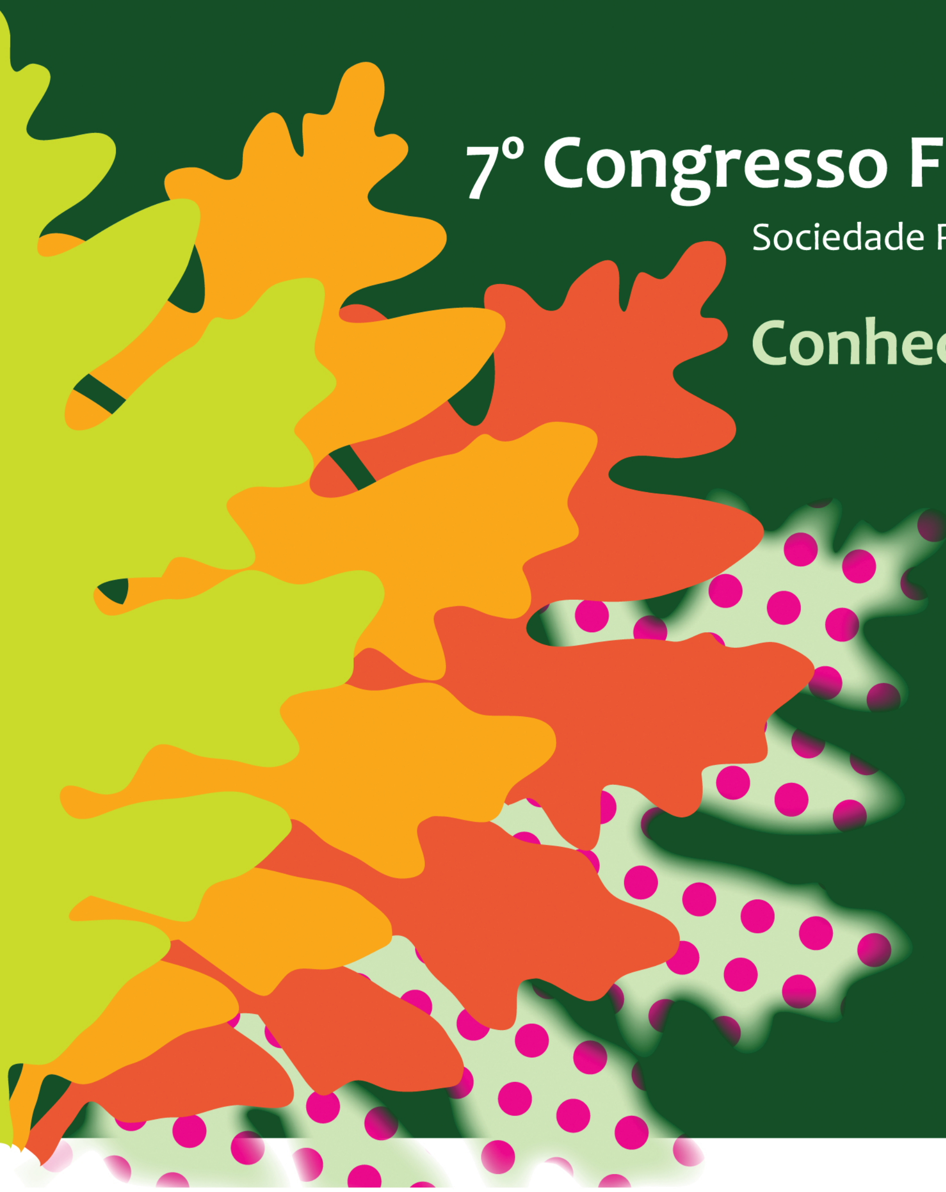

7º Congresso Florestal Nacional

Sociedade Portuguesa de Ciências Florestais

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Vila Real / Bragança
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CITAB – Centre for the Research and Technology of Agro-Environmental and Biological Sciences

