ASSESSING METAL POLLUTION IN PONDS CONSTRUCTED FOR CONTROLLING RUNOFF FROM RECLAIMED COAL MINES

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ABSTRACT

Constructing ponds to protect downstream ecosystems is a common practice in opencast coal mine reclamation. As these ponds remain integrated in the landscape, it is important to evaluate the extent of the effect of mine pollution on these ecosystems. However, this point has not been sufficiently addressed in the literature. The main objective of this work was to explore the metal pollution in manmade ponds constructed for runoff-control in reclaimed opencast coal mines over time. To do so, we evaluated the concentration of 10 heavy metals in the water, sediment and *Typha* sp. in 16 runoff ponds ranging from 1 to 19 years old that were constructed in reclaimed opencast coal mines of northeastern Spain. To evaluate degree of mining pollution, we compared these data to those from a pit-lake created in a local un-reclaimed mine and to local streams as an unpolluted reference, as well as comparing toxicity levels in aquatic organisms. The runoff ponds showed toxic concentrations of Al, Cu and Ni in the water and As and Ni in the sediment, which were maintained over time. Metal concentrations in runoff ponds were higher than in local streams, and macrophytes showed high metal concentrations. Nevertheless, metal concentrations in water and sediment in runoff ponds were lower than those in the pit-lake. This study highlights the importance of mining reclamation to preserve the health of aquatic ecosystems and suggests the existence of chronic metal toxicity in the ponds, potentially jeopardizing pond ecological functions and services.

Key words: runoff control; manmade ponds; heavy metals; reclamation; restoration; coal mining; post-mining landscapes

INTRODUCTION

Surface coal mining operations remove the soil and rocks over the coal seam (overburden) to gain access to the underlying coal. Despite reclamations, surface mining produces major environmental disturbances due to excavation operations, including deforestation, topsoil loss, topological alterations, soil compaction, hydrological changes and aquatic contamination (Shrestha and Lal 2006; Cravotta 2008; Pond et al. 2008; Palmer et al. 2010). Among all disturbances, the heavy metal pollution derived from acidic mine drainage (hereafter called AMD) is one of the greatest threats to the aquatic ecosystems because heavy metals degrade the aquatic habitat and are potentially toxic to aquatic organisms (Dunbabin and Bowmer 1992; MacDonald et al. 2000; Cravotta 2008).

The main goal of mine reclamation is to isolate the pollutants from the ecosystems located downstream of the mine sites. This objective should be achieved in combination with the final use of the reclaimed mine (e.g., production of biomass for energy and sustain natural grassland and forest) because the resulting ecosystem will remain integrated in the landscape (Bungart and Hüttl 2001; Nicolau 2003; Gould 2012; Vickers et al. 2012). The control of the offsite effects are addressed by the design of stable relief forms and safety structures, such as wetlands and ponds that guarantee the non-emission of sediments and contaminants from restored sites to adjacent natural watercourses (Sawtsky et al. 2000; Nicolau 2003; Wong 2003). These water bodies are normally constructed with two objectives: the control of the runoff generated in the reclaimed mines and the specific treatment of AMD.

The water bodies constructed to retain the runoff may be affected by metal pollution although water has neutral pH and sediment does not show red, orange or yellow iron precipitates. In reclaimed mines, coal mineral could be present in the overburden materials used to reconstruct the topography, and metals could be released from the oxidation of pyrite present in the coal mineral (Johnson 2003; Sheoran and Sheoran 2006; Cravotta 2008; Griffith et al. 2012). The manmade wetlands and ponds remain integrated in the landscape after the end of mining reclamation and may provide new ecological functions and services to society, such as aquatic fauna habitats and recreational areas. But these functions ultimately depend on the quality of the ecosystem. Therefore, to know the extent to which wetlands and ponds are affected by metal pollution is an important issue that nevertheless was insufficiently addressed in the extant literature.

The main objective of this work was to explore the metal pollution in manmade ponds constructed for runoff-control in reclaimed coal mines (hereafter called runoff ponds). Specifically, we were interested in evaluating the temporal changes in metal concentrations to determine if toxic concentrations of metals were present in the aquatic ecosystem. The temporal study of the metal pollution for runoff ponds was done using a chronosequence approach. A comprehensive assessment of the runoff ponds was conducted through a study of water, sediment and aquatic macrophytes,

which are three main factors involved in the process of heavy metal removal (Dunbabin and Bowmer 1992; Sheoran and Sheoran 2006).

MATERIAL AND METHODS

Site description

The study was conducted in the Teruel coalfield, a mountainous area that is located in central-eastern Spain (Fig. 1) and characterized by a continental Mediterranean climate. In this area, coal extraction requires the construction of an external dump. As mining advances through the coalfield along the coal seam, the overburden is used to refill the previously mined pits, and the post-mining topography is created according to different reclamation objectives. We selected 16 manmade ponds created during mine reclamation to control the runoff from reclaimed mines (Fig. 1B). Pond age ranged from 1 to 19 years old, so we used a space-for-time approach to evaluate metal pollution over time. Due to logistic constraints in the samplings, chronosequences are frequently used instead of long data series (Majer and Nichols 1998; Walker et al. 2010; Hart and Davis 2011). The runoff ponds were designed mimicking natural ecosystems so that they would not require permanent human management. The runoff ponds were oval shaped, and the area ranged from 0.2 to 3.9 ha with an exception of one of them, which had an area of 22 ha. Littoral vegetation was dominated by *Typha* sp. distributed in an average band of 1.5 m around the pond. All ponds were permanent and endorheic; except for two ponds that were connected to a small stream, the water arrived from superficial and sub-superficial runoff during rain events.

