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STREAM SEDIMENTS POLLUTION: A COMPOSITIONAL BASELINE ASSESSMENT AT THE CAVEIRA MINE, PORTUGAL

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Abstract

A high concentration of Potentially Toxic Elements (PTE) can affect ecosystem health. It is therefore essential that spatial trends of pollutants are assessed and controlled. River sediment pollution is widespread in mining communities around the world, including in developing countries. This study, as part of the GeoMaTre project, restoration of water bodies impacted by mine drainage, an ongoing collaborative project (2021-2024) between the Polytechnic Institute of Castelo Branco and the University of Évora, Portugal, aimed to evaluate the potential risk of PTEs pollution in stream sediments under the direct influence of Caveira mine, a Cu-Pb-Zn-Ag-Au old mine included in the Iberian Pyrite Belt, South Portugal. Quantifying pollution implies first the understanding of pollution-free stream sediment. Often, this background, or pollution baseline, is undefined or only partially known. Given that the concentration of chemical elements is compositional, as the attributes vary together, a compositional approach was used aiming to find a compositional balance, based on Compositional Data (CoDa) principles. A dataset of 33 samples was collected from within 0 to 10 cm depth, in a grid of 1Km x 1Km and thirteen chemical elements, including PTEs of variable toxicity (As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn, V) and major elements from lithogenic sources (Fe, Al), were analyzed in preserved samples at about 4°C. The most extractable forms of metals (except for Hg) were obtained by partial digestion with aqua regia (HCl and HNO₃) in a high-pressure microwave digestion unit, followed by ICP-OES analysis. Hg was analyzed determined by a mercury analyzer based on thermal decomposition, gold amalgamation, and cold vapor atomic absorption spectroscopy detection.

Very high levels of Pb, As and Hg were found in sediments in a stream closer to the mine tailings pile and in an accumulation area where it flows into a larger waterway. These concentrations, reaching 3.8% Pb, 750µg⁻¹ As and 340 µg⁻¹ Hg, are well beyond the intervention values imposed by the Netherlands legislation (2009), one of the only European legislation that includes reference values for freshwater sediments. In some of these locations, Zn contents above the legislated reference values (120 µg⁻¹) corroborate the nature of the ore previously exploited, pyrite mineralization enriched in Cu, Pb, Zn, Au, and Ag.

The methodological approach implied the geological background selection in terms of a trimmed subsample that can be assumed as non-pollutant (Al and Fe) and the selection of a list of pollutants based on the based on expert knowledge and previous studies (As, Zn, Pb, and Hg); Identifying a compositional balance, including pollutant and non-pollutant elements, with sparsity and simplicity as properties, is crucial for the construction of the novel Compositional Pollution Indicator (CPI).

A sequential stochastic Gaussian Simulation was performed on the new CPI. The results of the 100 computed simulations are summarized through mean image maps and probability maps of exceeding a given statistical

threshold, thus, allowing the characterization of the spatial distribution and variability of the CPI. A better understanding of the trends of relative enrichment and PTEs fate is discussed.

Keywords: Caveira mine; Stream sediment; Compositional Indicator; Sequential Gaussian Simulation; Probability map.