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Heavy metal pollution downstream the abandoned Coval da Mó mine (Portugal) and associated effects on epilithic diatom communities

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ABSTRACT

This study examined trace-element concentrations in 39 sediment samples collected in the vicinity of the abandoned Coval da Mó mine, and evaluated the anthropogenic contaminant effects and other environmental variables in the taxonomic composition, structure and morphological changes of benthic diatom communities.

The results show the existence of extremely high contamination in Pb, Zn and Cd (the mean values exceed the background values 376, 96 and 19 times, respectively) on the first 2.5 km in the water flow direction. Also Co, Cu, Mn and Ni are present in high concentrations. Dilution by relatively uncontaminated sediment reduces metal concentrations downstream, but Zn concentrations increase downstream Fílvida stream, as a result of several factors such as sewage and agriculture.

To evaluate the biological effects caused by Pb, Cd and Zn, three sites were selected. In the stressed environment, near the mining area (C232), diatoms were extremely rare, however there was a slight recovery at site C79 located 2 km downstream. *Fragilaria capucina* var. *rumpens*, *Fragilaria* cf. *crotonensis* and *Achnanthidium minutissimum* showed abnormal valves which may be related to high levels of metals.

Six km downstream, in Fílvida stream (C85), an increase in species richness and diversity was registered while the relative percentage of valve teratologies was lower. In the absence of OM, nutrients and low pH the diatom community patterns must be attributed to the metal concentration at some sites. Considering that community diversity can be affected by abiotic and biotic variables and valve deformations are caused by a small number of variables, basically metals, and acid conditions, we consider the presence of teratologies as an indication of the presence of metals.

1. Introduction

Human activities such as mining may greatly increase trace-element concentrations in the environment (Brigham, 2002). The wastes from mining activity, containing high metal concentrations, represent a source of metal contamination for a long time following extraction. Because of chemical and geotechnical instabilities of these materials, and other potential environmental constraints, the wastes result in long-term public concerns. The mining wastes contribute with sediment, acidity, metals, and secondary precipitates to streams, which may render local watersheds inhospitable to aquatic biota (Kucken et al., 1994; Lottermoser et al., 1999; Gold et al., 2002; Olaveson and Nalewajko, 2000; Sabater, 2000; Hirst et al., 2002; Hammarstrom et al., 2003; Lacoul and Freedman, 2006).

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The traditional approach to investigate the environmental impacts of an abandoned mining site is based on geochemical survey methodologies.

Streambed sediments can be a useful medium for trace-element analyses. Streambed sediments can accumulate chemicals over time, and may be useful archives of past contamination. If significant trace-element contamination is introduced to a stream – either transiently or continuously – streambed sediments should accumulate some portion of the elements through chemical and physical sorption processes.

Measurement of metals total concentration in sediments is useful to detect changes in the stream due to different possible phenomena such as erosion and leaching to groundwater, but it does not give any indication about the chemical form of metals in sediments (Pagnanelli et al., 2004). The knowledge about metal partitioning among different geochemical phases is particularly important to assess the potentially bioavailable fractions and any risks of ecotoxicity.

Numerous geochemical studies on total trace metal concentrations or related to partitioning of trace metals in different geochemical phases have been performed in order to study water contamination by heavy metals after cessation of sulphide-ore mining activities (Nordstrom, 1982; Leenaers, 1989; Boulet and Larocque, 1998; Edelgaard and Dahlströ, 1999; Leblanc et al., 2000; Schroth, 2001; Bird et al., 2003; Ferreira da Silva et al., 2005, 2006; Sánchez España et al., 2005).

Diatom communities possess many of the attributes required for indicator organisms because they are widely distributed, occupying an essential position at the base of aquatic food chains as they are important primary producers in many freshwater environments. They may attach to substrates, therefore integrating the real habitat conditions and responding quicker to environmental changes than higher level organisms, because of their short life cycle. In addition, algal assemblages are rich in species, composed of some tens of taxa with environmental tolerances and preferences (Lange-Bertalot, 1979; Ter Braak and Van Dam, 1989; Cox, 1991; Van Dam et al., 1994; Kelly and Whitton, 1989; Pan et al., 1996; Stoermer and Smol, 1999). The susceptibility of freshwater diatom communities to metals has been reported under field and laboratory conditions (Say, 1978; Leland and Carter, 1984; Deniseger et al., 1986; Genter et al., 1987; Gray and Hill, 1995; Gustavson and Wängberg, 1995; Genter, 1996; Medley and Clements, 1998; Paulsson et al., 2000).