In addition to the 16 runoff ponds, we sampled one pit-lake from an un-reclaimed coal mine within the same study area. Pit-lakes, which are formed when water fills excavated mining pits, are typically deep lakes with vertical walls. The pit-lake surface was 7.6 ha, and the pit-lake was narrow, deep, without a littoral zone and vegetation and enclosed by steep rock walls averaging 10 m high. The low water level and steep banks, typical characteristics of the un-reclaimed pit-lakes in the study area, make sampling extremely difficult and dangerous, and these conditions prevented us from including other pit-lake replicates in the study. The sampled pit-lake was older than 25 years old.

Finally, unpublished data of metal content in local streams were also considered to compare with data collected in the runoff ponds and used as a reference. Stream water and sediment samples were collected from 26 points along the mainstream (Martín River) and their principal tributaries in spring and summer of 2008 (Fig. 1A). Only dissolved metals in water and total metals in sediment are available.

Sample collection and processing

Water

In the spring and summer of 2009, the water conductivity ($\mu\text{S cm}^{-1}$) and pH were measured *in situ* at each pond using calibrated portable probes (WTW Multiline P4, Weilheim, Germany). All the material used for metal analysis was soaked in 10% HNO_3 (Sastre et al. 2002). The water was collected using polyethylene bottles at a depth of 15-20 cm. Samples were placed in portable refrigerators and immediately transported to the lab for further analyses. In the lab samples were stored in a refrigerator until the analysis were done. The alkalinity (mg l^{-1}) was determined by pH potentiometric automatic titration with 0.004 N H_2SO_4 (Metrohm, Herisau, Switzerland) within the 24h after collection. The water samples were filtered through pre-ashed and deionizer water cleaned 0.45 μm cellulose acetate filters. The dissolved SO_4^{2-} (mg l^{-1}) was determined by ion chromatography (Metrohm 861 Advanced Compact IC, Herisau, Switzerland). In addition, we determined ten dissolved trace metals (mg l^{-1}), Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn, using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES iCAP6300Duo; Thermo Fisher, Waltham, MA, USA). After filtering, water aliquots for metal analysis were immediately acidified to $\text{pH} < 2$ with ultrapure HNO_3 and kept at 4°C until analysis. The analyses performed in the lab followed standard American Public Health Association methods (APHA et al. 1992). Solution standards were appropriately diluted and used to calibrate the ICP-OES before metal determinations. Quality control for metal analysis was attained by including blanks and sample duplicates. The limits of detection in to water samples were $\text{Al} = 0.04 \text{ mg l}^{-1}$, $\text{As} = 0.08 \text{ mg l}^{-1}$, $\text{Cd} = 0.01 \text{ mg l}^{-1}$, $\text{Cr} = 0.01 \text{ mg l}^{-1}$, $\text{Cu} = 0.01 \text{ mg l}^{-1}$, $\text{Fe} = 0.02 \text{ mg l}^{-1}$, $\text{Mn} = 0.002 \text{ mg l}^{-1}$, $\text{Ni} = 0.03 \text{ mg l}^{-1}$, $\text{Pb} = 0.07 \text{ mg l}^{-1}$ and $\text{Zn} = 0.005 \text{ mg l}^{-1}$.

Sediment

One composite sample of sediment was collected from three points in the littoral zone of each pond, where *Typha* sp. grows, in the spring and summer of 2009. Sediment samples were taken using a hand corer sediment sampler 50 mm dia. The sampling was limited to the superficial sediment (i.e., top ~10 cm) because most physical and chemical changes in sediments occur within the upper 10 cm layer (Meyer et al. 2008). The sediment pH and conductivity ($\mu\text{S cm}^{-1}$) were measured in the lab in a solution of 10 g of fresh sediment dispersed in deionized water ($\text{pH}: 2.5:1 \text{ g ml}^{-1}$, conductivity: $5:1 \text{ g ml}^{-1}$) after shaking for 30 min. The collected sediments were air dried and sieved into fractions. The $< 2 \text{ mm}$ fraction was used to determine the total sulfur (%) using an elemental analyzer (LECO SC-144DR; Leco Instruments, St. Joseph, MI, USA). The $< 63 \mu\text{m}$ fraction was used to determine the total and extractable metals ($\text{mg kg}^{-1} \text{ DW}$): Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn (Förstner and Wittmann 1983; Casas et al. 2003). Total metal concentration was analyzed per the US Environmental Protection Agency 3051A Method (US EPA 2007), and the extractable metals were obtained using acetic acid (Davidson et al. 1994; Rauret 1998; Pueyo et al. 2001). In both cases, sediment digestion was performed by microwave extraction (Speedwave MWS-3, Berghof, Germany). Total and the extractable metals were determined using the ICP-OES following

American Public Health Association methods (APHA et al. 1992), in the same way as in water samples. The limits of detection to sediment were 0.01 mg l^{-1} for the 10 studied metals.

Vegetation (Typha sp.)

