

## PILOT ASSESSMENT OF CONTAMINANT ELEMENTS IN SOILS AND CRYPTOGAM PLANTS FROM EMISSIONS FROM AN ORE PROCESSING PLANT, ZLATNA REGION, ROMANIA

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**ABSTRACT.** Soil samples were collected from 7 sampling stations (in duplicate) and associated terricolous lichen (*Cladonia fimbriata* and *Cladonia coniocraea*) and moss (*Bryum argenteum*) samples along an W-E transect from Zlatna plant. *Cladonia* and moss samples were digested with HNO<sub>3</sub> + H<sub>2</sub>O<sub>2</sub> mixtures and analyzed for Pb, Zn, Cu using acetylene-air flame atomic absorption spectrometry. Chemical analyses of bulk samples for soil-surface horizons were digested with Lunge mixture and analyzed also with FAAS. Lead and Cu contents decreased more-or-less linearly with increasing distance from the ore-processing plant and soil pH values increased as a function of distance. Soils (surface horizons) are acidic virtually throughout the area. Lichen and moss metal content was significantly higher than soil metal content. Metal concentrations are amongst the highest reported for natural ecosystems, the most serious being for Pb.

### INTRODUCTION

Romania is confronted with serious problems of environmental pollution as a consequence of intensive industrialisation. One 'intensely polluted zone' is the Zlatna region of central Transilvania. A copper ore processing plant in the centre of Zlatna town lying in a sheltered valley produces acidic emissions and large amounts of metal particulates, both causing extreme environmental degradation throughout the locality [1]. Forest soils of the area are eroded, acidified and sparsely vegetated: trees are visibly damaged and agriculture in some parts of the area is noticeably affected [2].

The ore used for copper smelting contains a range of trace metals including: Pb, Zn, Cd, Sb, Bi, As, Ag, Au. The smelting process results in a

concentration of these elements and smelter particles ranging from < 5 to 100 µm in diameter, many in the size class commonly referred to as PM10, are released directly to the atmosphere. During oxidation of the Cu sulphide concentrate, S is partitioned into the volatile phase to produce SO<sub>2</sub>, which at Zlatna is released directly into the environment - up to 1305 µg/m<sup>3</sup> SO<sub>2</sub> /30-minute mean concentration was recorded in the town centre in 1996. Unfortunately, only the old factory is currently functioning and this has a very inefficient filter: the retention of dust being only about 50% efficiency. Emissions are released directly to the atmosphere, via the two chimneys from the smelting and conversion works, both 100 m in height.

This study forms part of an ongoing study into the impact of pollution in Zlatna region. Previous studies have focussed on macrolichen transplants [3, 4] and bioaccumulation of lead by *Acarospora smaragdula* [5]. The purpose of this pilot study is to sample native cryptogamic plants (mosses and lichens) and associated soils along a WE gradient transect in the Ampoi Valley to a site 25 km downwind from the smelter. The present paper compares the contents of Cu, Pb and Zn in lichens (*Cladonia fimbriata* and *Cladonia coniocraea*), mosses (*Bryum argenteum*) and soils. A combination of plant and soil chemical data will enable determination of functional relationships, which may be useful for predicting the response of the ecosystem to future change and which may also facilitate the planning of strategies for managing the ecosystem for multiple land use (e.g. agriculture, silvaculture, etc.).

## EXPERIMENTAL

**Sampling and sample digestion procedure.** Soil samples were collected from 7 sampling stations (in duplicate) and associated terricolous lichen (*Cladonia fimbriata* and *Cladonia coniocraea*) and moss (*Bryum argenteum*) samples. The sampling points are marked (Figure 1).

Approximately 1000 g brown forest soil samples (soil-surface horizons, 10 cm depth) were collected using a trowel and were placed into plastic bags. These samples were air-dried at room temperature prior to grinding in agate mortars, sieving (at -80 mesh) and dissolution. The results represent the average of 2 soil samples/site made in duplicate each one.

The moss and lichen samples were carefully removed by hand from their substrate and covered in tissue paper. These were then stored in plastic flasks prior to drying and cleaning. It was made a mixture of the two *Cladonia* species, and analysed in duplicate for each site.

