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Surface water and groundwater in a waste disposal area from dimension stone processing

Águas superficiais e subterrâneas em uma área de disposição de resíduos do beneficiamento de rochas ornamentais

Mirna Aparecida Neves[1], *Eduardo Baudson Duarte*[2], *Edlayne Pimentel Moraes*[3]

ABSTRACT

Processing of dimension stones involves the transformation of rock blocks into plates. This process generates a very fine-grained residue as mud, composed of rock powder, abrasive inputs, and water. During the polishing of plates, this residue can acquire phenolic resins, chlorides, and other chemical compounds. The effluent from polishing is usually mixed with sawdust and disposed of in industrial landfills and, eventually, clandestine deposits. This study presents an assessment of the quality of surface water and groundwater around an old deposit of residues from the processing of dimension stones located in the municipality of Cachoeiro de Itapemirim, south of the State of Espírito Santo, Southeast region of Brazil. Groundwater samples were collected in monitoring wells, and surface water was collected in drainage channels located upstream and downstream of the deposit. The study analyzed the pH, total dissolved solids, alkalinity, total phenols, chlorides, and dissolved metals. Considering the Resolutions of the National Environmental Council nº 357/05—for surface waters—and 396/08—for groundwater, the contents of Fe, Mn, and phenols are above the permitted limit, while Cu and Pb are close to it. The other parameters are within the permitted range but indicate an entry of pollutants from the drainage of urban effluents into the phreatic aquifer, which is also observed by monitoring rainfall, groundwater level depth, pH, and electrical conductivity. The study indicates that, if stored per current environmental regulations, residues from the processing of dimension stones present a controllable risk concerning environmental quality. On the other hand, the most significant impact on water quality in the studied area is that of domestic effluents.

Keywords: abrasive mud, water quality, environmental monitoring.

RESUMO

O beneficiamento de rochas ornamentais envolve a transformação de blocos rochosos em placas. Esse processo gera um resíduo de granulação muito fina, sob a forma de lama, composto de pó de rocha, insumos abrasivos e água. Durante o polimento das placas, o resíduo pode adquirir resinas fenólicas, cloretos e outros compostos químicos. O efluente do polimento geralmente é misturado ao da serragem e descartado em aterros industriais e, eventualmente, em depósitos clandestinos. Este estudo apresenta uma avaliação da qualidade das águas superficiais e subterrâneas no entorno de um antigo depósito de resíduos do beneficiamento de rochas ornamentais localizado em Cachoeiro de Itapemirim, sul do estado do Espírito Santo, sudeste do Brasil. Amostras de água subterrânea foram coletadas em poços de monitoramento e as águas superficiais em canais de drenagem localizados a montante e a jusante do depósito. Foram analisados pH, sólidos totais dissolvidos, alcalinidade, fenóis totais, cloretos e metais dissolvidos. Considerando-se as Resoluções do Conselho Nacional de Meio Ambiente nº 357/05 — para águas superficiais — e 396/08 — para águas subterrâneas —, os teores de Fe, Mn e fenóis estão acima dos valores máximos permitidos, enquanto Cu e Pb estão próximos a eles. Os demais parâmetros estão na faixa permitida, mas indicam a entrada de poluentes oriundos de efluentes urbanos para o aquífero freático, o que também é observado pelo monitoramento da precipitação, profundidade do freático, pH e condutividade elétrica. O estudo mostra que, se armazenados de acordo com as regulamentações ambientais vigentes, os resíduos provenientes do processamento de rochas ornamentais apresentam um risco controlável com relação à qualidade ambiental. Por outro lado, o impacto mais significativo na qualidade da água na área estudada é proveniente do lançamento de efluentes domésticos *in natura* no corpo d´água.

Palavras-chave: lama abrasiva; qualidade da água; monitoramento ambiental.

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Introduction

Dimension stone business has stood out in the international market due to the growing construction sector, in addition to the modern trend of using natural materials in some niches of architectural fashion. Although this production contributes to the economic growth of many developing countries, it claims attention for the environmental impacts related to generation of wastes, such as the residual sludge (Zichella et al., 2020).

According to Jalalian et al. (2021), about 51% of the crude rock extracted from quarries turns into waste and roughly 41% of the rock blocks that arrives at dimension stone processing plants becomes waste for producing finished plates. The processing of dimension stones involves the sawing of blocks to compose plates and polishing these plates for finishing and shine. The sawing of blocks on conventional looms uses a sawdust pulp composed of steel shot, lime, and water, which is discarded after wear. There are also diamond wire or multiwire looms, which do not use abrasive mud but generate a muddy residue, basically composed of rock dust and water. After sawing of the blocks, the raw plates are subjected to polishing, generating a residue composed of water, rock dust, various types of abrasive inputs, phenolic resins, coagulants, and other products. The waste generated at this stage is generally mixed with sawdust, partially dehydrated, and discarded in industrial deposits or landfills. Careful sorting according to the type of residue would enable the million tons of waste stored in landfills to be transformed in raw material for manufacture of other products (Yurdakul, 2020).

Although many studies have focused on the possibility of using dimension stone wastes to manufacture a wide range of by-products, such as concrete (Gautam et al., 2021), ceramics (Chiara et al., 2020), ecological bricks (Barros et al., 2020), mineral fertilizer (Theodoro et al., 2021), and others, research about environmental changes due to the storing of these wastes is not so common. Some works focused the impacts of dimension stone extraction on air, surface water, groundwater, and soil quality in the neighborhood of quarrying areas (Ahmed et al., 2020; Kalu and Ogbonna, 2021), but water quality has not yet been studied near the waste landfills of processing plants.

Indeed, the residue from dimension stone processing is generally considered an inert material, containing elements that are naturally present in rocks, but its very fine graining indicates the possibility of leaching potentially toxic compounds in the environment (Simão et al., 2021). Fine residues, even if they come from rocks, can significantly affect the physical and chemical properties of native soil (Singhal et al., 2020), which can change the natural characteristics of surficial and groundwater.

The geological substrate of the state of Espírito Santo is composed mainly of crystalline rocks, such as gneiss and granite, that form a crystalline aquifer system. In this aquifer type, the phreatic zone is commonly present in the weathered mantle that covers the fresh rock (Lachassagne et al., 2021). The weathered mantle acts as a water collector and stores groundwater that slowly feeds the deeper aquifer present in discontinuities of the non-altered rock (Zarate et al., 2021). At this layer, local flows predominate and the groundwater is more easily affected by surface pollutants (Bon et al., 2021).

