



Hazardous elements present in coal nanoparticles in a Caribbean port region in Colombia

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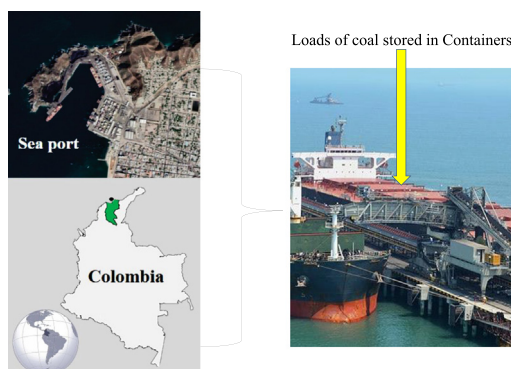
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HIGHLIGHTS

- Potentially toxic elements derived from coal, present in marine ports
- Environmental recovery project needs for marine ports impacted by coal
- Coal-derived nanoparticles (NPs) accumulate legacy liabilities generated by coal in seaports.

GRAPHICAL ABSTRACT



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ABSTRACT

Scientific works examining coal-derived nanoparticles (NPs) containing potentially toxic elements (PTEs) confined in marine suspended sediments (MSSs) in port regions worldwide is an understudied topic, despite the fact that coal NPs have tremendous negative impacts on marine estuaries. The general objective of this study is to analyze the NP levels of coal, including PTEs, contained within MSSs in the general vicinity of the largest Caribbean port in Colombia. The morphology, size, chemical composition, and agglomeration states of NPs within MSSs of the sampled beaches were calculated through modern electron microscopy. The methodology used to detect chemical elements, unfortunately with EDS, it is not possible to precisely specify the chemical elements of low atomic weight (e.g. H, O, F, etc.) Therefore, with the EDS available today, it is only possible to have an idea of the chemical composition of each detected particle. Thus, it was possible to obtain the average frequency of the chemical elements identified in the 23 analyzed sampling points. Through the results, more than one thousand particles were detected in the most abundant phases, thus, the most frequent particles in the results of this manuscript were described. Sample point 8, located closest to the coal export port, had a higher concentration of nano-toxic elements (Al, Fe, Si, K, Mg, K) most concerning for human health in addition to being harmful to marine life. This study suggests that public policies dealing with MSS

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pollution need to be discussed by public managers to avoid further and sustained environmental degradation. The need to create projects will subsidize legacy liabilities generated by coal in seaports in other regions of the world.

1. Introduction

The negative environmental impacts caused by hazardous elements in the form of nanoparticles in marine estuaries require the attention of scientists on a global scale. In order to identify which chemical elements of coal are capable of generating an environmental imbalance in order to mitigate possible impacts caused by these hazardous elements to the marine ecosystem (Qi et al., 2020; J. Wang et al., 2020; Y. Wang et al., 2020; Neckel et al., 2021; Oliveira et al., 2021). It is worth remembering that coal is defined as a solid and flammable organic rock, formed through the transformation of organic matter via biogeochemical processes during geologic burial (Baker, 2022; Wang et al., 2023). Coal stands out as an important source of abundant energy in Colombia, while containing toxic nanoparticles in its chemical structure that are harmful to human health (Silva et al., 2020; Neckel et al., 2021). This does not mean that coal itself is a harmful substance in the solid organic rock phase (Wang et al., 2019). However, coal pollution is composed of inorganic elements and polycyclic aromatic hydrocarbons that are extremely harmful to the health of the population, as coal contains highly carcinogenic compounds (Burns, 2014; Radford et al., 2021; Silva et al., 2021a, 2021b; Xu et al., 2022).

One of the areas most likely to be contaminated by coal are port regions, due to migration of small pieces of coal during transport by trucks and loading of ships destined for export (Dong and Wang, 2012; Burns, 2014). Coal that enters bodies of water is highly harmful to marine species because it has a high sulfur content in its composition, characterized by SO₂ (sulfur dioxide) and SO₃ (sulfuric oxide), which can even modify the hydrogen potential (pH) of water, making it acidic, which could compromise the survival of some species of marine fauna and flora close to ports that export coal on a global scale (Qi et al., 2020; Y. Wang et al., 2020; Silva et al., 2021a; Tretyakova et al., 2021; Zazouli et al., 2021).

Coal supplies one-third of the energy used worldwide and accounts for 40% of worldwide electricity generation, in addition to playing a crucial role in industries such as steel making (IEA, 2017). In Latin America, the main countries with coal reserves and production are Colombia (6746 Mt reserves, annual production - 85.5 Mt), Brazil (4.632 Mt reserves, annual production - 7.9 Mt), and Venezuela (479 Mt reserves, annual production - 0.8 Mt) (WEC, 2017). In Colombia, the departments with the largest coal reserves and production for 2017 were Cesar and La Guajira (SIMCO, 2017). The coal extracted from mines must be transported to strategic points such as seaports for export. Currently, Colombia is an important producer of this mineral resource in South America, with the Santa Marta area being one of the largest coal exporting ports in the country (Caballero-Gallardo et al., 2015). Seaports and large industries within and/or near populated areas are due to the flexibility of local and national administrative laws/policies that regulate their operation.

