

Characterization of drilling cuttings generated in oil and gas pre-salt drilling activities and leaching studies of contaminants present in these samples employing saline and aqueous solutions

Andréia Silveira Freire Soares (✉ andreiasfs07@gmail.com)

Rio de Janeiro State University: Universidade do Estado do Rio de Janeiro <https://orcid.org/0000-0002-3074-8728>

Mônica Regina da Costa Marques

Rio de Janeiro State University: Universidade do Estado do Rio de Janeiro

Luciana da Cunha Costa

Rio de Janeiro State University: Universidade do Estado do Rio de Janeiro

Research Article

Keywords: pre-salt drilling cuttings, leaching, metal ions, total organic carbon, solid residues.

Posted Date: June 14th, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1629655/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

This article describes the characterization of pre-salt drilling cuttings generated during offshore activities. Samples were submitted to leaching by employing saline and aqueous solutions to evaluate the leaching of contaminants in marine and aqueous environments. The results of tests on samples indicated that some of the heavy metals had high levels of contamination. The metals present in the highest concentrations in saline and aqueous leachates were Si and Ba. Probably, the presence of Ba in the leachates was associated with leaching of barite. The metals Cd, Cu, Ni and Zn were present in varied concentrations in the saline leachates, and the metals Si, Ba, Cu and Zn were found in the aqueous leachates. There was a tendency of higher concentration of TOC in saline leachates derived from samples containing aqueous-based fluids, which may be related to the greater leaching tendency of polymers and emulsifiers in this medium.

Highlights

- Heavy metals and TOC contents in pre-salt drilling cuttings with aqueous or non-aqueous fluids were measured.
- Most pronounced concentrations of Ba, Al, Fe, Cu, Pb, Mn, Si and Zn were found in cuttings containing non-aqueous fluids.
- Leaching experiments were conducted involving aqueous and saline solutions to simulate the bioavailability of the contaminants in sea and sanitary landfills.
- Environmentally hazardous metals such as Ba, Cd, Cu, Ni and Zn were present in the saline leachates in varying concentrations, while Cu and Zn were present in the aqueous leachates.

1 Introduction

Drilling cuttings are fragments of rock generated as the reservoir well is drilled by the bit, and brought to the surface by drilling fluids (Seyedmohammadi et al., 2017; Neff, 2007; Agha et al., 2002; Melton et al., 2000). The chemical characteristics of these residues are the result of the combination of properties of the rock formation and chemical parameters of the drilling fluids (Seyedmohammadi et al., 2017). Most of the metals present in drilling residues are also present in barite and bentonite clay, used as weighting material in the preparation of fluids, or in sedimentary rocks penetrated by the drill bit (Neff, 2007; Neff, 2010). Additionally, these cuttings may have high levels of organic contaminants such as petroleum hydrocarbons, polycyclic aromatic hydrocarbons, and/or polychlorinated biphenyls derived from drilled reservoirs or from the organic base used in the preparation of the drilling fluids (Melton et al., 2000; Farkas et al., 2017).

The removal and transport of cuttings fragments to the platform is only possible with the use of drilling fluids. According to the main constituent, these fluids are classified as water-based drilling fluids (WBDFs), non-aqueous drilling fluids (NADFs) and gas-based drilling fluids (GBDFs) (Apaleke et al., 2012). NADFs are traditionally subdivided into oil-based drilling fluids (OBDFs), enhanced mineral oil-

based drilling fluids and synthetic-based drilling fluids (SBFs) (USEPA, EPA-821-B-00-013, December 2000). These fluids have several specific functions, as well as advantages and disadvantages, that determine their conditions of use (Zhuang et al., 2019; Apaleke et al., 2012). As a result, drilling fluids can differ dramatically in their composition. The increased search for hydrocarbon reserves and the shift to offshore areas and/or deeper reservoirs, such as subsalt reserves, makes the performance and functionality of these drilling fluids more critical (Nrior & Odokuma, 2015).

During the drilling of phases I and II (without riser), the fluids used (seawater and WBDFs), together with the generated cuttings, do not return to the surface. The cuttings fragments are deposited around the wellhead. However, during phases III and subsequent drilling (riser phase), the fluids used together with the generated cuttings return to the surface. After reaching the platform or rig, the fluid and cuttings mixture is separated through a solids control system, containing a vibrating screen, degasser, desander, slurry cleaner and centrifuge system, which also separate solids depending on size (Kazamias & Zorpas, 2021; International Association of Oil & Gas Producers, Report 543/2016). The objective of these devices is to recover as much drilling fluid as possible to reduce environmental liabilities. It is estimated that about 10 to 15% of the drilling fluid remains adhered to the cuttings after the separation process, influencing the composition of the solid waste. Therefore, the cuttings retained in the solids are passed through a dryer to further reduce the adhered fluid, which passes from 20–45% after exit from the screen, to 3–10% after passing through the dryer (International Association of Oil & Gas Producers, Report 543/2016).

In general, WBDFs and drilling cuttings containing these fluids, depending on their composition, can be discharged into the sea after use, when permitted by local environmental regulations. However, NADF fluids cannot be disposed of this way. These fluids are generally reprocessed and recycled until their rheological properties are lost. When this happens, they are brought ashore for reprocessing or disposal.

There is much discussion about the strategies for management and treatment of these wastes (Kazamias & Zorpas, 2021; Almeida et al., 2017; Ball et al., 2012; Abbe et al., 2011; Page et al., 2003; Veil, 2002). The environmental and economic impacts associated with the management and disposal of these residues permeate this discussion. In offshore areas, disposal is done in the open sea, where dilution and rapid dispersion take place. However, increasing environmental concern over this practice has led to many restrictions in environmental regulations around the world. When these residues are brought to land, they are disposed of in class 2 sanitary landfills, intended for non-hazardous wastes. In these facilities, the cuttings are subject to contact with rainwater, which can carry contaminants to the soil.

The physical-chemical properties of cuttings are inherently variable, depending on several factors, such as type of drilled rock, depth and structure of the well, fluids used in the drilling process and composition of hydrocarbons, among others (Kujawska & Pawlowska, 2022; Abbe et al., 2011). The variability of cuttings means there is no standardized formula for the composition of samples that can be used to determine the toxicology and environmental impacts (Page et al. 2003), making the characterization work

of these samples very important from an environmental point of view. Thus, the characterization of cuttings is a fundamental step in defining the most appropriate treatment and management strategies.

The presence of metal ions in raw materials used in the preparation of fluids, such as barite and bentonite, can cause environmental damage if these ions are in a soluble and bioavailable form (Neff, 2008). Yu et al. (2021) reported that the adverse effects of metals in the environment are not only related to their total concentration, but also strongly depend on chemical partition processes. Chemical partition data of metals in sediments are preferred in studies of the ecological risk. Metals related to human contamination in sediments are typically found in the clay fraction. Fe-Mn oxides and organic matter are subject to ion exchange, complexation and chemical adsorption, presenting greater bioavailability and posing more serious risks to aquatic ecosystems. Therefore, partial chemical characterization of metals in sediments is preferred when investigating anthropogenic pollution and potential eco-hazards. Klein (1989), when analyzing the interaction of these metals with the biota and environment, observed that the quantification of solubilized ions and their speciation is more important than the total determination of the concentration of these ions by using acid digestion methods or alkaline melting of the samples.

Many researchers have analyzed leaching of samples of cuttings derived from offshore exploration and shale gas operations. Studies have also been conducted involving leaching of contaminants from oil drilling fluids, the raw materials used in the preparation of these fluids and sediment samples, by using aqueous solutions, dilute acid solutions or sequential extraction to separate water-soluble, acid-soluble, oxidizable and reducible fractions (Wang & Xiong, 2021; Xu et al., 2018; Zha et al., 2018; Piszcz-Karaś et al., 2016; Piszcz-Karaś et al., 2014; Edge et al., 2016; Leonard & Stegemann, 2010; Grant & Briggs, 2002; Sørheim et al., 2000; Terzaghi et al., 1998). It is necessary to expand leaching studies in saline and aqueous solutions.

Bioavailability is the main environmental concern related to the offshore and onshore disposal of drilling fluids and cuttings from offshore oil exploration and production activities. The expansion of studies on leaching from these pre-salt cuttings samples in saline and aqueous solutions will contribute to a better understanding of the environmental impact of disposing of these residues at sea or in sanitary landfills.

This study was conducted on two steps: characterization of pre-salt cuttings containing aqueous or non-aqueous based fluid (in solid state) with respect to particle size distribution, content of metal ions and total organic carbon (TOC) content; and analysis of leaching in saline or aqueous solutions by employing these cuttings according to the Brazilian standard ABNT Standard NBR 10.004/2004 and ABNT Standard NBR 10.006/2004. The leachates were characterized by determining pH, salinity (g L^{-1}), conductivity (mS cm^{-1}), total dissolved solids, free oil content (static iridescence), metal content and total organic carbon (TOC). The results were compared with parameters established in Brazilian environmental regulations. specifically Normative Instruction 01/2018 from the Brazilian Institute of the Environment and Renewable Natural Resources (IBAMA), and Normative Instructions 430/2011 and 357/2005 from the National Environmental Council (CONAMA).

2 Materials And Methods

For this study, ten cuttings samples from pre-salt drilling activities were used: five samples containing adhered aqueous fluid (WF) and five samples with adhered non-aqueous (NAF) fluid. These samples were called 1-WF, 2-WF, 3-WF, 4-WF, 5-WF, 6-NAF, 7-NAF, 8-NAF, 9-NAF, 10-NAF. The samples were packaged in plastic bottles and refrigerated.

2.1 Pretreatment of the samples

The cuttings samples were submitted to drying (60°C) in a forced-air oven (Solid Steel, SSDicr model) until constant weight (72 hours). To evaluate the granulometric distribution, the samples were subjected to separation in an electromagnetic stirrer (Bertel, model 0604), by using sieves of 4.75, 0.425, 0.075 and 0.005 mm.

Before the experiments involving leaching, acid digestion and determination of the total organic carbon content, the cuttings samples were manually crushed using a mortar and pestle until obtaining a fine sediment with granulometry < 0.005 mm. The samples were submitted to quartering to ensure homogenization, placed in previously identified glass containers and kept in a vertical desiccator, with silica gel at controlled temperature.