Around the world, the production and management of solid waste has been controlled by environmental regulations, either general or specific to each industrial sector. The European Directive 2006/21/EC (European Commission, 2006) stipulates the conditions under which waste may be generated, as well as stored, monitored and controlled. This objective is achieved through recovery and recycling, in accordance with the principles of the circular economy. In the US, the Code of Federal Regulations (United States, n.d.) stipulates the criteria for the classification of waste management facilities and their associated practices. Its application is predominantly directed at non-hazardous solid waste, such as that generated in the processing of dimension stone. This waste is classified as either industrial or "special".

In the state of Espírito Santo, the main Brazilian producer of dimension stone, the issue is regulated by the State Institute of Environment and Water Resources of Espírito Santo (IEMA), through the Normative Instructions 11/2016, 12/2023, and 13/2023 (Espírito Santo, 2016; 2023a; 2023b), which determine the rules for managing residues from processing of dimension stones. However, old deposits arranged incorrectly are widespread, creating environmental liabilities for the sector. Studying and monitoring these areas is essential to check possible interactions between the industrial waste and the environment. The municipality of Cachoeiro de Itapemirim is the main producer of dimension stones in Espírito Santo, a state that accounts for 82% of the sector's exports (FINDES, 2023). Thus, the production of wastes from this industrial sector becomes a regional concern, as the growth of production implies an increase in the volume of effluents.

In an attempt to assess the impact of industrial waste disposal on water quality, the data revealed influences from urban sewage discharges. This highlights the importance of a systematic analysis of the urban environment, considering the interconnectedness of natural processes. These data illustrate the situation regarding basic sanitation in Brazil: many municipalities still lack infrastructure for domestic sewage collection, and full treatment remains far from universal, reinforcing the urgency of effective public policies. In this sense, Law 14.026/2020, which updates the Legal Framework for Sanitation (Brasil, 2020) and the goals of the National Basic Sanitation Plan (PLANSAB) (Brasil, 2010), aims to ensure sanitation by 2033, in line with the commitments made to Sustainable Development Goal 6 (SDG 6) of the United Nations, which aims to promote the availability and sustainable management of water and sanitation for all by 2030.

This study analyzes the quality of surface water and groundwater in an old area of disposal of fine residues from the processing of dimension stones in Cachoeiro de Itapemirim (ES), where they have been stored in direct contact with soil for decades. In addition to analyzing the water's physicochemical parameters, the study also presents its variations concerning rainfall.

Materials and Methods

Study area

The old deposit of dimension stone waste studied here is located in Cachoeiro de Itapemirim, south of the state of Espírito Santo, approximately 136 kilometers away from the capital, Vitória. According to the Brazilian Institute of Geography and Statistics (IBGE, 2022), in 2022, the municipality of Cachoeiro de Itapemirim had 185,786 inhabitants, a demographic density of 214.89 inhabitants/km^2, and sanitary sewage in around 89% of the territory.

According to the Köppen climate classification, the region presents a tropical climate with dry winter (Aw) and a subtropical high-altitude climate, with dry winter and mild summer (Cwb) and dry winter and hot summer (Cwa) (Alvares et al., 2013). Rainfall has two distinct periods: a rainy season from November to March, and a drier season from April to October (Figure 1).

The rocks comprising the region's geological substrate are gneisses of granitic, granodioritic to tonalitic composition (Santiago et al., 2022). Alluvial sediments also occur, which can be sandy, sandy-clayey, and clayey, with pebbles of various lithological types. Due to the hot and humid climate, a mantle of alteration (or weathering mantle) covers the crystalline rocks of the geological substrate. This unconsolidated mantle, together with the alluvial sediments, stores a phreatic aquifer with granular porosity, which is essential for recharging the underlying aquifer and serving as a protective barrier for deeper circulating waters (Oliveira et al., 2022).

The groundwater aquifer in the weathering mantle and alluvial deposits supplies small-scale water, mainly for domestic use. Therefore, monitoring water quality is extremely important, as there is a risk of pollution/contamination by effluents, not only of industrial origin, but also by untreated urban sewage, which is very common in the region. Similar conditions are reported in many Brazilian cities such as Belo Horizonte/MG (Dantas et al., 2021), Campinas/SP (Santos et al., 2022), and Rio de Janeiro/RJ (Delaunay et al., 2024), as well as in other countries such as China (Wang et al., 2022), Romania (Mihali and Dippong, 2023) and Argentina (Paná et al., 2024), where the discharge of raw sewage significantly compromises the quality of water resources. According to the Water and Sewage Diagnostic (Brasil, 2023), 43.7% of Brazilian municipalities still lack a sewage treatment system, relying instead on alternative solutions such as septic tanks, rudimentary cesspits, open ditches, and discharge into waterways.

Field data collection

Surface and groundwater samples were collected upstream and downstream of the waste deposit (Figure 2). The upstream points are safely unaffected by the waste disposal, while the downstream points are located to receive fluids from the waste if released from them.

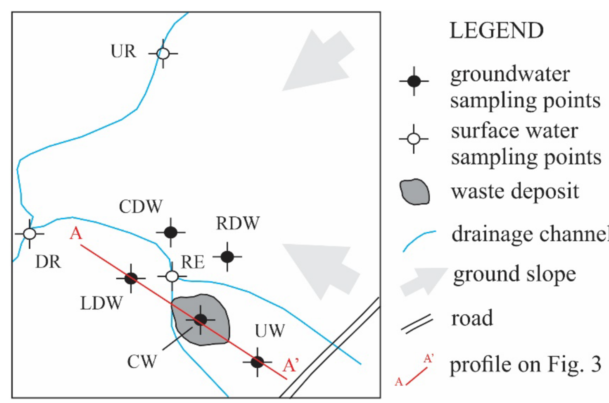

Figure 2 – Location of the waste deposit and surface and groundwater sample collection points.
UW: upstream well; CW: well in the center of the deposit; LDW: left side downstream well; CDW: central downstream well; RDW: right side downstream well; UR: upstream river; DR: downstream river; RE: river receiving urban effluents.

