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Coal as a marine pollutant

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COAL AS A MARINE POLLUTANT

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Declaration

I certify that all the material in this dissertation that is not my own work has been identified, and that no material is included for which a degree has previously been conferred on me.

The contents of this dissertation reflect my own personal views, and are not necessarily endorsed by the University.

(Signature): ....

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I always kept myself motivated to not resign on this project that I believe is crucially important and of interest not only for the General Maritime Directorate in Colombia (DIMAR), but also for Colombia as a country. That is because Colombia has the largest reserve of coal in Latin America and is one the principal coal exporters worldwide. Colombia as well has a grand variety of marine ecosystems demanding a proper balance between the exploitation of mineral resources and protection of such ecosystems.

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Abstract

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Coal is a sedimentary rock that is formed by the burial of plant and animal remains in swamps, which are subjected to major transformation processes due to increased temperature and pressure during geological periods. Unburnt coal is considered a significant source of energy not only for its abundance but also due to its low cost. Even though coal is mainly used in electricity generation, it has other important applications such as its use in steel, cement and fuel production, among others. Nonetheless, this mineral chiefly formed by organic and inorganic constituents, contains some compounds and elements, which can be potentially toxic such as trace metals and the Polycyclic Aromatic Hydrocarbons (PAHs).

In addition, it has been demonstrated on many occasions and by significant examples that coal has adverse impacts on human health. Interestingly, despite the above, there are few studies on the impacts of coal on the marine environment, which illustrates that this topic still remains as an unexplored issue. On the one hand, unburnt coal could cause physical effects such as turbidity and abrasion due to contact between coal particles and animal and plant species. On the other hand, unburnt coal could release some toxic elements, which could jeopardize the health of a substantial amount of species in marine and estuarine ecosystems. Due to this fact, this dissertation mainly aims, through a comprehensive analysis, to establish the different chemical and physical impacts of unburnt coal on the marine environment and its organisms.

To achieve this goal, the most significant research on the physical and chemical effects of unburnt coal on water bodies and aquatic organisms was studied and analyzed. The results show that unburnt coal may release some trace metals and PAHs after entering seawater. The elements and compounds formerly mentioned could exceed the established limits and, hence become potentially toxic elements for a great many marine species such as fish, crustaceans, and mollusks, not only in the juvenile stage but also in the adult phase.

Key words: Unburnt coal, pollutant, marine environment, trace metals, polycyclic aromatic hydrocarbons (PAHs), marine organisms.

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List of Abbreviations

AGI	American Geosciences Institute
ANR	Alpha Natural Resources
ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
BGS	British Geological Survey
BRC	Banco de la República de Colombia [Bank of Republic of Colombia]
CGR	Contraloria General de la República [The National Comptroller's Office]
CIOH	Centro de Investigaciones Oceanográficas e Hidrográficas del Caribe [Center for Oceanographic and Hydrographic Research of the Caribbean]
DIMAR	Dirección General Marítima [General Maritime Directorate].
DOE	US Department of Energy
EPA	US Environmental Protection Agency
GDP	Gross Domestic Product
GMI	Global Methane Initiative
IEA	International Energy Agency
INPA	International Network for Acid Prevention
INVEMAR	Instituto de Investigaciones Marinas y Costeras [Institute of Marine and Coastal Research of Colombia]

KGS	Kentucky Geological Survey
LIMCOL	Liga Marítima de Colombia [Maritime League of Colombia]
MAVDT	Ministerio de Ambiente, Vivienda y Desarrollo Territorial de Colombia [Ministry of Environment, Housing and Territorial Development of Colombia]
MME	Ministerio de Minas y Energía de Colombia [Ministry of Mines and Energy of Colombia]
PNNC	Parques Nacionales Naturales de Colombia [National Parks of Colombia]
UJTL	Universidad de Bogotá Jorge Tadeo Lozano [University of Bogotá Jorge Tadeo Lozano]
UPME	Unidad de Planeación Minero Energética de Colombia [Mining and Energy Planning Unit of Colombia]
WCA	World Coal Association
WCI	World Coal Institute
WHO	World Health Organization

1 INTRODUCTION

“Many of life's failures are people who did not realize
How close they were to success when they gave up."
Thomas A. Edison

“Tell me and I forget. Teach me and
I remember. Involve me and I learn.”
Benjamin Franklin

“Most of the large errors occur when one rushes.”