2.2 Determination of the metal content of drilling cuttings samples

The concentration of metals (Al, Cd, Pb, Cu, Cr, Fe, Mn, Mo, Ni, Si, Zn and Ba) was determined by flame atomic absorption spectrometry - FAAS (Varian, AA240). The concentrations of Hg and As were determined by FAAS with use of the VGA-77 accessory to generate cold steam. Before the analysis, the samples were submitted to acid digestion to convert them into a suitable form for analysis. The digestion of the sample is a fundamental step in the process of determining the metal content (Zhang & Hu, 2019; Hu & Qui, 2014). In this study, partial acid digestion of the samples was used, considered adequate for determining the concentration of environmentally available ions not attached to the siliceous matrices (Duzgoren-Aydin et al., 2011). This digestion, carried out using a mixture of HNO₃ and H₂O₂, 1:1 v/v, 10 mL of acid solution and 0.25 g of sample, was assisted by microwave for 10 minutes, at power of 50 watts, according to EPA 3050B (USEPA, EPA 3050B, December 1996). The solutions obtained were filtered, completed to 200 ml with Milli-Q water, and acidified with 5% v/v HNO₃. This procedure was performed in triplicate.

The commercial sample Buffalo River Sediment, despite not containing all the metals of interest for this study, was used as a reference for validation of the method. All results were within the acceptance criteria of 80–120% as suggested by the Association of Official Analytical Chemists (AOAC) and Brazilian guidelines INMETRO DOQ-CGCRE-008 (08/2018). To calculate the working range, a calibration curve was plotted by using a standard solution of the metal of interest and 7 concentration points. The evaluation of the linearity of the working curve, homoscedasticity and determination of the limits of detection (LD)

and quantification (LQ) of the metals was carried out using the Action Start® software (Table 1). The analyte recovery was estimated by analyzing samples spiked with known amounts of the metal. The acceptance criterion for recovery was 80–120%.

Table 1
Detection and quantification limits of metals determined by atomic absorption spectrometry.

Metals	Samples		
	DL	QL ¹	QL ²
	(mg L ⁻¹)	(mg L ⁻¹)	(mg Kg ⁻¹)
Al	0.2430 ± 0.0004	0.0750 ± 0.0004	18.41 ± 0.01
As*	2.62 ± 0.02	7.94 ± 0.02	198.7 ± 0.9
Ba	0.460 ± 0.001	1.394 ± 0.001	34.85 ± 0.03
Cd	0.248 ± 0.003	0.752 ± 0.003	1.88 ± 0.08
Cu	0.0065 ± 0.0003	0.0196 ± 0.0003	0.490 ± 0.008
Cr	0.045 ± 0.001	0.138 ± 0.001	3.45 ± 0.03
Fe	0.0115 ± 0.0003	0.035 ± 0.0003	0.873 ± 0.008
Hg*	1.841 ± 0.009	0.144 ± 0.009	139.5 ± 0.2
Mn	0.103 ± 0.006	0.313 ± 0.006	7.8 ± 0.2
Mo	0.320 ± 0.001	0.971 ± 0.001	27.27 ± 0.02
Ni	0.048 ± 0.001	0.105 ± 0.001	2.63 ± 0.02
Pb	0.0541 ± 0.0007	0.1638 ± 0.0007	4.09 ± 0.02
Si	0.4330 ± 0.0003	1.313 ± 0.0003	32.827 ± 0.008
V	0.1810 ± 0.0004	0.5480 ± 0.0004	13.71 ± 0.01
Zn	0.0193 ± 0.003	0.0585 ± 0.003	1.46 ± 0.08

DL: detection limit of the AAS equipment, based on reading standards in MilliQ water; QL¹: quantification limit of the equipment, based on the reading of standards in Milli-Q water; QL²: Limit of quantification of the method, calculated by multiplying the LQ¹ by the dilution factor for reading the sample

2.3 Determination of total organic carbon content of cuttings

The determination of the total organic carbon (TOC) content of the cuttings was carried out by using a Shimadzu TOC-L total carbon analyzer with an SSM – 5000A accessory for solids analysis. The total organic carbon content was indirectly obtained through the difference between the total carbon content (TC) and the inorganic carbon content (IC). In the solid state, the TC content was obtained through total combustion of the sample in an oven at 900 °C and the IC content was obtained through acidification with 1:1 phosphoric acid and heating in an oven at 200 °C. For TC and IC, the standard for preparing the calibration curve was glucose. The linearity of the calibration curve was evaluated using the Action Start statistical software, which revealed an R^2 of 0.9996, and absence of extreme points. A mass of approximately 20 mg of the fine dry sediment sample was used for the TC and IC analyses. The limit of quantification was 0.36% for TOC.

2.4 Fixed bed leaching studies employing saline and aqueous media

Bioavailability assays were performed in aqueous and saline media by using the method described by the Brazilian Association of Technical Standards (NBR 10004/2004 and NBR 10006/2004). This method is based on studies of leaching of solid waste in an aqueous medium, allowing the classification of these wastes (non-hazardous, class II) into inert or non-inert waste, depending on the presence of contaminants of environmental concern in the leachate.

The cuttings samples with \emptyset particles smaller than 0.005 mm (200 g) and distilled water (1 L) or saline solution (prepared by dissolving 69 g of commercial salt in 1 L of water) were transferred to a jar test device (Milan model JT101) and stirred (50 rpm) for 5 minutes. The sample was then kept in contact with the solutions for 7 days at room temperature. At the end of this procedure, the samples were filtered and the respective leachates were separated for characterization.

2.5. Characterization of aqueous and saline leachates

Data on pH, salinity (g/L), conductivity (mS/cm) and total dissolved solids (g/L) of aqueous and saline leachates were obtained by multi-parameter analysis (Hanna, model HI 2550). These data were obtained at the beginning (after contact between cuttings and solutions) and at the end of the leaching tests. The evaluation of free oil was performed visually in aqueous and saline solutions. Observations were made and recorded at the end of the leaching tests.

To determine the content of metals in the leachate, the samples were filtered through a nylon membrane (0.45 μm porosity) and acidified with a 5% v/v aqueous HNO_3 solution. The metal concentration of most metals was determined by flame atomic absorption spectrometry (FAAS) (Varian AA240). The concentration of Hg and As was determined using cold steam generation, as described in item 2.3.

The determination of the TOC content of the aqueous and saline leachates was carried out using a total carbon analyzer (Shimadzu TOC-L). To determine the Cl content, the standard used was sodium bicarbonate, and for TC the standard used was potassium biphthalate. The linearity of the calibration

curve was evaluated using the Action Start statistical software, which revealed R^2 of 0.9997 and absence of extreme points.

3 Results And Discussion

The results of total organic carbon and metals were compared with current Brazilian regulations, in particular IBAMA Normative Instruction 01/2018, which, despite being revoked in 2019, was used as a reference for having specific conditions for disposal of drilling cuttings generated in offshore operations and drilling fluids used in these operations. The main regulations consulted are mentioned below. A summary of the maximum discharge limits is presented in Table 2.

IBAMA Normative Instruction 01: Regulates the disposal of fluids, cuttings and cement pastes from offshore well drilling activities (Brazil, 2018);

CONAMA Resolution 430: Establishes conditions and standards for effluent releases (Brazil, 2011);

CONAMA Resolution 357: Establishes parameters for the classification of water bodies (Brazil, 2005);

ABNT Standard NBR 10.004/2004: Classifies solid waste potential risks according to its potential risks to the environment and health.

ABNT Standard NBR 10.006/2004: Classifies solid waste according to its potential risks (inert/non-inert) to the environment and public health, so that these wastes can be handled and disposed of properly.

Table 2

Maximum limits for discharge according to rules and regulations of Brazilian environmental agencies

Parameters	Normative Instruction 01/2018 IBAMA	ABNT NBR 10.004/2004	CONAMA 430/2011	CONAMA 393/2007	CONAMA 357/2005
	Notes	Maximum limit	Maximum limit	Maximum limit	Maximum limit
Density	WF (a), NAF (b), WBCF (c)	annotate			Class 1 saline water framework
Salinity	WF (a), NAF (b), WBCF (c)	annotate			
pH	WF ^(a) , WBCF (c)	annotate		5 a 9	
Temperature	WF (a), NAF (b), WBCF (c)	annotate		Less than 40°C	
Sedimentable Materials				1 mL L ⁻¹	
Ag			0.05 mg L ⁻¹	0.1 mg L ⁻¹	0.005 mg L ⁻¹
Al			0.2 mg L ⁻¹		1.5 mg L ⁻¹
As			0.01 mg L ⁻¹	0.5 mg L ⁻¹	0.01 mg L ⁻¹

(a)WF: water-based drilling fluids (b) NAF: non-aqueous drilling fluids (c) WBCF: aqueous-based complementary fluids

Parameters	Normative Instruction 01/2018 IBAMA		ABNT NBR 10.004/2004	CONAMA 430/2011	CONAMA 393/2007	CONAMA 357/2005 Class 1 saline water framework
	Notes	Maximum limit	Maximum limit	Maximum limit	Maximum limit	Maximum limit
Ba			0.7 mg L ⁻¹	5.0 mg L ⁻¹		1.0 mg L ⁻¹
Cd	barite	3 mg kg ⁻¹ ₁	0.005 mg L ⁻¹ ₁	0.2 mg L ⁻¹		0.005 mg L ⁻¹
Cr			0.05 mg L ⁻¹	0.1 mg L ⁻¹ for Cr ⁺⁶ and 1.0 mg L ⁻¹ for Cr ³⁺		0.05 mg L ⁻¹
Cu			2 mg L ⁻¹	1.0 mg L ⁻¹		0.005 mg L ⁻¹
Fe			0.3 mg L ⁻¹	15.0 mg L ⁻¹		0.3 mg L ⁻¹
Hg	barite	1 mg kg ⁻¹ ₁	0.001 mg L ⁻¹ ₁	0.01 mg L ⁻¹		0.0002 mg L ⁻¹
Mn			0.1 mg L ⁻¹	1.0 mg L ⁻¹		0.1 mg L ⁻¹ ₁
Na			200 mg L ⁻¹			
Ni				2.0 mg L ⁻¹		0.025 mg L ⁻¹
Pb			0.01 mg L ⁻¹	0.5 mg L ⁻¹		0.01 mg L ⁻¹
Se			0.01 mg L ⁻¹	0.3 mg L ⁻¹		0.01 mg L ⁻¹
Si						
Sn				4.0 mg L ⁻¹		
V						
(a)WF: water-based drilling fluids (b) NAF: non-aqueous drilling fluids (c) WBCF: aqueous-based complementary fluids						