In the summer of 2009, we collected three plants of *Typha* sp. at the perimeter of each runoff pond. The plants were carefully washed using tap and distilled water, cleaned by immersion in 0.01 M ethylenediaminetetraacetic acid (EDTA) to remove any absorbed metals and finally rinsed with deionized water (Carranza-Alvarez, Alonso-Castro et al. 2008). Later, the plants were dried to constant weight at 60°C . The metal concentration in the tissues of *Typha* sp. varied, with root > rhizome > leaf (Dunbabin and Bowmer 1992; Sasmaz et al. 2008), so the dried plants were separated into leaf, root and rhizome and grounded in a laboratory mixer mill (MM400 Retsch, Haan, Germany) using teflon recovered grinding jars and balls. The plant material was digested with nitric acid to solubilize metals (Meeravali and Kumar 2000; Sastre et al. 2002) using a microwave system to reduce the total analysis time and the risk of sample contamination (Nadkarni 1984; Smith and Arsenault 1996; Sastre et al. 2002). Finally, Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn were determined in ICP-OES following APHA et al. (1992) methods as describe above for the water samples. The limits of detection to plant tissues were 0.01 mg l^{-1} for the ten studied metals. The metal concentration in the plant tissues was expressed in $\text{mg kg}^{-1} \text{ DW}$.

Data analyses

Water and sediment

Changes in the water and sediment characteristics in the runoff ponds were assessed over time by linear mixed-effect models (LMM). The LMM allowed for the detection of trends in the change of the environmental variables and control for the effect of the sampling season. For each variable, we built a model in which the fixed factor was the age of the ponds, and sampling season was used as random variable. LMM analyses were conducted with R software v.2.15.1 (R Core Team 2012). We used the function “lme” of the “nlme” package (Pinheiro et al. 2012). The “lme” function assumes that both the random effects and the errors follow normal distributions. All the water and sediment variables, except pH, were transformed with the $\log(x+1)$ to improve model fitting.

The metal toxicity in the runoff ponds was evaluated using several criteria obtained from the literature. To evaluate water pollution, we used the criteria established by the Environmental Protection Agency of United States for the indefinite (CCC: Criterion Continuous Concentration) and brief (CMC: Criteria Maximum Concentration) exposure of aquatic organisms without producing unacceptable effects (US EPA 2002). In addition, we used the toxic concentration of dissolved metals to plants defined by Markert (1992). The sediment metal pollution was evaluated using the quality guidelines for freshwater ecosystems proposed by MacDonald et al. (2000) that provide an accurate basis to predict the absence of sediment toxicity (TEC: Threshold Effect

Concentration) and the presence of sediment toxicity (PEC: Probable Effect Concentration). Moreover, Kruskal-Wallis analyses between metal concentration of runoff ponds and streams were conducted with R software v.2.15.1 (R Core Team 2012), to evaluate the mining effect over aquatic ecosystems located in reclaimed areas. We used the function “kruskal.test” of the “stats” package (Hollander and Wolfe 1973). In addition, the metal concentrations in the runoff ponds were compared to the metal concentration in the pit-lake created within the un-reclaimed coal mine.

Aquatic macrophytes

We assessed the influence of mining on the macrophytes by comparing the metal concentration of the *Typha* sp. to the average concentration of metals in plants growing in natural ecosystems following Markert (1992). We did not use a chronosequence approach to analyze metal content in *Typha* sp. because the time that each plant was exposed to the metals in the runoff pond could not be determined.

RESULTS

Metal pollution evaluation

In runoff ponds, heavy metals were rarely detected in water. As, Cd, Fe and Pb were below the limits of detection and Cr was only detected in the pit-lake, therefore were not shown in the figures. Water Al, Cu, Mn, Ni and Zn concentrations were above detection limits and shown in Figure 2. The water in the runoff ponds had a neutral pH (7.67 ± 0.16). The water pH in the pit-lake was acidic (3.48 ± 0.06) and alkalinity was not detected. The concentrations of sulfate, Al, Cu, Mn, Ni and Zn in the pit lake were several orders of magnitude higher than the runoff ponds (Fig. 2 from (a) to (i)). According to the criteria proposed by the US EPA (2002), the dissolved Al, Cu and Ni concentrations in the runoff ponds were above CCC criteria and only the Cu concentration were above CMC criteria. Ni was in the same order of magnitude than CCC, Al was four times greater than the CCC criteria, and mean Cu was six times greater than CCC and four times greater than CMC. The pit-lake showed Al, Cr, Cu, Ni, and Zn metal concentrations above CCC criteria and Al, Cr, Cu and Zn concentrations above CMC criteria. In fact, the differences between the pit-lake and reference levels were much higher than between the runoff ponds and the reference levels (Fig. 2 from (e) to (i)); notably, the Al and Cu metal concentrations in the pit-lake were more than 100 times greater. Among all metals in runoff ponds and the pit-lake, only Al in the pit-lake (Fig. 2(e)) exceeded the toxicity values established for plants in Markert (1992).

Total metal concentrations in sediment were detected in a high percentage of samples (from 60 to 100 %) for most of the studied metals, with the exception of Cd, which was below its limit of detection. Extractable concentrations of metals in sediments were detected in less than 50% of samples and As, Cd, Cr and Pb were below limit of detection (data not shown in figures).

Concentration of Al, As, Cr, Cu, Fe, Mn, Ni, Pb and Zn, to both, total and extractable fractions, were shown in Figure 3. In the sediment, the pH was neutral in the runoff ponds (7.32 ± 0.19) and acidic (4.73 ± 1.23) in the pit-lake, and the total sulfur was three times higher in the pit-lake than in the runoff ponds (Fig. 3 (a) and (c) respectively). Despite these results, we did not detect differences in the total and extractable heavy metals among runoff ponds and the pit-lake (Fig. 3 from (d) to (l)). In both water bodies, only As and Ni exceeded the quality guidelines established by MacDonald et al. (2000) for sediments in freshwater ecosystems. Notably, mean Ni was 20 times higher than the threshold value of TEC criteria, and approximately 10 times higher than PEC in both the runoff ponds and the pit-lake.