1.1 The Origins of Coal

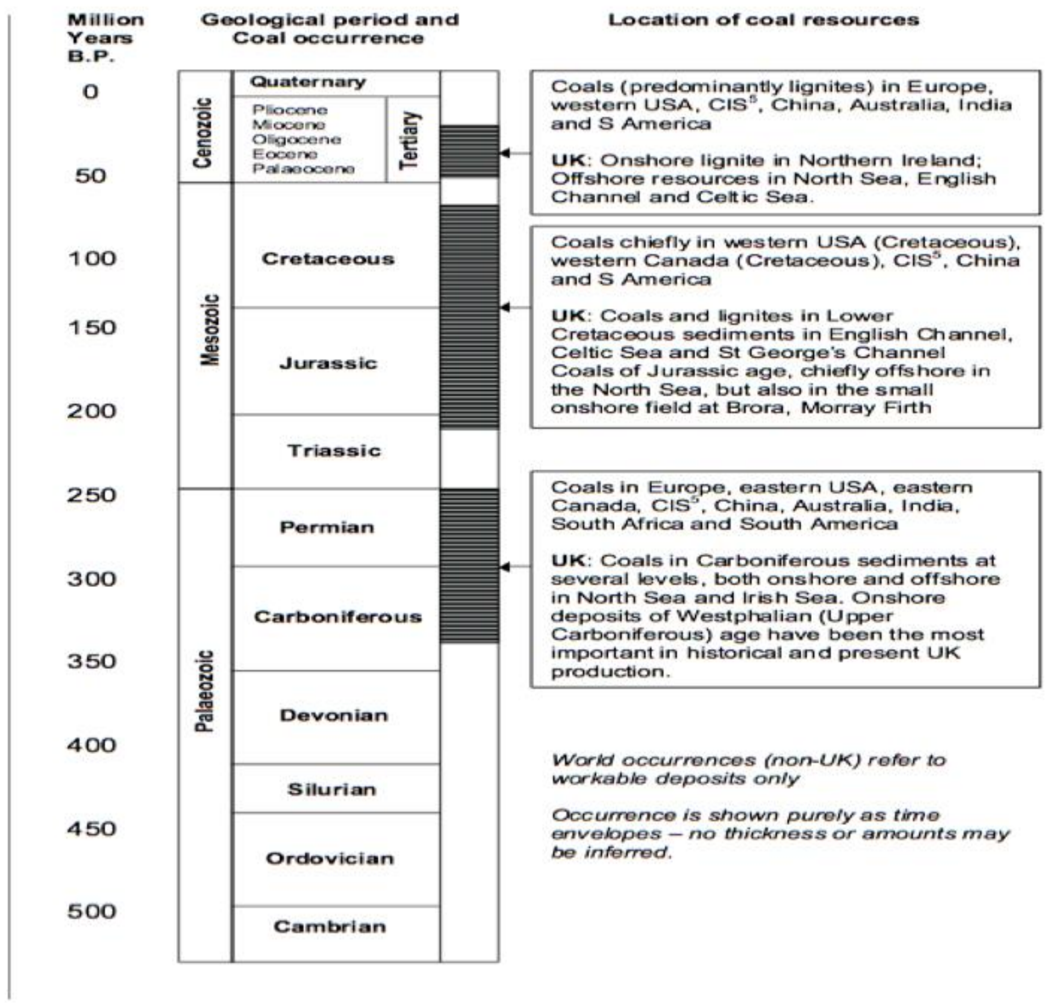
"Coal has been an indispensable component of civilization for centuries and has fueled the industrial and economic development of many coal rich countries around the world over the past 150 years" (Stout & Emsbo-Mattingly, 2008). Moreover, “Coal has a very long and varied history. Some historians believe that coal was first used commercially in China. There are reports that a mine in northeastern China provided coal for smelting copper and for casting coins around 1000 BC” (WCI, 2005). Coal was the primary source of energy that was used in ancient times. It even remained as the most important source of energy for human consumption until the 1960’s when it was replaced by oil. However, its high consumption has remained due to the fact that it is an abundant and economic source of energy, which is highly available in current markets.

Archeologists have also found evidence that the Romans in England used coal in the second and third centuries (100–200 AD). The first scientific reference to coal may have been made by the Greek philosopher and scientist Aristotle, who referred to a charcoal like rock. It was during the Industrial Revolution in the 18th and 19th centuries that demand for coal surged. The introduction of the steam engine by James Watt in 1769 was largely responsible for the growth in coal use (Ghosh & Prelas, 2009). “Coal is the altered remains of prehistoric vegetation that originally accumulated as plant material in swamps or over deltas. With burial caused by movements of the earth’s crust, the plant material underwent physical and chemical changes and was further transformed into coal” (Barranco, 2001).