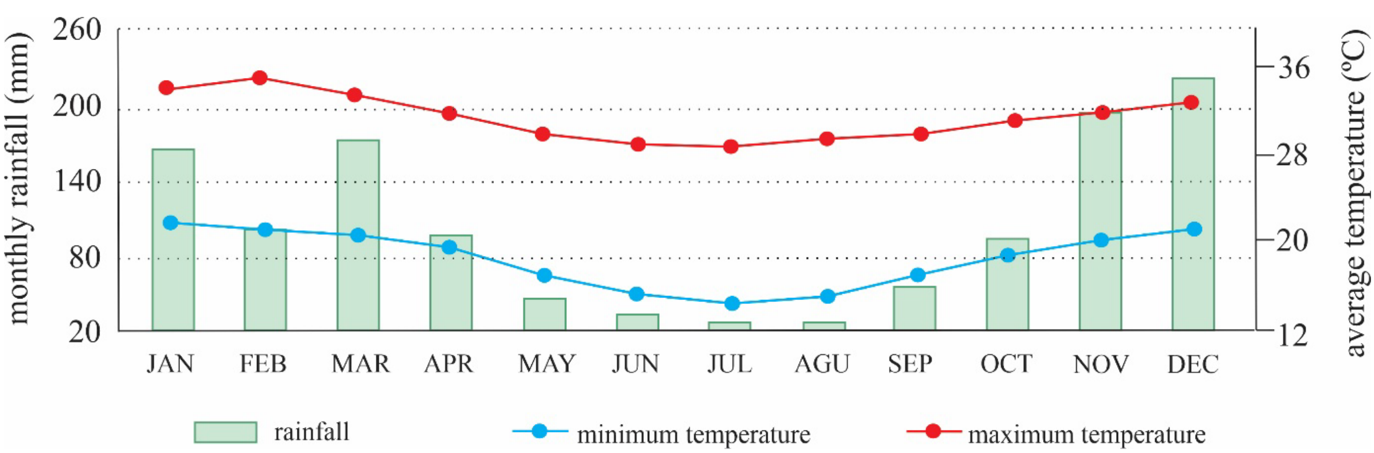

Figure 1 – Temperature and rainfall in Cachoeiro de Itapemirim (ES)—monthly averages from 1982 to 2013.
Source: Incaper (2023).

Thus, surface water was collected in drainage channels that cross the area (UR and DR), one of which receives urban effluents (RE). Groundwater was collected in monitoring wells drilled strategically concerning the waste deposit, according to NBR 13.895/97 (ABNT, 1997). One of the wells is upstream of the deposit (UW), and the other three are downstream, one on the right side (RDW), another on the left side (LDW), and the third between them, in the central position (CDW). Although not foreseen in the regulations, a well was also drilled in the center of the waste deposit (CW), reaching the geological substrate (Figure 3).

The monitoring wells were protected with a polyvinyl chloride (PVC) cover and slab and a box with a concrete cover (Figure 4). The water level depth was measured using a level gauge, and rainfall was measured using a rain gauge installed in the study area. The groundwater flow network was constructed through the water level depth data subtracted from the terrain elevation. Due to the area's climatic conditions, the drainage channels were considered effluents, i.e., they supply the water table aquifer.

Groundwater samples were collected with disposable bailers after pumping and recovering the water level in the wells. Still in the field, the following parameters were measured in the collected samples: pH, temperature, electrical conductivity (EC), and total dissolved solids (TDS), using a previously calibrated portable multiparameter. The aliquots were stored in bottles previously sanitized with HNO_3 solution, and refrigerated at near 4°C before the proceedings to analyze alkalinity, chlorides, phenols, and dissolved elements. The bottles were stored in Styrofoam with ice and sent to the Applied Geology Laboratory of the Department of Geology (CCENS/UFES).

Data acquisition in the laboratory

The preservation of samples and sampling techniques were carried out in accordance with the NBR 9898/1987 (ABNT, 1987), and analysis followed the Standard Methods for the Examination of Water and Wastewater (APHA; AWWA; WEF, 2022). The samples remained refrigerated in the laboratory, where they were separated into aliquots for the different analytical procedures.

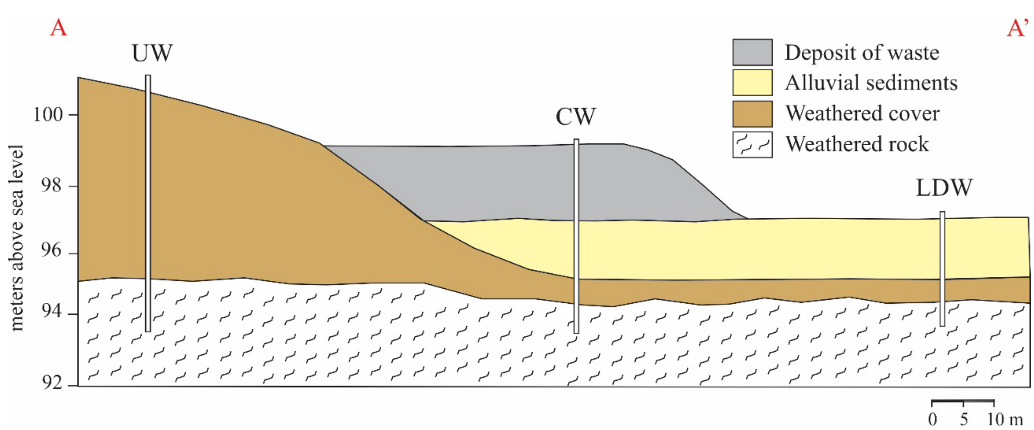

Figure 3 – Profile showing the position of monitoring wells and materials found in the geological substrate. In addition to the upstream (UW) and downstream (CDW) wells recommended by the environmental standard, a well was also drilled in the center of the waste deposit (CW) (profile position A – A' illustrated in Figure 2).

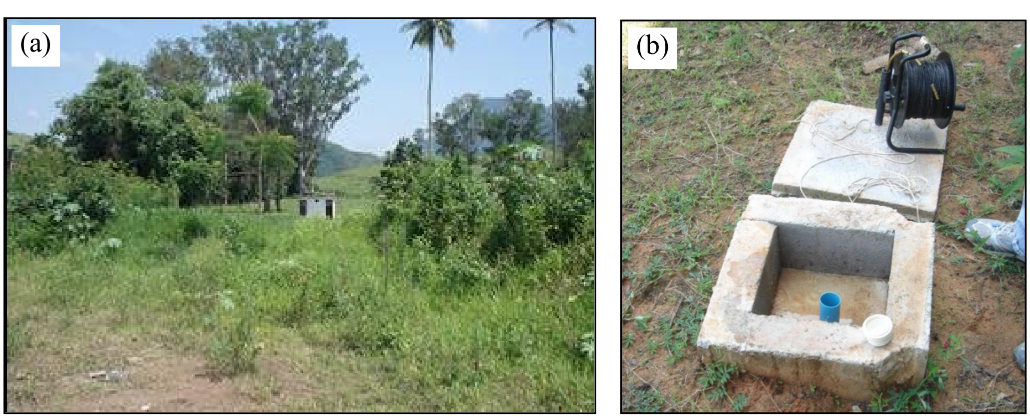

Figure 4 – (a) View of the site of the old waste deposit, already occupied by vegetation, and (b) open monitoring well for collecting water and measuring the groundwater level (WL).

