Chemosphere 194 (2018) 158–170

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Metal(loid) accumulation in aquatic plants of a mining area: Potential for water quality biomonitoring and biogeochemical prospecting

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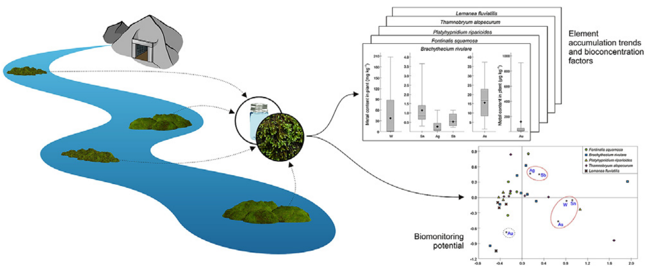
HIGHLIGHTS

- This work focused on multi-element accumulation by aquatic plants in field conditions.
- A set of plant species was found with the ability to accumulate several elements.
- The studied aquatic bryophytes can be suitable for water quality biomonitoring.
- *Thamnobryum alopecurum* and *Brachythecium rivulare* reveal high accumulative capacity.
- The alga *Lemanea fluviatilis* hold promise in the context of some metals (Rb, Ta, Au).

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 20 June 2017
Received in revised form
21 November 2017
Accepted 22 November 2017
Available online 23 November 2017

Handling Editor: Martine Leermakers

Keywords:
Algae
Bryomonitoring
Central Portugal
Mosses
Nature-based technique
Phytotechnology

ABSTRACT

Aquatic bryophytes can accumulate extremely high levels of chemical elements because of their unique morphology and physiology which is markedly different from vascular plants. Four aquatic mosses—*Fontinalis squamosa*, *Brachythecium rivulare*, *Platyhypnidium riparioides*, *Thamnobryum alopecurum*—and a freshwater red alga *Lemanea fluviatilis* along with water samples from the streams of Góis mine region in Central Portugal were analyzed for 46 elements. Despite being below detection levels in the water samples, the elements Zr, V, Cr, Mo, Ru, Os, Rh, Ir, Pt, Ag, Ge and Bi were obtained in the plant samples. The moss *T. alopecurum* had the highest mean concentrations of 19 elements followed by *B. rivulare* (15 elements). Maximum accumulation of Rb, Ta and Au, however, was seen in the alga *L. fluviatilis*. Bioconcentration factors $> 10^6$ were obtained for a few metals. The investigation confirms that aquatic bryophytes can be suitable for water quality biomonitoring and biogeochemical prospecting in fresh water bodies owing to their high accumulative capacity of multi-elements from their aquatic ambient.

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https://doi.org/10.1016/j.chemosphere.2017.11.139
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1. Introduction

Aquatic bryophytes are often conspicuous in mountain stream ecosystems marked by extreme physical fluctuations. They influence both biodiversity and water chemistry (Gecheva and Yurukova, 2014; Vieira et al., 2005). They are not always sensitive to pollutants at levels that would harm other organisms (Glime and Keen, 1984) and are considered excellent biomonitors of metals and other contaminants (Zechmeister et al., 2003). Also, they are easy to collect and transplant, can be harvested any time of year, and samples can be kept many years for later analysis. Chemical analyses of contaminants in bryophyte samples reflect the state of environmental contamination (Ganeva, 1998). This is because they accumulate extremely high levels of heavy metals based on their high-cation-exchange tissue capacity, lack of cuticle and high surface-to-volume ratio (Tyler, 1990). Being composed of sheets of tissue, they are in close contact with the environment and hence respond more rapidly to environmental changes as compared to the vascular plants.

Possible use of bryophyte species for biomonitoring of water quality has been discussed broadly in recent years (Ceschin et al., 2012; Gapeeva et al., 2010; Hájek et al., 2014). They have been successfully used as passive and active bioindicators/biomonitors of surface water (rivers, lakes) contamination by metals in several European countries, such as Belgium (e.g., Mouvet, 1984; Vanderpoorten, 1999), Bulgaria (e.g., Gecheva et al., 2015), England (e.g., Kelly et al., 1987; Vincent et al., 2001), Germany (e.g., Kapfer et al., 2012; Samecka-Cymerman et al., 2002) and Portugal (e.g., Figueira and Ribeiro, 2005; Vieira et al., 2011, 2012; Pratas et al., 2017), and predictive models including mosses as bioassessment tools have been devised (Feio et al., 2012; Tremp et al., 2012; Vieira et al., 2014). Passive biomonitoring deals with observation and analysis of native species, while active biomonitoring is based on bryophytes transplantation for a fixed exposure period (Gecheva and Yurukova, 2014). Thus, bryophytes can be used as a low cost methodology for monitoring water quality. They also have the potential to phytoremediate contaminated waters, acting as natural 'green' filters. In fact they might have a distinct advantage over vascular plants in this, due to their unique anatomy as mentioned above.

A wide variety of aquatic mosses have been used worldwide for biomonitoring purposes. In a review, Debén et al. (2015) estimated that 58% of the 71 species tested had been used only once. They also found that in 68% cases the moss belonged to the genus *Fontinalis* (*F. antipyretica* Hedw., *F. squamosa* Hedw., *F. dalecarlica* Bruch & Schimp., *F. duriaei* Schimp. and *F. hypnoides* Hartm.) followed, in order of frequency, by *Platyhypnidium riparioides* (Hedw.) Dixon (30%) and *Brachythecium rivulare* Schimp. (10%).