Scientists suggest two main theories regarding coal formation. On the one hand, the first theory asserts that coal was formed in situ in the same place where vegetation grew and fell, thus this deposit is called autochthonous in origin. It is believed that the starting constituents of coal are trees, plant debris and bark that accumulated and settled in swamps. This is an important reason why coals are quite different around the world because of the kinds of materials involved in the formation processes (i.e. type of vegetation that started the process that lead to the formation of coal), the degree of coalification or metamorphism (i.e. rank of coal), and the types of impurities (i.e. grade of coal). Nevertheless, regarding the bearing constituent of plants there is a great controversy, particularly cellulose and lignin, on formation of the coal.

In addition, peat is the unconsolidated accumulation of plant remains. The beginning of the majority of deposits of coal began with thick peat bogs where the water was nearly stagnant and debris of plants accumulated. Then microbiological action converted plant debris into peat. Over the time, these layers of peat were covered with sediment (Williams, Hofmann, & Glasspool, 2008) and underwent heat and pressure from subsidence of the swamps (WCI, 2005). Besides, "the cycles of accumulation and sediment deposition continued and were followed by diagenetic (i.e., biological) and tectonic (i.e., geological) actions and, depending upon the extent of temperature, time, and forces exerted, formed the different ranks of coal observed today" (Ghosh & Prelas, 2009).

The second theory establishes that formation of coal occurred through vegetal matter accumulation, which has been moved by water to another place. This theory is called allochthonous origin. More specifically, the fragments of plants were transported by streams and deposited on the sea bottom or in lakes where they built up strata, which then became compressed into coal (Ghosh & Prelas, 2009). Additionally, the geological period and coal occurrence is shown in Figure 1. Owing to the fact that a single theory could not explain the origin of all coal deposits in the world, there are these two theories.



Source: BGS. (2010). *Coal. Definition, mineralogy and deposits (pp. 18).* Keyworth, UK: British Geological Survey.

Figure 1. Coal occurrence in the stratigraphic column.

1.2 Rationale

As a result of the sinking and spilling of coal by the barge number 115 in Ciénaga, Colombia, national authorities such as the General Maritime Directorate (DIMAR, for its acronym in Spanish) started to think about whether coal is a marine polluting agent.

Coal spills in Colombia have occurred with very high frequency. For instance, between 2006 and 2010, 9 barges with 600 tons of coal in each one, sunk into the marine environment (Patiño, 2013), which means nearly two barges per year. Rivers are also exposed to this threat, an example is 1.500 tons of coal spilled into the Magdalena river in 1995 (Value, 1995), the largest tributary into the Caribbean Sea (Restrepo, Kjerfve, Hermelin, & Restrepo, 2006). It has long been recognized that Colombia has not handled this problem with the required priority. The lack of environmental impact assessment suggests that this problem must be dealt with at a very high level. In other words, each incident should be followed by an environmental impact study, which not only clearly establishes its effects on the aquatic ecosystem, but also recommends how to prevent and/or mitigate these accidents. Nonetheless, the effects caused by this mineral in water bodies and their living resources, are at present largely unknown. This issue has been disregarded as the assumption has been that there are no impacts of coal in the aquatic environment. , However, although the quality of Colombian coal is quite high (Tewalt, Finkelman, Torres, & Simoni, 2006), (GMI, 2011), (UPME, 2005), it also contains several elements such as sulphides, metals and ashes, which could react when introduced into bodies of water and become potential pollutants. In addition, coal particles will be deposited on the seabed and on the shoreline and cause an impairment (Vivas-Aguas et al., 2011) in these ecosystems.

In addition, Colombia is one of the main producers and exporters of coal in the world (IEA, 2012). Furthermore, Colombia has at least seven important coal ports, where there is a high risk of spillage during coal operations. Moreover, this phenomenon is affecting marine life and important activities such as fishing and tourism in these areas. Therefore, the Colombian authorities need to take action and develop management procedures in order to fully assess the impacts of the spillage of coal in the marine and aquatic environments and prevent or mitigate such spilling.