Metal concentration in streams are shown in Table 1. Al, Cd, Cu, Ni, Pb and Zn were below the limit of detection in water samples and Cd in sediment samples. The comparison of runoff ponds and stream metal concentration showed that dissolved Al, Cu, Ni were present in runoff pond but absent in streams and also that Mn showed a higher concentration in runoff ponds (Kruskal-Wallis test, $P < 0.001$). Dissolved Fe was present in streams and absent in runoff ponds, but was only detected in 20% of the stream samples. Total sediment concentration of As, Cu, Fe and Zn were higher in runoff ponds than in streams (Kruskal-Wallis test, $P < 0.001$, $P = 0.014$, $P = 0.002$ and $P = 0.018$ respectively). Al total concentration in sediment was significantly higher in the streams (Kruskal-Wallis test, $P = 0.028$) although mean concentrations in runoff ponds and in streams were in the same order of magnitude.

Finally, concentration of metals in plants were found in most of samples in a high percentage, with the exception of Cd and Cr that were below limits of detection. Metal concentration in plants (except Cd and Cr) were shown in Figure 4. The *Typha* sp. exceeded the average metal concentration of Al, As, Fe and Ni in a great percentage of samples, especially in the roots and rhizomes where was near 100% (Fig. 4 a, b, d and f). It is noteworthy that Fe was more than 100 times higher than the mean concentration in plants defined by Markert (1992).

Changes over time

Runoff ponds had similar values in the heavy metals carried by water, as well as in pH, conductivity alkalinity and sulfate concentration, regardless of age (LMM analysis, $P > 0.05$). The conductivity, total sulfur, As, Fe and Zn in the sediment increased with pond age (LMM analysis: $t = +2.687$, $P = 0.012$; $t = +3.572$, $P = 0.001$; $t = +2.662$, $P = 0.013$; $t = +4.284$, $P < 0.001$; and $t = +2.169$, $P = 0.038$ respectively). Despite the increase over time, toxic levels of As in the sediment to the aquatic organisms were maintained above TEC and below PEC thresholds.

DISCUSSION

Ponds exhibit toxic metal concentrations for aquatic life

The references used to detect metal toxicity in the aquatic organisms showed potentially toxic levels of Al, Cu and Ni in water and As and Ni in sediment (MacDonald et al. 2000; US EPA 2002). In addition, the higher metal concentration in runoff ponds than in local streams evidenced the effect of metal pollution from coal mining. Ponds are generally considered to be good metal sinks (Dunbabin and Bowmer 1992; Mitsch and Wise 1998; Sheoran and Sheoran 2006; Merricks et al. 2007). However, the case of the Teruel coalfield showed that the pond's ability to retain metals in the sediment did not completely reduce the water's metal concentration below levels toxic to the aquatic organisms. CCC, CMC, PEC and TEC criteria consider the negative effects that heavy metals could cause for a wide range of aquatic organisms (plankton, macroinvertebrates and fishes). Therefore, the persistent metal concentration above toxic levels over time may compromise the composition and development of the entire aquatic community. For example, metal pollution in aquatic sites could reduce the taxonomic richness of macroinvertebrate communities and induce a shift toward more tolerant taxa (Clements 1994; David 2003; Merricks et al. 2007; Loayza-Muro et al. 2010). Indeed, a low macroinvertebrate biodiversity was found in the studied runoff (Miguel-Chinchilla 2013; Miguel-Chinchilla et al. 2014). In addition, in fishes, heavy metals may restrict the presence of some species, reduce embryonic survival and increase the frequency of body malformations and deaths (Dubé et al. 2005; Lindberg et al. 2011; Witeska et al. 2013).

Although metal concentrations in the runoff ponds were not above levels considered to be toxic to plants (Markert 1992), the effects of the high metal concentrations were reflected in the study of the *Typha* sp. We detected Al, As, Fe, and Ni concentrations in the *Typha* sp. that were well above concentrations considered to be normal for plants (Markert 1992) and higher than the metal concentration of *Typha* sp. growing in non-polluted sites (Babcock et al. 1983; Samecka-Cymerman and Kempers 2001). *Typha* sp. is known to accumulate high amounts of metals in their tissues (McNaughton et al. 1974; Ye et al. 2003; Demirezen and Aksoy 2004), and our results are consistent with these previous findings. This accumulation of metals in the plant tissues could be a long-term problem because when plants die, metals in their tissues return to the ecosystems into detritus and during decomposition become more available, particularly to deposit feeders (Dorgelo et al. 1995; Weis and Weis 2004). Remarkably, *Typha* sp. was almost the only macrophyte in the runoff ponds. This observation suggests that other plants were less competitive than *Typha* and unable to establish due to prevalent heavy metal levels in the runoff ponds, indicating that ponds ultimately suffered from undesirable heavy metal pollution.

The accumulation of metals in the pond may not necessary indicate that ponds will be their final sink (Dunbabin and Bowmer 1992). Even if ponds have an endorheic character (similar to our study case), possible negative effects over downstream ecosystems should be considered. For example, metal exportation outside the reclaimed mines could happen during high storm events (Mitsch and

Gosselink 2000; Griffith et al. 2012) and through the food web (Braune et al. 1999; Parker 2004; Croteau et al. 2005).