Blank samples, which consist of ultrapure water, were added to check for possible analytical interferences.

The alkalinity was determined by titration, using sulfuric acid solution, sodium carbonate solution, and bromocresol green indicator. The titration was done in triplicate, and the value used to calculate alkalinity was the average of the values found. The total phenol concentration was measured using a Hanna Instruments kit, to prepare a color solution, coupled with a total phenols stock solution and standard phenol solutions. Chloride analysis was performed by preparing a chloride stock solution, standard solutions, and a color solution with $Hg(SCN)_2$ and $Fe(NO_3)_3.9H_2O$. The total phenol and chloride concentrations were determined employing an ultraviolet-visible (UV-VIS) spectrophotometer, using 510 nm wavelength to calibrate the absorbance readings. The concentration of chemical elements dissolved in the water samples was measured after filtering with a 0.45 µm porosity membrane. An aliquot of each filtered sample was stored in a previously cleaned polyethylene bottle and acidified with nitric acid (HNO_3) until reaching a pH below 2. Analytical blanks composed of Milli-Q standard ultrapure water were also prepared, which went through all the procedures applied to the samples studied. The vials were stored in a refrigerator until analysis. The concentrations of Ca, Mg, Na, Al, Fe, Mn, Zn, Pb, and Cu were measured using inductively coupled plasma optical emission spectrometry (ICP-OES) on a Thermo Scientific iCAP 6300 Duo model instrument, with radio frequency power of 1,150 W, cyclonic nebulization chamber, and gas flow of 0.50 $L.min^{-1}$, with three reading repetitions for each element.

Data treatment

Box plot graphs were constructed using the R 2.15.0 software (R Core Team, 2020). The graphical representation in the box plot allows a visual comparison between two or more data groups, in addition to demonstrating how the variables are distributed concerning homogeneity, the central tendency values, their arrangement, and the existence or absence of outliers. The parameters present in the box plot include median, first and third quartiles, mean, maximum and minimum values, and outliers (Figure 5). The box in the graph corresponding to the range of the first and third quartiles represents 25 and 75% of the observed sample values and gives an idea of how dispersed the sampled values are. The median or second quartile is the value that divides in half, i.e., 50% of the elements in the sample are less than or equal to the median.

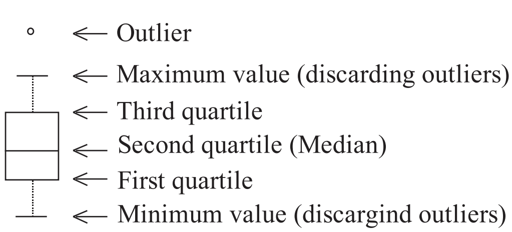

Figure 5 – Elements that comprise the box plot graph.

The other 50% of the elements are greater than or equal to the median, the horizontal lines correspond to the maximum and minimum values (except for outliers), and outliers are anomalous or discrepant values that deserve greater attention.

The measured values were compared with the thresholds (THR) determined by the National Environmental Council Resolutions (*Conselho Nacional de Meio Ambiente*—CONAMA) for surface water and groundwater (Brasil, 2005; 2008). Some of the parameters analyzed are not mentioned in these resolutions, but they are presented for comparing upstream and downstream points in relation to the environmental liability.

It is worth noting that the analysis of these parameters and the integrated monitoring approach allow for a detailed and updated characterization of the local environmental situation, representing an advance in knowledge, since similar studies in the region have not yet been carried out.

Results and Discussion

Physicochemical parameters of surface water and groundwater

This item presents the values of pH, TDS, alkalinity, phenols, chlorides and concentration of dissolved chemical elements, which were analyzed in surface and groundwater collected in the disposal area of fine waste from dimension stone processing.

Hydrogen ion potential

The pH is an important parameter to be analyzed in the studied area, as it is usually high in dimension stone wastes, due to the lime used in the rock sawing on conventional looms.

The pH values measured in the water samples (Figure 6) are generally within the limits required by CONAMA Resolution 357 (Brasil, 2005) for Class 1 freshwater and expected for groundwater (Hem, 1989).

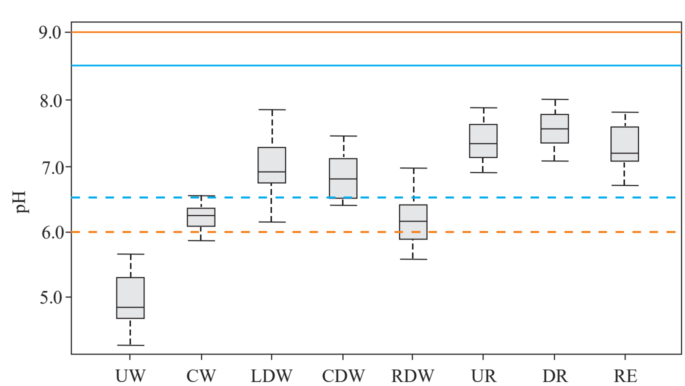

Figure 6 – Distribution of pH values at collection points. The intervals between the dotted and solid lines, orange and blue, indicate the range of values considered normal in surface water and groundwater (Hem, 1989).
UW: upstream well; CW: well in the center of the waste deposit; LDW: left side downstream well; CDW: central downstream well; RDW: right side downstream well; UR: upstream river; DR: downstream river; RE: river receiving urban effluents.

Exceptions are observed in the UW, which presents some values below the common groundwater pH. The waters in the CDW and LDW have higher pH values than in the CW. The surface waters, both at the downstream and upstream points, as well as the RE point also show the higher values. Therefore, it can be stated that the deposition does not cause harmful changes regarding pH-values in the studied area.