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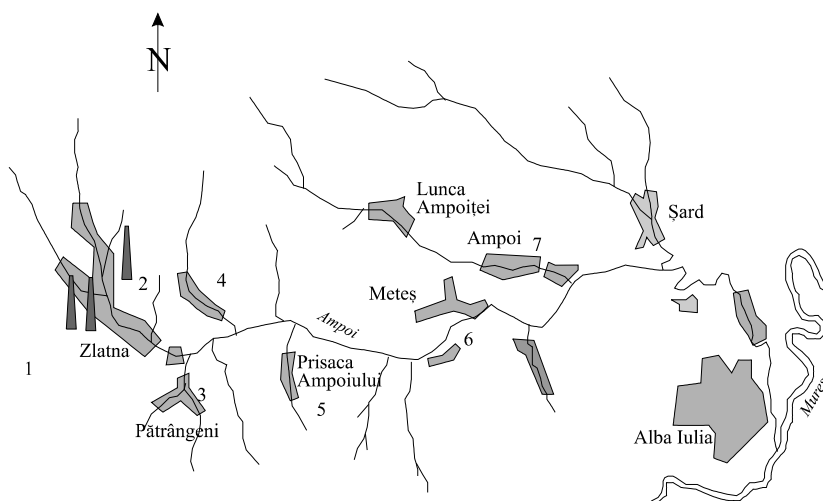


Fig. 1. The sketch map of the Zlatna region and the location of the studied sites.

**Dissolution procedure for soil samples.** In the acid digestion procedure (Lunge method) [6], 0.2 g of finely ground soil sample was weighed. Ten millilitres of 1:1 HCl were added to the sample and the solution was fumed to near dryness. After cooling, 10 ml of 1:3 HCl:HNO<sub>3</sub> (v/v) (Lunge mixture), was added, and again the acid was fumed off to near dryness. The residue was dissolved in 25 ml 1:4 HCl and heated for approximately 15 min. The sample was then transferred into a 50 ml volumetric flask and diluted to volume with distilled water.

**Dissolution procedure for vegetable samples.** Samples were hand-cleaned to remove foreign material and oven dried at 108<sup>o</sup> C for 8-10 hrs. Each sample was carefully ground in a porcelain mortar. Approximately a 0.5 g portion was digested in a glass vessel using 14 ml HNO<sub>3</sub>; this was carried out for over night at room temperature then heated 3 hrs at 120<sup>o</sup> C. It was then cooled, 6 ml H<sub>2</sub>O<sub>2</sub> added, and reheated to 120<sup>o</sup>C until no brown fumes were given off. The resulting sample was cooled and bulked to 50 ml.

**Reagent and standard solution.** Nitric acid (65% m/v), hydrochloric acid (37% m/v) and H<sub>2</sub>O<sub>2</sub> (30% m/v) (Merck, Darmstadt, Germany) were used for the soils, mosses and lichen digestion. The blank sample contained only the reagents used for digestion. All solutions were stored in plastic vials cleaned with acid solution and rinsed with distilled water.

Single element stock solutions of 1000 mg L<sup>-1</sup> were prepared by dissolution of high-purity metal (Merck, Darmstadt, Germany) in a minimum volume of HNO<sub>3</sub> (Cu, Pb) or HCl (Zn) and diluted to 1 L.

**Instrumentation.** Flame atomic absorption measurements were performed on a Perkin-Elmer Model 2100 atomic absorption spectrometer operating with acetylene-air flame and optimised standard operating conditions. Linear curves from mono-element external standards were used for quantification.

**Soils pH determination.**

*Procedure.* Weigh 25 g of soil in a clean beaker. Add 25 ml distilled water and stir for 15 minutes. Calibrate the pH meter prior to use by inserting the combination glass electrode in a buffer solution of pH 7.0. Adjust the pH meter to read pH 7.0. Rinse the electrode with distilled water and place it in a buffer solution of pH 4.0 to read pH 4.0. Rinse the electrode again with distilled water and place it in the soil suspension above. Read the pH in the scale of the pH meter.

Soil pH is strongly affected by acid emissions from the Zlatna plant (Table 1).