Metal pollution persists in runoff ponds over time

The temporal approach used in this study indicates that metal pollution in the runoff ponds persisted even 19 years after their construction. Similarly, other studies revealed that heavy metal pollution in streams close to reclaimed coal mines was detected even more than 20 years after mining reclamation finished (Hartman et al. 2005; Clements et al. 2010; Hopkins et al. 2013). The increase of total sulfur, As, Fe and Zn in sediments over time may evidence a continuous introduction of metals into the runoff ponds. When coal mine spoils are exposed to natural weathering conditions, the pyretic minerals contained in the coal are oxidized in presence of oxygen and water, producing sulfuric acid and releasing heavy metals (Johnson 2003; Sheoran and Sheoran 2006; Cravotta 2008). Thus, sulfates and metals could move from the reclaimed mines into the runoff ponds during rain events dissolved in the water runoff. Moreover, soil and overburden erosion during storm events could mobilize sulfur and metals in suspension.

Despite continuous metal introduction into the runoff ponds, the pH, alkalinity, SO_4^{2-} and dissolved heavy metals in water and the extractable metals in sediment did not change over time. These results suggest that during the studied period, represented by the chronosequence, the runoff ponds had a chemical equilibrium that may be favored by carbonate parent material that provides extensive internal buffering capacity (Pond et al. 2008; Bernhardt and Palmer 2011; Griffith et al. 2012). Nevertheless, the observed chemical equilibrium in the runoff ponds may be altered by sediment pH changes in the future. This can sometimes occur when reduced sediment become oxidized, then stored metals may be released to more mobile forms (Gambrell 1994).

Relevance of mine reclamation

The concentration of heavy metals in the water of the runoff ponds was significantly lower than the concentration of heavy metals found in the pit-lake located in the un-reclaimed mine. Although the pit-lake was formed in a limestone area more than 25 years ago, it had a low pH and high concentrations of sulfate and heavy metals typical in this type of lakes (Blodau 2006; Yucel and Baba 2012). The concentrations of most of the studied metals in the water of the pit-lake were above the levels considered to be toxic for the aquatic organisms. Moreover, the combination of the acidic pH and the toxic level of Al could contribute to the absence of macrophytes and aquatic plants in the pit-lake (Markert 1992; Samecka-Cymerman and Kempers 2001; Brix et al. 2002). Therefore, if opencast coal mines had not been reclaimed in our study area, it is expectable that acidic and metal polluted lakes with poor conditions to sustain a biological community would have formed. In accordance to previous works (Younger 2001; Rodrigue et al. 2002; Wei et al. 2011), our study highlighted the relevance of opencast coal mine reclamation.

335

336 CONCLUSIONS AND MANAGEMENT IMPLICATIONS

337 Currently, the study of mining pollution is primarily focused on the study of downstream
338 ecosystems, and on constructed wetlands and ponds to specific AMD treatment. Nevertheless,
339 reclaimed mines also support aquatic ecosystems that could be highly affected by mining as shown
340 by our results. Even though reclamation of opencast coal mines plays a key role in reducing metal
341 pollution and obtaining functional ecosystems in post-mining landscapes, mine reclamation does not
342 completely avoid metal pollution, supporting higher concentration in the constructed runoff ponds
343 than in local streams. Metal concentrations were maintained over time, and in some cases even
344 increased, indicating that metal pollution may be a chronic problem. This is a relevant issue that may
345 determine the future land use of the reclaimed mines. Monitoring and control of post-mining areas
346 are therefore necessary on a long-term basis.

347

348 Runoff ponds are efficient tools to reduce mining pollution of natural ecosystems under the
349 condition that runoff is managed through endorheic basins. Nevertheless, we advocate a more
350 ambitious goal in restoration of opencast coal mines: metal pollution in manmade ponds should be
351 targeted to be reduced to the lowest level possible. The reclamation of opencast coal-mining
352 landscapes should focus on maintaining self-organized ecosystems in combination with the final use
353 of the post-mining area (Hobbs and Norton 1996). Topography, soil, water and vegetation should be
354 collectively considered in mining management projects to design landscapes that reduce the mining
355 pollution not only downstream but also *within* the reclaimed mines (Nicolau 2003). The selection of
356 the overburden with the best physical and chemical characteristics in the most superficial layers and
357 the design of a topography that minimizes erosion are important points to consider in post-mining
358 area management to reduce the metal pollution in constructed ponds and their associated aquatic and
359 terrestrial ecosystems.