Authors who measured the pH directly in the sludge used for sawing rocks, still within the company's circulation system, report noticeably higher values, which would classify them as corrosives (Delgado et al., 2006; Freitas et al., 2012). On the other hand, Venturoti et al. (2019) measured pH values of 10.4 in the sludge decanted in the company's tank and 8.5 in the effluent stored in landfills. This shows that the pasty sludge, collected within the companies' production system, is different from the residue stored after dehydration by pressing or air drying. This was also found by Neves et al. (2013), who attribute the stabilization of waste pH over time to interactions with atmospheric CO_2.

Total dissolved solids

The TDS, estimated here through EC, means the quantity of chemical compounds dissolved in water, mainly the inorganic charge (Hounslow, 1995). The relationship between EC and TDS indicates the degree of water salinity, which is a growing water quality challenge in the world, that can negatively impact water use and food security, as well as biodiversity and ecosystems (Thorslund and Vliet, 2020). The CONAMA Resolutions 357/2005 for surface water (Brasil, 2005) and 396/2008 for groundwater (Brasil, 2008) allow the maximum values for the TDS to be 500 and 1,000 mg L^{-1}, respectively. All surface water and groundwater samples are below these THR.

When comparing the CW data with all points corresponding to groundwater, the highest concentration is found in the LDW and not in the CW, which corresponds to the waste disposal area (Figure 7). This shows that another source of saline fluids may exist, so the total concentration of dissolved solids is greater than in the CW. For surface waters, the RE point has a higher concentration than all the points analyzed, and there is no significant difference between the upstream and downstream points. Thus, the residue does not interfere with the increase in total solids dissolved in surface waters. Furthermore, sewage drainage may be the source of fluids contributing to the increase in TDS in the downstream well to the left of the deposit (LDW).

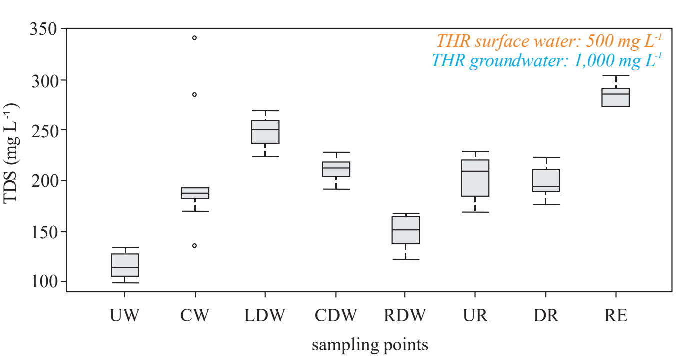

Figure 7 – Distribution of total dissolved solids (TDS) values at collection points.
UW: upstream well; CW: well in the center of the waste deposit; LDW: left side downstream well; CDW: central downstream well; RDW: right side downstream well; UR: upstream river; DR: downstream river; RE: river receiving urban effluents; THR: threshold values.

Alkalinity

The alkalinity of a solution is defined as its capacity for neutralizing acids (Hounslow, 1995). Commonly, alkalinity in natural waters is due to the presence of dissolved carbon dioxide, bicarbonate and carbonate, but it may also be due to other species such as NH_4OH (Hem, 1989). So, in the studied area, both the waste deposit and the sewage drainage could be sources of fluids capable of increasing the alkalinity of surface and groundwater.

The distribution of alkalinity values (Figure 8) shows that, in groundwater, the UW has the lowest values compared with the CW and DWs. The CW does not show a significant difference in alkalinity compared with the downstream wells, although the LDW again shows a tendency towards higher values. For surface waters (UR, DR, and RE), the RE point presents the highest alkalinity, including a value higher than the CW point. The surface water monitoring points upstream and downstream of the deposit do not differ significantly from each other. Thus, the residue does not interfere with the increase in alkalinity in surface water and groundwater.

Phenols

Regarding total phenol, the CONAMA Resolution 357/2005 for surface water (Brasil, 2005), in Class 2 rivers, and the CONAMA 396/2008 for groundwater (Brasil, 2008), in the more restrictive use, allow limits of 0.003 and 0.002 mg L^{-1}, respectively. Such highly restrictive limits are due to the dangerous toxicity of phenol compounds, which provoke mutagenesis and carcinogenesis toward humans and other living organisms (Michalowicz and Duda, 2007).

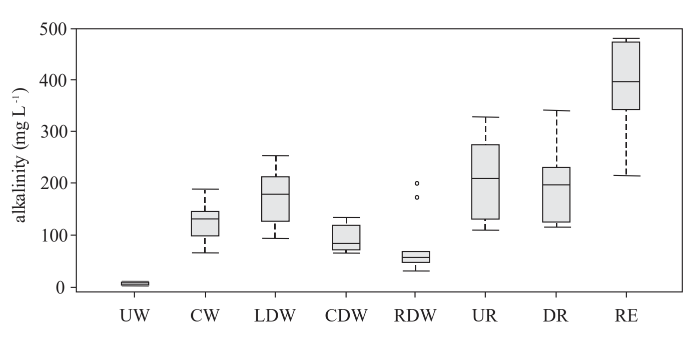

Figure 8 – Distribution of alkalinity values at collection points.
UW: upstream well; CW: well in the center of the waste deposit; LDW: left side downstream well; CDW: central downstream well; RDW: right side downstream well; UR: upstream river; DR: downstream river; RE: river receiving urban effluents.

The presence of phenols in water can be related with degradation of pesticides and can also come from industrial and municipal sewage. According to Liu and Mabury (2020), synthetic phenolic antioxidants are used in a wide range of products to retard oxidative reactions and have been detected in various environmental matrices including air particulates, sea sediment, and river water.

In this work, at all sampling points, values were found above the limits established by those resolutions (Figure 9). The CW presents higher values than the other sampling points. However, downstream wells (DWs) do not present a significant difference compared with UW, indicating that there may be other source(s) of phenols reaching groundwater. Supporting this fact, the phenol levels measured in surface waters (UR, DR, and RE) are significantly higher than in groundwater, including those observed in CW. The surface water monitoring points upstream and downstream of the deposit do not show significant differences, while the highest values stand out at the RE point.

Chlorides

Chloride is present in all natural waters, but mostly the concentrations are low (Hem, 1989). In the studied area, at all points, the measured levels of this anion (below 250 mg L^{-1}) comply with the limits established by CONAMA Resolutions 357 (Brasil, 2005) and 396 (Brasil, 2008).