**Table 1.**  
pH values of the soil samples collected on 16 May 1999.

Sample	Sampling point definition	pH
1a 1b	Site 1 300 m SSW of two smelter chimneys above house	3.93 3.82
2a 2b	Site 2 opposite site 1, 500 m NE from new factory	3.78 3.83
3a 3b	Site 3 P <sup>3</sup> atrângeni (station)	4.00 4.01
4a 4b	Site 4 opposite Patrangeni forest (300 m below calcareous stone with cross)	4.42 4.46
5a 5b	Site 5 Presaca Ampoiului	4.38 4.25
6a 6b	Site 6 Metes	5.32 5.05
7a 7b	Site 7 Ampoita	4.58 7.17

Down-valley of the plant soils display low pH due to acid deposition. The acidity of the soils decreases with increasing distance from the plant. This is in agreement with the prevailing wind direction and the dispersal (and dilution) of pollutants from the smelter plant (west-east). Soil pH at site 4, is slightly buffered by the local calcareous (limestone) bedrock (Wildflisch Formation), but the soils are still very acidic. Soils at site 7 show a large variation in pH values due to the soils in the area being largely agricultural and recently ploughed.

**Results and discussion**

The variation in Pb, Cu and Zn concentrations in moss samples collected along the 25 km is represented in Figure 2. Lead concentrations show the greatest variation between sample sites, and also the highest concentrations overall. Zinc is not present in very high concentrations; variation between sites 1,2,4 and 5 is very little. Copper shows a similar degree of variation as lead, but is not present in such high concentrations; it is greater than zinc since the primary ore (chalcopyrite) does not contain much zinc.

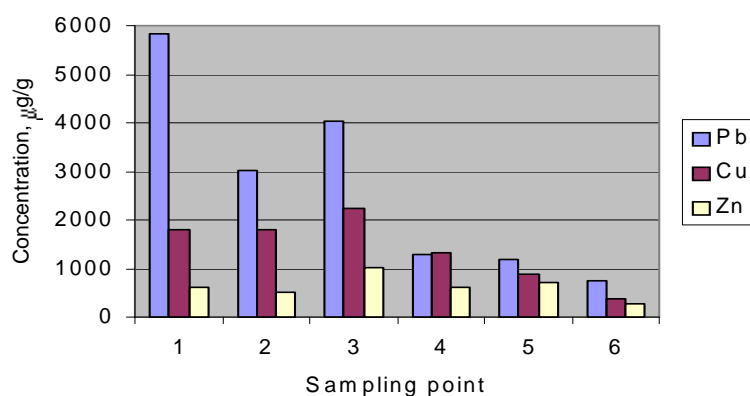


Fig. 2 Pb, Cu and Zn concentration in mosses.

lected along the Ampoi Valley is represented in Figure 3. Lead is once again the greatest concentrations in comparisons with the other studied elements. In sites 1 and 2 *Cladonia fimbriata* and *Cladonia coniocraea* (fruticulous lichens) could not be found at all; this effect is probably due to the fact that SO<sub>2</sub> and the metals are too concentrated in these areas for these lichens to exist.

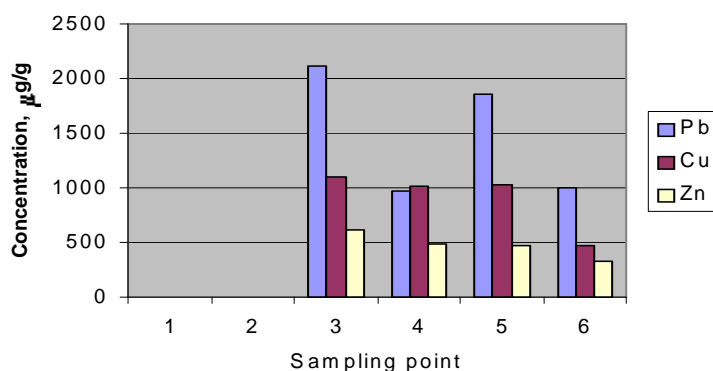


Fig. 3 Pb, Cu and Zn concentration in lichens.

The degree of accumulation of the analysed elements is different for soils, mosses, lichens and oak leaves. In Figure 4 the Cu, Zn and Pb concentrations in the studied samples versus the distance from the polluted source are represented comparatively. It is interesting to compare lichens and mosses data (perennial plants) with oak leaves chemical data (deciduous trees).