CIMO – Centro de Investigação de Montanha

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Large spill of mining wastes in Portelo stream: Impacts on ecosystem integrity and on angling potential

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Abstract: Streams located at Montesinho Natural Park (NE Portugal) have high potential for brown trout (*Salmo trutta*) angling. However, in this territory there are several abandoned mine sites. Therefore, the continuous drainage of fine grained tailings can be particularly problematic due to arsenic, copper, aluminium and zinc. However, until now no significant disturbance was detected in water quality and in biota. Nevertheless, there has never been such a large spill of mining wastes as that occurred in January 2010. As a consequence of intense precipitation, several millions of cubic meters of wastes were spilled into Portelo stream. The large amount of wastes covered the riverbed with a layer of mud reaching more than half a meter in areas close to the mine. Both riparian and agricultural areas were also affected by the sediments from mine. Wastes were spilled downstream by several strong rain events. Thus, the objective of the present research was to evaluate the impact of this event on ecosystem integrity and ultimately on angling potential. To achieve the proposed objective the water from four sampling points along the affected stream was sampled for the following metals - Al, Mn, Co, Cu, Ni, Cd and As. Concomitantly, macroinvertebrate and fish assemblages were also assessed. Temporal differences between stations were not detected. On contrary spatial differences were found. As expected, the stations located near the mine showed the highest levels of contamination and disturbance. Consequently, in these stations no macroinvertebrates and fish were found during the period of study.

Key-words: Mine spilling, macroinvertebrates, headwater stream, ecosystem integrity, angling potential

1. INTRODUCTION

Continuous effects of mining activity on water quality and aquatic biota have been documented in a wide range of aquatic systems (NELSON and ROLINE 1996; 1999; MARQUÉS et al. 2003; GERHARDT et al. 2004; BRUNS 2005; FREUND and PETTY 2007; BESSER et al. 2007; van DAMME et al. 2008; GRAY and DELANEY 2008; POULTON et al. 2010). On contrary, studies concerning the sudden release of millions of cubic meters of waste products from ore-processing facilities in streams are scarce. These accidental spills intensify water pollution and have strong impacts in biota (PRAT et al. 1999; SOLÁ et al. 2004). The physicochemical effects of these events on aquatic ecosystems lead to abrupt changes in: (1) pH and conductivity; (2) metal concentration; (3) water transparency and riverbed structure. The consequences for biota depend on local, meteorological, geographic and environmental conditions, making the impact of these events unpredictable. Aquatic assemblages are quite well adapted to variable hydrological regimes, allowing them to tolerate certain changes. However, occasionally, the tolerance thresholds of many species are surpassed, and the structure of the assemblage changed irreversibly in some cases (MARQUÉS et al. 2003).

Portugal has about 175 old abandoned mine sites. Some of them are seriously degraded, containing large volume of old mining residues with significant environmental impact on local or regional scales (SANTOS OLIVEIRA et al. 2002; CABRAL-PINTO and SILVA 2005). An unprecedented large spill of mining wastes occurred in the abandoned Sn Portelo mine (NE Portugal) in January 2010. As a consequence of intense rainfall, several millions of cubic meters of wastes and acid water were spilled into Portelo stream. These wastes covered the riverbed with a layer of fine grained particles, reaching 50 cm in areas closer to the mine. Both riparian and agricultural areas were also affected by spreading of this mine wastes. Since no record of mining wastes has been found in these habitats previously, the aim of the present study was to evaluate the amplitude of the initial effects of the spill on the aquatic ecosystem. Therefore, during the first semester after the contamination event dissolved concentrations of Al, As, Cd, Co, Cu, Mn and Ni were assessed. Conductivity, pH and concentration of Suspended Particulate Matter (SPM) were also monitored. Concomitantly, the effects of spill on the macroinvertebrate assemblages and on angling potential were assessed.