Coal mining is a major economic activity in many countries (Caballero-Gallardo and Olivero-Verbel, 2016; Bie et al., 2021), influencing local economic development and supporting local economies. Coal dust and nanoparticle (NPs) emissions related to human health and environmental impacts are generated during mining, transportation, and use of the coal itself (Omeland et al., 2013; Liu and Liu, 2020; Fang et al., 2021; Silva et al., 2021a, 2021b). NPs are dispersed through the surrounding air and enter the environment through deposition (Gautam et al., 2012; Saikia et al., 2018; Liu et al., 2020; Fang et al., 2021). In human and animal models, acute and chronic exposure to NPs cause inflammatory effects, activation of antioxidant enzymes, increased markers of lipid peroxidation, and decreased antioxidant defenses (Buzea et al., 2007; Liu and Liu, 2020). Potentially toxic elements (PTEs) are among the major pollutants associated with coal NPs (Martinello et al., 2014; Saikia et al., 2018). These are ubiquitous, persistent, bioaccumulative, biomagnifiable, highly harmful pollutants at relatively low concentrations, in addition to being non-degradable (Alharbi and El-Sorogy, 2017; Benitez-Polo and Velasco, 2020). They are

prevalent in aquatic sediments, making the total content of PTEs a good indicator of the pollution status of ecosystems (Merhaby et al., 2015; Gao et al., 2018; Jones et al., 2019; Neckel et al., 2021; Timoszczuk et al., 2021). These marine suspended sediments (MSSs) act as secondary sources of pollution as associated PTEs can be released to the water column by changes in environmental factors, such as pH, conductivity, temperature, dissolved oxygen, salinity, and sediment alterations (Merhaby et al., 2015; Zhao et al., 2018; Bie et al., 2021). Leading to a potential risk to ecosystems and biota (Duodu et al., 2016; Neckel et al., 2021).

The exposure to high levels of PTEs can cause acute and chronic toxicity, which can damage the central and peripheral nervous system, blood composition, lungs, kidneys, liver, and can even cause death. PTEs are also known to cause mutagenic and carcinogenic effects in the population (Burns, 2014; Jaishankar et al., 2014; Timoszczuk et al., 2021). Local communities heavily involved in coal mining and transportation are exposed to PTEs in dust and environmental matrices through exposure routes such as ingestion, inhalation, and dermal absorption (Buzea et al., 2007; Liu et al., 2020; Timoszczuk et al., 2021). Globally, coal mining and transportation activities have incredible effect on environmental and human health, including NPs containing PTEs confined in MSSs (Cutroneo et al., 2017; Yu et al., 2017). The transference of NPs to MSSs and fluvial sediments display significant multiple-dimensional variability from marine toxicological effects (Fernandez-Maestre et al., 2018). The impacts of incorrect coal disposal are leading to significant harms on a worldwide scale (Jones and Ruppert, 2017; Saikia et al., 2018; J. Wang et al., 2020). The increasing buildup of coal in beach-soil leads to the discharge of PTEs, eventually contaminating topsoil, water bodies, and negatively impacting marine algae development (J. Wang et al., 2020; Zhao et al., 2020; Bie et al., 2021).

This study, which examines a port in Colombia's Caribbean region, is extremely important due to the fact that there are few studies carried out in such a location, examining coal nanoparticles to date (Benitez-Polo and Velasco, 2020; Silva et al., 2021a, 2021b). As such, no article on coal contamination in ports was identified in the literature review for this article. Whereas Colombia exports nearly 95% of its mined coal, the dearth of publications examining this important topic is alarming. The region under study is an area located within the Caribbean, which therefore has a direct influence, demonstrated through statistical averages, in relation to each of the 23 sampled points. There being no Caribbean studies on contamination by coal, the present study is highly justifiable.

The general objective of this study is to analyze the NP levels of coal, including PTEs, contained within MSSs in the general vicinity of the largest Caribbean port in Colombia. The analytical approach discussed is constructed in the grouping of dissemination of coal NPs and physicochemical data collection applied to PTEs, based on the need for future public policies and environmental recovery projects to mitigate the impacts caused by coal in a seaport. Thus, it is highlighted in this study that coal, iron oxides, aluminum oxides would be poorly soluble in marine environments (Neckel et al., 2021; Spellman et al., 2022; Zhang et al., 2022), however, according to Szykiewicz et al. (2009), Martínez-López et al. (2020) and Whitworth et al. (2020), sulfates present in coal, such as gypsum and jarosite, are very soluble in water, easily compromising the quality of oceanic fauna and flora, in addition to becoming for Dai et al. (2021), Giordani et al. (2022) and Silva et al. (2022) hazardous elements that can compromise human health through the release of nanoparticles.

2. Methodology

2.1. Study area

The city of Santa Marta is part of the tourist, cultural and historical district of the Colombian Caribbean. Its economy is based on tourism,

commerce, port activity, and fishing. It is located at 2 m above sea level, with nearby mountainous terrain reaching elevations of up to 5775 m. It has about 500,000 inhabitants (DANE, 2019). The urban and rural area is 2381 km², a semi-arid climate predominates the urban area. Due to the difference in the topography of the city, all thermal floors are present (CIOH, 2021).

