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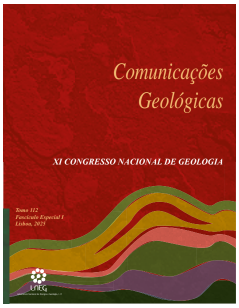
Influence of sulphide mine tailings on drainage water quality, 60 years after its abandonment. A case study in SW Portugal

Influência dos rejeitos de uma mina de sulfuretos na qualidade da água de drenagem, 60 anos após o seu abandono: Caso de estudo no SW de Portugal



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Abstract: The GeoMatRe project aims to find low-cost solutions for water and sediment rehabilitation using raw geomaterials, in abandoned mines of the Iberian Pyritic Belt. One of our case studies is the Caveira mine in southwestern Portugal, where large piles of mining waste, containing significant amounts of metals, record the long history of its exploitation for gold (Au) and silver (Ag). After the exhaustion of its reserves, the extraction of the remaining metals (cooper (Cu), lead (Pb) and zinc (Zn)) and sulphur (S) continued, until its abandonment during the 60s of 20th century. This work has two objectives: (i) to study the influence of mine and mine tailings drainage on water quality by analysing the dissolved and particulate material in drainage waters, and (ii) to determine whether there are differences in the contamination level of these waters according to the different weather conditions of the last two winters.

Keywords: Potentially toxic elements, Sulphide mine, Caveira mine, Water quality.

Resumo: O projeto GeoMatRe tem como objetivo encontrar soluções de baixo custo para a remediação de águas e sedimentos utilizando geomateriais, em minas abandonadas da Faixa Piritosa Ibérica. Um dos nossos casos de estudo é a mina de Caveira, no sudoeste de Portugal, onde grandes quantidades de resíduos mineiros acumulados, contendo quantidades significativas de metais, registam a longa história da sua exploração de ouro (Au) e prata (Ag). Após o fim das suas reservas, a extração dos restantes metais (cobre (Cu), chumbo (Pb) e zinco (Zn)) e enxofre (S) continuou, até ao seu abandono durante os anos 60 do século XX. Este trabalho tem dois objetivos: (i) estudar a influência da drenagem da mina e dos rejeitos mineiros deixados ao abandono, sobre a qualidade da água, através da análise do material dissolvido e particulado nas águas de drenagem, e (ii) determinar se existem diferenças nos sues níveis de contaminação em função das diferentes condições meteorológicas dos dois últimos Invernos.

Palavras-chave: Elementos potencialmente tóxicos, Mina de sulfuretos, Mina de Caveira, Qualidade da água.

1. Introduction

The GeoMatRe project, funded by the La Caixa Foundation, aims to evaluate the effectiveness of the use of geomaterials in the retention of potentially toxic elements in the effluents of abandoned mines in the Iberian Pyrite Belt (IPB). One of the case studies carried out in this project is the Caveira polymetallic sulphide mine, located in the NW region of the IPB (Figura 1). The mine area exhibits significant geological complexity, characterized by an antiform structure with a N-S orientation. The core is formed by phyllites and quartzites (Middle-Sup. Famenian), and the flanks are composed of sedimentary and volcanic sequences of the volcano-sedimentary complex (VSC). Fine volcanogenic sediments are found in the western part of this structure, while the eastern part contains chloritic shales, black shales, and intercalations of chert and jasper. To the N of the antiform, basic intrusions appear, and on both flanks, masses of sulphides occur, in the contact between the lower volcanites of the VSC and the black shales that define the limit of the VSC with the underlying phyllites and quartzites (Matos and Martins, 2006). The mineralizations are essentially composed of pyrite, with a lesser predominance of chalcopyrite, galena and sphalerite (Reis *et al*., 2012). In addition to these mineralisations, there are also stratiform Fe and Mn deposits and phyllonitic mineralisations of Cu, Sb, Pb and Ba. Despite its small size, the mine is dominated by an important heap leach, with several smaller areas with waste of varying nature, estimated globally at 2 Mt (Mateus *et al*., 2008; Reis *et al*., 2012).