2. STUDY AREA

The abandoned Sn Portelo mine is located in Montesinho Natural Park (NE Portugal) (Figure1). Mining wastes accumulated in a small riverbed during the last twenty years were spilled into Portelo Stream in January 2010.This headwater stream flows through granitic and schistic substrates for about 20 Km. It is a tributary of Sabor River, which flows into Douro River. Riparian vegetation is mainly composed of *Alnus glutinosa*. Fish assemblages are dominated by brown trout (*Salmo trutta*). Chub (*Squalius carolitertii*) and nase (*Pseudochondrostoma duriense*) can also be present (OLIVEIRA et al. 2007). The study area has an enormous potential for brown trout angling. Apart from past mining activities, direct human influence in the area is reduced being confined to small villages, where the main activity is extensive agriculture. The four sampling sites were located within the 20 km closest to the mine (Figure1; Table 1).

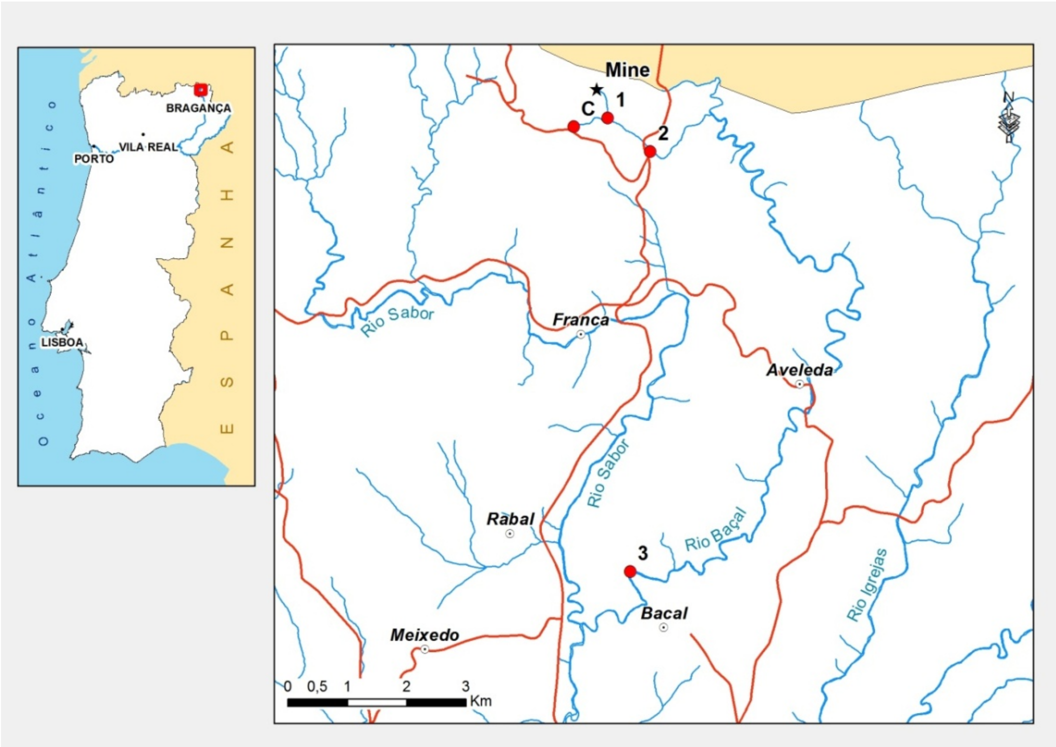

Figure 1- Location of the sampling stations.

A control site (C) was selected in an unaffected tributary, without influence of the mining area. A sampling site (1) was located closer to the mining area around 250 m downstream. The second site (2) was located 5 Km downstream from 1. The last site (3) was located in Sabor River, after receiving waters from Portelo stream and is located 15 Km downstream mine facilities. All sites presented similar characteristics of slope, water current velocity, riparian cover and human occupation. The sampling sites were located in a non-regulated river sections. For this reason and because of the influence of Mediterranean climate the flow may vary from 0.3 to 1 m^3s^{-1}. The total annual precipitation in the region varied between 800 and 1000 mm. Most of the precipitation events occur between October and March with an inter-annual irregular variation pattern. The rain fall during this period was around 400 mm (PORTUGUESE METEOROLOGY INSTITUTE, 2010). However, 2010 was considered a wet year, since the total precipitation occurring between January and July was 727 mm.