Millions of metric tons of coal are moved annually through four port terminals, the Port of Santa Marta, Prodeco (Glencore subsidiary), Drummond and Colombia Natural Resources (Benitez-Polo and Velasco, 2020). The seaport is operated by the Sociedad Portuaria Regional de Santa Marta, and it exported 3,008,407 tons, 2,357,434 tons and 989,945 tons for the years 2018, 2019 and 2020, respectively (Statistical Bulletin, Port Traffic in Colombia, 2020).

Although the Covid-19 pandemic caused a huge reduction in Colombian coal exports, the impacts on beaches where coal has been exported in recent years have not been reduced. This fact is mainly due to the lack of good environmental legislation and the lack of scientific studies in the region under study (Carmona and Jaramillo, 2020; Rojas et al., 2020; Akinyemi et al., 2021; Neckel et al., 2021; Oliveira et al., 2021). This initial study will serve for future recovery work in this and other areas where coal is exported in Colombia. Rojas et al. (2020) and Akinyemi et al. (2021) highlight the need to carry out studies that identify the levels of contamination by coal in Colombia in order to motivate further research at a global level; which will point to future solutions aiming at mitigating the harmful problems to marine estuaries and the human health of the Caribbean population, stimulated by sulfur dioxide and sulfuric oxide, arising from the reactions of coal in the environment.

2.2. Sampling

Great amounts of coal are transported through Colombian Caribbean areas (Carmona and Jaramillo, 2020; Rojas et al., 2020; Akinyemi et al., 2021). It should be remembered that the effects of coal pollution become

lethal to many oceanic animals (Tretyakova et al., 2021). The NPs on the beaches of the Colombian Caribbean are mainly due to inefficient transport of coal (Benitez-Polo and Velasco, 2020; Akinyemi et al., 2021; Rojon et al., 2021). The coal released during transport to the seaport can be transferred to: industrial wastewater, domestic sewage and the ocean (Ge et al., 2021). It should be noted that the environmental and human health risks posed by MSSs in this study were carried out as designated in previous works (Carmona and Jaramillo, 2020; Rojas et al., 2020; Akinyemi et al., 2021; Silva et al., 2021a, 2021b).

In the regional port area of Santa Marta (Colombia), for this study, 23 samples of MSSs were collected, with samples taken at a spacing of 100 m apart (Fig. 1), based on the collection methodology laid out by Goellner et al. (2021) and Neckel et al. (2021), who emphasize this distance of 100 m as the possibility of better understanding the variation of contaminants present in a given region. Sampling took place in 2019, 2020 and 2021, in both the summer and winter seasons of each year. The 23 samples (5 kg each) were obtained with the aid of a shovel and stored in a sterilized glass container, being transported in a sealed Styrofoam box, protected from high variations in ambient temperature.

Average temperatures of the region sampled in this study range from 23.4 °C to 32.6 °C. The annual relative humidity is 76% and the annual solar brightness average is 245 h. The average annual precipitation is 453 mm, with 31 mm falling on average in the dry season (December to April) and 422 mm falling during the rainy season (May to November). The influence of the trade winds predominates, especially in the dry season, with the highest percentages blowing from the north (26%) and from the northeast (15%). The average annual speed is 3.0 m/s, with the highest values between January and March (3.4 to 4.1 m/s) (CIOH, 2021).

The coal studied in this manuscript has a density less than water which, in theory, suggests that it is partially suspended in marine waters (Johnson and Bustin, 2006; Dai et al., 2021). However, coal pyrites or coal Ferminerals, among other associations, are more clustered and denser. These coal portions do not always remain on the surface of the sea water, instead

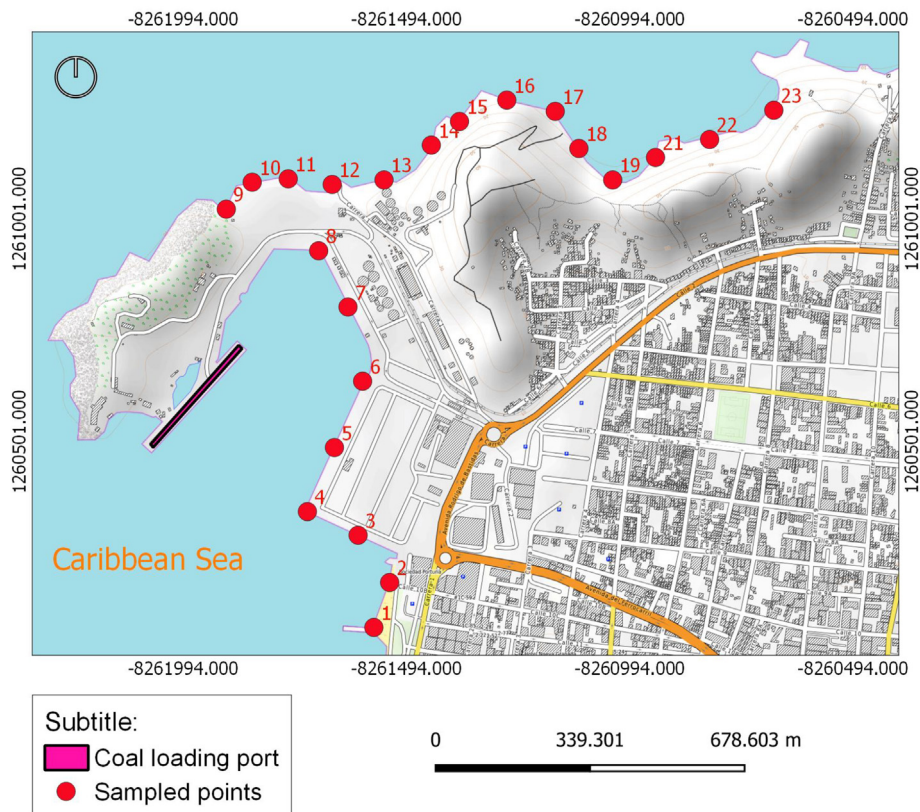


Fig. 1. Illustration of the Caribbean coal export port area. Note the tourist beaches in close proximity to and surrounding the port, with the identification of the location of the 23 sampled points, during the years 2019, 2020 and 2021.