CW does not present a significant difference of chlorides compared with the UW (Figure 10). Chloride values in the LDW tend to be higher than in the UW, while the RDW and CDW points present lower values. For surface waters (UR, DR, and RE), the RE point presents the highest chloride values, including a value higher than the CW point. The surface water monitoring points upstream and downstream of the deposit do not differ significantly from each other.

Therefore, the residue does not interfere with the increase in chlorides in surface water and groundwater, with the possibility that the LDW is receiving a supply of these ions from the sewage channel (RE).

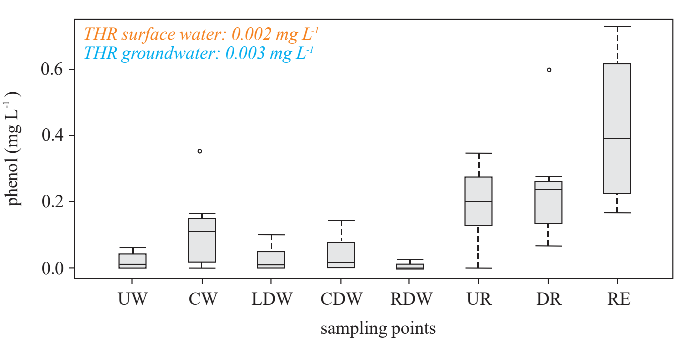

Figure 9 – Distribution of phenol values at collection points.
UW: upstream well, CW: well in the center of the waste deposit, LDW: left side downstream well, CDW: central downstream well, RDW: right side downstream well, UR: upstream river, DR: downstream river, RE: river receiving urban effluents, THR: threshold values.

The leachate from domestic and municipal solid waste usually contains inorganic components like chlorides, due to the salt used in the kitchen (Ren et al., 2020). Therefore, the sewage channel can provide fluids rich in these substances to surface and groundwater.

Dissolved chemical elements

Table 1 presents the concentration of dissolved chemical elements in surface water and groundwater samples. Even though Ca and Mg have no restrictions regarding their concentration in water, they are presented here to verify the presence of fluids coming from the deposit, as residues from the processing of dimension stones are known to be rich in these elements (Neves et al., 2021). However, the same pattern observed in the previous parameters, where CW does not present the highest values and LDW shows a similarity with RE, occurs in the levels of these chemical elements. In the case of surface water, the UR values also show that other sources of these elements exist, possibly discharges of domestic sewage upstream of the studied area.

The other elements analyzed have maximum values allowed by CONAMA resolutions. Among them, those that exceeded the THR at specific collection points are Fe, Mn, and Cu.

The Fe content is notably high in the CW, reflecting the presence and release of this element from the residue. The residues generated in conventional looms are rich in Fe from steel shot (Neves et al., 2021); because of that, Zichella et al. (2020) propose a treatment before disposal consisting of dividing the sludge in two by-products using a magnetic segregation technique. The magnetic product, rich in metals including Fe, can be reused in other productive sectors or disposed of in landfills (with an economic advantage due to the smaller volume of material to be discharged). The amagnetic product, rich in silicates from rocks, could be reused in the building sector. Despite the high Fe content, this element does not have high mobility in the environment (Hem, 1989), which is why it is not observed at high levels in DWs. On the other hand, Mn has sources in the waste deposit, sewage drainage, and unknown sources upstream. Surface waters also presented Mn contents above the THRs of Conama for Class 2 rivers.

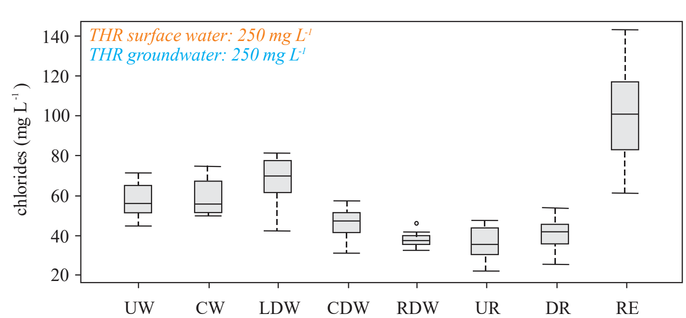

Figure 10 – Distribution of chloride values at collection points.
UW: upstream well; CW: well in the center of the waste deposit; LDW: left side downstream well; CDW: central downstream well; RDW: right side downstream well; UR: upstream river; DR: downstream river; RE: river receiving urban effluents; THR: threshold values.

Table 1 – Concentration of chemical elements (in mg L^{-1}) dissolved in surface water and groundwater collected at sampling points.

	Ca	Mg	Na	Al	Fe	Mn	Zn	Pb	Cu
UW	3.30±1.69	5.41±0.99	20.50±0.02	0.01±0.02	0.03±0.04	0.24±0.15	0.01±0.02	0.01±0.02	*nd*
CW	11.87±1.93	6.61±2.04	43.50±22.32	*nd*	5.22±4.61	0.54±0.28	*nd*	0.01±0.01	*nd*
LDW	30.83±8.81	16.33±2.25	27.67±2.02	*nd*	0.03±0.05	0.09±0.05	*nd*	*nd*	0.01±0.01
CDW	8.83±1.76	7.00±2.00	30.17±10.56	*nd*	0.06±0.10	0.020±0.04	*nd*	*nd*	*nd*
RDW	9.00±5.77	5.33±2.02	27.83±13.42	*nd*	*nd*	0.04±0.03	*nd*	*nd*	*nd*
UR	31.50±5.57	11.5±4.44	20.00±3.91	0.04±0.07	0.93±0.68	0.33±0.31	0.05±0.09	0.01±0.01	*nd*
DR	34.17±4.19	10.33±3.40	22.83±3.01	0.06±0.10	0.46±0.54	0.12±0.21	*nd*	*nd*	*nd*
RE	38.00±6.56	16.50±6.50	50.00±21.11	0.070±0.11	1.17±0.36	0.39±0.07	*nd*	*nd*	0.01±0.01
THR*	---	---	---	0.10	0.30	0.10	0.18	0.01	0.009
THR**	---	---	200.00	0.20	0.30	0.05	2.00	0.01	0.20

Nd: not detected; UW: upstream well; CW: well in the center of the waste deposit; LDW: left side downstream well; CDW: central downstream well; RDW: right side downstream well; UR: upstream river; DR: downstream river; RE:- river receiving urban effluents. Values in red are above the threshold values; *threshold of CONAMA 357/05 – surface water; **threshold of CONAMA 396/08 – groundwater.

