METAL CONTAMINATION MONITORING WITH AQUATIC BRYOPHYTES: IMPACT OF AN ABANDONED MINE SITE ON THE RIVER MERSE (CENTRAL ITALY)

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Introduction

Mine waters, such as acid mine drainage (AMD), have severe impacts on receiving water bodies and on exposed plants and animals. In contrast to present-day regulated mine sites, historic mine sites are often a special cause of concern due to uncontrolled mine waters which result in toxic discharges to adjacent freshwaters and/or groundwater (Lottermoser, 2010).

The River Merse flows through an isolated valley of Southern Tuscany (Central Italy), mostly protected by a natural reserve. The watershed of the Merse drains the *Colline Metallifere*, for centuries a major Italian mining district with large pyrite (FeS_2) deposits and veins bearing Ag, Cu, Pb, Zn and other ores. Mining activities in this district came to an end about 30 years ago, leaving behind a legacy of abandoned tailings and spoils of mining plants, often located in direct proximity to watercourses.

In April 2001, acute pollution of the upper course of the Merse gained the attention of local population and media, when huge quantities of AMD waters from the abandoned mine of Campiano reached the river trough a small tributary. Promptly, a monitoring system and hydraulic countermeasures for the containment of mine waters were implemented by the Local Authorities. Remediation operations, which included specific AMD treatment technologies, ceased in 2009 when a project for a complete reclamation of the Merse-Campiano area was adopted.

Aquatic moss are efficient accumulators of trace metals and ideal indicators of contamination in freshwater ecosystems. The moss *Rhynchostegium riparioides* is among the most commonly used and proven biomonitors in river quality assessment, especially in chronic exposures to metals (Debén et al., 2015). In this study, *R. riparioides* was used to quantitatively assess impact from potentially toxic elements in the river Merse. By comparing data from different biomonitong campaigns carried out in 2015, 2009 and 2004, this research also aimed at assessing temporal trends in trace element contamination and, indirectly, efficacy of AMD water management strategies that were adopted.

Methods

Submerged tufts of *R. ripariodes* were collected from 8 sites from the River Merse. Approximately 100 g fresh weight of moss samples were taken at each location from an area of about 10 m^2. In the laboratory, bryophyte samples were washed carefully with distilled water and the apical shoots of the moss (2– 4 cm) cut by hand and dried at 40°C for 48 h. Samples were mineralized in closed PTFE vessels with a solution of HNO_3, and H_2O_2 using a microwave oven. Concentrations of Cd, Co, Cr, Cu, Fe, Pb, Mn, Ni and Zn were determined by a ETAAS and ICP-AES. Hg and As concentrations were determined by CVAAS and HGAAS, respectively. Analytical quality control was performed by inserting reagent blanks, duplicate samples and CRMs (1515a "Apple Leaves" from NIST) into each batch of analysis.

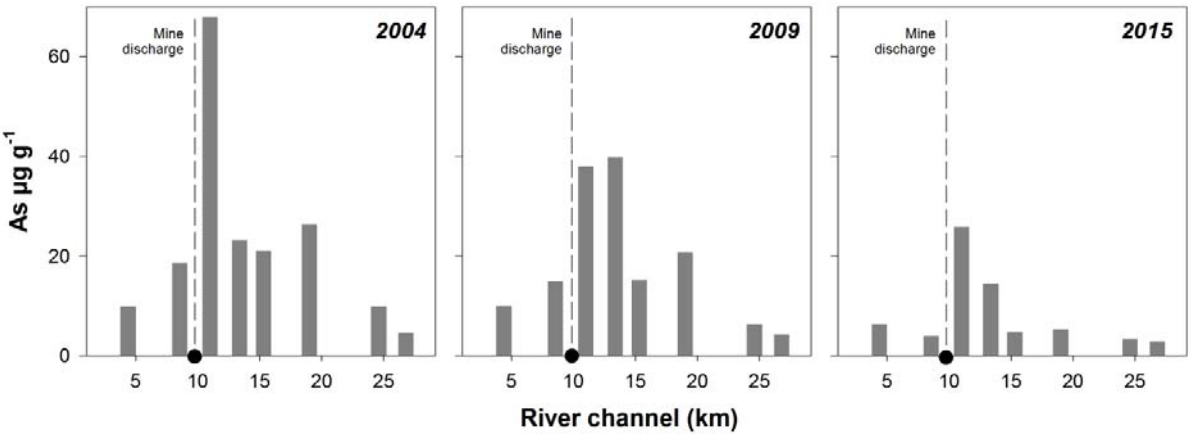
Results

Concentrations (mean ± sd) of trace elements in *R. riparioides* collected in 2015 from the upper (0-15 km) and lower (15-30 km) course of the River Merse are shown in Table 1. Cu was the metal showing the greatest variability (range: 17.9-843 µg g^{-1}) with the lowest Cu concentration in the lowland sampling sites. As, Cd, Co, Hg and Pb concentrations, although relatively less variable (85< CV < 96%), showed a similar pattern to that of Cu which was attributable to seepage waters flowing from the mining district. For As (and for the other elements of this group), temporal trends shown in Figure 1 highlighted a decrease in contamination as consequence of the AMD treatment plant put in place to contain acute pollution episodes recurring in this tract of the river since 2001.

Table 1. Trace element concentrations (mean ± standard deviation; µg g^{-1}) in samples of *R. riparioides* collected in the upper (0-15 km) and lower (15-30 km) tracts of the river Merse in May 2015.

River course	As	Cd	Co	Cr	Cu	Fe	Pb	Mn	Ni	Hg	Zn
upper	12.6 (±9.86)	2.38 (±1.26)	8.42 (±5.01)	13.7 (±6.14)	315 (±372)	9153 (±6054)	39.1 (±16.4)	922 (±572)	13.9 (±2.01)	0.28 (±0.26)	394 (±210)
lower	4.05 (±1.17)	0.42 (±0.23)	2.77 (±1.38)	19.4 (±10.4)	39.6 (±8.57)	5560 (±2552)	7.86 (±2.64)	555 (±389)	13.7 (±4.36)	0.14 (±0.04)	144 (±35.6)

Figure 1. Comparison of As concentrations (µg g^{-1} dw) in *R. riparioides* collected in 2015 and in previous monitoring campaigns (2004, 2009) from 8 sites along the River Merse, upstream and downstream of the main tributary connected with the mine of Campiano (dashed line).



Conclusion

Biomonitoring by *R. riparioides* allowed to characterize trace element contamination of the River Merse and provided quantitative basis to assess remediation measures recently adopted in the area. Moreover, excessive levels of potentially toxic elements, such as As and Cd, evidenced by the most recent *R. riparioides* data, prompted urgent completion of environmental reclamation (i.e. cleanup and disposal of mine waste piles and tailings still in the banks of the upper course of the river) to reduce toxic metal loads to the aquatic and riparian environment.

References

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