This mine was explored intermittently since the Roman occupation, with a focus on Au and Ag, until the end of the 60s of the 20th century, at that time more focused on the exploration of Cu, S and pyrite (Matos and Martins, 2006; Mateus *et al*., 2008). After its cessation, the mine was abandoned and no mitigation measures were taken to prevent acid drainage (Reis *et al*., 2012). The drainage in the Caveira mine converge to the Grândola stream (Mateus *et al*., 2008). The marked erosion that occurs in the main mine heap allows the dispersion of metals such as Cu, Pb, Zn, As, Mo, Se, Cd, Fe and Hg in sediments and surface waters (Matos and Martins, 2006).

2. Material and methods

Surface water and sediment sampling campaigns were carried out in February 2022 and February 2023 on a sampling grid covering approximately 1 km^2. The two sampling campaigns presented significantly different hydrological conditions. The average rainfall

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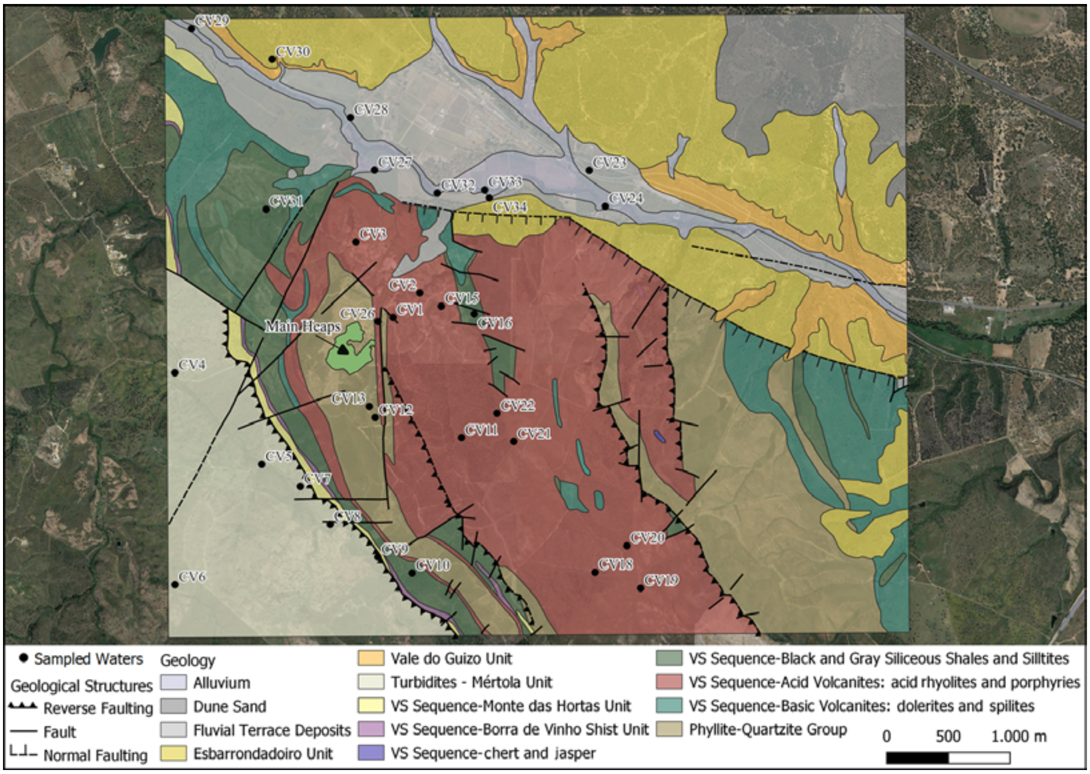

Figure 1. Geographical and geological setting of the study area and surface water sampling points (Adapted from LNEG, 2010).

Figura 1. Enquadramento geográfico e geológico da zona de estudo e pontos de amostragem das águas superficiais (adaptado de LNEG, 2010).

for the 3 months preceding the 2022 campaign was 24 mm, while for the 2023 campaign, it was 51 mm (SNIRH, 2023). One of the objectives of the campaigns was to study the influence of the mine tailings on the water quality that percolates through them. To this purpose, a total of 18 water samples were collected in the first campaign, because of the scarcity of surface water due to weather conditions, and 31 samples in the second campaign, which were subsequently analysed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) for dissolved and total (dissolved + particulate) phases of elements, each sample with two replicates. For the analysis of elements in total forms, the water samples were first digested in an acidic medium using a high-pressure microwave unit. The sulphate content was determined using a molecular absorption spectrophotometer, while Hg analysis was conducted using an Hg analyser with gold amalgamation. Additionally, pH, turbidity, and electrical conductivity analysis were taken using selective electrodes.