360

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369 REFERENCES

- 370 APHA, AWWA, WPCF (1992) Métodos normalizados para el análisis de aguas potables y
371 residuales. Ediciones Díaz de Santos
- 372 Babcock MF, Evans DW, Alberts JJ (1983) Comparative uptake and translocation of trace elements
373 from coal ash by typha latifolia. *Sci Total Environ* 28:203–214. doi: 16/S0048-
374 9697(83)80019-9
- 375 Bernhardt ES, Palmer MA (2011) The environmental costs of mountaintop mining valley fill
376 operations for aquatic ecosystems of the Central Appalachians. *Ann N Y Acad Sci* 1223:39–
377 57. doi: 10.1111/j.1749-6632.2011.05986.x
- 378 Blodau C (2006) A review of acidity generation and consumption in acidic coal mine lakes and their
379 watersheds. *Sci Total Environ* 369:307–332. doi: 10.1016/j.scitotenv.2006.05.004
- 380 Braune B, Muir D, DeMarch B, et al. (1999) Spatial and temporal trends of contaminants in
381 Canadian Arctic freshwater and terrestrial ecosystems: a review. *Sci Total Environ* 230:145–
382 207. doi: 10.1016/S0048-9697(99)00038-8
- 383 Brix H, Dyhr-Jensen K, Lorenzen B (2002) Root-zone acidity and nitrogen source affects Typha
384 latifolia L. growth and uptake kinetics of ammonium and nitrate. *J Exp Bot* 53:2441–2450.
385 doi: 10.1093/jxb/erf106
- 386 Bungart R, Hüttl R. (2001) Production of biomass for energy in post-mining landscapes and nutrient
387 dynamics. *Biomass Bioenergy* 20:181–187. doi: 10.1016/S0961-9534(00)00078-7
- 388 Casas JM, Rosas H, Sole M, Lao C (2003) Heavy metals and metalloids in sediments from the
389 Llobregat basin, Spain. *Environ Geol* 44:325–332.
- 390 Clements WH (1994) Benthic Invertebrate Community Responses to Heavy Metals in the Upper
391 Arkansas River Basin, Colorado. *J North Am Benthol Soc* 13:30–44. doi: 10.2307/1467263
- 392 Clements WH, Vieira NKM, Church SE (2010) Quantifying restoration success and recovery in a
393 metal-polluted stream: a 17-year assessment of physicochemical and biological responses. *J*
394 *Appl Ecol* 47:899–910. doi: 10.1111/j.1365-2664.2010.01838.x
- 395 Cravotta C (2008) Dissolved metals and associated constituents in abandoned coal-mine discharges,
396 Pennsylvania, USA. Part 1: Constituent quantities and correlations. *Appl Geochem* 23:166–
397 202. doi: 10.1016/j.apgeochem.2007.10.011
- 398 Croteau MN, Luoma SN, Stewart AR (2005) Trophic Transfer of Metals along Freshwater Food
399 Webs: Evidence of Cadmium Biomagnification in Nature. *Limnol Oceanogr* 50:1511–1519.
400 doi: 10.2307/3597695
- 401 David CPC (2003) Establishing the impact of acid mine drainage through metal bioaccumulation
402 and taxa richness of benthic insects in a tropical Asian stream (the Philippines). *Environ*
403 *Toxicol Chem* 22:2952–2959. doi: 10.1897/02-529
- 404 Davidson CM, Thomas RP, McVey SE, et al. (1994) Evaluation of a sequential extraction procedure
405 for the speciation of heavy-metals in sediments. *Anal Chim Acta* 291:277–286.

Demirezen D, Aksoy A (2004) Accumulation of heavy metals in *Typha angustifolia* (L.) and *Potamogeton pectinatus* (L.) living in Sultan Marsh (Kayseri, Turkey). *Chemosphere* 56:685–696. doi: 10.1016/j.chemosphere.2004.04.011

Dorgelo J, Meester H, Velzen C van (1995) Effects of diet and heavy metals on growth rate and fertility in the deposit-feeding snail *Potamopyrgus jenkinsi* (Smith) (Gastropoda: Hydrobiidae). *Hydrobiologia* 316:199–210. doi: 10.1007/BF00017437

Dubé MG, MacLatchy DL, Kieffer JD, et al. (2005) Effects of metal mining effluent on Atlantic salmon (*Salmo salar*) and slimy sculpin (*Cottus cognatus*): using artificial streams to assess existing effects and predict future consequences. *Sci Total Environ* 343:135–154. doi: 10.1016/j.scitotenv.2004.09.037

Dunbabin JS, Bowmer KH (1992) Potential use of constructed wetlands for treatment of industrial wastewaters containing metals. *Sci Total Environ* 111:151–168. doi: 10.1016/0048-9697(92)90353-T

Förstner U, Wittmann GTW (1983) Metal pollution in the aquatic environment. Springer

Gambrell R (1994) Trace and toxic metals in wetlands - A review. *J Environ Qual* 23:883–891.

Gould SF (2012) Comparison of Post-mining Rehabilitation with Reference Ecosystems in Monsoonal Eucalypt Woodlands, Northern Australia. *Restor Ecol* 20:250–259. doi: 10.1111/j.1526-100X.2010.00757.x

Griffith MB, Norton SB, Alexander LC, et al. (2012) The effects of mountaintop mines and valley fills on the physicochemical quality of stream ecosystems in the central Appalachians: A review. *Sci Total Environ* 417–418:1–12. doi: 10.1016/j.scitotenv.2011.12.042

Hart TM, Davis SE (2011) Wetland development in a previously mined landscape of East Texas, USA. *Wetl Ecol Manag* 19:317–329. doi: 10.1007/s11273-011-9218-2

Hartman KJ, Kaller MD, Howell JW, Sweka JA (2005) How much do valley fills influence headwater streams? *Hydrobiologia* 532:91–102. doi: 10.1007/s10750-004-9019-1

Hobbs RJ, Norton DA (1996) Towards a Conceptual Framework for Restoration Ecology. *Restor Ecol* 4:93–110. doi: 10.1111/j.1526-100X.1996.tb00112.x

Hollander M, Wolfe DA (1973) Nonparametric statistical methods. John Wiley & Sons, New York

Hopkins RL, Altier BM, Haselman D, et al. (2013) Exploring the legacy effects of surface coal mining on stream chemistry. *Hydrobiologia* 713:87–95. doi: 10.1007/s10750-013-1494-9

Johnson DB (2003) Chemical and microbiological characteristics of mineral spoils and drainage waters at abandoned coal and metal mines. *Water Air Soil Pollut Focus* 3:47–66.