Parameters	Normative Instruction 01/2018 IBAMA		ABNT NBR 10.004/2004	CONAMA 430/2011	CONAMA 393/2007	CONAMA 357/2005
	Notes	Maximum limit	Maximum limit	Maximum limit	Maximum limit	Maximum limit
Zn			5 mg/L	5.0 mg L ⁻¹		0.09 mg L ⁻¹
(a)WF: water-based drilling fluids (b) NAF: non-aqueous drilling fluids (c) WBCF: aqueous-based complementary fluids						

3.1 Granulometric characterization of drilling cuttings samples

The granulometric distribution of the drilling cuttings, previously dried in an oven at 600 °C until constant weight, varied widely in all samples analyzed. The largest proportion of the samples was composed of the fine sand fraction (4.75 – 0.425 mm), (51-77.6%), followed by the coarse sand fraction (≥ 4.75 mm) (9.3–42.7%), silt (0.425 – 0.075 mm) (3,7-11.4%), and clay (< 0.005 mm) (1-3.2%) (Fig. 1). These results show that the pre-salt cuttings samples collected were not composed exclusively of clay particles, but by a mixture of this fraction with larger particles such as coarse and fine sand and silt. The irregular distribution of cuttings samples can be associated with the type of bit used in the well drilling process, type of rock and fluid adhered in the samples.

3.2 Determination of metal concentration of drilling cuttings samples

Figure 2 presents data on the concentration of the metals Al, Fe, Si, Ni, Zn, Pb, Cu, Mn, Cr, Si and Ba in pre-salt cuttings containing aqueous and non-aqueous fluids adhered. The concentrations of As, Hg, Cd, V and Mo were below the limit of quantification, which were 0.199 mg Kg⁻¹, 0.139 mg Kg⁻¹; 1.88 mg Kg⁻¹, 13.7 mg Kg⁻¹ and 27.27 mg Kg⁻¹, respectively. Al, Fe and Ba were the metals present in the highest concentrations in these samples. The high concentration of Ba in these cuttings is commonly associated with the use of barite as a weighting material in the preparation of fluids. Barite is considered a carrier of several metals of environmental concern, since the high concentration of Ba in these samples normally coincides with high concentrations of other toxic metals in these samples (Neff, 2008). It has often been

assumed that the toxicity of barite is directly comparable to other suspended particulate materials, due to the perceived low bioavailability of the metals associated with this component.

However, some studies point to greater toxicity of barite in relation to these particulate materials (Junttila et al, 2018). In general, the greatest concentrations of Ba, Al, Fe, Cu, Pb, Mn, Si and Zn were found in cuttings samples containing non-aqueous fluids, but the highest concentrations of Ni and Cr were found in samples containing aqueous fluids. The 7-NAF sample had the highest concentration of Ba and also the highest concentration of most other metals.

Several studies have indicated that drilling fluids are also carriers of contamination by metals (Stuckman et al., 2019; Araka et al., 2019; Kogbara et al., 2017; Pozebon et al., 2005; Terzaghi et al., 1998). Since the fluid impregnated in the cuttings is not totally removed in the secondary treatment, they may contain contaminants. Neff (2008) pointed out that many of the metals detected in drilling fluids are present as trace impurities in samples of barite and bentonite as well as the rock formations from which these cuttings originate. The higher concentration of metals in samples containing non-aqueous fluids can be explained by two aspects: (i) in general, non-aqueous based fluids have a higher concentration of barite in their formulation, while WBDFs contain around 15% barite, and NADF's contain around 33% of this component; and (ii) NADF's are constantly recycled and reused until loss of rheological properties, so it is possible to assume a progressive increase in the concentration of metals in these fluids as a function of time. However, these aspects have not been explored in the literature.

3.3 Determination of total organic carbon content (TOC)

The percentage of total organic carbon (TOC) is a fundamental parameter that describes the abundance of organic matter in drilling cuttings. The total organic carbon consists of the sum of contamination derived from fluids (polymers, emulsifiers, paraffins, olefins, esters, ethers, acetals) and contamination due to the presence of formation oil in these samples (total HTP petroleum hydrocarbons, mixture of aliphatic and aromatic substances and PAHs). IBAMA Normative Instruction 01/2018 specifies restrictions on the offshore disposal of cuttings adhered in non-aqueous based drilling fluids, in relation to the content of adhered organic base. Currently, this disposal is only allowed if the adhered organic base content is less than 4.9% by mass (accumulated average per well) in the case of n-paraffins, internal olefins (IOs), linear alpha olefins (LAOs), polyalpha olefins (PAOs) and treated mineral oil-based fluids, or 9.4% organic base in the case of esters, ethers and acetals.

Figure 3 shows the TOC results for the pre-salt cuttings with aqueous and non-aqueous fluids adhered. Considering that the total organic carbon content is related to the content of organic base adhered to the samples, determined by applying the retort method, this parameter was expressed as a percentage and the results achieved correlated with the limit of organic base adhered to these samples according to NI 01/2018. The TOC values ranged from 0.34% (3-WF) to 6.35% (7-NAF). In general, samples containing non-aqueous fluids adhered had a higher TOC content than samples with aqueous fluids adhered, which is probably related to the greater sorption of these fluids by the cutting particles. Considering the relationship between content of adhered organic based fluid and content, it is possible to suppose that

only the 7-NAF sample contained organic compounds above the limit imposed by NI 01/2018 (4.9%), which may be related to less efficient drying of this sample on the platform or the presence of contamination by formation oil from the production zone retained in the pores of this sample.

Junttila et al. (2018) characterized contaminated sediments and cuttings from different drilling depths. They observed a relationship between the concentration of metals and the TOC content of the samples. Samples with higher TOC also showed higher concentrations of Cu, Hg and Pb. In this present study, we observed that the cuttings containing non-aqueous based fluid adhered, in addition to having a higher content of TOC, also contained higher concentrations of most metals. The 7-NAF sample containing 6.35% TOC also showed higher contents of the metals Ba, Fe, Pb, Cu, Si, Mn, Zn, which may be related to the higher concentration of barite in this sample, and interaction between the adhered base and the metals through sorption processes that would keep these metals attached to the cuttings.

3.4 Static sheen test of drilling cuttings samples

The static sheen test assesses contamination of the fluid with free oil according to the protocol “EPA 40: Protection of Environmental - Part 435 - Oil and Gas Extraction Point Source Category - Appendix 1 to Subpart A of Part 435 - Static Sheen Test (EPA Method 1617)” (USEPA, EPA-821-R-11-004, December 2011). Prohibition of free oil is intended to minimize the formation of sheen on the surface of the receiving water.

According to IBAMA Normative Instruction 1/2018, all water-based drilling and complementary fluids and/or drilling cuttings impregnated with water-based and non-aqueous fluids must meet the standard for disposal overboard of absence of gloss in the static sheen test. We applied the sheen test to the leachates obtained after 7 days of contact between these samples and the aqueous and saline solutions (Table 3). We observed that the samples 3-NAF, 4-WF, 5-WF, 8-NAF and 9-NAF generated turbidity in aqueous and saline media, indicating leaching of insoluble contaminants from these media. The cuttings samples with non-aqueous fluids 8-NAF, 9-NAF and 10-NAF formed a glossy film on the surface of the medium, which may indicate the presence of oil in these samples. However, for these same samples, smaller particles of the cuttings itself were observed floating during the sheen test and in the leaching tests. CONAMA Resolution 430 (Brazil, 2011) specifies that effluents must be discharged only when floating materials are virtually absent. The presence of free oil in water-based fluids and cuttings is usually easily identified. However, for cuttings containing adhered synthetic-based fluids, the presence of oleaginous compounds and barite itself present in the composition of these SBFs can mask the presence of O&G and crude oil contaminants, generating a false negative result (USEPA, EPA-821-B-00-013, December 2000).

Table 3 - Physical aspect of saline and aqueous leachates – Static iridescence test.

Sample	Observation effects on the surface					
	Turbidity		Effect on surface (brightness, increased reflectance and film or free oil drops)		Floating Material	
	Aqueous	Saline	Aqueous	Saline	Aqueous	Saline
1-WF	VA		VA		VA	
2-WF	VP		VA		VA	
3-WF	VA		VA		VA	
4-WF	VP		VA		VA	
5-WF	VP		VA		VA	
6-NAF	VA		VA		VA	
7-NAF	VA		VA		VA	
8-NAF	VP		VP		VP	
9-NAF	VP		VP		VP	
10-NAF	VA		VP		VP	

VA- Virtually Absent; VP- Virtually Present.