The data was previously normalised subtracting the mean and dividing by the standard deviation, for all the samples and considering the surveyed elements. Furthermore, a script was executed in R using the "corrplot" function to calculate all the possible linear correlations between the various elements analysed by ICP-OES. Additionally, a spatial analysis was conducted using QGIS software, which included interpolation performed with Inverse Distance Weighting (IDW) within a 10-meter radius to assess the dispersion of elements and the migration of contamination plumes.

3. Results and Discussion

3.1. Physicochemical parameters

After analysing the physicochemical parameters of the collected surface waters, we can observe some differences in the key water quality parameters measured in the two sampling campaigns: in February 2022 and February 2023 (Tab.1). In particular, the data reveals that the water pH decreased in 2023 compared to the previous campaign, shifting from a median value of 7.21 in 2022 to 6.45 in 2023, with a pH maximum of 8.33 in 2022 and 7.08 in 2023, and a minimum pH of 1.1 in 2022 to 1.42 in 2023. The higher level of acidification of the waters can be attributed to the influence of the sulphide wastes piled up in the mining area, under the considerably wetter winter of 2023 (with more than the double of the precipitation recorded in 2022) contributing to increased leaching of these materials accumulated in the mine's tailings piles. Furthermore, we observe an inverse trend in the turbidity of the surface waters. The data indicates that, overall, turbidity was relatively higher during the 2022 campaign. This increase may suggest a higher concentration of dissolved metals and/or metal-rich suspended particles in the waters, which is corroborated by the higher electrical conductivity in 2022, whereas in 2023, data show an effect of solubilisation of these waters due to the increased precipitation rates.

Finally, the results of electrical conductivity reveal that in February 2022, higher values were recorded, suggesting a higher concentration of ions in the water, with maximum values of 8315 µ(m)S/cm, minimum of 85.46 µ(m)S/cm, and medians of 889 µ(m) S/cm. In February 2023, electrical conductivity decreased, possibly due to changes in the hydrological conditions and to an increase of ions dilution as consequence of higher rates of rainfall, with a maximum conductivity of 2539 µ(m)S/cm, a minimum of 11.78 µ(m) S/cm, and a median of 583 µ(m)S/cm.

These variations reflect the complex interaction between mining residues and the hydrogeochemical context, revealing an apparent deterioration of water quality in the drier year of 2022 and a leaching

Table 1. Results of analyses of physicochemical water parameters.

Tabela 1. Resultados das análises dos parâmetros físico-químicos das águas.

February 2022

		Conductivity	Turbidity
Sample	**pH**	**µ(m)S/cm**	**NTU**
CV1	1.23	8250	14.3
CV2	1.1	8315	31.9
CV3	3.31	5367	41.6
CV5	6.64	789	41.5
CV10	7.29	490	8.8
CV13	8.33	673	4.81
CV15	5.76	156	466
CV22	8.25	1315	19.3
CV23	6.96	896	36.4
CV24	6.26	1008	49.5
CV26	1.33	85,46	1.47
CV27	7.24	1752	24.2
CV28	7.19	870	6.02
CV29	7.45	863	12.8
CV30	7.92	882	2.12
CV31	8.28	749	10.7
CV32	7.23	929	11.5
CV33	7.28	930	5.64

February 2023

		Conductivity	Turbidity
Sample	**pH**	**µ(m)S/cm**	**NTU**
CV1	1.58	23.22	3.22
CV2	1.68	19.26	2.17
CV3	4.53	2539	42.5
CV4	6.68	816	3.13
CV5	6.73	822	2.12
CV6	6.57	1075	24.7
CV7	6.55	720	1.71
CV8	6.45	764	14.8
CV9	6.59	748	0.9
CV10	6.61	573	54.5
CV11	5.48	220	1472
CV12	5.6	91	101
CV13	7.04	691	35.1
CV15	5.77	403	7.44
CV16	4.94	935	33.2
CV18	6.21	391	272
CV19	6.5	271	7.61
CV20	6.17	84	203
CV21	6.07	1206	27.3
CV22	6.33	610	2.56
CV23	6.54	752	13.8
CV24	5.93	618	3.42
CV26	1.42	31.47	48.4
CV27	6.96	896	1.42
CV28	7.07	517	2.58
CV29	6.45	524	2.16
CV30	7.08	512	4.43
CV31	6.94	583	21.9
CV32	6.65	577	2.15
CV33	5.85	585	5.57
CV34	1.78	11.78	1.69