Table 1

Toxic chemical elements and their associations with nanoparticles detected in marine suspended sediments.

Phases	Elements detected
Amorphous nanoparticles (inorganic and organic phases)	Ag, As, Cd, Co, Cr, Cu, Ga, Ge, Hg, Li, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Th, Ti, Tl, U, V, W, Zn, REEs
Arsenopyrite	As, Cd, Se
Carbon nanotubes	As, Cd, Ce, Co, Cr, Cu, Ga, Ge, Hg, La, Li, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Th, Ti, Tl, U, V, W, Zn
Clays	Al, As, Ba, Be, Br, Cd, Ce, Co, Cr, Cu, Hf, Li, Mg, Mn, Mo, Pb, Sb, Se, Sn, Ti, U, V, Zn, Zr, REEs
Fullerenes (C ₆₀ , C ₇₀ , C ₈₀)	As, Br, Co, Cu, Cl, Cr, F, Hg, I, Mo, Pb, Se, Ti
Galena	As, Cu, Pb, Hg
Graphenes	As, Cd, Co, Be, Cr, Cu, Ni, Mo, Se, REEs
Sulfates	
Aluminum-sulfates	Ga, Ge, Hg, Li, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Th, Ti, Tl, U, V, W, Zn, REEs
Iron-sulfates	Ag, As, Cd, Co, Cr, Cu, Ga, Ge, Hg, Ni, Pb, Sb, Se, Sn, Sr, Th, Ti, U, V
Pyrite	As, Cd, Co, Cr, Fe, Ge, Hg, Ni, Pb, Sb
Pyrrhotite	Ag, As, Bi, Cd, Co, Cu, Hg, Mn, Ni, Pb, Sb, Se, Sn, Ti, Zn
Hidroxiides	
Aluminum hidroxiides	As, Co, Ga, Ge, Hg, Li, Mg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Sr, Th, Ti, Tl, U, V, W, Zn, REEs
Iron hidroxiides	As, Ag, Cd, Co, Cr, Cu, Ga, Ge, Hg, Ni, Pb, Sb, Se, Sn, Sr, Th, Ti, U, V

REEs = rare earth elements.

aggregating with marine sediments (Dai et al., 2020; Sutcu et al., 2021; Marghany, 2022). This demonstrates greater reliability of this study's findings in relation to the 23 points collected in sediment samples, constantly receiving uncontrolled discharges of spilled coal during ship loading at the port.

Collected samples were stored in sealed glass test tubes and kept in a thermal Styrofoam box before being immediately submitted to the Laboratory of Analytical Chemistry of Barraquinhos, Coast University - CUC, in Colombia, where they were dried at 25° C for 76 h to prevent the volatilization of some elements. Subsequently, they were transferred to desiccators, and each sample was centrifuged at 4000 rpm to ensure complete separation. To analyze both polar and non-polar

particles, high purity ethanol and hexane (Aldrich brand) were used, respectively.

In the laboratory the 23 samples were centrifuged to minimize the interference of NPs as filtering and other sampling procedures can always change the occurrence mode of NPs containing PTEs (Khan et al., 2021). It should be noted that the MSSs were sampled in triplicate (Dong and Lin, 2015; Rojas et al., 2020; Akinyemi et al., 2021; Silva et al., 2021a, 2021b), in order to strengthen the results obtained in this study. Consequently, all the quantitative samples from the 23 collection points of MSSs (Fig. 1) totaled 138 samples submitted for laboratory analysis. As each sample was tripled over the collection time, a total of 414 samples (bodies of evidence) were analyzed, demonstrating a greater reliability of the results obtained in this study.

2.3. Analytical procedure

Considering sampled NPs are highly heterogeneous and their reactivity with the environment is very wide, it was necessary to use different equipment to ensure the reliability of the results presented in this study (Korkanç et al., 2019). For the most abundant mineralogical phases, X-ray diffraction (XRD) was used as it is the most reliable technique in determining the most abundant phases (Boukir et al., 2019; Korkanç et al., 2019; Stanchik et al., 2021; Piffet et al., 2022). However, XRD does not have the robustness required to analyze phases that are below 1–5% (Stanchik et al., 2021; Piffet et al., 2022).