3.5 Determination of physicochemical parameters of saline and aqueous leachates.

The saline and aqueous leachates were evaluated regarding the physicochemical parameters total dissolved solids (TDS), pH, salinity and conductivity. Physicochemical analyses play the most important role in measuring the remobilization of metals from sediments (Acosta et al., 2011; Liu & Shen, 2014). The evaluation of the physicochemical parameters of the leachates was carried out by using the coarse cuttings samples, without grinding. The results presented in Fig. 4 already discounted the blank of each parameter. Parameters of the blank test were (i) saline leachate: conductivity: 95.5 mS cm^{-1} , salinity: 66.48 g L^{-1} , TDS: 48 g L^{-1} and (ii) aqueous leachate: conductivity: 0.002 mS cm^{-1} , salinity: 0.008 g L^{-1} , TDS: 0.002 g L^{-1} . The aqueous leachates did not show significant variations in the conductivity and salinity parameters at the beginning and end of the leaching test (Fig. 4-a and Fig. 4-b). However, for saline leachates, there were significant variations in these parameters at the end of the contact time, which may be related to greater leaching of inorganic contaminants such as carbonate, bicarbonate, chloride, sulfate, phosphate, nitrate, calcium, magnesium, sodium and metal ions in this medium of higher ionic concentration. Total suspended solids (SST) make up most of the pollutant loads from drilling activities, consisting of cuttings particles and solids present in the composition of fluids. The analyzed samples had a large increase in the TDS parameter (Fig. 4-c) at the end of the leaching tests, probably reflecting the leaching of cuttings particles containing a high proportion of silt and clay, in

addition to the leaching of barite particles and the clays used in the preparation of fluids for saline media (USEPA, EPA-821-B-00-013, December 2000).

pH is a key parameter that controls the behavior of metal ion transfer in sediments. The extent of release of these ions depends strongly on the overall pH of the solubilization environment (Stuckman et al., 2019). According to Peng et al. (2009), the decrease in sediment pH favors competition between H^+ ions and dissolved metals by ligands such as OH^- , CO_3^{2-} , SO_4^{2-} , Cl^- , S^{2-} and phosphates. Subsequently, there is a decrease in the adsorption ability and bioavailability of the metals, followed by an increase in the mobility of heavy metals. Sometimes just a few pH units lower can cause the percentage of heavy metals attached to sediment particles to fall from almost 100–0%. There was significant pH variation from acidic to neutral to basic in the leaching tests in aqueous medium as a function of contact time (Fig. 4-d). This result may indicate the leaching of inorganic contaminants such as carbonate, bicarbonate and phosphate in sufficient concentration to cause the pH variation of the medium. According to petroleum industry standards, all drilling fluids and complementary fluids during the activity must meet the temperature limit $\leq 40^\circ C$ and pH between 5 and 9. In general, all saline leachates had pH below 9, indicating that these cuttings could be discharged in the sea if the other discharge parameters were also attained. The samples 1-WF, 3-WF, 4-WF, 6-NAF, 7-NAF and 8-NAF generated aqueous leachates with pH above 9, indicating a greater need for control in the disposal of these cuttings in landfills. No correlation was observed between variations in the parameters conductivity, salinity, TDS and pH and the type of fluid adhered to the drilling cuttings, as well as granulometric distribution of the samples, concentrations of metals (determined through acid digestion of the samples) and contents of total organic carbon of solid samples.

3.6 Leaching tests in saline medium

Discharge into the ocean is the main cuttings management strategy in offshore operations (Almeida et al., 2017). As already mentioned, these residues return to the platform where they are separated from the fluids by a solids control systems, followed by treatment in dryers aiming at reducing the content of adhered organic base material below the limit established by environmental legislation. Therefore, the performance of this equipment is monitored by tests of static sheen and retort (Petri Junior et al. 2017; Santos & Veloso, 2013). When the cuttings meet the parameters set out in environmental legislation, they are discarded at sea. This strategy is adopted in several oil producing countries.

The environmental impact of releasing drilling waste into the sea is influenced by several factors, such as: physical-chemical properties of these wastes (size of the particulate material, density, type and concentration of contaminants, degree of solubility of the contaminants in saline environment), volume of waste discharged, discharge flow, total water column depth, prevailing current velocity, deposition rate and plume type (Lelchate et al., 2020). Studies of leaching of contaminants from drilling cuttings in saline environments are scarce in the literature, despite the great importance of ascertaining the environmental impact of discharging these residues into the sea.

In this work, saline leaching tests were performed using an adaptation of the ABNT Standard NBR 10.004/2004 and ABNT Standard NBR 10.006/2004 standard to assess the mobility and potential bioavailability of contaminants present in solid residues in aqueous solution. Since there are no regulatory parameters for bioavailability of contaminants, we used the parameters established in IBAMA Normative Instruction (TOC, an indirect measure of the adhered organic base and metals content) for evaluation and compared the results with the limits established in CONAMA Resolution 430 (Brazil, 2011), which contains standards for discharge of industrial or domestic effluents, and CONAMA Resolution 393 (Brazil, 2007), which defines the parameters for disposal of produced water at sea. In addition, we compared the results with the standards established for the classification of Class I saline waters, according to CONAMA Resolution 357 (Brazil, 2005). This last analysis was carried out considering CONAMA Resolution 393 (Brazil, 2007), which establishes that saline water will be considered as will be considered Class 1 Saline Water in the area where the platform is located when there are no specific parameters.

Figure 5 shows the concentrations of metals in saline leachates. The concentrations of As, Hg, Mn, Cr, Mo, Cd, Al and V were below the detection limit of the FAAS equipment, for all analyzed cuttings samples.

Microstructural analysis by X-ray diffraction (XRD) showed that many samples contained aluminosilicate minerals due to the high content of SiO_2 and Al_2O_3 , in addition to the presence of CaO , BaO , Fe_2O_3 , SO_3 , K_2O , MgO , Na_2O , TiO_2 , SrO and SO_4^{2-} , as also found by Xie et al., (2022), Piszcz-Karaś et al. (2019), Abbe et al. (2011), and Leonard & Stegemann, 2010). The mineral impurities in barite included SiO_2 , CaCO_3 , SrSO_4 , FeO_3 , which are also abundant in the marine environment. In some situations, barite is replaced by hematite (Fe_2O_3) in the preparation of WBDF to be used in deep water drilling (USEPA, EPA-821-B-00-013, December 2000). The presence of Si, Fe and Al in the cuttings samples or leachate is not considered a reason for environmental concern because these metals are natural constituents of rocks and sediments.

Si and Ba were found in high concentrations in the pre-salt samples with adhered fluid (Fig. 3-a) and also in the saline leachates derived from these samples (Fig. 5-a). The Si concentration in saline leachates ranged from 6.46 mg L^{-1} to 56.08 mg L^{-1} , whereas the concentration of Ba in these leachates ranged from 2.24 mg L^{-1} to 14.98 mg L^{-1} . The solubility of barite in seawater has been reported to be around $80 \text{ } \mu\text{g L}^{-1}$ (Bakhtyar & Gagnon, 2011). Thus, the Ba carried from the cuttings samples and present in the saline leachates was probably in the form of BaSO_4 , which is considered a non-bioavailable form of this metal (Sørheim, 2000). The highest concentration of Ba was found in the saline leachate obtained from the 8-NAF sample, which also had the highest clay fraction content, indicating there may be a correlation between the size of cuttings particles and BaSO_4 leaching in the saline solutions. The 8-NAF cuttings sample also showed turbidity, gloss effect, increased reflectance and presence of floating material in the static iridescence test.

Barite contains high concentrations of barium and a range of heavy metal and metalloid impurities (such as arsenic, chromium, copper, lead, nickel and zinc) in low concentrations. In mineralized forms, these are

environmentally unavailable sulfide salts thus, barite can be considered a carrier of these contaminants of environmental concern (Edge et al., 2016). Some works have described a relationship between the concentration of Ba in cuttings and concentration of other metals in these samples (Lourenço et al., 2013).

It was not possible to observe a correlation between the content of Ba leached from the cuttings samples and the content of the other metals also leached. However, it was possible to observe a trend of higher concentration of metals in saline leachates derived from cuttings containing non-aqueous based fluids. In general, NADFs contain a higher content of barite than WBDFs (IPIECA/IOGP, 2009). These latter fluids are reused until their rheological properties are lost. Fine solid particles such as barite and clays are also reused in the preparation of other fluids. It is possible that the recycling of fluids and fine particles led to the progressive increase in the concentration of metals found in these media. Furthermore, it is also possible to assume that organic bases can act as adsorbents of these metal ions.

Fe, when analyzed directly in solid cuttings, was present in high concentration (Fig. 3-a). However, the results of this metal in the saline solution showed concentrations below the legal limits according to CONAMA Resolution 430 (Brazil, 2011) and Resolution 357 (Brazil, 2005).

The Cd concentration in the saline leachate ranged from 0.04 to 0.15 mg L⁻¹; the Cu concentration ranged from 0.03 to 0.42 mg L⁻¹; the Ni concentration varied from 0.24 to 0.93 mg L⁻¹; and the Zn concentration ranged from 0.17 to 0.63 mg L⁻¹. Pb was found only in sample 6-NAF. The other samples contained concentrations of this metal below detection limit. The concentration of Pb in sample 6-NAF was 0.88 mg L⁻¹. In general, the saline solution derived from sample 6-NAF, containing non-aqueous fluid, had higher concentration of most of these metals.

Comparing these data with the limits specified in Brazilian environmental regulations (Table 2) reveals that the concentrations of Cd, Cu, Ni and Zn were below the limit established in CONAMA Resolution 430 (Brazil, 2011), which establishes parameters for the disposal of effluents, but above the limits established in CONAMA Resolution 357 (Brazil, 2005), regarding the classification of class I saline water (more restrictive rules). The concentration of Pb in saline leachate derived from sample 6-NAF was above the regulatory threshold. As these metals are of environmental concern. These findings suggest the need for treatment to minimize the impacts caused by these materials when discharged in marine environments.

The TOC levels in the saline leachates are shown in Fig. 6. There was no correlation between the TOC content of the solid cuttings samples (Fig. 3) and the TOC content of the saline leachates. As previously mentioned, while the TOC content in the cuttings is related to the combination of organic components present in the fluids and contamination of the samples by formation oil, the TOC content in saline leachates is related to the greater or lesser tendency of these organic compounds to solubilize in this medium. There was a tendency of higher concentration of TOC in saline leachates derived from samples containing aqueous-based fluids, which may be related to a greater tendency of leaching of polymers and emulsifiers (components of the fluids) in this medium.

3.7 Leaching tests in aqueous medium

The cuttings samples were also subjected to leaching tests with distilled water for 7 days to classify these residues as inert or non-inert, according to ABNT Standard NBR 10.004/2004 and ABNT Standard NBR 10.006/2004. In this study, the samples were treated with aqueous solutions and the leachate generated was analyzed and compared to the maximum limits established with this standard. This analysis is required for classification of Class II wastes (non-hazardous wastes) as inert or non-inert, by simulating the leaching of contaminants in an aqueous medium such as rainwater or their release when sent to sanitary landfills.

The concentrations of As, Hg, Mn, Cr, Mo, Cd, Al, Ni, Fe, Pb, Ba, Cu, Zn and V in the aqueous leachate were below the detection limit of the equipment for all cuttings samples analyzed.