Table 2. Sulphate content in water

Tabela 2. Teor de sulfatos nas águas

February 2022

Samples	SO42- (mg/L)
CV 1	6195.10
CV 2	4368.45
CV 3	1208.55
CV 5	145.20
CV 10	30.85
CV 13	24.59
CV 15	424.11
CV 22	78.70
CV 23	83.91
CV 24	135.47
CV 26	6489.00
CV 27	483.83
CV 28	21.92
CV 29	27.17

February 2023

Samples	SO42- (mg/L)
CV1	4531.33
CV2	4237.51
CV3	4263.76
CV4	123.52
CV5	117.63
CV6	175.34
CV7	114.77
CV8	129.10
CV9	114.78
CV10	136.31
CV11	454.02
CV12	280.32
CV13	99.82
CV15	42.38
CV16	212.81
CV18	111.17
CV19	8.87
CV21	93.29
CV22	48.69
CV23	146.03
CV24	149.92
CV25	<1
CV26	7585.48
CV27	154.51
CV28	83.43
CV29	61.81
CV30	89.00
CV31	84.01
CV32	76.87
CV33	93.77
CV34	14967.46

and dilution effect in 2023, which experienced higher precipitation, resulting in a slight improvement of water quality.

3.2. Geochemical data

Unlike the high levels of Hg observed in the sediments of some areas of the watercourse flowing through the tailings pile (Mota *et al.*, 2022), the Hg analyses revealed very low levels in the waters of both campaigns, with no substantial differences between the two years, with maximum values recorded at 0.3 ppm, and the vast majority below the equipment's detection limits (<1pbb). This fact may indicate that Hg is exclusively in its immobile phase, since its solubility does not depend on the pH conditions of the environment (Ferreira da Silva *et al.*, 2015).

The sulphate data in the waters collected in both campaigns (Tab. 2) exhibit noteworthy differences. In February 2022, sulphates ranged from a minimum of 21.92 mg/L to a maximum of 6489 mg/L, with a median value of 109.69 mg/L. In contrast, in February 2023, sulphate levels displayed a wide range, ranging from <1 mg/L (below the equipment's detection limit) to a maximum of 14967.46 mg/L, with a median value of 120.58 mg/L.

This clear difference in sulphate concentrations can be attributed to factors such as fluctuations of weather conditions subsequent to the seasonal effects observed, and, mostly, to the influence of leaching water on sulphide wastes disposed in the abandoned mine. The noteworthy increase of sulphate levels in 2023 suggests higher leaching rates of these compounds from the mining area, as they exhibit high chemical mobility under various geochemical conditions (Weightman, 2021), particularly under conditions of increased precipitation. The higher leaching of sulphates can also influence the pH, as their solubilization generates sulfuric acid (H_4SO_4) (Tomiyama and Igarashi, 2022). This underscores the mine's importance as a potential source of contamination and acidity for the surrounding waters.

The data for both the dissolved phase and the total content of elements (dissolved + particulate) in the water also exhibit some variability according to the hydrological year. Figure 2 illustrates the total content distribution of Al, As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Zn for both sampling campaigns and across all collected samples. It can be observed that Ca, Co, Mg, and Mn are elements that display higher levels in February 2022, which may be related to their association with sulphates or other salts, such as hexahydrite ($MgSO_4.6H_2O$), epsomite ($MgSO_4.7H_2O$), and gypsum ($CaSO_4.2H_2O$), as identified by Ferreira da Silva *et al.*, 2015 in the same study area under dry conditions.

Al, As, Cd, Cr, Cu, Fe, K, Na, Ni, Pb, and Zn exhibit higher solubility, as evidenced by their increased concentrations during the February 2023 sampling campaign. This highlights the significant influence of the mine tailings heaps on the contaminant dispersion, as under oxidizing conditions, the dissolution of sulphides is

