Mt. Amiata were already described by BARGAGLI (1990) as being probably due to the high dispersal power of this atmophile element.

As compared to unpolluted areas of Tuscany and the control site, only the concentrations of Co, Mo and Sb turned out to be significantly higher in lichens from the geothermal site. This result agrees with the data of LOPPI (1995) for the geothermal area of Travale-Radicondoli, which showed that concentrations of Co, Mo and Sb are higher in geothermal than in background areas. Furthermore, for the same area, LOPPI and BARGAGLI (1996) reported strong correlations between the concentrations of Co, Mo and Sb in the lichen *Parmelia caperata*.

All three elements are used in alloys for geothermal pipes and Mo is also used as corrosion inhibitor (ADRIANO 1986). This could represent their common

Tab. 1. Mean values ± standard deviation (μg/g dw) of trace elements in lichen samples from the geothermal (Piancastagnaio) and control sites. Background = mean values found in unpolluted areas of Tuscany. * = significant difference at $p<0.05$ between geothermal and control site

	Piancastagnaio	Control site	Background
Al	1923 ± 1122	2595 ± 1565	987
Ba	29.5 ± 20.9	21.1 ± 10.7	24.5
Cd	0.28 ± 0.19	0.17 ± 0.08	0.26
Co *	0.49 ± 0.18	0.22 ± 0.09	0.23
Cr	5.9 ± 3.6	5.2 ± 2.9	2.3
Cu	12.8 ± 4.9	11.8 ± 8.7	10.8
Fe	1130 ± 574	2209 ± 1070	785
Mn	50.6 ± 29.7	49.9 ± 10.8	47.2
Mo *	1.01 ± 0.52	0.22 ± 0.08	0.21
Pb	13.2 ± 6.4	17.8 ± 6.7	14.1
Sb *	0.56 ± 0.25	0.31 ± 0.10	0.28
Sr	21.6 ± 9.2	15.7 ± 7.4	16.4
Ti	77.4 ± 60.1	76.2 ± 29.4	47.7
V	2.89 ± 1.59	2.87 ± 0.88	2.69
Zn	78.4 ± 16.7	58.3 ± 25.2	36.9

source and explain their relatively high concentrations in geothermal areas. Also, BRONDI et al. (1986) found that the concentration of some trace elements in geothermal steam is mainly due to release from pipes and not to natural processes. However, Sb is known to be an element of geothermal origin (NICHOLSON 1993) and there are indications that Mo is also present in geothermal fluids in greater amounts than in cold waters (BRONDI et al. 1986). The only data available for the geothermal power plants at Piancastagnaio (ENEL 1996) indicate Sb emission rates into the atmosphere in the range 0.6–0.9 g/h.

Cobalt, Mo and Sb are relatively non-toxic to animals and man (ADRIANO 1986). For Sb, despite some indications of toxicity, this concerns soluble compounds, while in the terrestrial environment it is mainly present in insoluble forms which are not concentrated in the food chain (ADRIANO 1986).

Very little is known about Co, Mo and Sb in lichens. Cobalt and molybdenum are essential elements for lichen metabolism and are generally found in higher concentrations in the peripheral part of the thallus, which is physiologically the most active (LOPPI et al. 1997). Their mean concentrations reported for several lichen species from Europe (FREITAS et al. 1995; QUEVAUVILLER et al. 1996) indicate ranges of 0.29–0.38 μg/g dw for Co and 0.22–0.42 μg/g dw for Mo. Antimony is non-essential to plants; it is generally released in the atmosphere by combustion processes in association with the fine particulate of stack emissions (ADRIANO 1986). Usually it is widely dispersed over large areas determining higher levels than the natural background, except in the most remote areas such as Antarctica (AINSWORTH and COOKE 1991). Mean concentrations of Sb in lichens from Europe and North America (FREITAS et al. 1995; OLMEZ et al. 1985; QUEVAUVILLER et al. 1996) indicate levels of 0.07–0.35 μg/g dw. According to HERZIG (1993), concentrations of Sb in *P. sulcata* are linearly correlated with air quality assessed by lichen bioindication, with the highest levels found in the vicinity of main streets or highways (0.49 μg/g dw) and in large settlements (0.41 μg/g dw). These observations are also confirmed by the data of GUEVARA et al. (1995), which reported Sb concentrations in the range 0.14–0.22 µg/g dw for lichens from rural areas and 0.59–1.12 µg/g dw for lichens from urban areas of Argentina.

Conclusions

From the results of the present survey it can be concluded that the geothermal power plants at Piancastagnaio do not represent a macroscopic source of atmospheric contamination by elements such as Al, Ba, Cd, Cr, Cu, Fe, Mn, Pb, Sr, Ti, V and Zn. On the other hand, there are indications that, the emissions from the geothermal power plants are a source of air pollution by Co, Mo and Sb.

However, the Mt. Amiata hydrothermal system is situated in a strongly mineralized area rich in cinnabar deposits (FERRARA et al. 1991) and for a better understanding of the contribution of geothermal exploitation to the atmospheric contamination of the area, it would be advisable to perform further investigations, taking into account also the nearby geothermal area of Bagnore (about 10 km W of Piancastagnaio), the thermal springs of Bagni S. Filippo (about 9 km N of Piancastagnaio) and the natural manifestations of sulphurous exhalations locally known as "putizze", which are scattered in the area.

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