3. MATERIAL AND METHODS

3.1. Water parameters

Conductivity, pH, temperature and dissolved oxygen were measured “in situ” with a multiparametric probe HANNA HI9828. Water was monthly sampled (from January to July 2010) in the four sampling sites. Samples were collected in 5-L polyethylene bottles previously acid-washed. Dissolved and particulate fractions were separated by filtration through cellulose acetate membranes (0.45 μm) and weighed. Samples for dissolved trace elements analysis were acidified with Suprapure HNO_3 (pH <2). Particle retained membranes were dried at 40° C and weighed to calculate the concentration of suspended particulate matter (SPM) and stored in freezer for metal analyses. Concentrations of Al, Mn, Co, Cu, Ni, Cd and As in dissolved fraction were determined using a quadrupole ICP-MS (Thermo Elemental, X-Series) equipped with a Peltier Impact bead spray chamber and a concentric Meinhard nebulizer. The experimental parameters were: forward power 1400 W; peak jumping mode; 150 sweeps per replicate; dwell time 10 ms; dead time 50 ns. Indium was the internal standard chosen. For the analyzed elements, coefficients of variation for counts (n=5) were lower than 2 % and a 10-point calibration within a range of 0.1 to 200 µg L^{-1} was used for quantification. Two procedural blanks were prepared using similar analytical procedures and reagents, and included within each batch of 10 samples. Procedural blanks always accounted for less than 1 % of element concentrations in the samples. The precision and accuracy of the analytical methodologies were controlled through repeated analysis of the elements studied in the certified reference material SLRS-5 from the National Research Council of Canada.

Potential toxicity of metal concentrations from water samples was examined by calculating toxic units (TU) for Al, Mn, Co, Cu, Ni, Cd and As according to NELSON and ROLINE (1999). TU for each metal concentration were calculated by dividing the measured concentrations by the values for *Daphnia magna* 48 lethal concentrations to 50% of the organisms (LC_{50}) found in BIESINGER and Christensen (1972), KHANGAROT and RAY (1989), SANKARAMANACHI and QASIM (1999) and FERREIRA et al. (2010). Individual TU were summed to determine the overall toxicity for each sampling period and sampling site. This methodology allows evaluate the biologically-relevant integration of metal effects using an indirect measurement of toxicity (YIM et al., 2006).

3.2. Macroinvertebrate assemblages

The macroinvertebrate assemblages were sampled according to INAG (2008). At each site, composite multi-habitat samples were taken using a hand net (25 x25 cm frame; 500 µm mesh size) and each microhabitat (e.g., riffle, pool, edge, vegetation) was sampled in proportion to its representation. Organisms were preserved in 70% ethanol and identified at least to genus level for most taxonomic families (except for some Diptera and Oligochaeta). To assess the relationship between water parameters and macroinvertebrate assemblage composition several metrics were selected: Diversity index (H’), evenness (J’), number of families in the orders Ephemeroptera, Plecoptera and Trichoptera (% EPT) and in Diptera-Oligochaeta (%), Northern Portuguese Invertebrate Index (IPtIN) (INAG 2009), Functional Feeding Groups (MERRITT and CUMMINS 1978) and Habits/Behavior were assigned according to the primary category documented by TACHET et al (2002) and complemented with information based upon MERRITT and CUMMINS (1996) and BARBOUR et al (1999). These metrics were identified as the most sensitive to disturbance in Northern Portugal catchments (VARANDAS and CORTES 2010; CORTES et al. 2011).

3.3. Fish assemblages

Fish were sampled by electrofishing (Hans Grassl ELT60, DC, 1.5W, 300-600 volts) in 100 m sections, concomitantly with macroinvertebrate sampling. Fish were returned to water after species identification.