There were high concentrations of Ba and Si in aqueous leachates derived from cuttings (Fig. 7-a). The presence of Si was identified in all leachates analyzed, while the presence of Ba was identified in five of these samples. The concentration of Ba varied from 4.2 mg L^{-1} to 17.5 mg L^{-1} , being highest in sample 6-NAF, containing non-aqueous fluid. The concentration of Ba in these aqueous solutions was higher than the limit established in ABNT Standard NBR 10.004/2004 and ABNT Standard NBR 10.006/2004 (0.7 mg L^{-1}). Like in saline leachates, Ba is probably carried to aqueous leachates as BaSO_4 , considered a non-bioavailable form of this metal.

It was also possible to observe the presence of Cu and Zn in these aqueous leachates (Fig. 7-b). The presence of Cu was identified in five samples (three samples derived from cuttings containing non-aqueous fluid and two samples derived from cuttings containing aqueous fluid). The Cu concentration in these samples ranged from 0.13 mg L^{-1} to 0.37 mg L^{-1} , being highest in the aqueous leachate derived from sample 5-NAF. The presence of Zn was observed in two samples, with concentrations of 0.35 mg L^{-1} and 0.44 mg L^{-1} , both derived from cuttings containing non-aqueous fluid. The concentrations of these metals in the aqueous leachates were lower than the limit recommended in ABNT Standard NBR 10.004/2004 and specified in CONAMA Resolution 430 (Brazil, 2011), but above the limits established in CONAMA Resolution 357 (Brazil, 2005), regarding the classification of class I saline water.

The aqueous leachates derived from the cuttings showed TOC concentrations ranging from 0.08 mg L^{-1} to 18.72 mg L^{-1} (Fig. 8). The TOC contents in the saline leachates were much higher than the TOC contents in the aqueous leachates, indicating greater leaching of the organic components of the fluids and organic contaminants present in these samples in the saline environment. The highest concentration of TOC was observed in the aqueous leachate derived from sample 6-NAF, containing adherent non-aqueous fluid, but the aqueous leachate derived from samples 2-WF and 5-WF also had high concentrations of TOC.

4. Conclusions

The granulometric distribution of the pre-salt drilling cuttings varied widely. Fine sand (4.75 – 0.425 mm) accounted for the greatest fraction (51 to 77.6%). The metals Al, Fe and Ba were present in highest concentrations in drilling cuttings. The most pronounced concentrations of Ba, Al, Fe, Cu, Pb, Mn, Si and Zn were found in cuttings containing non-aqueous fluids, but the highest concentrations of Ni and Cr were found in samples containing aqueous fluids. In general, samples containing non-aqueous fluids also had a higher concentration of TOC, which was probably related to the presence of non-aqueous fluid adhered to the particles. The sheen test was performed for saline and aqueous leachates. The cuttings with non-aqueous fluid (8-NAF, 9-NAF and 10-NAF) had a glossy film, possibly indicating the presence of oil in these samples. There were significant variations in the conductivity and salinity parameters at the end of the leaching test in saline medium, which may be related to the greater leaching of inorganic contaminants in this medium. These samples also had a high increase in the TDS parameter at the end of the leaching tests, probably reflecting the leaching of cuttings (silt and clay fractions) and barite and clay particles used in the preparation of fluids. The metals present in highest concentrations in saline and aqueous leachates were Si and Ba. In the saline medium, the concentration of Ba varied from 2.24 mg L⁻¹ to 14.98 mg L⁻¹ and in the aqueous medium from 4.2 to 17.5 mg L⁻¹. Probably the presence of Ba in the leachates was associated with leaching of barite, considered a non-bioavailable form of this metal. The metals Cd, Cu, Ni and Zn were present in the saline leachates in varying concentrations. It was also possible to identify the presence of Pb in the saline leachate, derived from only one of the cuttings samples (6-NAF). It was also possible to identify the presence of Si, Ba, Cu and Zn in the aqueous leachates, and the concentrations of Si and Ba were highest in this medium. The concentrations of the other metals were below the detection limit. There was a tendency of higher concentration of TOC in saline leachates derived from samples containing aqueous-based fluids, which may be related to a greater tendency of leaching of polymers and emulsifiers in this medium. The studies carried out suggest the need for appropriate treatment and disposal to minimize the environmental impacts caused by pre-salt cuttings, especially those containing adhered non-aqueous based fluid.

Declarations

Data availability

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Ethical Approval

Not applicable

Consent to Participate

Not applicable

Consent to Publish

Not applicable

Authors Contributions

Andreia Silva Freire Soares was responsible for investigation, methodology and writing the original draft. Luciana da Cunha Costa was responsible for writing (review & editing). Mônica Regina da Costa Marques was responsible for conceptualization, funding acquisition and writing (review & editing).

Funding

This work was supported by Rio de Janeiro State Research Foundation (FAPERJ) (grant number: SEI 260003/011353/2021 and E-26/010.1011.142/2018), National Council for Scientific and Technological Development (CNPq) and Coordination for the Improvement of Higher Education Personnel) (CAPES).

Competing Interests

The authors declare no competing interests.

References

1. Abbe OE, Grimes SM, Fowler GD (2011) Decision support for the management of oil well drill cuttings. *J Waste Manag* 164: 213-220. <https://doi.org/10.1680/warm.2011.164.4.213>
2. Acosta JA., Jansen B, Kalbitz K, Faz A, Martinez-Martinez S (2011) Salinity increases mobility of heavy metals in soils. *Chemosphere* 85: 1318-1324. <https://doi.org/10.1016/j.chemosphere.2011.07.046>
3. Agha GU, Irrechukwu DO (2002) Experiences in the management of drilling fluids and the regulatory control of associated cuttings in the nigerian oil and gas industry. Paper presented at the SPE International Conference on Health, Safety and Environment in Oil and Gas Exploration and Production, Kuala Lumpur Malaysia. Paper Number: SPE-73932-MS, 2002. <https://doi.org/10.2118/73932-MS>
4. Almeida PC, Araújo OQF, Medeiros JL (2017) Managing offshore drill cuttings waste for improved sustainability. *J Clean Prod* 165: 143-156. <https://doi.org/10.1016/j.jclepro.2017.07.062>
5. Araka PP, Okparanma RN, Ayotamuno JM (2019) Diagnostic screening of organic contaminant level in solidified/stabilized pre-treated oil-based drill cuttings. *Heliyon* 5: e02644. <https://doi.org/10.1016/j.heliyon.2019.e02644>
6. Brazilian Association of Technical Standards, 2004 (in Portuguese).
7. ____ NBR 10004: Solid waste - Classification.
8. ____ NBR 10006: Procedure for obtaining solubilized extract from solid waste.

9. Apaleke AS, Al-Majed A, Hossain ME (2012) Drilling Fluid: State of The Art and Future Trend. Society of Petroleum Engineers, North Africa Technical Conference and Exhibition, 20-22 February, 2012, Cairo, Egypt. <https://doi.org/10.2118/149555-MS>
10. Association of Official Analytical Chemists (AOAC) and Brazilian guidelines (2018), Guidance on validation of analytical methods, INMETRO DOQ-CGCRE-008 (08/2018).
11. Ball AS, Stewart RJ, Schliephake K (2012) A review of the current options for the treatment and safe disposal of drill cuttings. *Waste Manag Res*, 30: 457-473. <https://doi.org/10.1177/0734242X11419892>
12. Bakhtyar S, Gagnon M (2011) Toxicity assessment of individual ingredients of synthetic-based drilling muds (SBMs). *Environmental monitoring and assessment*, 184: 5311-5325. <https://doi.org/10.1007/s10661-011-2342-x>.
13. Brazil (2005). Ministry of the Environment. Resolution CONAMA 357/2005: Establishes provisions for the classification of water bodies as well as environmental directives for their framework, establishes conditions and standards for effluent releases and makes other provisions (in Portuguese).
14. Brazil (2007). Ministry of the Environment. Resolution CONAMA n° 393/2007 providing for the continuous disposal of process or production water on offshore oil and natural gas platforms (in Portuguese).
15. Brazil (2010). Law 12.305/2010. Institutes the National Policy on Solid Waste; alters Law No. 9,605 of 12 February 1998; and makes other provisions (in Portuguese).
16. Brazil (2011). Ministry of the Environment. Resolution CONAMA n° 430/2011. Regulates the conditions, parameters, standards and directives for the management of effluent releases into receptor water bodies, partially changing and complementing Resolution 357/2005 (in Portuguese).
17. Brazil (2018). Brazilian Institute for the Environment and Renewable Natural Resources IBAMA IN 01/2018. It defines guidelines that regulate the environmental conditions for the use and disposal of fluids, drilling cuttings and cement pastes in the activities of offshore well drilling and oil and gas production, establishes the Fluid and Cuttings Monitoring Project, and other measures (in Portuguese).
18. Duzgoren-Aydin NS, Avula B, Willett KL, Khan IA (2011) Determination of total and partially extractable solid-bound element concentrations using collision/reaction cell inductively coupled plasma-mass spectrometry and their significance in environmental studies. *Environ Monit Assess*, 172: 51-66. <https://doi.org/10.1007/s10661-010-1317-7>.
19. Edge KJ, Johnston EL, Dafforn KA, Simpson SL, Kutti T, Bannister RJ (2016) Sub-lethal effects of water-based drilling muds on the deep-water sponge *Geodia barrette*. *Environ Pollut*, 212: 525-534. <https://doi.org/10.1016/j.envpol.2016.02.047>
20. Farkas J, Bådsvik CY, Altin D, Nordtug T, Olsen AJ, Hansen BH (2017). Acute and physical effects of water-based drilling mud in the marine copepod *Calanus finmarchicus*. *J Toxicol Environ Health Part A*, 80: 907–915. <https://doi.org/10.1080/15287394.2017.1352197>