Glime and Keen (1984) found that *Fontinalis* could survive at water concentrations of Cd up to 35 $\mu g\ L^{-1}$, whereas waterfleas and salmonid fish die at 1.2 $\mu g\ L^{-1}$. Caines et al. (1985) evaluated the connection between heavy metal concentrations in a liverwort (*Scapania undulata* (L.) Dumort.), mosses (*F. squamosa*, *P. riparioides*), and water in Scotland. Natural background levels for Cd, Cr, Cu, Pb and Zn in four moss species (*F. antipyretica, F. squamosa, P. riparioides,* and *Amblystegium riparium* (Hedw.) Schimp.) and sediments were reported from Portugal (Gonçalves et al., 1992). In this study, Cr and Zn were accumulated by plants 107 and 70 times more than their respective background levels. Also the accumulation of highly toxic elements, such as As and U, in *F. antipyretica* has been reported by several authors (Favas et al., 2012, 2014b; Cordeiro et al., 2016). In turn, López and Carballeira (1993b) found that *F. antipyretica*, *P. riparioides*, and *B. rivulare* displayed intermediate capacities to accumulate metals.

Platyhypnidium riparioides (synonym *Rhynchostegium riparioides* (Hedw.) C. Jens.) has been confirmed as a geographically and ecologically widespread species excellent for monitoring heavy metals (Wehr and Whitton, 1983a). This moss was broadly included in biomonitoring researches in Belgium (Wehr et al., 1983), Bulgaria (Gecheva et al., 2011; Yurukova and Gecheva, 2012), England (Jackson et al., 1991) and Spain (García-Álvaro et al., 2000).

Brachythecium rivulare has been found useful in biogeochemical prospecting for minerals (Samecka-Cymerman and Kempers, 1992, 1993; Pirc, 2003). *Brachythecium* spp. were also used for biomonitoring Mn, Mo and Ni (Vukojević et al., 2009), and Cd and Cr (Xu et al., 2012) from atmospheric deposition and contaminated water, respectively.

Some algae also show a high capacity for accumulation of heavy metals due to their tolerance mechanisms (Suresh and Ravishankar, 2004) and simple morphology like bryophytes. Several species of the green algae *Enteromorpha* and *Cladophora*, occurring in freshwater, brackish and/or marine conditions, have been utilized to measure heavy metals in many parts of the world (Al-Homaidan et al., 2011). For example, *Ascophyllum nodosum* (L.) Le Jolis, *Sargassum* spp., *Fucus vesiculosus* L., *Microasterias denticulata* Brébisson ex Ralfs have been reported to accumulate metal(loid)s like Pb, Ni, As, Zn, Au, Cu, Cd, Co, and Hg (Kuyucak and Volesky, 1989; Holan and Volesky, 1994; Kumar and Oommen, 2012; Volland et al., 2012). Relationships between Zn, Cd and Pb concentrations in three algae (*Lemanea fluviatilis* (L.) C. Agardh, *Cladophora glomerata* (L.) Kützing, *Stigeoclonium tenue* (C. Agardh) Kützing), one liverwort (*S. undulata*) and three mosses (*A. riparium*, *F. antipyretica* and *P. riparioides*) were established in Belgium, France, Germany, Ireland, Italy and Great Britain (Kelly and Whitton, 1989).

In this context, the present investigation has been undertaken with the following objectives: (a) to evaluate the degree of metal(loid) contamination of the streams in the study area; (b) to determine the metal(loid) concentrations in the surface water and four aquatic mosses and one alga; (c) to relate the metal(loid) concentrations in water and mosses/alga species; and (d) to identify mosses/alga species with the biomonitoring/biogeochemical prospecting potential based on accumulation pattern.

2. Materials and methods

2.1. Study area

The mining area of Góis, which includes the Escadia Grande mine (Au) and the Vale de Pião mine (Sn–W), is located in Central Portugal, about 40 km east of the city of Coimbra. Topographic elevations vary between 179 m and 859 m (Fig. 1). It is a densely forested area with rugged relief drained by the Ceira River and its tributaries (Pratas et al., 2017). In recent years, the average monthly precipitation in the area varied from a minimum of 16.2 mm in August to a maximum of 153.6 mm in December, and the average annual precipitation was 1011 mm (SNIRH, 2016).

This area is situated in the tin–tungsten sector of the Central Iberian Zone, close to its boundaries with another geotectonic zone, the Ossa Morena Zone (Pratas et al., 2017). The principal types of rocks of the region are included in the Neoproterozoic metasedimentary sequence of Beiras Group (Dúrico-Beirão Supergroup or Schist-Graywacke Complex) (Meireles et al., 2013). These lithological sequences are mainly formed by black phyllites, siltstones, mudstones and graywackes, which display low-grade regional metamorphism in the chlorite zone. In some places, like in the Senhora da Guia area, there are evidences of contact metamorphism (occurrence of spotted schists) (Oliveira, 1990; Parra, 1990).

This is a vast mining field, with several mineral occurrences of

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