To carry out this study, it was necessary to use a field emission scanning electron microscopy (FE-SEM), allowing, according to Boukir et al. (2019) and Stanchik et al. (2021), a high level of analytical scope to the collected samples, to be completed by the use of a high resolution transmission electron microscope (HR-TEM), coupled with an energy dispersive X-ray microanalysis (EDS) system. As many NPs are found inside of larger particles, it was necessary to use the Focused Ion Beam (FIB) to prepare/cut the ultra-fine particles, and thus study the mineralogy and chemical composition of their interiors (Neckel et al., 2021). Only with the combination of this equipment it is possible to correctly determine the geochemistry of NPs containing PTEs in areas contaminated by coal. Similar analytical procedures have been reported by several studies (Saikia et al., 2018; Silva et al., 2021a, 2021b). Thus, the results presented here in this work become relevant to science at a global level. The bulk chemical composition was

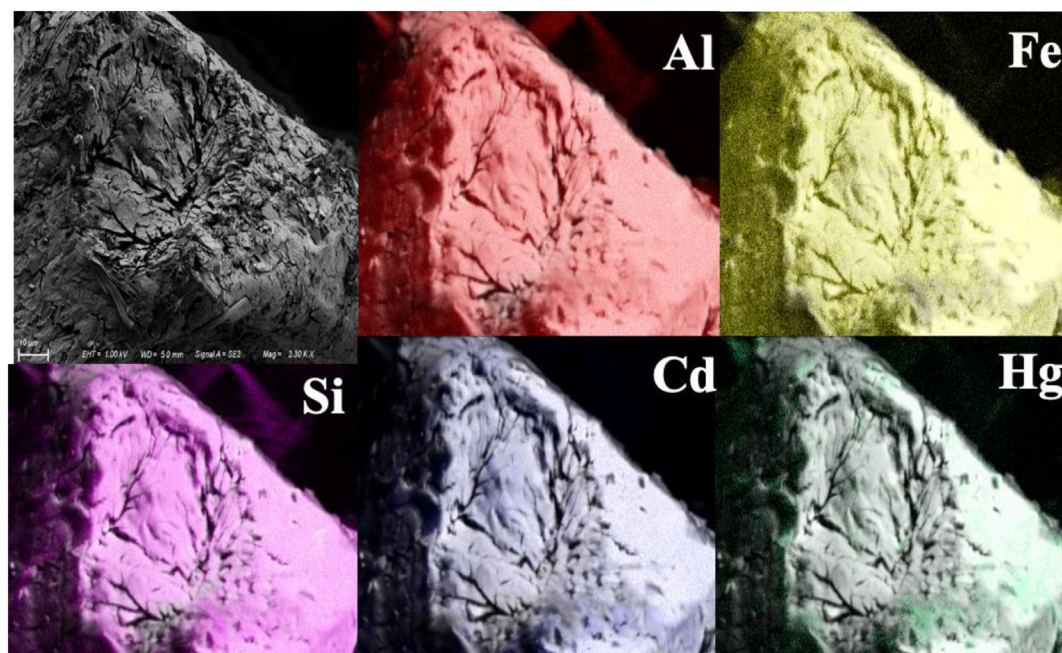


Fig. 2. Example of an amorphous particle clustered with multiple other particles. The chemical composition varies depending on where it is analyzed with EDS, however almost all agglomerations contain only non-toxic elements, and only about 40% of all amorphous particles contained PTEs.

determined by inductively coupled plasma-mass spectrometry (ICP-MS) (Silva et al., 2021a, 2021b), in terms of the chemical composition of the elements detected. This technique reveals only a general understanding of each applied procedure to the samples, through advanced microscopes, the geochemistry of NPs can be well evaluated, demonstrating the high reliability of the results of this study, through statistical mean values in relation to the 23 sampled points, thus considering the chemical elements detected in greater quantity.

3. Results and discussion

The most abundant phases, according to XRD, were the amorphous phases, in addition to the abundant mineralogical quartz particles, some clays, and sulfates. According to Zheng et al. (2019) and Qin et al. (2021) the presence of high levels of sulfates are usually directly associated with the presence of coal, which in areas of abundant water cause immersions of aqueous solutions of sulfate. What demonstrates the influence of coal in the port region, and the excess of sulfate, according to Bartley et al. (2010) and Wignall et al. (2020) can directly compromise the marine fauna and flora. Additionally, this can have negative impacts on human health and the local economy, as excess aquatic sulfate can threaten tourism and the local availability of fish. Many local residents in the vicinity of the study area practice subsistence fishing.

As shown by EDS coupled with electron microscopy, the amorphous particles are the NPs that contain the highest proportion of PTEs. Table 1 illustrates the main interactions between PTEs and NPs. The authors detected more than 30 elements that are toxic to the environment and human health in the different phases analyzed. It should be emphasized that the amorphous phases, in addition to carbon nanotubes, and Fe, Al-NPs were the phases that contained PTEs most often. Therefore, it is easy to see the geochemical importance of such phases in the transport and immobilization of hazardous elements including rare earth elements.