3.4. Statistical analysis

Samples were pooled in three distinct periods: Winter (W); Spring (Sp) and Summer (S). Non-Metric Multidimensional Scaling (NMDS) was used to examine spatial and seasonal patterns in water parameters and macroinvertebrate abundance data on the basis of similarity (Bray-Curtis distance). NMDS analysis produces a two-dimensional plot where data are arranged in a continuum in such a way that samples close together are similar and samples which are far apart are dissimilar. Species abundance data were Log (X+1) transformed to balance the contributions from the few very abundant species with the many rare species. Differences between sites and seasons were tested by a One-Way ANOSIM test. A One-Way ANOVA was performed as a complement to the multivariate analysis mentioned above in order to assess differences in water parameters between sites and seasons. The assumption of normal distribution of the variables was assessed by the Kolmogorov-Smirnov test and homogeneity of variance using the Levene test. When normality and homogeneity of variances were not observed, the nonparametric Kruskal-Wallis test followed by multiple comparisons of orders means was applied, as described in Maroco (2010). Multivariate analysis was performed using PRIMER Version 5 and other routines were carried out using SPSS Version 16.

4. RESULTS

4.1. Water parameters

During the first six months the studied variables, apart from SPM concentrations, did not show significant seasonal variations. The lowest values for pH and the highest concentrations of heavy metals were always found at site 1 located in Portelo stream, downstream of the mine. Herein pH was always below 4.8. Concerning dissolved metals, Al was the most abundant element followed by Mn, Cu, Co, Cd and As. Metal concentrations decreased from site 1 to 2 (Table1). Regarding site 3, the metal concentrations, pH, conductivity and SPM concentrations were generally similar to those observed in the control (C). Differences between sites were confirmed by the statistical analysis performed (Table1). Moreover, these data are in line with the ordination plot of NMDS based on pH, conductivity, SPM and metal concentrations (Figure 2) which indicated the existence of two groups: One formed by sites 1 and 2 (the more contaminated areas located in Portelo stream just downstream mine) and the other by the site 3 (located in Baçal River), site C and site 2 in summer. This fact was due to a decrease on SPM concentrations at this site in summer. Calculated Toxic Units (TU) were lower than 1 for Al, Mn, Co, Ni, Cd and As at all sampling sites. Conversely, TU values for Cu were higher than 1 at site 1 for all seasons (>40 in winter; >30 in spring; > 20 in summer) and at site 2 in winter and spring (>10). At site 2 in summer TU for Cu was lower than1.

Table 1 – Some general features of the sampling sites. Mean values and range of water parameters measured at sampling stations.