It is known that untreated wastewater contains a wide variety of inorganic, organic, and biological contaminants (Alansi et al., 2021; Vasudevan et al., 2021; Ullah et al., 2022). Various research studies (Yu et al., 2022) have shown that vegetable leaves present an accumulation of metals as Cd, Cr, Ni, Zn, Fe, Pb, and Cu, in areas irrigated or in contact with urban effluents. This may explain the high levels of Fe and Mn in the area, including at collection points outside the influence of the landfill.

The concentration of Cu is above the THR only at the RE point. Even if the concentration is low, this fact shows that the sewage channel is a crucial contamination source in the studied area. Pb should be better investigated in a future study using the inductively coupled plasma mass spectrometry (ICP-MS) technique (the present study used inductively coupled plasma optical emission spectroscopy—ICP-OES, whose detection limit is very close to the THR in the equipment used), since it is very close to the THRs, including in the UW.

Variations with rainfall

Figure 11 shows measurements of the groundwater level (WL) depth and rainfall in the study area. There is a rapid response to an increase in the WL (decrease in WL depth) to increased rainfall, showing that the aquifer's recharge at the site is rapid. In fact, the geological substrate at the site, composed of weathered and sedimentary materials (mantle of alteration of crystalline rocks and river sediments, respectively), favors the infiltration of rainwater. However, in the UW, located in the weathering mantle, the WL rise response is slower than in DWs drilled in alluvial sediments.

pH and EC values, considered indirect water quality indicators (Saalidong et al., 2022), were also compared to rainfall indices (Figure 12). Values of pH and EC decrease with increasing rainfall, indicating dilution and demineralization of groundwater with recharge events. However, in the LDW, the behavior is the opposite, showing that there is more significant mineralization of the water with the increase in rainfall. This fact corroborates that these waters contain components originating from sewage drainage, which is proven by monitoring the parameters presented previously.

Flow network

Based on the WL and the surface drainage channels, the equipotential and flow lines of the phreatic aquifer were traced (Figure 13). Groundwater movement converges into the area's main channel, which flows NE to SW on the left side of the map.

The underground flow network shows that the LDW's position means it receives fluids from both the deposit and the drainage channel that receives domestic sewage. The variations in the water quality parameters presented above, mainly in the samples collected inside the waste deposit (monitored by the CW) and in the drainage channel (monitored by the RE), indicate that the latter is mainly responsible for the changes observed in the LDW. The rainfall monitoring data and its influence on WL, pH, and EC (Figures 11 and 12) support what is observed through the flow network and the position of the water monitoring points.

The observed pattern, with an influence of more than one pollution source for the phreatic aquifer, shows the need to implement a routine for monitoring water quality in areas of dimension stone waste disposal, in addition to channeling and treating urban effluents. It is known that the shallow aquifer present in the alluvium and the weathered rock in crystalline terrains is the recharge area of the deeper aquifer (Lachassagne et al., 2021) that is widely used for water supply and needs to be protected.

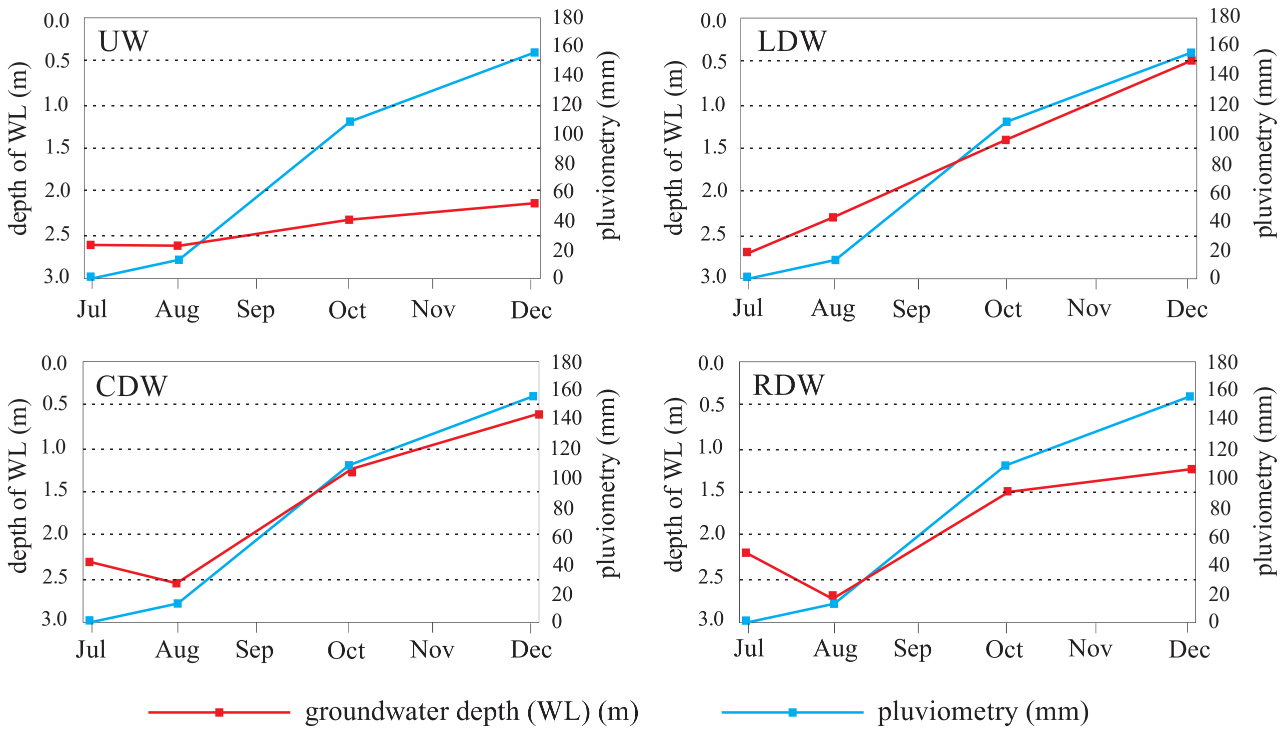

Figure 11 – Variation in groundwater level (WL) depth (red line) in monitoring wells and rainfall (blue line) measured at the site.
UW: upstream well; LDW: left side downstream well; CDW: central downstream well; RDW: right side downstream well.