Lindberg TT, Bernhardt ES, Bier R, et al. (2011) Cumulative impacts of mountaintop mining on an Appalachian watershed. *Proc Natl Acad Sci* 108:20929–20934. doi: 10.1073/pnas.1112381108

Loayza-Muro RA, Elías-Letts R, Marticorena-Ruiz JK, et al. (2010) Metal-induced shifts in benthic macroinvertebrate community composition in Andean high altitude streams. *Environ Toxicol Chem* 29:2761–2768. doi: 10.1002/etc.327

MacDonald DD, Ingersoll CG, Berger TA (2000) Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. *Arch Environ Contam Toxicol* 39:20–31.

Majer, Nichols (1998) Long-term recolonization patterns of ants in Western Australian rehabilitated bauxite mines with reference to their use as indicators of restoration success. *J Appl Ecol* 35:161–182. doi: 10.1046/j.1365-2664.1998.00286.x

Markert B (1992) Presence and significance of naturally-occurring chemical-elements of the periodic system in the plant organism and consequences for future investigations on inorganic environmental chemistry in ecosystems. *Vegetatio* 103:1–30.

McNaughton SJ, Folsom TC, Lee T, et al. (1974) Heavy Metal Tolerance in *Typha Latifolia* without the Evolution of Tolerant Races. *Ecology* 55:1163–1165.

Meeravali NN, Kumar SJ (2000) Comparison of open microwave digestion and digestion by conventional heating for the determination of Cd, Cr, Cu and Pb in algae using transverse heated electrothermal atomic absorption spectrometry. *Fresenius J Anal Chem* 366:313–315. doi: 10.1007/s002160050061

Merricks TC, Cherry DS, Zipper CE, et al. (2007) Coal-mine hollow fill and settling pond influences on headwater streams in southern West Virginia, USA. *Environ Monit Assess* 129:359–378.

Meyer CK, Baer SG, Whiles MR (2008) Ecosystem Recovery Across a Chronosequence of Restored Wetlands in the Platte River Valley. *Ecosystems* 11:193–208. doi: 10.1007/s10021-007-9115-y

Miguel-Chinchilla L (2013) Physicochemical and Macroinvertebrate Community Trends in Manmade Ponds Constructed in Reclaimed Opencast Coal Mines. Universidad de Alcalá

Miguel-Chinchilla L, Boix D, Gascón S, Comín FA (2014) Macroinvertebrate biodiversity patterns during primary succession in manmade ponds in north-eastern Spain. *J. Limnol.* 73:

Mitsch WJ, Gosselink JG (2000) *Wetlands*, 3rd ed. Wiley

Mitsch WJ, Wise KM (1998) Water quality, fate of metals, and predictive model validation of a constructed wetland treating acid mine drainage. *Water Res* 32:1888–1900. doi: 10.1016/S0043-1354(97)00401-6

Nadkarni RA (1984) Applications of microwave oven sample dissolution in analysis. *Anal Chem* 56:2233–2237. doi: 10.1021/ac00276a056

Nicolau JM (2003) Trends in relief design and construction in opencast mining reclamation. *Land Degrad Dev* 14:215–226.

Palmer M, Bernhardt E, Schlesinger W, et al. (2010) Mountaintop Mining Consequences. *Science* 327:148–149. doi: 10.1126/science.1180543

Parker GH (2004) Tissue metal levels in Muskrat (*Ondatra zibethica*) collected near the Sudbury (Ontario) ore-smelters; prospects for biomonitoring marsh pollution. *Environ Pollut* 129:23–30. doi: 10.1016/j.envpol.2003.10.003

Pinheiro J, Bates D, DebRoy S, et al. (2012) nlme: Linear and Nonlinear Mixed Effects Models. R Package Version 3.1-111

Pond GJ, Passmore ME, Borsuk FA, et al. (2008) Downstream effects of mountaintop coal mining: comparing biological conditions using family- and genus-level macroinvertebrate bioassessment tools. *J North Am Benthol Soc* 27:717–737. doi: 10.1899/08-015.1

Pueyo M, Rauret G, Luck D, et al. (2001) Certification of the extractable contents of Cd, Cr, Cu, Ni, Pb and Zn in a freshwater sediment following a collaboratively tested and optimised three-step sequential extraction procedure. *J Environ Monit* 3:243–250. doi: Article

R Core Team (2012) R: A language and environment for statistical computing. R foundation for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria

Rauret G (1998) Extraction procedures for the determination of heavy metals in contaminated soil and sediment. *Talanta* 46:449–455.

Rodrigue JA, Burger JA, Oderwald RG (2002) Forest Productivity and Commercial Value of Pre-Law Reclaimed Mined Land in the Eastern United States. *North J Appl For* 19:106–114.

Samecka-Cymerman A, Kempers AJ (2001) Concentrations of heavy metals and plant nutrients in water, sediments and aquatic macrophytes of anthropogenic lakes (former open cut brown coal mines) differing in stage of acidification. *Sci Total Environ* 281:87–98.

Sasmaz A, Obek E, Hasar H (2008) The accumulation of heavy metals in *Typha latifolia* L. grown in a stream carrying secondary effluent. *Ecol Eng* 33:278–284.