1.3 Purpose of the Project

> “Coal, a generating source of foreign currency and employment, accounts for 47% of the national mining activity and represents 1% of the Colombian gross national product with a little more than $3.4 trillion pesos. In recent years, coal has consolidated itself as the second national exportation product after oil and it is estimated that under the current market conditions, between the 2010 and 2015, it may exceed oil exportation” (UPME, 2005)

Although coal is one of the most important resources of Colombia, its exploitation and transport could endanger certain ecosystems associated with coal activities. For instance, in most of the ports of the Magdalena department, coal is transported by barges (MME, 2010) from the dock to the ship (Patiño, 2013). A significant number of these barges have sunk due to different causes, spilling the product into the sea. The spilling of coal into the marine environment has traditionally not been considered a source of marine pollution (CGR, 2012). However, very few studies have in fact been carried out to assess the real damage to the aquatic and marine ecosystems, and only a few of them have examined whether unburnt coal represents a threat to the marine environment. Therefore, this dissertation aims to study and analyze different impacts such as physical, chemical and biological effects of unburnt coal on the marine environment.

It is important to establish that this study will not analyze or provide any recommendations regarding methods of storage and transportation of coal.

1.4 Research Methodology

Bearing in mind that the main goal of this research is to determine whether coal is a pollutant of the marine environment, it is necessary to study and analyze the physical, chemical and biologic impacts of coal on the environment above mentioned. Hence, it will carry out a qualitative research study, through the study and analysis of different studies conducted. Likewise, this valuable information will require a comprehensive analysis in order to obtain expected results. In addition, conclusions and recommendations will be presented as an outcome of this research.

Firstly, qualitative information will be provided by the Marine and Coastal Research Institute (INVEMAR, for its acronym in Spanish). This important research institution of Colombia has led and developed different research projects on coal and its effects on the marine environment. INVEMAR has made significant findings that will be taken into account in this dissertation. The Universidad Jorge Tadeo Lozano of Colombia has also made several important investigations in this field, as have some universities such as the University of Newcastle, Australia, and the University of California, United States, among others. Secondly, this information will be fully analyzed focusing on studied cases, which show successful results. Thirdly, the coal composition and what impacts the different constituents of coal will have on marine species as a result of a spill will be covered as well. Finally, the conclusion of the research will be given. In brief, some important recommendations will be provided in order to prevent or mitigate possible pollution because of a coal spillage.

1.5 Difficulties Encountered During the Research

Undoubtedly, the greatest difficulty encountered during the present investigation was to obtain scientific information about the impacts of coal on the marine environment. Additionally, there is a lot of speculation about coal pollution in marine organisms and their environment. As a consequence, it was not possible to make use of this information because of lack of scientific soundness. In Colombia for example, there are only a few studies and most of them are inconclusive. Similarly, the literature on coal remains limited worldwide. One reason is that many researchers consider natural coal as an inert mineral. This alleged “inert" state is said not to represent any threat to the marine environment or its living resource, which discourages the development of studies that seek to identify and analyze the impacts of this mineral on the marine environment. Despite this, there were studies that led to an analysis of these effects.

2 LITERATURE REVIEW

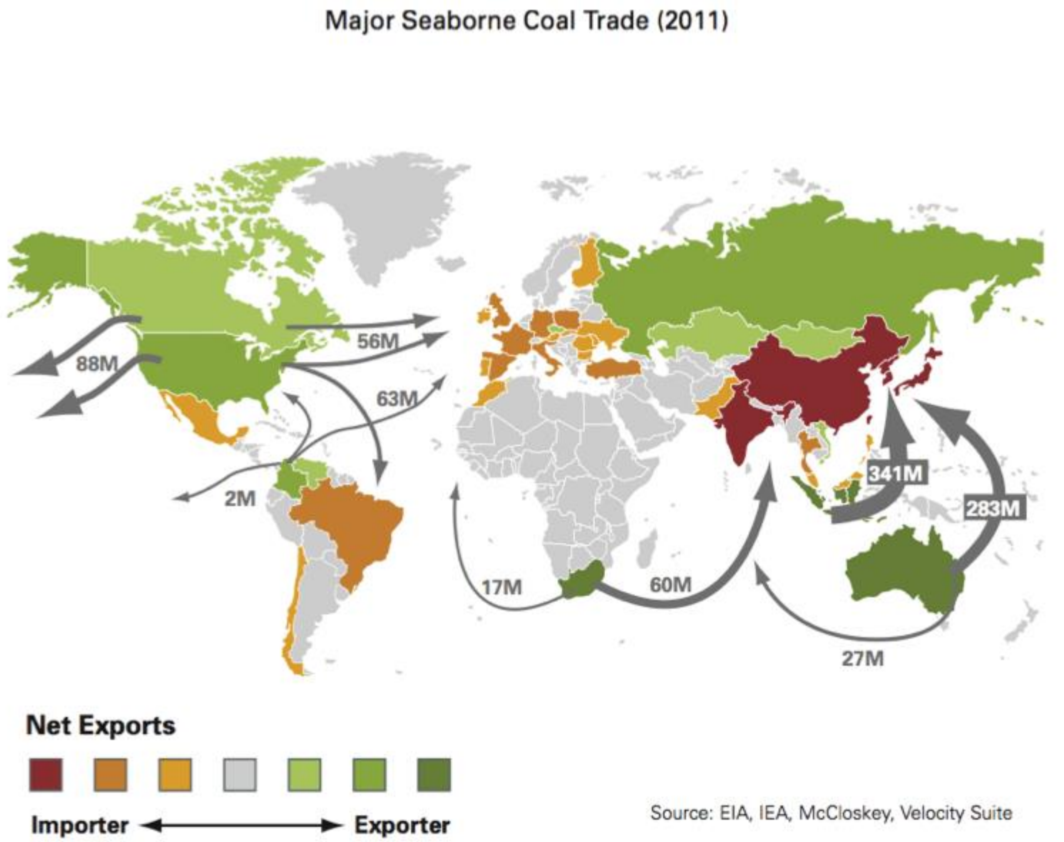
The following review will provide a general overview of coal such as its origins and formation, classification, properties and structure. The review will also provide a summary of global reserves, uses and production of coal is presented. In addition a comprehensive background to the Colombian coal will be given since the area of the case study of this project is located in the coastal area of the Department of Magdalena (Colombia). Furthermore this review will be a complete support for subsequent chapters of this dissertation.