21. Grant A, Briggs AD (2002) Toxicity of sediments from around a North Sea oil platform: are metals or hydrocarbons responsible for ecological impacts? *Mar Environ Res*, 53: 95–116.
[https://doi.org/10.1016/S0141-1136\(01\)00114-3](https://doi.org/10.1016/S0141-1136(01)00114-3).
22. Hu Z, Qi L (2014) Sample Digestion Methods, *Treatise on Geochemistry (Second Edition)* 15: 87-109.
<https://doi.org/10.1016/B978-0-08-095975-7.01406-6>
23. International Association of Oil & Gas Producers. Environmental fates and effects of ocean discharge of drill cuttings and associated drilling fluids from offshore oil and gas operations. Report 543, March 2016
24. International Petroleum Industry Environmental Conservation Association and International Association of Oil & Gas Producers, IPIECA/IOGP. Drilling fluids and health risk management. A guide for drilling personnel, managers and health professionals in the oil and gas industry. IOGP Report 396. London, UK. 1-60, 2009.
25. Junttila J, Dijkstra N, Aagaard-Sørensen S (2018) Spreading of drill cuttings and sediment recovery of three exploration wells of different ages, SW Barents Sea, Norway. *Mar Pollut Bull*, 135: 224-238.
<https://doi.org/10.1016/j.marpolbul.2018.06.064>
26. Kazamias G, Zorpas AA (2021) Drill cuttings waste management from oil & gas exploitation industries through end-of-waste criteria in the framework of circular economy strategy. *J Clean Prod*, 322: 129098, 2021. <https://doi.org/10.1016/j.jclepro.2021.129098>
27. Klein W (1989) Mobility of environmental chemicals, including abiotic degradation. *Ecotoxicology and Climate*. Ecotoxicology and Climate, Bourdeau P, Haines JA, Klein, W, Murti CRK, John Wiley & Sons Ltda.
28. Kogbara RB, Dumkhana BB, Ayotamuno JM, Okparanma RN (2017) Recycling stabilised/solidified drill cuttings for forage production in acidic soils. *Chemosphere* 184: 652-663.
<https://doi.org/10.1016/j.chemosphere.2017.06.042>.
29. Kujawska J, Pawlowska M (2022) The effect of amendment addition drill cuttings on heavy metals accumulation in soils and plants: Experimental study and artificial network simulation. *J Hazard Mater* 425: 127920. <https://doi.org/10.1016/j.jhazmat.2021.127920>.
30. Lechat F, Dussauze M, Lemaire P, Theron M, Toffin L, Le Floch S (2020) Measuring the biological impact of drilling waste on the deep seafloor: an experimental challenge., *J Hazard Mater* 389: 122132. <https://doi.org/10.1016/j.jhazmat.2020.122132>
31. Leonard SA, Stegemann JA (2010) Stabilization/solidification of petroleum drill cuttings: Leaching studies. *J Hazard Mater*, 174: 484-491. <https://doi.org/10.1016/j.jhazmat.2009.09.078>
32. Liu E, Shen J (2014) A comparative study of metal pollution and potential eco-risk in the sediment of Chaohu Lake (China) based on total concentration and chemical speciation. *Environ Sci Pollut Res*, 21: 7285–7295. <https://doi.org/10.1007/s11356-014-2639-8>
33. Lourenço RA, Araujo Júnior MAG, Meireles Júnior RO, Macena LF, Lima EFA, Carneiro MER (2013) Aliphatic and polycyclic aromatic hydrocarbons and trace elements as indicators of contamination

- status near oil and gas platforms in the Sergipe–Alagoas Basin (Southwest Atlantic Ocean). *Cont Shelf Res*, 71: 37–44. <https://doi.org/10.1016/j.csr.2013.09.015>
34. Melton HR, Smith JP, Martin CR, Nedwed TJ, Mairs HL, Raught DL (2000) Offshore discharge of drilling fluids and cuttings – a scientific perspective on public policy. Conference: Rio Oil and Gas Expo and Conference, Rio de Janeiro, RJ (Brazil).
 35. Neff JM (2010) Fate and Effects of Water Based Drilling Muds and Cuttings in Cold Water Environments. Shell Exploration and Production Company, Houston, Texas, 2010.
 36. Neff JM (2008) Estimation of Bioavailability of Metals from Drilling Mud Barite. *Integr Environ Assess Manag* 4: 184-193. https://doi.org/10.1897/ieam_2007-037.1
 37. Nrior RR, Odokuma LO (2015) Comparative toxicity of drilling fluids to marine water shrimp (*Mysidopsis bahia*) and brackish water shrimp (*Palaemonetes africanus*). *J Environ Sci Toxicol Food Technol* 9: 2319-2399. <https://doi.org/10.9790/2402-09727379>
 38. Page PW, Greaves C, Lawson R, Hayes S, Boyle F (2003) Options for the Recycling of Drill Cuttings. SPE/EPA/DOE Exploration and Production Environmental Conference, San Antonio, Texas, Paper Number: SPE-80583-MS. <https://doi.org/10.2118/80583-MS>
 39. Peng JF, Song YH, Yang P, Cui X, Qiu G (2009) The remediation of heavy metals contaminated sediment. *J Hazard Mater*, 161: 633-640. <https://doi.org/10.1016/j.jhazmat.2008.04.061>
 40. Petri Júnior I, Martins AL, Ataíde CH, Duarte CR (2017) Microwave drying remediation of petroleum-contaminated drill cuttings. *J Environ Manage* 196: 659-665. <https://doi.org/10.1016/j.jenvman.2017.03.068>
 41. Piszcz-Karaś K, Klein M, Hupka J, Łuczak J (2019) Utilization of shale cuttings in production of lightweight aggregates. *J Environ Manage* 231: 232–240. <https://doi.org/10.1016/j.jenvman.2018.09.101>
 42. Piszcz-Karaś K, Luczak J, Hupka J (2016) Release of selected chemical elements from shale drill cuttings to aqueous solutions of different pH. *Appl Geochem* 72: 136-145. <https://doi.org/10.1016/j.apgeochem.2016.07.006>
 43. Piszcz-Karaś K, Luczak J, Hupka J (2014) Mobility of shale drill cuttings constituents. *Physicochem Probl Miner Process*, 50: 795–810. <https://doi.org/10.5277/ppmp140230>
 44. Pozebon D, Lima EC, Maia SM, Fachel JMG (2005) Heavy metals contribution of non-aqueous fluids used in offshore oil drilling. *Fuel*, 84: 53–61. <https://doi.org/10.1016/j.fuel.2004.08.002>
 45. Santos GB, Veloso J (2013) The challenges for the treatment of drilling fluid wastes generated by E&P industry in Brazil, SPE Latin-American and Caribbean Health, Safety, Environment and Social Responsibility Conference, Lima, Peru. SPE 165613, 2013. <https://doi.org/10.2118/165613-MS>
 46. Seyedmohammadi J (2017) The effects of drilling fluids and environment protection from pollutants using some models. *Model Earth Syst Environ*, 3: 23. <https://doi.org/10.1007/s40808-017-0299-7>
 47. Sørheim R, Amundsen CE, Kristiansen R, Paulsen JE (2000) Oily Drill Cuttings - From Waste to Resource, Society of Petroleum Engineers, SPE 61273. <https://doi.org/10.2118/61273-MS>

48. Stuckman MY, Lopano CL, Berry SM, Hakala JA (2019) Geochemical solid characterization of drill cuttings, core and drilling mud from Marcellus Shale Energy development. *J Nat Gas Sci Eng* 68: 102922. <https://doi.org/10.1016/j.jngse.2019.102922>
49. Terzaghi C, Buffagni M, Cantelli D, Bonfanti P, Camatini M (1988) Physical-chemical and ecotoxicological evaluation of water based drilling fluids used in italian off-shore. *Chemosphere* 37: 2859–2871. [https://doi.org/10.1016/s0045-6535\(98\)00328-2](https://doi.org/10.1016/s0045-6535(98)00328-2)
50. USEPA (Environment Protection Agency of United State of America) EPA-821-R-11-004, Analytic Methods for the Oil and Gas Extraction Point Source Category. December 2011.
51. USEPA (Environment Protection Agency of United State of America) EPA-821-B-00-013, Development Document for Final Effluent Limitations Guidelines and Standards for Synthetic-Based Drilling Fluids and other Non-Aqueous Drilling Fluids in the Oil and Gas Extraction Point Source Category. December 2000.
52. USEPA (Environment Protection Agency of United State of America) EPA-3050-B, Acid Digestion of Sediments, Sludges and Soils, December 1996.
53. Veil JA (2002) Drilling Waste Management: Past, Present, and Future, SPE Annual Technical Conference and Exhibition, San Antonio, Texas. <https://doi.org/10.2118/77388-MS>
54. Wang C-q, Xiong D-m (2021) Leaching assessment of aerated concrete made of recycled shale gas drilling cuttings: Particular pollutants, physical performance and environmental characterization. *J Clean Prod* 282: 125099. <https://doi.org/10.1016/j.jclepro.2020.125099>
55. Xie B, Qin J, Sun H, Wang S, Li X (2022) Release characteristics of polycyclic aromatic hydrocarbons (PAHs) leaching from oil-based drilling cuttings. *Chemosphere* 291: 132711. <https://doi.org/10.1016/j.chemosphere.2021.132711>
56. Xu T, Wang L, Wang X, Li T, Zhan X (2018) Heavy metal pollution of oil-based drill cuttings at a shale gas drilling field in Chongqing, China: A human health risk assessment for the workers. *Ecotoxicol Environ Saf* 165: 160–163. <https://doi.org/10.1016/j.ecoenv.2018.08.104>
57. Yu Z, Liu E, Lin Q, Zhang E, Yang F, Wei C, Shen J (2021) Comprehensive assessment of heavy metal pollution and ecological risk in lake sediment by combining total concentration and chemical partitioning. *Environ Pollut* 269: 116212, 2021. <https://doi.org/10.1016/j.envpol.2020.116212>
58. Zha X, Liao X, Zhao X, Liu F, He AQ, Xiong WX (2018) Turning Waste drilling fluids into a new, sustainable soil resources for landscaping. *Ecol Eng* 121: 130-136. <https://doi.org/10.1016/j.ecoleng.2017.06.026>
59. Zhang W, Hu Z (2019) Recent advances in sample preparation methods for elemental and isotopic analysis of geological samples. *Spectrochim. Acta B*, 160: 105690. <https://doi.org/10.1016/j.sab.2019.105690>
60. Zhuang G, Zhang Z, Jaber M (2019) Organoclays used as colloidal and rheological additives in oil-based drilling fluids: An overview. *Appl Clay Sci* 177: 63–81. <https://doi.org/10.1016/j.clay.2019.05.006>