	Sampling sites				Significance[1]
	1	2	3	C	
Latitude	41º56.003'N	41º55.730N	41º51.827N	41º55.930N	
Longitude	6º44245'W	6º43.752	6º44.078W	6º44.281'W	
Sediment (%)					
>2mm	0.9	66.9	18.6	67.8	
< 2mm	99.1	33.1	81.4	32.2	
Altitude	838	775	600	761	
T(ºC)	9.7 (7.2-19.0)[a]	9.9 (7.3-20.4)[a]	9.4 (5.1-20.4)[a]	8.2 (6.1-18.9)[a]	ns
pH	4.58 (4.02-4.72)[a]	5.38 (4.96-6.60)[b]	6.54 (6.10-7.30)[c]	6.15 (5.80-6.65)[b,c]	***
Conductivity (μS/cm)	159.5[a] (144.0-174.5)	73.0[b] (64.7-81.2)	42.1[c] (37.5-81.9)	29.1[d] (25.0-36.3)	***
Dissolved Oxygen (mg/L)	8.60[a] (7.00-9.37)	8.82[a] (7.60-10.10)	9.65[a] (7.60-12.00)	8.10[a] (7.20-9.80)	ns
SPM (mg/L)	6.49×10^{3} [a] $(0\text{-}2.71\times10^{4})$	2.70×10^{3} [a] $(0\text{-}5.43\times10^{3})$	29.0[a,b] (0-143)	0.0715[b] (0-4.70)	*
Ni (μg/L)	64.6 (61.4-131)[a]	25.4 (12.6-38.0)[b]	1.68 (0.94-2.55)[c]	1.46 (1.08-1.89)[c]	***
Cd (μg/L)	6.55 (4.71-9.97)[a]	2.28 (0.75-3.55)[b]	0.085 (0.01-0.18)[c]	0.10 (0.03-0.20)[c]	***
Al (μg/L)	1114 (859-1253)[a]	196 (5.00-295)[b]	4.80 (0.90-11.0)[c]	11.9 (0.50-24.7)[b,c]	***
Cu (μg/L)	325 (247-656)[a]	97.3 (5.16-144)[b]	<DL (<DL-1.13)[c]	0.14 (<DL-0.79)[c]	***
Mn (μg/L)	746 (252-1216)[a]	207 (133-342)[b]	21.6 (11.6-27.3)[c]	2.12 (<DL -4.59)[d]	***
As (μg/L)	2.32 (1.11-9.50)[a]	1.79 (1.04-3.04)[a,b]	1.85 (1.60-8.47)[a]	0.83 (0.56-2.09)[b]	*
Co (μg/L)	68.4 (40.9-228)[a]	26.8 (5.27-52.2)[b]	1.12 (0.09-2.45)[c]	0.46 (0.05-0.71)[c]	***

Data expressed as median (range). Values followed by the same letter under the same row were not significantly different. [1]Significance: *p<0.05, ** p< 0.01, *** p<0.005, [ns] no significant

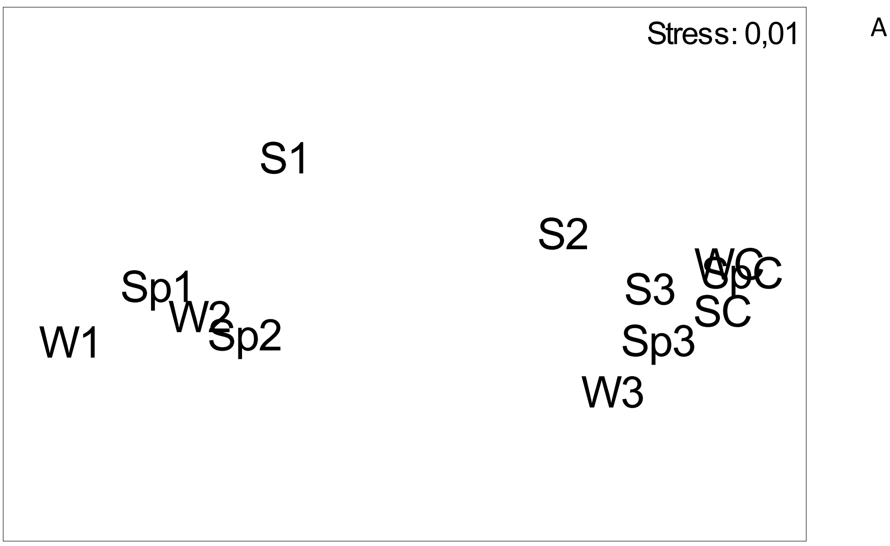

Figure 2- Results of NDMS ordination for water parameters.