Coal is a sedimentary rock, composed principally of a variety of accumulated organic materials, which are associated with mineral elements that become ash after a complete combustion process (Rađenović, 2006). It is also defined as a group of several ingredients made up of inorganic and organic matters. Biological components in the marsh are derived principally from plant remains, which have suffered different grades of decay and physical and chemical modification after burying (Zeng, 1997). Nevertheless, "The major disadvantages of coal come from the adverse environmental effects that accompany its mining, transport and combustion" (Katzer et al., 2007).

Coal transport by ships is a global industry with demand worldwide. Therefore vessels need to cover long distances in order to satisfy market requirements. Likewise, ports are well-organized to provide facilities to guarantee the safe transportation of coal from one place to another. However, accidents happen for many reasons and sometimes, the coal still is spilled into the marine environment. A recent example occurred with the barge number 115 in Ciénaga, Colombia. In addition, in most cases coal dust is scattered during operations as has happen in most of coal ports around the world. Moreover, Colombia is the fifth net exporter of coal with 82 Mt after Indonesia, Australia, United States and Russian Federation (IEA, 2013). Thus, risks for accidents are directly related to the volume of coal to export. In addition, due to the lack of facilities for appropriate handling of coal in ports, it could be said that the risk of spilling this mineral in operation areas is considerably high. Toxic elements contained in minerals of coal may cause potential environmental effects on soil, air and water related with its physiological toxicity, even at a low exposure level (Zhou, Liu, Fang, Wu, & Lam, 2014). Consequently, it can be said that coal could endanger marine flora and fauna. For these reasons, special measures should be taken into account in order to prevent and/or mitigate impacts of coal on the marine environment.

This paper intends to show whether coal is a marine polluting agent. To accomplish this, it is necessary to study scientific information related to coal ports around the world, keeping in mind those countries where major coal transportation takes place, such as Indonesia, Australia, the United States, Canada, China and Colombia. In fact, this topic was mainly chosen because Colombia still does not have a coal management policy under which, a clear course of action about storage, loading, unloading and transportation of coal by ships can be established in order to prevent marine pollution. This research is relevant not only because it will seek an answer to a very important problem in Colombia, but it also will help to organize a port management plan for coal operations.

According to Jaffrennou et al., (2007b) during a simulation of accidental coal immersion, it was established that despite the longtime of immersion, it was perceived that an important fraction of coal remained, absorbing light. Thus, if a spillage happens in any area where organisms depend on light to live, coal could have a negative impact on the flora and the fauna. More specifically, coal in the marine environment would impede light propagation, which would have a detrimental effect on the photosynthesis processes of many organisms such as phytoplankton. Similarly, it was clearly demonstrated in another study that sediments and seabed, inhabited by benthos organisms are clearly affected because of the disturbance of the bottom due to coal deposition (Johnson & Bustin, 2006). These studies show that coal particles affect organisms both in the water and at the seabed.