Sastre J, Sahuquillo A, Vidal M, Rauret G (2002) Determination of Cd, Cu, Pb and Zn in environmental samples: microwave-assisted total digestion versus aqua regia and nitric acid extraction. *Anal Chim Acta* 462:59–72. doi: 10.1016/S0003-2670(02)00307-0

Sawtsky L, McKenna G, Keys MJ, Long D (2000) Towards Minimising the Long-term Liability of Reclaimed Mine Sites. In: Haigh MJ (ed) *Reclaimed Land Eros. Control Soils Ecol.* Taylor & Francis, pp 21–36

Sheoran AS, Sheoran V (2006) Heavy metal removal mechanism of acid mine drainage in wetlands: A critical review. *Miner Eng* 19:105–116. doi: 10.1016/j.mineng.2005.08.006

Shrestha RK, Lal R (2006) Ecosystem carbon budgeting and soil carbon sequestration in reclaimed mine soil. *Environ Int* 32:781–796. doi: 16/j.envint.2006.05.001

Smith FE, Arsenault EA (1996) Microwave-assisted sample preparation in analytical chemistry. *Talanta* 43:1207–1268. doi: 10.1016/0039-9140(96)01882-6

US EPA (2002) National Recommended Water Quality Criteria: 2002. Office of Water, EPA-822-R-02-047. United States Environmental Protection Agency, Washintong, DC, USA. Accessed 23 Jun 2013

Vickers H, Gillespie M, Gravina A (2012) Assessing the development of rehabilitated grasslands on post-mined landforms in north west Queensland, Australia. *Agric Ecosyst Environ* 163:72–84. doi: 10.1016/j.agee.2012.05.024

- Walker LR, Wardle DA, Bardgett RD, Clarkson BD (2010) The use of chronosequences in studies of ecological succession and soil development. *J Ecol* 98:725–736. doi: 10.1111/j.1365-2745.2010.01664.x
- Wei X, Wei H, Viadero Jr. RC (2011) Post-reclamation water quality trend in a Mid-Appalachian watershed of abandoned mine lands. *Sci Total Environ* 409:941–948. doi: 10.1016/j.scitotenv.2010.11.030
- Weis JS, Weis P (2004) Metal uptake, transport and release by wetland plants: implications for phytoremediation and restoration. *Environ Int* 30:685–700.
- Witeska M, Sarnowski P, Ługowska K, Kowal E (2013) The effects of cadmium and copper on embryonic and larval development of ide *Leuciscus idus* L. *Fish Physiol Biochem Adv Online Publ.* doi: 10.1007/s10695-013-9832-4
- Wong M. (2003) Ecological restoration of mine degraded soils, with emphasis on metal contaminated soils. *Chemosphere* 50:775–780. doi: 10.1016/S0045-6535(02)00232-1
- Ye ZH, Lin ZQ, Whiting SN, et al. (2003) Possible use of constructed wetland to remove selenocyanate, arsenic, and boron from electric utility wastewater. *Chemosphere* 52:1571–1579. doi: 10.1016/S0045-6535(03)00497-1
- Younger PL (2001) Mine water pollution in Scotland: nature, extent and preventative strategies. *Sci Total Environ* 265:309–326. doi: 10.1016/S0048-9697(00)00673-2
- Yucel DS, Baba A (2012) Geochemical Characterization of Acid Mine Lakes in Northwest Turkey and Their Effect on the Environment. *Arch Environ Contam Toxicol* 64:357–376. doi: 10.1007/s00244-012-9843-7

Table 1: Mean and standard deviation of metal concentrations of streams located in the river basin where mines are located. Dissolved metals in water (mg l⁻¹) and total metals in sediment (mg kg⁻¹) are shown. ND= no data.

	Water (mg l ⁻¹)		Total Sediment (mg kg ⁻¹)	
	Average	SD	Average	SD
Al	<0.04	-	21237.85	9447.13
As	ND	-	10.06	4.02
Cd	<0.01	-	<2.50	-
Cr	<0.01	-	26.69	9.79
Cu	<0.01	-	3.52	3.32
Fe	0.011	0.028	22764.96	5310.63
Mn	0.024	0.077	364.01	163.58
Ni	<0.03	-	199.90	301.44
Pb	<0.07	-	22.31	9.08
Zn	<0.05	-	46.75	43.08

Figure 1: Study site. Section A: location of the study site (inset) and Martín river basin showing sampling points in the local streams. Section B: Mining area showing the 16 runoff ponds constructed in reclaimed opencast coal mines and the pit-lake located in an un-reclaimed opencast coal mine.

Figure 2: Scatter plots of the water characteristics in relation to the runoff pond age. Circles represent spring data, and squares represent summer data. The pit-lake (age = 25 yr) values were shown in the grey area of the graphic. Dashed lines indicate reference criteria to metal pollution CMC: Criteria Maximum Concentration (US EPA 2002) CCC: Criterion Continuous Concentration (US EPA 2002); PTC: average toxic concentration to plants (Markert 1992). When a range of references exists, H represents the high value and L represents the low value.

Figure 3: Scatter plots of the sediment characteristics in relation to runoff pond age. Circles represent spring data, and squares represent summer data. The pit-lake (age = 25 yr) values were shown in the grey area of the graphic. Dashed lines indicate reference criteria to metal pollution TEC: threshold effect concentration and PEC: probable effect concentration (MacDonald et al. 2000).

Figure 4: Metal concentration in *Typha* sp. root, rhizome and leaf tissues. Dashed lines indicate the averaged range of metal concentrations for plants (Markert 1992), with H indicating the high and L the low value of the range. M indicates a unique mean value when a range of references does not exist.