(Symbols: W- winter; Sp- spring; S- summer)

4.2. Macroinvertebrate assemblage

Assemblages at sites 1 and 2 were strongly impacted. In fact, no individuals were sampled during the surveyed period. It was found sensitive taxa simultaneously at sites C and 3, like Ephemeroptera (*e.g., Habrophlebia fusca, Ecdyonurus gr. venosus* and *Calliarcys humilis*), Plecoptera (*e.g., Leuctra* sp., *Capnioneura* sp. and *Isoperla* sp.) and Trichoptera (*e.g., Allogamus* sp., *Sericostoma* sp. and *Philopotamus* sp.). The occurrence of these insects indicated that in site 3 the disturbance caused by the mine spill seemed to be negligible. This idea is reinforced by the different macroinvertebrate metrics, which evidence that macroinvertebrate assemblages found in site 3 were similar to those determined in the undisturbed site C (Table 2). Therefore, the assemblages found in site 3 could have been also the reflex of lower SPM and metals concentrations and higher pH values than those determined in sites 1 and 2. The ordination plot of the NMDS based on macroinvertebrate data grouped site 1 with site 2 and site 3 with site C, reflecting the scenario above mentioned (Figure 3). Furthermore, ANOSIM analysis stressed the results of NMDS (R=0.75; p=0.001).

Table 2- List of macroinvertebrate metrics and indices used to evaluate sites C and 3.

Metric name	WC	SpC	SC	W3	Sp3	S3
Diversity (H')	3.00	2.77	2.80	2.59	2.27	2.36
Evenness (J')	0.82	0.84	0.80	0.76	0.76	0.74
% EPT families	0.53	0.63	0.44	0.44	0.65	0.30
***% Diptera+Oligochaeta* families**	0.30	0.24	0.23	0.18	0.19	0.24
IPtIN *	0.86	0.84	0.77	0.70	0.70	0.59
Habits/behavior (% of total taxa)						
Sprawlers	0.32	0.26	0.15	0.28	0.25	0.09
Clingers	0.47	0.52	0.47	0.31	0.35	0.52
Swimmers	0.08	0.07	0.06	0.06	0.15	0.09
Burrowers	0.13	0.15	0.15	0.22	0.25	0.26
Divers	0.03	0.00	0.06	0.03	0.05	0.09
Skaters	0.00	0.00	0.06	0.06	0.00	0.00
Climbers	0.00	0.00	0.00	0.03	0.00	0.00
Functional feeding groups (% of total taxa)						
Shredders	0.29	0.30	0.15	0.22	0.20	0.09
Predators and Parasites	0.21	0.15	0.32	0.34	0.30	0.26
Gathering collectors	0.24	0.26	0.24	0.25	0.35	0.22
Filtering Collectors	0.11	0.15	0.12	0.06	0.05	0.13
Scrapers	0.16	0.15	0.18	0.13	0.10	0.30

W: winter; Sp: spring; S :summer. * reference values 0.98; >0.86 Excellent/Good; 0.60 Good/Fair; 0.40 Fair/Poor; 0.20 Poor/Very poor

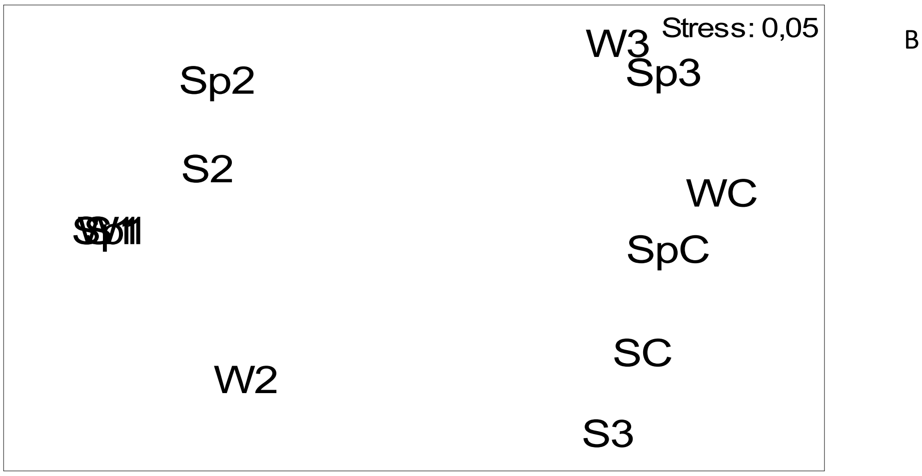

Figure 3 - Results of NDMS ordination for macroinvertebrate assemblages
(Symbols: W- winter; Sp- spring; S- summer).