The amorphous phases varied between NPs and particles larger than 10 μm (Fig. 2). Highly agglomerated particles composed of Al, Fe, Si, K, Mg, K, and other non-toxic elements were the most numerous. However, about 40% of the 728 (corresponding to 100% of the total elements) amorphous NPs detected in the sampled area contained PTEs (e.g. As, Cd, Hg, and Pb)

(Table 2 contains the elements with the most quantitative representation in relation to the total number of identified elements). Pb is a dangerous element that can cause different types of cancer in both adults and children (Gao et al., 2021; Nag and Cummins, 2021; Neckel et al., 2021; Zhang et al., 2021). Thus, highlighting that each part of the human body has a distinct reactivity with each element, being able to absorb these dangerous elements differently (Dehdashti et al., 2020; Kumar Shakya and Singh, 2022; Urquhart et al., 2022). It should be noted that unfortunately the reactivity of amorphous particles is still limited to the fact that we do not have analytical procedures to determine whether such NPs are capable of adsorbing without again leaching the PTEs they contain in their structures and agglomerations. It is of great importance that future studies help in this determination of NPs (Saikia et al., 2018; Silva et al., 2021a, 2021b; Timoszczuk et al., 2021). It should be remembered that only amorphous NPs in extraction areas contaminated by coal export and transport have not been studied. Several authors of previous coal studies have demonstrated similar contaminations and reactivity of clustered amorphous phases containing PTEs (De Vallejuelo et al., 2017; Benitez-Polo and Velasco, 2020).

One of the most interesting NPs detected in this study were the fullerenes C_{60} aggregates (Fig. 3). Due to the 3D-dimensional form of C_{60} , its unsaturated bonds and its electronic structure, C_{60} has exceptional geochemical characteristics. In this work only C_{60} was detected. However, that does not mean that C_{70} and C_{80} cannot be present. Several toxicological and bioaccumulation studies indicate that C_{60} may pose a high danger to species (e.g. mitochondrial dysfunction by means of diverse deadly devices) in contact with such NPs in marine environments (Marisa et al., 2021; Oliveira et al., 2021; Timoszczuk et al., 2021).

Despite the robustness of the equipment used (e.g. XRD, FE-SEM, and HR-TEM) many NPs of high environmental and health importance would not have been detected without the use of FIB. This is due to the fact that many NPs are inside larger sized particles, either uncalcined, dormant or have been formed in such a way that they occur while allowing the disintegration of some dangerous elements present in coal along with NPs (Bie et al., 2021; Marisa et al., 2021).

Fig. 4 shows the interior of an amorphous particle on its outside, yet containing multiple crystalline phases inside. Among the mineralogical phases of greatest importance in Fig. 4, jarosite stands out as more than

Table 2

Average results of the analyses carried out at the 23 points sampled, located in the port region of the Colombian Caribbean during the years 2019, 2020 and 2021, in both summer and winter seasons.

Elements identified in the 23 sampled points																									
Points	(%)							(ppm)																	
	Al	Fe	K	Mg	Na	P	Ti	As	Ba	Cd	Co	Cr	C	Cu	Hg	Mn	Ni	Pb	Sb	Sn	Se	Ta	Th	U	Zn
1	11.8	5.0	3.1	0.9	0.3	1.6	0.4	42.9	533	0.6	4.8	150	28.1	36.3	31.7	147	34.8	47.1	15.8	4.3	113	1.4	16.2	5.1	47.4
2	11.2	5.1	3.2	0.8	0.5	1.5	0.6	42.6	555	0.8	5.5	150	23.5	37.4	33.2	142	33.1	50.2	15.2	4.2	112	0.2	16.5	4.3	48.0
3	13.5	5.8	3.4	0.9	0.7	1.8	0.8	46.2	570	0.8	5.6	142	27.7	37.6	37.1	90	35.5	51.7	15.2	4.3	122	0.3	18.7	4.5	49.6
4	15.8	4.6	3.8	0.7	0.5	1.7	0.7	47.1	518	1.0	5.8	147	32.2	20.5	34.7	106	40.2	55.6	16.4	4.1	123	0.1	19.1	4.8	50.5
5	19.9	8.3	6.7	1.2	0.4	1.7	0.5	48.5	160	1.0	5.4	148	33.5	32.9	37.6	163	42.9	60.5	15.6	4.5	124	0.6	20.5	5.7	51.5
6	23.7	8.2	7.0	1.3	0.8	1.6	0.9	54.2	80	1.3	6.2	161	45.7	40.5	39.4	158	32.7	59.1	17.8	4.1	129	0.7	21.3	5.8	51.7
7	23.2	9.5	11.1	1.1	0.4	1.4	0.8	54.0	602	1.1	6.7	158	47.8	20.3	40.5	122	36.8	60.8	17.4	4.4	138	1.8	21.2	5.9	52.5
8 ^a	25.1	9.5	12.2	1.8	0.5	1.5	1.3	55.8	569	1.3	7.1	162	47.9	22.3	40.8	143	35.6	70.5	23.0	4.4	145	1.9	21.8	5.9	54.8
9	23.6	3.5	3.9	0.9	0.2	1.2	0.7	43.7	205	0.8	2.1	158	28.2	13.7	29.0	132	19.9	25.0	8.5	2.3	123	0.1	12.9	3.5	29.4
10	23.2	6.8	3.8	0.9	0.2	0.9	0.6	43.8	180	0.7	2.2	157	28.4	13.4	29.4	133	11.2	35.8	9.9	2.1	120	0.1	11.6	4.2	22.1
11	20.1	6.3	3.7	0.9	0.1	0.8	0.7	43.3	193	0.7	1.9	145	16.0	23.1	20.4	80	18.6	22.5	15.3	2.0	121	0.2	11.2	4.1	23.0
12	19.6	6.4	3.9	0.7	0.3	1.5	0.5	43.2	370	0.8	1.2	154	22.3	12.8	21.7	101	23.1	23.9	12.8	2.9	123	0.2	11.4	3.3	26.3
13	19.7	5.3	3.1	0.9	0.1	1.2	0.8	43.7	426	0.9	2.8	132	22.1	11.1	15.1	110	15.0	20.3	9.3	2.4	118	0.3	10.7	2.9	22.8
14	16.9	6.1	3.1	0.8	0.5	0.7	0.7	43.5	283	0.6	2.4	138	12.2	12.9	13.7	119	12.0	16.7	8.8	2.0	115	0.7	8.3	2.8	21.2
15	16.2	4.3	3.4	0.5	0.6	0.9	0.4	42.9	70	0.3	1.8	146	19.8	23.2	9.3	117	18.2	17.6	9.0	1.9	120	0.4	8.7	2.7	21.3
16	16.5	5.6	3.1	0.5	0.6	1.0	0.5	43.1	119	0.2	2.2	146	22.7	16.5	7.9	89	11.4	16.1	7.3	2.1	180	0.3	9.3	2.6	21.0
17	9.5	5.5	2.8	0.6	0.4	0.8	0.5	42.4	207	0.4	1.7	142	13.3	19.0	7.2	92	9.3	12.2	13.5	2.2	109	0.1	7.6	2.9	15.7
18	12.6	4.5	3.3	0.7	0.7	0.7	0.4	43.7	501	0.7	1.8	150	12.9	10.6	1.6	95	20.6	11.4	12.0	1.9	108	0.2	6.8	2.0	14.8
19	12.4	4.2	3.0	0.6	0.3	0.9	0.6	42.2	110	0.6	1.2	147	11.6	9.1	3.6	73	16.8	10.3	6.8	1.8	101	0.1	7.9	1.9	16.4
20	12.2	6.4	3.1	0.6	0.4	0.7	0.3	41.3	95	0.4	1.5	146	11.3	3.6	2.9	68	27.1	10.6	9.3	1.0	98	0.1	7.3	2.2	13.5
21	10.8	4.3	2.7	0.4	0.3	0.6	0.3	41.6	60	0.4	1.3	149	9.5	1.1	3.8	130	32.5	12.7	10.1	1.4	105	0.4	7.6	2.1	15.4
22	8.8	4.7	3.2	0.4	0.1	1.1	0.4	41.1	110	0.3	1.4	148	11.8	12.3	3.3	107	16.7	13.9	9.2	1.3	101	0.2	7.1	2.3	10.3
23	9.2	4.7	3.1	0.5	0.3	0.4	0.3	41.2	180	0.5	1.7	148	11.3	16.0	2.8	95	12.6	11.8	8.6	2.3	97	0.1	7.5	2.6	11.1