Source: ANR. (2012). *Alpha Handbook Coal. A reference guide for coal, ironmaking, electricity generation, and emissions control technologies. (pp. 144).* Bristol, VA: Alpha Natural Resources.

Figure 2. Major seaborne coal trade (2011).

2.1 Coal General Overview

2.1.1 Trade of Coal

"Coal is a global industry, with coal mined commercially in over 50 countries and coal used in over 70" (WCI, 2005). At the same time, coal covers huge distances by sea to reach markets all over the world as shown in Figure 2. Furthermore, the seaborne trade in steam coal has increased on average by about 7% each year and seaborne coking coal trade has increased by 1.6% a year during the last twenty years. In general the international trade in coal reached 1142Mt in 2011, although this amount only represents about 16% of total coal consumed since the majority of coal is utilized in the countries in which it is produced. Additionally, The Pacific market currently represents about 57% of the seaborne steam coal trade in the world, where Indonesia appears as the largest coal exporter in the world exporting over 300Mt of coal in 2011 as shown in Table 1. Australia remains as the largest supplier of coking coal in the world with 50% of world exports (WCA, 2014).

2.1.2 Coal Transportation

According to WCA (2014) the distances to be covered define the way that coal is transported as shown in Figure 3. Usually coal transportation is carried out by truck or conveyor over short distances. In addition, barges and trains are utilized for longer distances within domestic markets. As an alternative, the coal can be mixed with water to form a coal slurry and transported through a pipeline. However, the greater distances in the international coal market are covered by vessels of different sizes.

Table 1. Exporters/importers 2012.

Source: WCA. (2014, Aug). *Coal market & transportation. World Coal Association.* Retrieved Aug, 2014, from http://www.worldcoal.org/coal/market-amp-transportation/

Top Coal Exporters (2012e)

	Total *of which*	Steam	Coking
Indonesia	383Mt	380Mt	3Mt
Australia	301Mt	159Mt	142Mt
Russia	134Mt	116Mt	18Mt
USA	114Mt	51Mt	63Mt
Colombia	82Mt	82Mt	0Mt
South Africa	74Mt	74Mt	0Mt
Canada	35Mt	4Mt	31Mt

Top Coal Importers (2012e)

	Total *of which*	Steam	Coking
PR China	289Mt	218Mt	71Mt
Japan	184Mt	132Mt	52Mt
India	160Mt	123Mt	37Mt
South Korea	125Mt	94Mt	31Mt
Chinese Tapei	64Mt	56Mt	8Mt
Germany	45Mt	36Mt	9Mt
UK	45Mt	40Mt	5Mt

2.1.3 Coal Production

Currently more than 4050 Mt of coal are consumed by the world, which in turn are used in a variety of sectors such as power generation, liquid fuel, steel and iron production and cement manufacturing. For example, “Coal is currently the predominant fuel for electricity generation worldwide” (Epstein et al., 2011). China, the USA, India, Australia and South Africa are the largest coal producing countries. Additionally, only around 18% of global hard coal production is put on the international market because the remaining 82% is utilized in the country in which it is exploited. Furthermore, in 2030 global coal production is expected to reach 7 billion tons with China accounting for around 50% of the increase over this period. Coking coal is projected to reach around 624 million tons, brown coal 1.2 billion tons and the steam coal production around 5.2 billion tons(WCI, 2005).

	Mode	Approximate Capacity (tons)
	Truck	< 25
	Rail car	100 to 125
	Unit train (100 to 150 cars)	10,000 to 18,750
	River barge	1,700
	River barge tow (~15 barges)	25,000
	Mode	**Deadweight Tonnage (Dwt)**
	Handysize	> 10,000 - 40,000
	Handymax/ Supramax	> 40,000 to 60,000
	Panamax/ Post-Panamax	> 60,000 to 100,000
	Capesize	100,000 +

Source: ANR. (2012). *Alpha Handbook Coal. A reference guide for coal, ironmaking, electricity generation, and emissions control technologies. (pp. 144).* Bristol, VA: Alpha Natural Resources.

Figure 3. Coal transportation systems.

2.1.4 Coal Consumption

According to WCI (2005) coal plays an essential role in power generation and this role is expected to continue. Similarly, coal currently provides 39% of the electricity of the world and it is going to remain over the next 30 years at similar levels. Besides, over the period 2002-2030, steam coal consumption is projected to grow by 1.5% per year.

It is clear and unequivocal that Asia, which currently accounts for 54% of global consumption of coal plays the most important role, where China (Hertsgaard, 2000)is responsible for the biggest market for coal in the world. There are also many countries that do not have sufficient natural energy resources to satisfy their energy needs and, hence need to import significant quantities of this product such as Japan, Chinese Taipei and Korea.