Many studies on metal polluted rivers have shown that diatoms respond to environmental degradation not only at the community level through shifts in dominant taxa and diversity patterns but also at the individual level with changes in frustule morphology. Size decrease (Gensemer 1990; Cattaneo et al., 1998, 2004) and frustule deformations (Harding and Whitton, 1976; Thomas et al., 1980; Adshead-Simonsen et al., 1981; Barber and Carter, 1981; Foster, 1982; Kelly and Whitton, 1989; Carter, 1990; Yang and Duthie, 1993; McFarland et al. 1997; Dickman, 1998; Gold et al., 2003; Cattaneo et al., 2004) have been correlated with high metal concentrations. An interesting review paper on teratologies in diatoms has recently been published (Falasco et al. 2009). This review highlights the main causes for frustule deformations. Although metal contamination is pointed out as one of the producers of teratological alterations in diatom frustules it is not the only one. Other physical and chemical parameters were pointed as potential deformation causers such as: drought conditions, light intensity, UV, salinity levels, nutrients and other toxic compounds such as cyanide, polycyclic aromatic hydrocarbons (PAH) and pesticides.

Several studies that aim to establish a relationship between the level of metal contamination and diatom species composition have been carried out (Besch et al., 1972; Say, 1978; Say and Whitton, 1980; Rushforth et al., 1981; Deniseger et al., 1986; Genter and Lehman, 2000; Sabater, 2000; Gold et al., 2002), thereby allowing the assessment of metals long-term effects within resident communities at polluted sites. Metal contamination may drive succession in algal communities towards more pollution tolerant species (Gustavson and Wängberg, 1995), resulting in an increased tolerance of communities (Blanck et al., 1988). It may also result in loss of species diversity (Leland and Carter, 1984; Medley and Clements, 1998).

The purpose of this study was to:

- characterize the aquatic environmental conditions in the Coval da Mó and Fílvida streams and determine the geochemical background of trace metals in streambed sediment in order to evaluate the degree of the dispersion of trace elements in streambed sediment.
- evaluate the trace-element concentrations found in surface water and their potential detrimental effects on aquatic habitat in Coval da Mó and Fílvida streams.
- compare communities growing at different sites along strong metal pollution gradients.

2. The study area

2.1. Environmental setting

The Coval da Mó old mining area is located 20 km northeast of the city of Aveiro in the drainage area of the Caima river (140 km^2), a tributary of the Vouga river (Fig. 1a). The mine is located in a mountainous region with rounded rolling hills and short narrow valleys that form a dendritic-type drainage network. Coval da Mó and Fílvida streams are small perennial impacted tributary streams with an approximate width of 1 m to 2.5 m, and 20 to 50 cm deep, respectively (Fig. 1b, c).

This area has a seasonal temperate climate, with a very well defined rainy and dry season. Most rainfall occurs between October and March and the dry season occurs from June to September (DGRAH, 1981). According to "Instituto Nacional de Meteorologia e Geofísica" (INMG) the long-term average annual precipitation is 1244 mm/year (precipitation range between 584 and 2514 mm/year — Borg and Hedlund, 2001). Temperatures range between 8.5 and 20.3 °C (annual mean of 13.7 °C).

Most of the landscape is forested (*Eucalyptus* sp. and *Pinus pinaster* type), with some grassland to the south. Major human land uses in this basin include agriculture, industry, mining, urban, and mixed use. Agricultural activities include the production of fruits, grains and vegetables.

2.2. Geological setting

Set in the Central Iberian Zone of the Iberian Massif, a tectonostratigraphic unit of the Iberian Peninsula first described by Ribeiro et al. (1979), the mine is located in terrains of the Beira Schist Complex, a meta-sedimentary formation mainly composed by phylites, metagreywacke and micaschists of still lower Cambrian age.

As mentioned before, the wall rock in the mine was mainly black, chloritic schist from the Beira Schist Complex of Cambrian age, in which faults and fracture lines of E–W, WNW–ESE and ENE–WSW directions were filled by the mineralizing solutions of probable late to post-Hercynian age (Thadeu, 1977).

2.3. Mining

The Coval da Mó mine is part of the mining complex of Braçal, situated in the Aveiro district, of the Beira Litoral Province, Central-West Portugal, about 30 km from Aveiro. Mining activities at this site started in 1856, but due to economical difficulties caused by the First World War period the mining complex was forced to close in 1918. Afterwards, the second mining period started during the Second World War in 1942, and lasted until the end of the 60's (total shutdown in 1972).

The main ore exploited in this mine was lead in the form of galena (PbS), and also some zinc [sphalerite — (Zn,Fe)S] and silver (in galena and sphalerite) as accessories. Gangue minerals are dolomite ($CaMg(CO_3)_2$), siderite ($FeCO_3$), some (not much) quartz (SiO_2), pyrite (FeS_2), some chalcopyrite ($CuFeS_2$) and other secondary alteration minerals as aragonite ($CaCO_3$) and anglesite ($PbSO_4$). Macroscopic observations permit to distinguish between three types of mineral association: *Type 1*: is richer in sphalerite and pyrite with main gangue mineral being quartz; *Type 2*: represents the main mineralized vein body consisting of galena in large cubic-octahedral crystals and white sparry dolomite; *Type 3*: consists of small veins and brecciation caused by fractures at near perpendicular attitude to main vein, mostly fully filled with massive sulphides (mainly galena or pyrite) and almost no content of gangue minerals (Marques de Sá, 2004, 2008).

The type of waste generated by mining activities in the Coval da Mó mining area was very large dumps of wall-rock and vein stones, debris and tailings.