^a Note: Point 8 is located near the port responsible for exporting coal from the Caribbean, Colombia to other countries in the world.

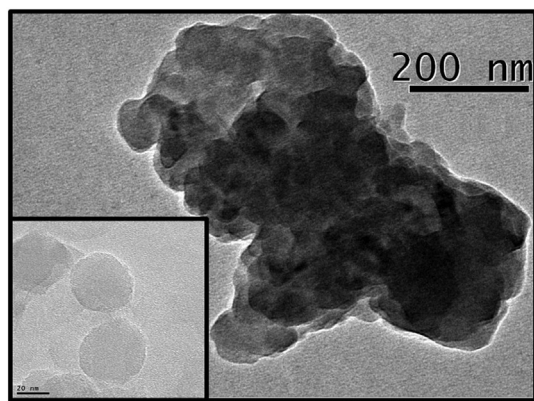


Fig. 3. HR-TEM illustration of C₆₀ agglomerated and the typical C₆₀ magnification.

95% of the analyzed crystals that contained elements such as, Cd, Co, Cr, Hg, Pb, Sb, Se, Sn and Zn (Table 2). Thus, it is highlighted that point 8, located closest to the port, is the one that concentrates the largest amount of identified chemical elements. In rare cases it is known to contain U and Th as well. According to Espitia-Pérez et al. (2018) and Akinyemi et al. (2021), Cr becomes highly enriched in ultra-fine particulates (PM_{2.5}), with higher amounts in coal mining areas, along roadsides in which coal is transported and in port regions.

This fact demonstrates the importance of using FIB for an adequate understanding of the coal NPs that impact several beaches around the world, in addition to the beach under study (Benítez-Polo and Velasco, 2020; Oliveira et al., 2021). The presence of jarosite crystals is probably due to the degradation of primary minerals present in the coal such as pyrite, calcite, and clays. Some crystals can be pure, however most often they are found with amorphous phases containing Al, Si, K, C and other elements. Another mineral of great importance in Fig. 4 is gypsum, as this mineral in the presence of water can be easily mobilized and change the

geochemical characteristics of the oceanic waters under study, in addition to affecting marine life.

Several authors confirmed the immunotoxicity, neurotoxicity and mutagenic risks including the induction of reactive oxygen species of similar NPs detected in this study (Burns, 2014; Cutroneo et al., 2017; Yu et al., 2017; Saikia et al., 2018; Zhao et al., 2020; Silva et al., 2021a, 2021b). Some studies emphasize that Ti-NPs as well as several carbon-NPs have neurotoxicological activities (Guan et al., 2018; Zha et al., 2019; Gao et al., 2021), so it is crucial that Colombian authorities pay greater attention to environmental legislation that prevents both aquatic organisms and humans from being contaminated by NPs derived from transport and export of Colombian coal.