Figures

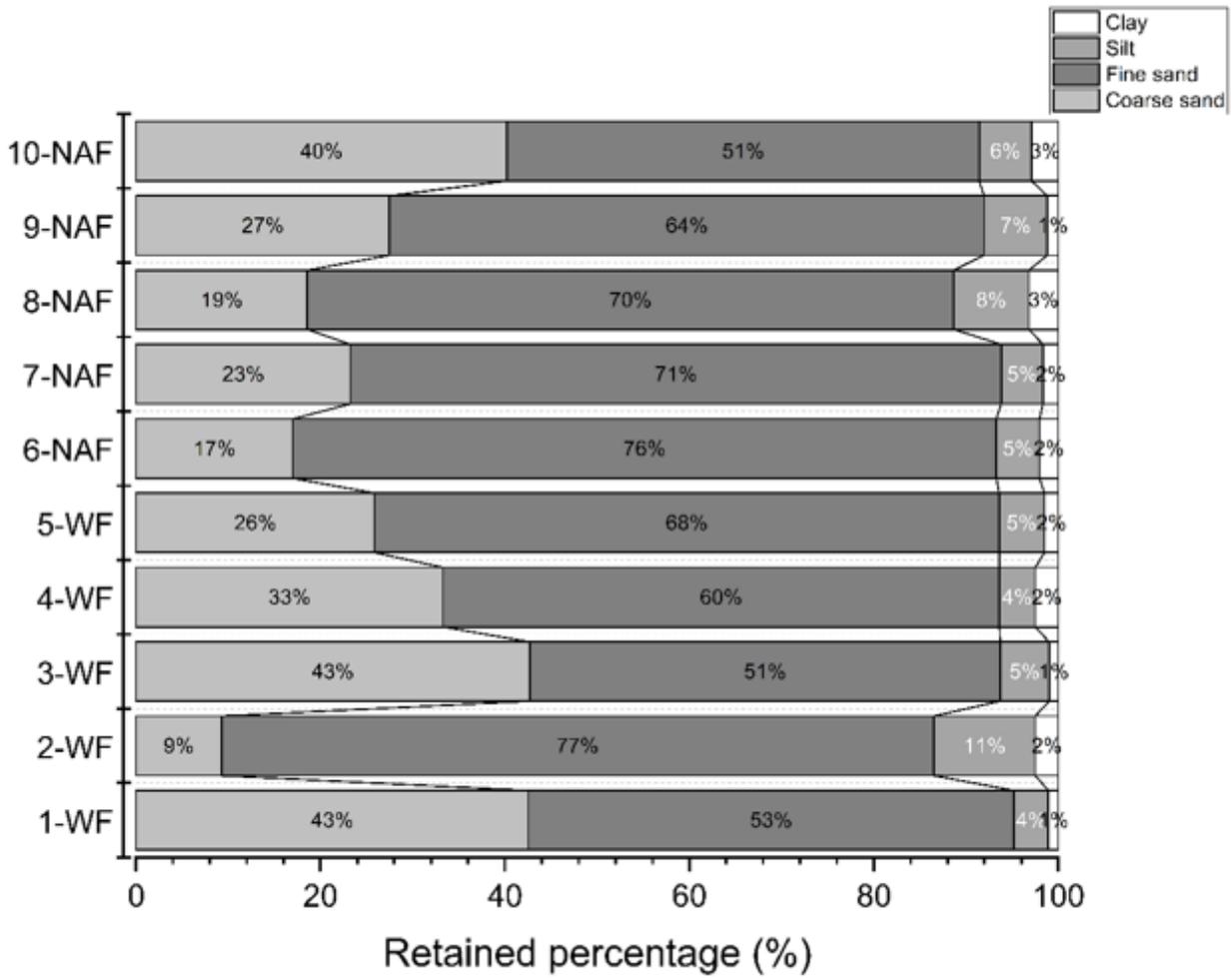
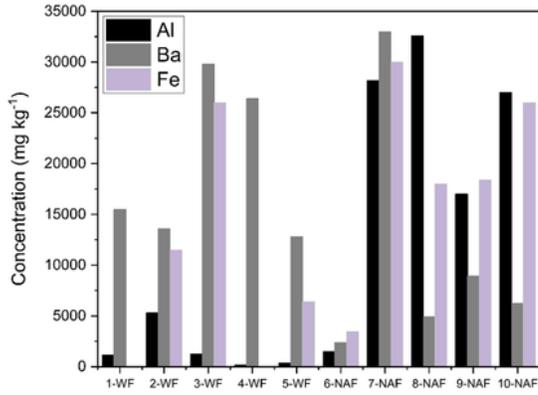
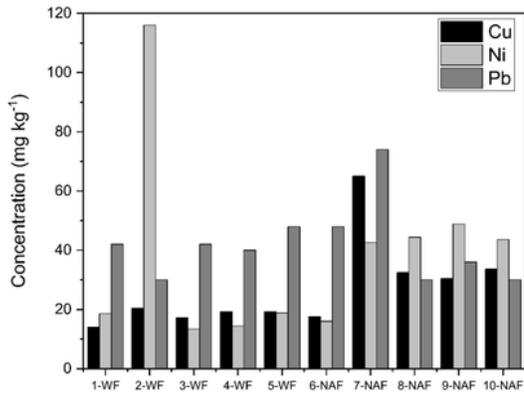


Figure 1

Grain size distribution of coarse sand, fine sand, silt and clay fractions in drill cuttings samples.



A



B

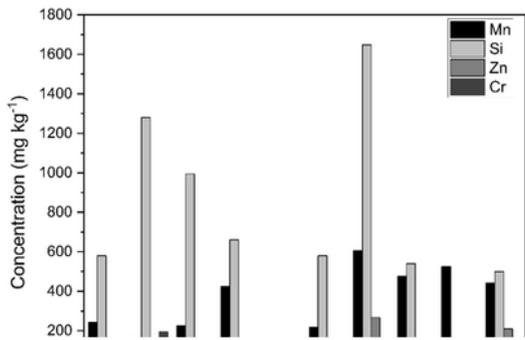


Figure 2

Content of metals (a) Al, Ba and Fe; (b) Cu, Cr, Ni and Pb; and (c) Mn, Si and Zn present in cuttings samples.

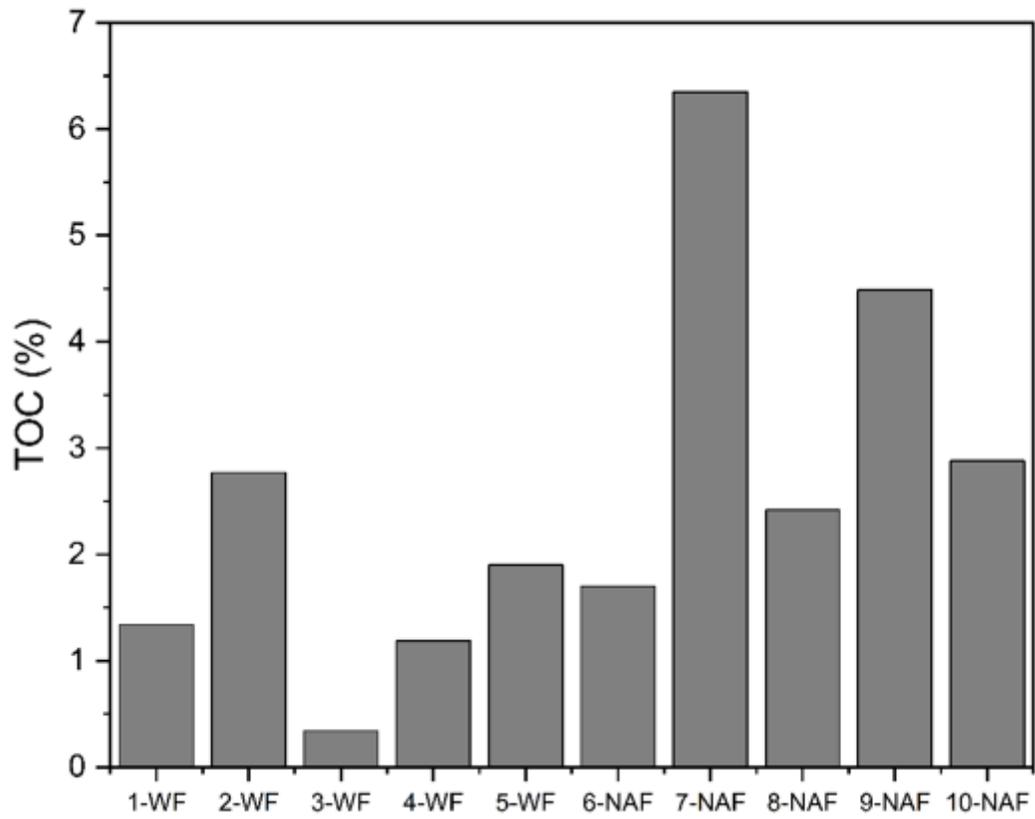


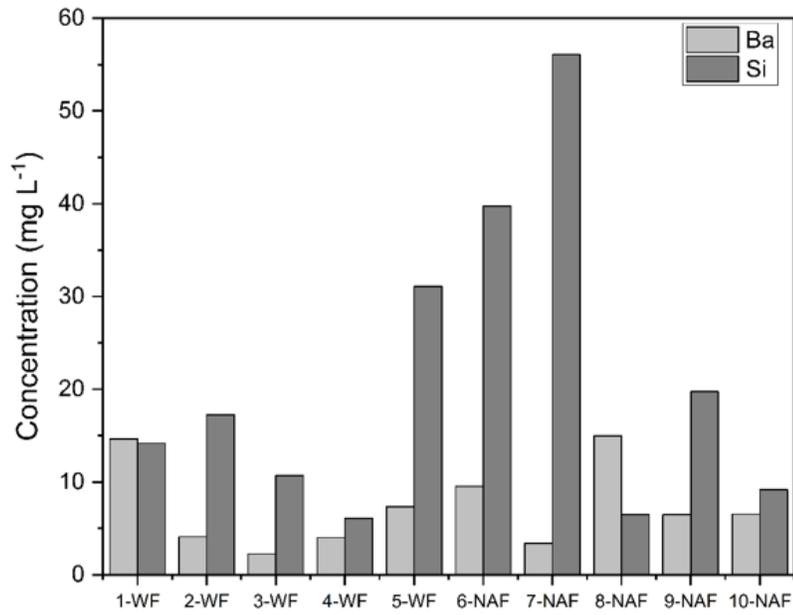
Figure 3

Total organic carbon (TOC) contents in cuttings samples with aqueous and non-aqueous fluids adhered.