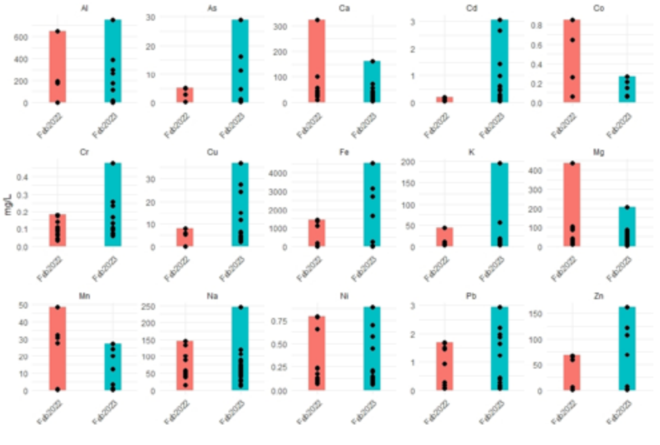

Figure 2. Comparison of the distribution of total content of chemical elements between the February 2022 campaign and the February 2023 campaign.

Figura 2. Comparação da distribuição do teor total de elementos químicos, entre a campanha de Fevereiro de 2022 e a campanha de Fevereiro de 2023.

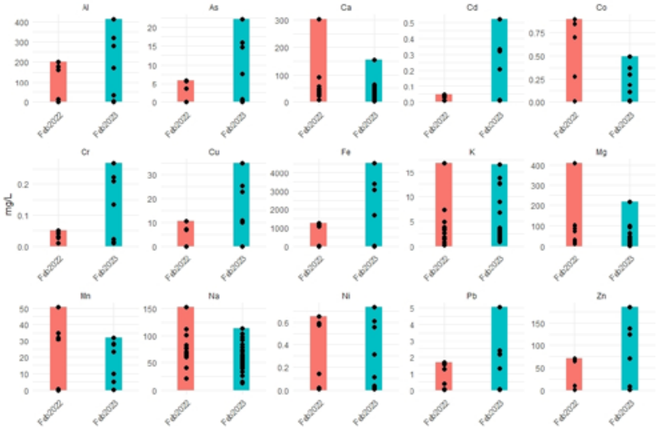

Figure 3. Comparison of the distribution of chemical element levels in the dissolved phase between the February 2022 campaign and the February 2023 campaign.

Figura 3. Comparação da distribuição dos teores de elementos químicos na fase dissolvida, entre a campanha de Fevereiro de 2022 e a campanha de Fevereiro de 2023.

accelerated. This is the case of pyrite (FeS_2), sphalerite (ZnS), arsenopyrite (FeAsS), or chalcopyrite ($CuFeS_2$) (Tomiyama and Igarashi, 2022), which release these metals into the environment. This fact can be corroborated by consulting the Figure 3, which presents the distributions of the dissolved aforementioned elements in both sampling periods for all the samples. Elements like Fe, Zn, Ni, Cu, and As seem to exhibit very similar distributions in relation to those found in Figure 2, indicating that these elements are predominantly in the dissolved phase. Thus, it may suggest that they are indeed a result of the leaching from the sulphides present in the tailings heap. The calculation of linear correlations between different elements can support this hypothesis. In Figure 4, the values of linear correlations among different chemical elements in the dissolved phase for 2023 and the total water chemistry in 2022, are represented. In the case of the total water chemistry for the February 2022 campaign, it is possible to identify a cluster of positive correlation with associations SO_4-Co-Ni-Zn-Fe-Cd-As. This suggests that these elements may behave similarly, mainly being associated with sulphides, as mentioned above. On the other hand, the results related to the dissolved phase in the February 2023 campaign corroborate the high chemical mobility of these metals, as also demonstrated in Figure 3, through the cluster of high linear correlation of the association Mn-Co-Cu-Cr-Ni-Al-Cd-As-Fe.

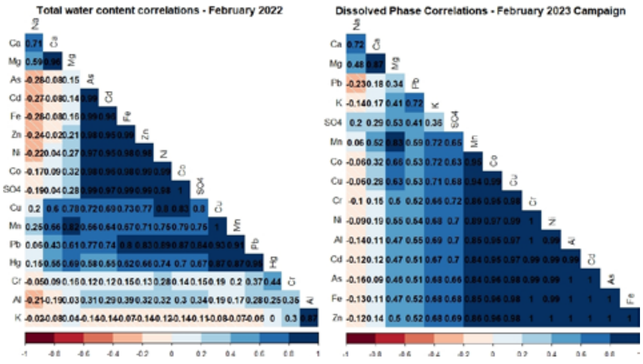

Figure 4. Representation of all possible linear correlations among the different chemical elements in the total chemistry of the water samples from the February 2022 campaign and the chemical content in the dissolved phase during the February 2023 campaign.