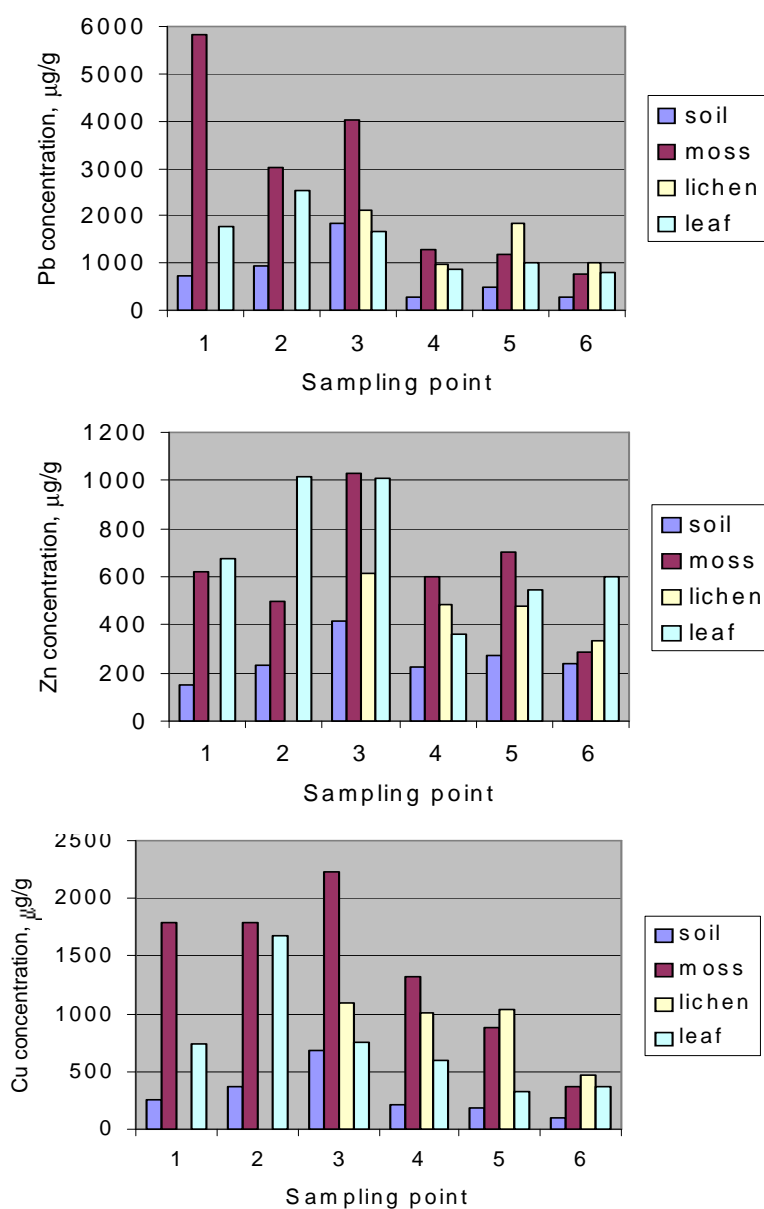


Fig. 4 Pb, Zn and Cu concentration in studied samples

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For copper the mosses accumulate the greatest concentrations. The trend of the concentrations for leaves, mosses and soils is such that levels of copper increase up to site 3, at which point they begin to decline as distance from the source increases. This is not the case for lichens: these can only exist from point 3 eastwards, and perhaps their copper levels do not show the same trend as, say mosses, due to their being saturated with copper.