2.1.5 Coal Reserves

Currently, the world recoverable coal reserves are estimated at 948 billion tons, which could last for 118 years at current consumption. In other words, these are the world reserves that can be economically extracted using the current technology. In spite of the fact that these reserves are spread around the world, the United States has more than all other countries (29%), followed by Russia (19%), China (14%), and Australia (9%)" (ANR, 2012).

2.1.6 Colombian Coal

According to UPME (2005) Colombia has the greatest reserves of coal in Latin America with 7.063 Million tons. In addition, it is the sixth exporter in the world with 6.3%. Colombia could guarantee more than 120 years of production with the current rate of exploitation. Owing to this fact, Colombia has sufficient coal to supply its internal demand and provide on a large scale to the international market. Moreover, coal represents 1% of the Gross Domestic Product (GDP) of Colombia. Recently, "Coal has consolidated itself as the second national exportation product after oil and it is estimated that under the current market conditions, between the 2010 and 2015, it may exceed oil exportation" (UPME, 2005).

According to Tewalt et al. (2006), most of the coal of Colombia is exported to the United States and European markets. Similarly, Colombia has been positioning itself in countries such as Guatemala, Jamaica, Dominican Republic, Puerto Rico and increasing exportations to Ecuador, Peru and Chile. The quality of Colombian coal is quite high. Hence, it is increasing its international market. For instance, in 2003 Colombia exported 45.3 million metric tons of coal, of which Europe received Europe 67%, North America 18%, Central and South America 6%, and other areas 9% (Tewalt et al., 2006).

2.2 Coal Classification, Properties and Structure

"Coal is a combustible dark-brown to black organic sedimentary rock that occurs in coal beds or coal seams" (Speight, 2012). Coal is made up primarily of carbon with variable amounts of sulphur, oxygen, nitrogen, and hydrogen and may as well contain gases and mineral matters as a portion of the coal matrix. Coals around the world show essential differences in their chemical and physical properties (Guerrero, 2012). This is linked to constituent minerals, organic matter, and the geological process, which it has undergone over the years. For instance, in a sample of three types of coals from South Africa, it was established that they had relevant differences to each other (Cabon, Burel, Jaffrennou, Giamarchi, & Bautin, 2007). As a consequence, there is no doubt that organic and inorganic components, burial pressure and thermodynamic processes undergone by coals throughout the time of formation, among others, could define their main features.

A great many of the classification systems of coal worldwide are focused on the use (Cortés, 2012) rather than science. Equally, coal is classified according to its different physicochemical properties (Achten & Hofmann, 2009). Generally, most are based on coal rank, which in turn is referred to as content of volatiles, sub-classified by calorific value, sulphur content, ash content (Ajiaco, 2011) and other variables (BGS, 2010).

For example, the American Society for Testing and Materials (ASTM) classifies coal under four different categories as shown in Table 2.

Table 2. ASTM classification system.

Source: Barranco, R. (2001). *The characterization and combustion of South American coals.* (Ph.D.), University of Nottingham.

Class/Group	Fixed Carbon Limits (% dmmf[a])	Volatile Matter Limits (% dmmf)	Gross Calorific Value[b] (BTU/Lb)	Agglomerating Character
I. Anthracitic				
1. Meta-anthracite	>98	<2	...	Non-agglomerating
2. Anthracite	92-98	2-8	...	
3. Semianthracite	86-92	8-14	...	
I. Bituminous				
1. Low Volatile	78-80	14-22	...	Commonly agglomerating
2. Medium Volatile	69-78	22-32	...	
3. High Volatile A	<69	>31	>14000	
4. High Volatile B	...	...	1300-14000	
5. High Volatile C	...	...	11500-15000	
			10500-11500	Agglomerating
I. Sub-bituminous				
1. Sub-bituminous A	...	...	10500-11500	Non-agglomerating
2. Sub-bituminous B	...	...	9500-10500	
3. Sub-bituminous C	...	...	8300-9500	
I. Lignitic				
1. Lignite A	...	...	6300-8300	Non-agglomerating
2. Lignite B	...	...	<6300	

[a] dmmf= Dry, Mineral Matter-Free Basis; [b] Moist, Mineral Matter-Free Basis. Moist refers to coal containing its natural moisture but not including visible water on the surface of the coal.