Figura 4. Representação de todas as correlações lineares possíveis entre os diferentes elementos químicos na química total das águas da campanha de Fevereiro de 2022, e do conteúdo químico na fase dissolvida na campanha de Fevereiro de 2023.

3.3. Influence of mine heaps and dispersion of elements

Water samples that show the most severe contamination levels, as defined by Decree-Law no. 218/2015 of October 7th, were CV1, CV2, CV3, and CV26. These samples are those located in the sectors of the streams closest to the tailings pile and, therefore, most influenced by its drainage. Figure 5 presents the log transformed concentrations of these contaminant elements measured in the dissolved phase for the two sampling campaigns, demonstrating the high influence of the mine's waste piles in the dispersion of these elements in the above-mentioned samples, with the exception of sample CV3. The latter does not show significant fluctuations between the two campaigns since it is located upstream in a watercourse, even presenting a slight increase in the levels of these contaminants, possibly due to the more oxidizing conditions observed in the February 2022 campaign.

After performing IDW interpolation, it was possible to visualize the migration of contamination plumes for various contaminants. Figure 6 represents the migration of Fe, the element with the highest content among the metallic elements, in the study area. During the drier campaign, Fe is more confined to the mining area, whereas in 2023, direct migration of Fe from the mining zone to downstream watercourses is evident. Thus, we can infer the direct influence of the Caveira mine's waste piles on the contamination of the surrounding water.

4. Conclusions

This study demonstrates the clear influence of the mine waste heap drainage on the water quality in the surrounding areas of the mine. The high chemical mobility observed in various metals, very low pH downstream of the mine, and high turbidity levels indicate that the leaching from the waste heaps is detrimental to the surrounding environment.

On the other hand, differences in the water chemistry related to different weather conditions were observed. The February 2022 campaign, following a very dry winter, generally showed lower pH, higher turbidity, and conditions conducive to the formation

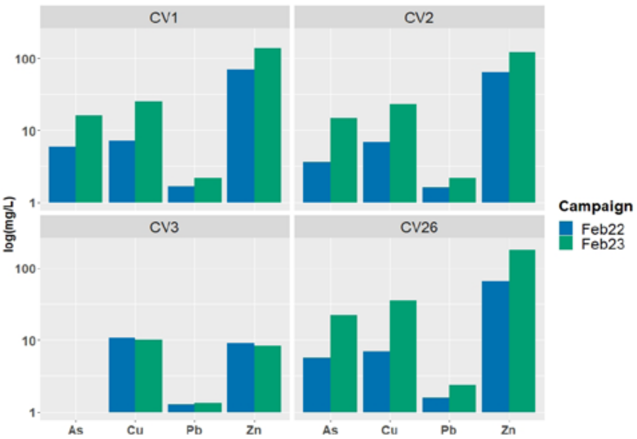

Figure 5. Concentrations of the main pollutants in the four most contaminated samples in the two sampling campaigns.

Figura 5. Concentrações dos principais poluentes nas quatro amostras mais contaminadas nas duas campanhas de amostragem.

of specific salts. In contrast, the February 2023 campaign demonstrated some dilution effects, particularly in relation to the physicochemical parameters of the water, slightly improving water quality in relation to these parameters. However, it was found that after a very dry period, in which conditions are conducive to the oxidation of sulphides, several metals were leached from the mining area into the watercourses, increasing the levels of contamination.

In order to conduct a more detailed study of the migration of the contamination plume, further sampling is needed under the same meteorological conditions as those described in this study. This will allow us to generate dispersion maps with shorter radii.

This study highlights the urgent need for environmental remediation measures in the Caveira mine waste heaps to prevent the ongoing source of the contamination observed.