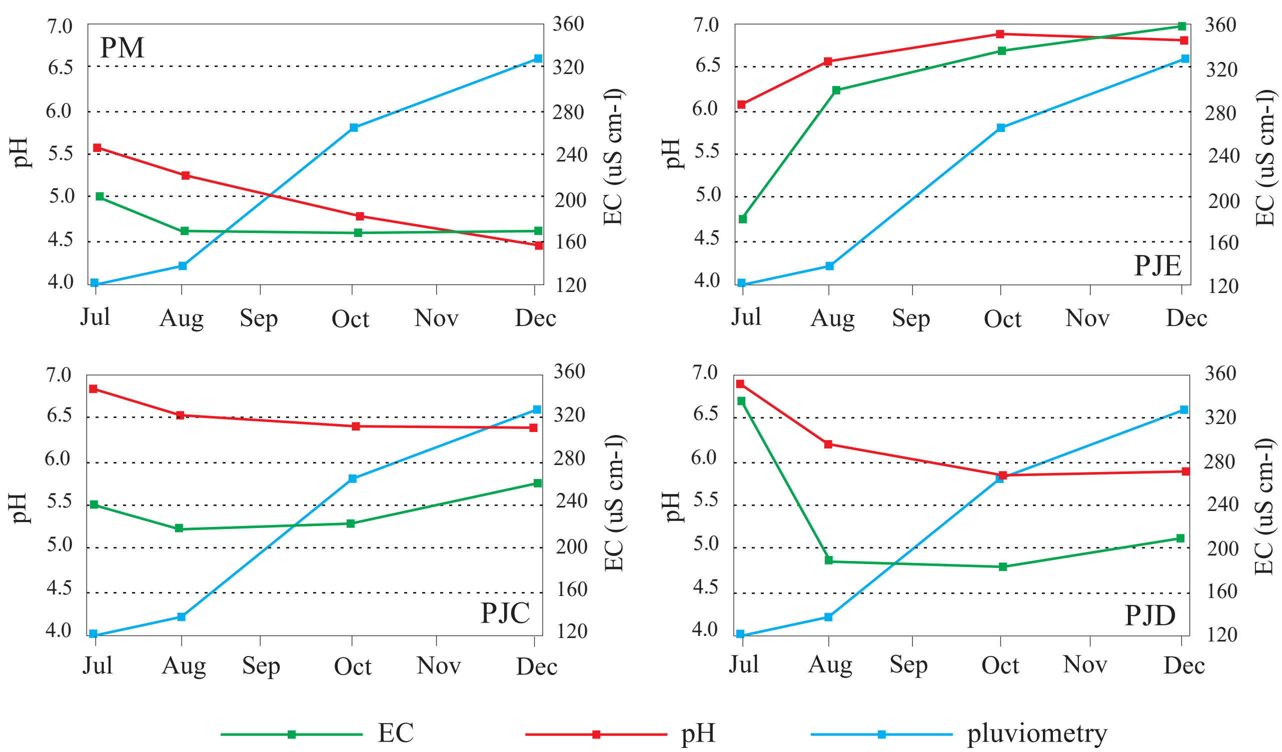

Figure 12 – Variation in pH (red line) and electrical conductivity—EC (green line) in groundwater and rainfall (blue line) measured at the site (rainfall values equal to those in Figure 10).
UW: upstream well; LDW: left side downstream well; CDW: central downstream well; RDW: right side downstream well.

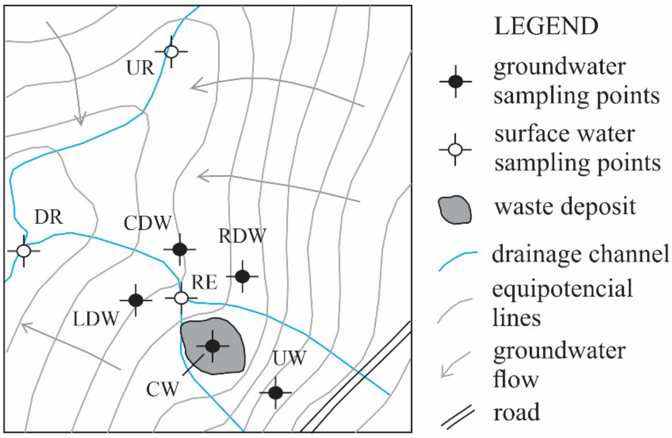

Figure 13 – Groundwater flow network with the position of the waste deposit and collection points for surface and groundwater.
UW: upstream well; CW: well in the center of the deposit; LDW: left side downstream well; CDW: central downstream well; RDW: right side downstream well; UR: upstream river; DR: downstream river; RE: river receiving urban effluents.

Conclusions

The dimension stone waste stored in the studied area does not alter surface water and groundwater pH values to levels that could harm the environment. Chloride, alkalinity, TDS, and the elements Al, Zn, Mn, and Na do not exceed the maximum limits of environmental resolutions.

On the other hand, Fe, Mn, and phenols occur above the THR at several sampling points. The behavior of these parameters does not indicate a source from the waste deposit but from a surface drainage channel that receives urban sewage discharge. The iron concentration is increased at the central waste disposal point, indicating that the waste is interfering with the iron value in groundwater. However, there is no evidence of mobility of this element, as in DWs it is below the THR.

The value distribution pattern of the studied parameters indicates an entry of effluents into the water table aquifer from the sewage drainage channel. The LDW point, in almost all parameters, has the highest values, including values higher than those measured in the CW, showing that another source of pollutants interferes with groundwater quality. While waters of most wells indicate dilution effects with increased precipitation, the LDW waters indicate the arrival of substances that cause an increase in pH and EC. Therefore, although the waste deposit from the processing of dimension stones studied here is located irregularly concerning environmental regulations, the most significant impact on water quality is from domestic effluents. It should, therefore, be noted that the storage of this waste, as long as it is carried out per environmental regulations, presents a controllable risk from an environmental point of view.

The data presented here may indicate ways to improve the monitoring of areas impacted by ornamental rock processing waste, as well as guide environmental management and recovery strategies. In addition, there are aspects that deserve further investigation, particularly with regard to the long-term behavior of contaminants and the effectiveness of various remediation techniques.

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Authors' Contributions

Neves, M. A.: Conceptualization; funding; investigation; methodology; project administration; resources; supervision; validation; visualization; writing – review & editing; **Duarte**, E. B.: Data curation; formal analysis; investigation; methodology; validation; **Moraes**, E. P.: Data curation; formal analysis; investigation; methodology; writing – original draft.

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