4. Conclusions

This study specified understandings about the association between the NPs found in MSSs sampled in the largest coal export port in Latin America and the anthropogenic actions that have emerged in the Caribbean area during the last several decades. By systematically analyzing the geochemical portions of NPs containing PTEs and the dangers they pose to the environment and human health, the presence of hazardous elements related to the transport of coal to the investigated port was identified. In this relationship, it can be seen that the 23 sampling points, as they stand out from the port, reduce the proposition of identified chemical elements, however, sampling point 8 stands out, which is located closer to the coal export port, containing higher concentrations of the following dangerous elements: Al, Fe, Si, K, Mg and K, as they are nano-toxic to human health and degrade the quality of the human environment.

The data from this study demonstrated the greater existence due to pollution by NPs and PTEs in the port networks of beaches in the Caribbean. The continuation of permanent NP analysis is essential to control coal contamination related to the studied port region. The authors suggest examining the feasibility of forming and enforcing public policies for the environmental monitoring of coal tailings released during transport in future studies. Future environmental recovery projects in the studied port region should also be taken into account regarding the mitigation of

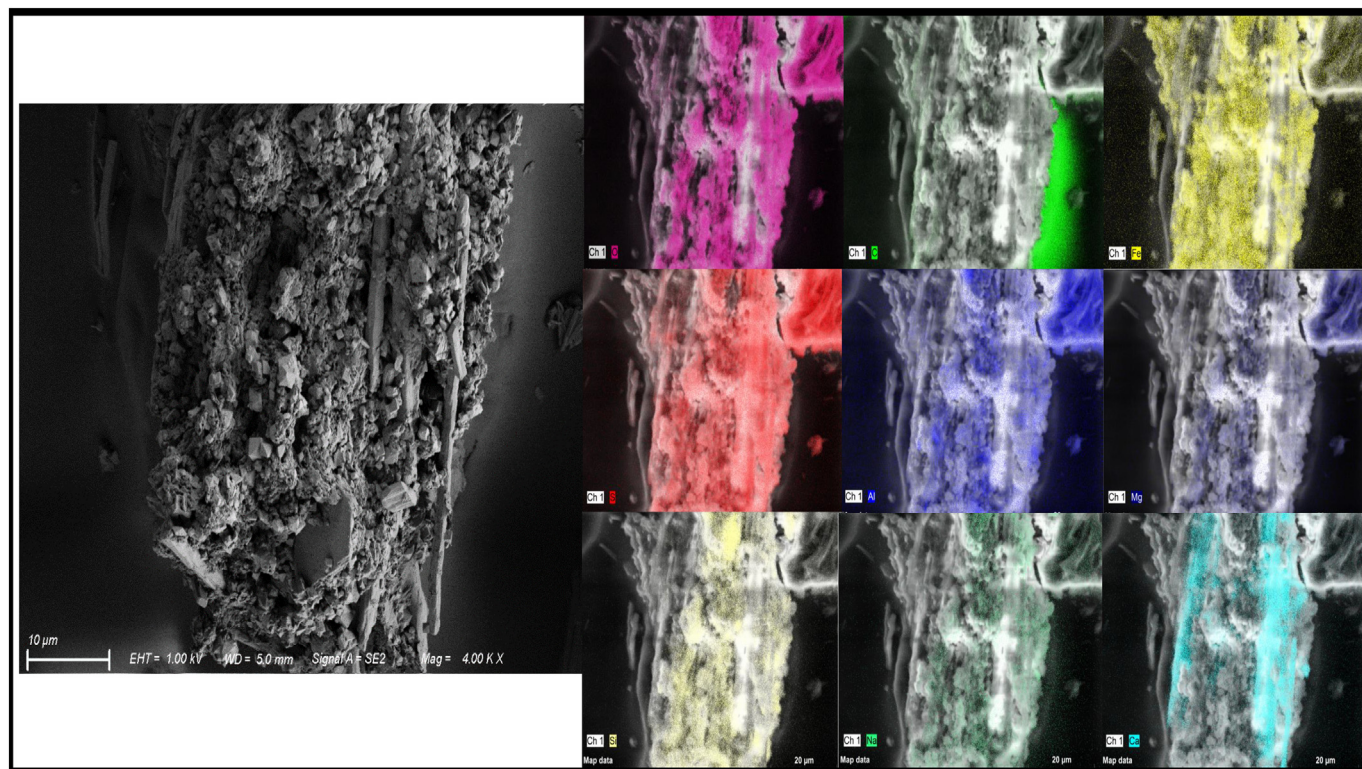


Fig. 4. Amorphous particle containing multiple minerals in its interior, the most abundant and sloping ones were jarosite and gypsum.

hazardous elements generated by coal. Also, there is a need for future studies to assess the real harmful impacts on the human health of port workers and the population residing nearby who may be exposed to hazardous elements present in coal through releases generated by transportation after the mining process and the process of loading coal onto ships in the port.

CRedit authorship contribution statement

Alcindo Neckel: Conceptualization, Funding acquisition.

Jorge Osorio-Martinez, Diana Pinto, and Brian W. Bodah: final manuscript writing.

Bashir Adelodun, and Luis F.O. Silva: review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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