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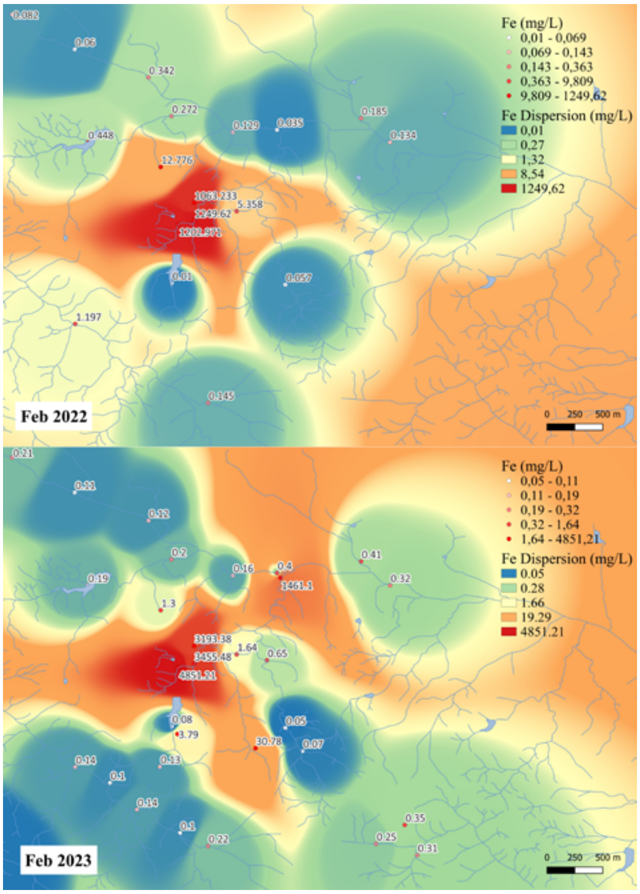

Figure 6. Dispersion of the Fe contamination plume between the February 2022 campaign, during the dry winter, and the February 2023 campaign, in the wetter winter.

Figura 6. Dispersão da pluma de contaminação de Fe entre a campanha de Fevereiro de 2022, no Inverno de seca, e a campanha de Fevereiro de 2023, no Inverno mais chuvoso.

References

Ferreira da Silva, E., Durães, N., Reis, P., Patinha, C., Costa, M.R., 2015. An Integrative Assessment of Environmental Degradation of Caveira Abandoned Mine Area (Southern Portugal), *Journal of Geochemical Exploration*, **159**: 33-47.

LNEG-LGM., 2010. Carta Geológica de Portugal à escala 1:1 000 000, edição 2010. Ministério da Economia, Inovação e Desenvolvimento. Unidade de Geologia, Hidrogeologia e Geologia Costeira, Laboratório Nacional de Energia e Geologia.

Mateus, A., Figueiras, J. X., Matos, J., Abel Gonçalves, M., Lopes, R., Labaredas, J., Beleque, A., 2008. Condicionantes impostas à dispersão de metais acumulados em escombreiras mineiras: o exemplo de Caveira (Faixa Piritosa Ibérica). In: Callapez, P. M., Rocha, R. B., Marques, J. F., Cunha, L. S., Dinis, P. M. (Eds.), *A Terra: Conflitos e Ordem. Homenagem ao Professor Ferreira Soares*. Museu Mineralógico e Geológico da Universidade de Coimbra, Coimbra, 373-382.

Matos, J. X., Martins, L. P., 2006. Reabilitação ambiental de áreas mineiras do sector português da Faixa Piritosa Ibérica: estado da arte e prespectivas futuras. *Boletín Geológico y Minero*, **117**: 289-304.

Mota, N., Fonseca, R., Araújo, J., Antunes, M., Valente, T., Barroso, A., Araújo, A., Albuquerque, T., 2022. A Geostatistical approach for Mercury spatial patterns assessment in sediments in an old mining region – the Caveira Mine case study, Portugal. Proceedings of the 14th International Conference on Geostatistics for Environmental Applications (GeoENV 2022). Ecology, Natural, Resources, Parma.

Reis, A. P., Ferreira da Silva, E., Cardoso Fonseca, E., Patinha, C., Barrosinho, C., Matos, J., 2012. Environment al Assessment of the Caveira Abandoned Mine (Southern Portugal): Part1: Characterization of Metal Contaminated Soil. *Soil and Sediment Contamination: An International Journal*, 21, **2**: 227-254.

Sistema Nacional de Informação de Recursos Hídricos (SNIRH), 2023. Dados de Base [Página de Internet] https://snirh.apambiente.pt/index.php?idMain=2&idItem=1.

Tomiyama, S., Igarashi, T., 2022. The potential threat of mine drainage to groundwater resources. *Environmental Science & Health*, **27**: 100347.

Weightman, E., 2021. Environmental geochemistry of mine waste and waters at Macraes gold mine, Otago. *Master thesis*. University of Otago, Dunedin, New Zealand.