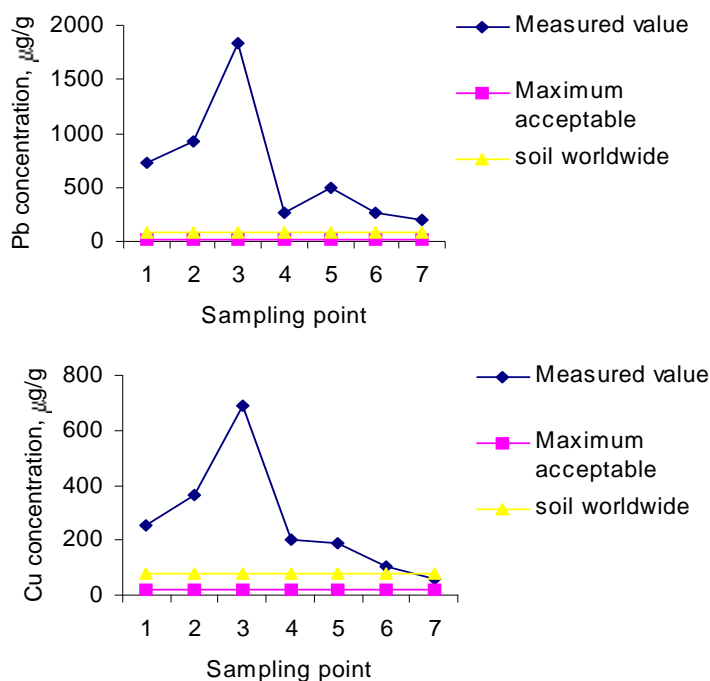
For zinc mosses and leaves show similar levels of concentration, in the lichens this metal decrease with the distance from the pollution source. The general trend is less clear than that of copper.

For lead the relationship of concentrations between each of the sample media is similar to that of copper. The general trend between sites is less clear, but there is some trend of decrease away from the source. Site 3 and 4 interesting as these are on opposite sides of the valley, equidistant from the plant and yet soil Pb values are much lower in 4 than 3. It shows that there is some local variation due to the topographical influences. As the soil pH is higher here (site 4) we would accept, the metals are not mobilised in these acidic conditions.

The soil concentrations are not very high compared to the vegetation samples, but show a trend of increasing towards site 3 and decreasing eastwards.

The fact that soils are much lower in concentration of the studied elements than the biological samples may be due acid rains leaching the lower horizons, and also because soils do not accumulate the metals biologically to the same degree.

The Cu, Zn and Pb concentrations find in soils were compared with the maximum value admitted by Romanian standards and with the soil worldwide (Figure 5).



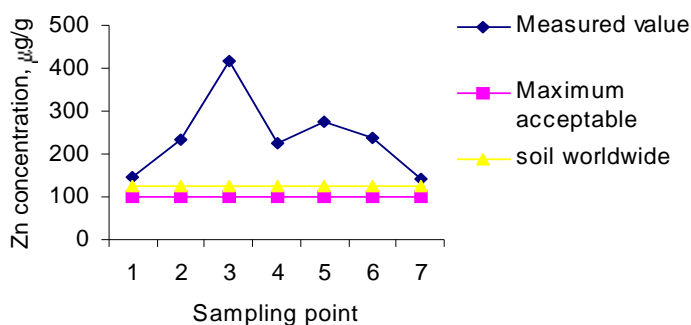


Fig. 5 Pb, Cu and Zn distribution in the sampling points along Ampoi Valley.

These graphs indicate the concentrations of copper, lead and zinc in soils along the transect in the Ampoi Valley. These are compared, in each case, with both the average concentration (worldwide- Pb: range 10 to 84 ppm, Cu: range 6 to 80 ppm, Zn: range 17 to 125 ppm [7]) and the maximum acceptable concentrations of these elements (Official Romanian Standard, 1997- Pb 20ppm, Cu 20ppm, Zn 100ppm ). In all situations the element concentrations exceed these maximum levels — by a considerable margin.

### Conclusions.

- Our pilot study identified a strong gradient of metal contamination in soils and biota as well as soil acidification along a WE transect from the plant.
- Highest impact of pollution is at site Patrangeni (3), 3.5 km from the plant.
- Local topographic influences may protect certain areas from metal deposition as at site (4) directly opposite the most contaminated site.
- Mosses accumulated higher levels of metals than lichens, leaves and soils.
- Extreme SO<sub>2</sub> contamination in the results in a low macrolichen diversity present in insufficient quantities in the vicinity of the plant to allow bulk chemical analysis by conventional means.
- We conclude that in view of the high soil and biotic metal concentrations which are significantly higher than recommended levels, this suggests there may be important health implications from ingestion of locally contaminated crops.
- We recommend that future biomonitoring studies should focus on utilising moss/lichen transplants using a grid system to minimise problems in obtaining sufficient samples *in situ* for analysis. This is necessary to assess the full extent of contamination.

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