Figure 4

Analysis of the physicochemical parameters of saline and aqueous leachates

(a)



(b)

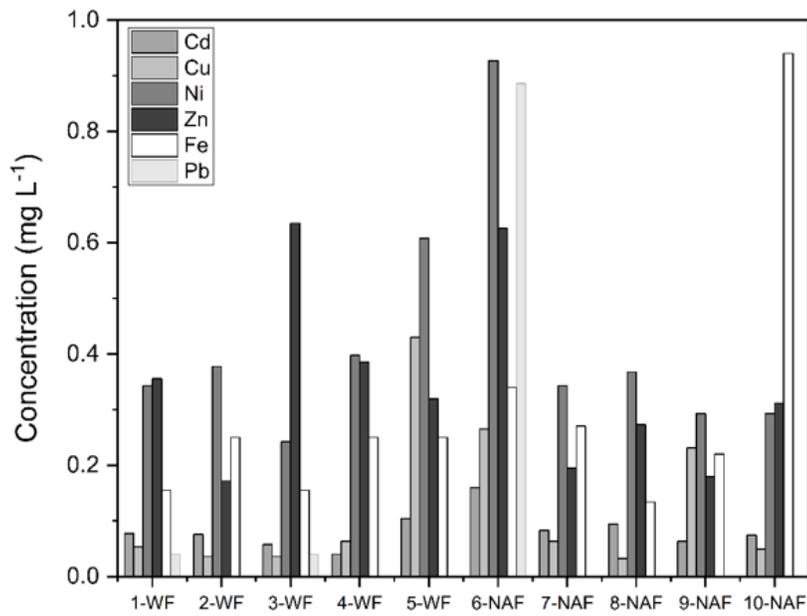


Figure 5

Metal contents of saline leachates derived from contact between cuttings and saline solutions.

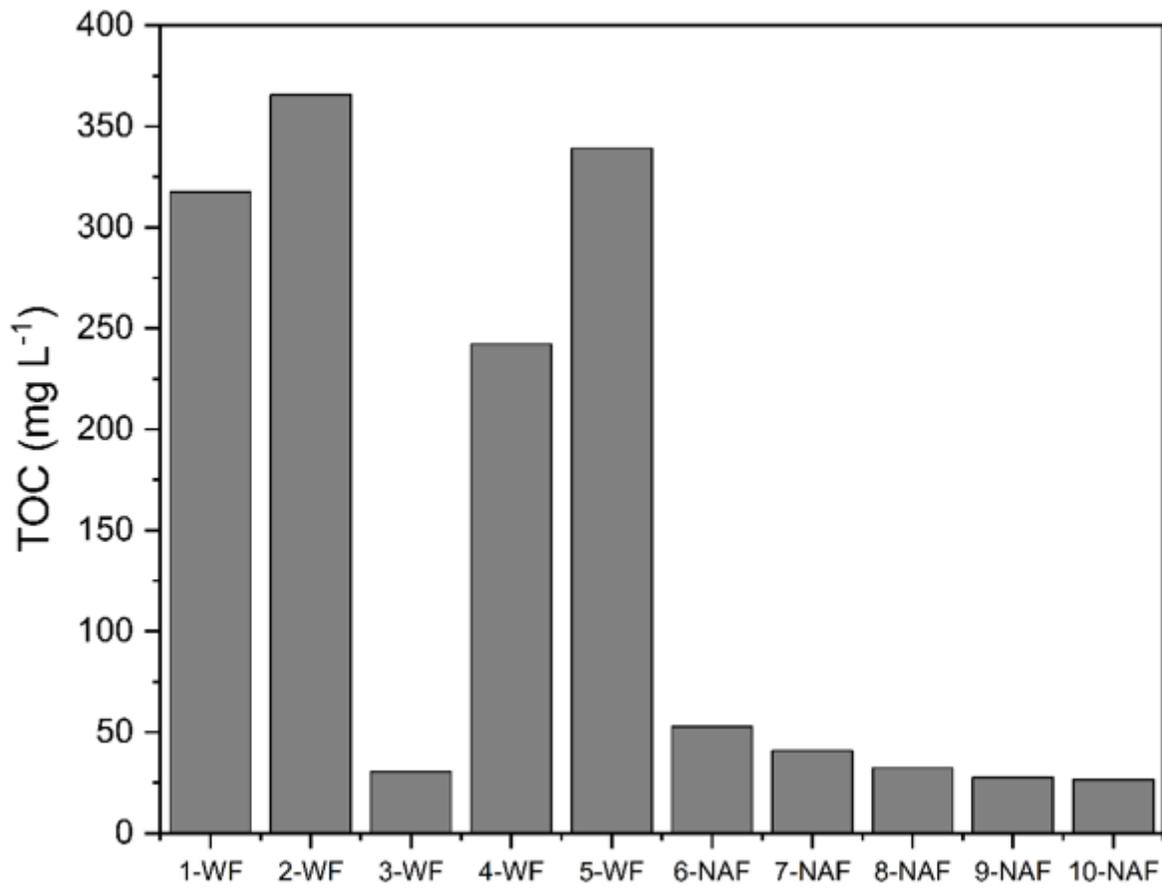
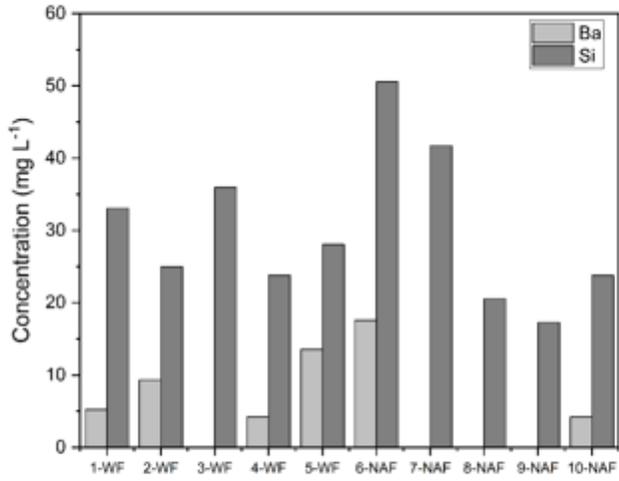


Figure 6

TOC content of saline leachates derived from contact between cuttings and saline solutions

(a)



(b)

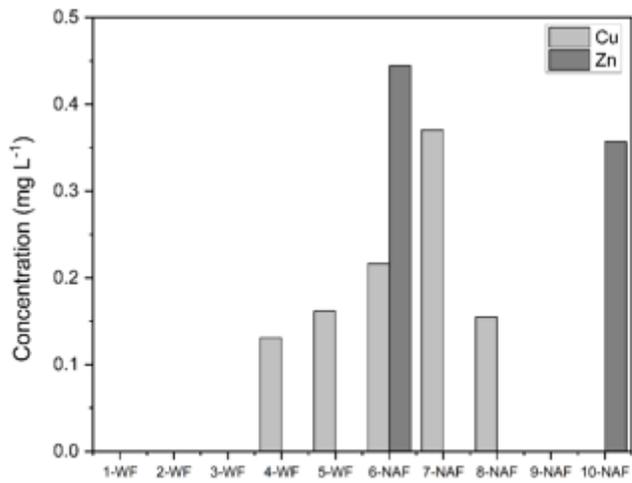


Figure 7

Metal contents of aqueous leachates derived from contact between cuttings and aqueous solutions.

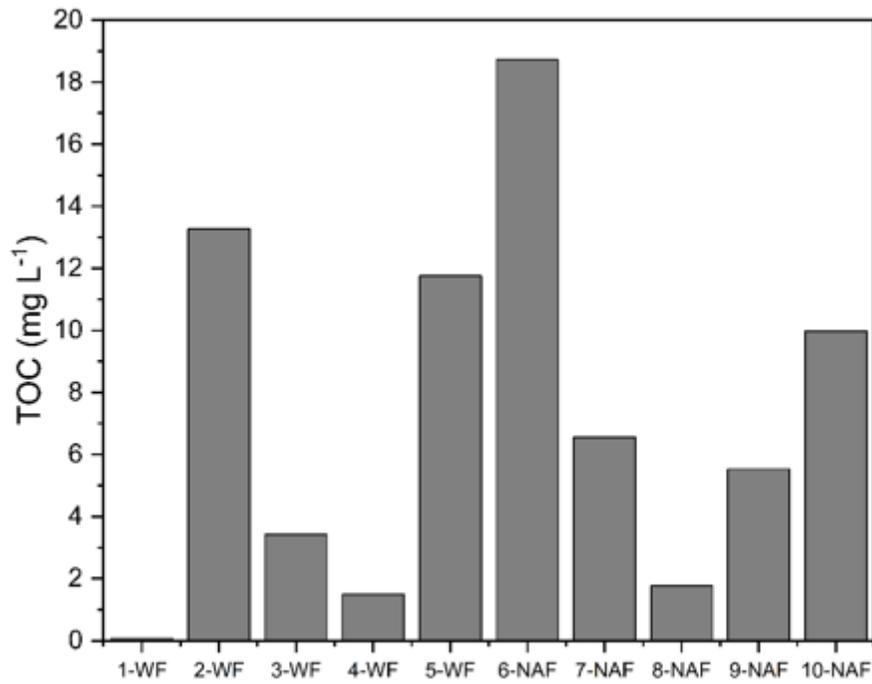


Figure 8

TOC content of aqueous leachates derived from contact between cuttings and aqueous solutions

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [GA.png](#)