4.3. Fish assemblages

In sites 1 and 2 no fish were sampled during the period of study. In site C only brown trout (*Salmo trutta*) was sampled. In site 3 fish assemblage was dominated by Calandino (*Squalius alburnoides*), Northern Iberian chub (*Squalius carolitertii*) and Northern straight-mouth nase (*Pseudochondrostoma duriense*).

5. DISCUSSION

The short-term effects of mine spill were harsher in the sites 1 and 2, which are located at the first 5-Km downstream the mine, including all extension of Portelo Stream. In this section, the highest metal concentrations and SPM load and the lowest pH values were detected.
PRAT et al. (1999) and SÓLA et al. (2004) showed that metal concentrations in water decreased exponentially with the distance to the mine during the Aznalcóllar mining spill. The observed decrease might result from metal sorption to particles, particle settling, oxide and/or hydroxide precipitation and dilution (NELSON and ROLINE 1996; POULTON et al. 2010). The mining spill impacts at site 3 (located around 20 km downstream from the mine) were not detectable. The spill occurred in winter during a heavy rainy period with consequently high stream and river discharges. Therefore, large amounts of sediments might have been flushed away. Furthermore, Sabor River receives water from other tributaries without mining activity. According to GRAY and DELANEY (2008) the dilution of metals load and the change of pH due to tributaries that have no mining impacts are important for maintaining aquatic life in these systems although, not significant enough to eliminate all risks to aquatic organisms. In fact, macroinvertebrate assemblages at site 3 were similar to the one reported at control site. Results concerning fish assemblage were in line with those obtained for macroinvertebrate assemblages. Fish assemblage composition and structure did not change significantly when compared with data obtained before the mining spill (TEIXEIRA, unpublished data).

Conversely, at sites 1 and 2 the mine spill had led to the total disappearance of the macroinvertebrates and fish. PRAT et al. (1999) reported that seven months after the Aznalcóllar mining spill a slight recovery in macroinvertebrate species number occurred even at the most affected sites. However, they verified that macroinvertebrate assemblage was substantially different from the reference station. Conversely, at stations located in Portelo stream no recovery has occurred. Even in samples performed in 2011 no animals were caught and principally, at station 1 low pH and high metal concentration still persisting (unpublished data). Furthermore, the loss of habitat had occurred as a result of the deposit on the riverbed of fine grained sediments. Portelo watershed is very small and the dilution effect from Sabor River did not occurred here so intensively. In the present study metal determination in sediments was not performed. According to MARQUÉS et al. (2003) and GRAY and DELANEY (2008) the critical factors responsible for disrupting the macroinvertebrate assemblage appears to be pH and metal concentrations or a combination of the two. It also should be stressed that the surface water quality has a greater influence than pore water quality in macroinvertebrate assemblages (NELSON and ROLINE 1996). It is true that the physical habitat alterations induced by spill inhibit biotic recovery. But the results obtained by NELSON and ROLINE 1996; 1999; PRAT et al. 1999; SÓLA et al. 2004; FREUND and PETTY 2007; POULTON et al. 2010) suggest that macroinvertebrate assemblages will recover quickly when adjacent colonist pools exist together with absence of degraded habitat and if inputs of metals could be mitigated or eliminated. A similar behavior was described for fish assemblages when impacted by mining pollution (FORD 1989; DIAMOND et al. 2002; RICCIARDI et al. 2009).

Since no mitigation or restorations measures were implemented, acid mine drainage and spilling may still occurring at Portelo currently, becoming more accentuated during rainfall periods. In the future if mitigation measures are not implemented it is possible that this abandoned mine might pose additional environmental risks, not only to the aquatic system but also for other natural values included in Montesinho Natural Park, threatening areas with high ecological, recreational and economic importance.

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