Nonetheless, the main objective of these classification systems is to classify coals according their characteristics. In relation to Barranco (2001) some investigators have pointed out two different types of coal classifications, which in turn work for different purposes namely: commercial system, which deals with factors such as particular end uses, market value, technological properties and suitability or utilization; and scientific system, concerned with aspects such constitution and basic or fundamental properties and origin. Consequently, most of the classification systems of coal include both commercial and scientific characteristics, but either of them may be taken into account for any coal classification around the world.

Coal classification systems depend on two principal chemical analyses, proximate and ultimate, which in turn provide percentages of the main chemical elements that compose the coal (carbon, nitrogen, oxygen, total sulphur and chlorine, hydrogen) and the volatile matter, relative amounts of moisture, ash and fixed carbon respectively. However, a number of other classification parameters such as technological properties of coal, including plasticity of coal, free swelling index, calorific value and fusibility of coal ash have been incorporated as second parameters to characterize coal in several fields of use (Barranco, 2001).

In addition, coal can be classified depending on the amount of carbon it contains and the amount of heat energy it can produce. It is, in other words, dependent on the length of time during which peat is heated and compressed, and becomes denser increasing the relative amount of carbon inside. Under more time and pressure, peat produces a sort of soft brown coal named lignite, which contains around 40% carbon. Moreover, lignite might become bituminous (Chudnovsky & Talanker, 2004) or soft coal over more time and under increasingly more pressure. Bituminous coal contains up to 85 percent carbon and its temperature of formation is between 100°C to 200°C. Then, under substantial pressure and heat, bituminous coal may become hard coal or anthracite, which is formed between 8 to 10 kilometers in depth, and at temperatures of 200°C to 300°C, reaching between 90 to 95 percent of carbon concentration (AGI, 2014). For instance, Colombia has coals of high rank because of high temperatures produced by local geological conditions (BGS, 2010). According to AGI (2014) the carbon concentration is also important because the greater the carbon percentage, the more energy contained by the coal.

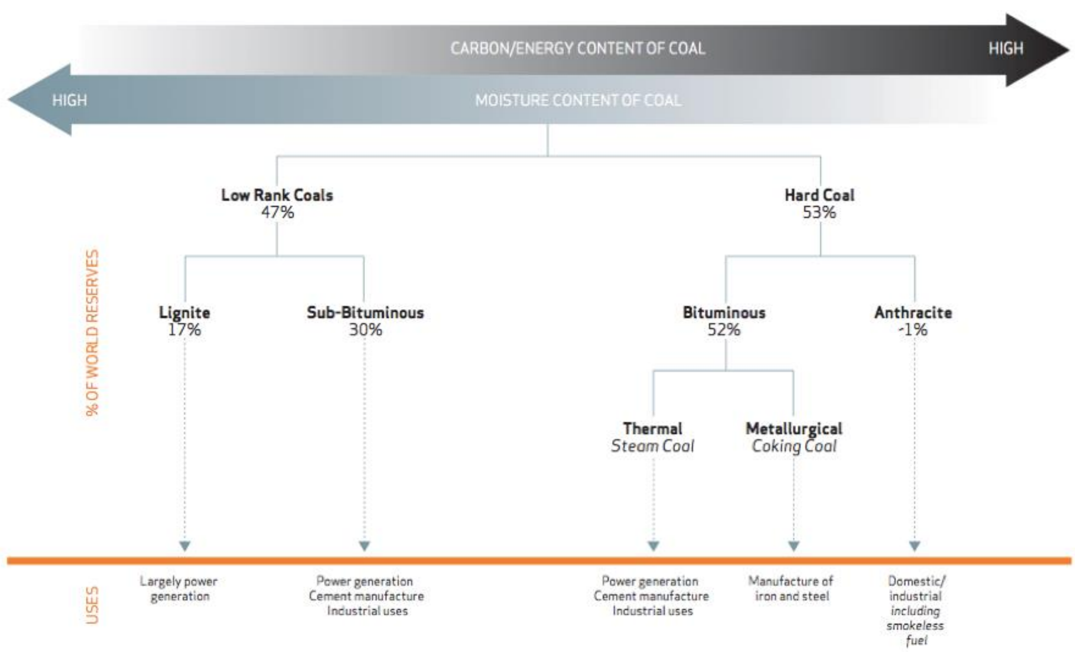
According to Barranco (2001), the American Society for Testing of Materials (ASTM) is the most commonly used of the several classification systems proposed so far. The ASTM system is hierarchical and is based upon proximate analysis, calorific value and agglomerating tendency as many others. Coals that show “a fixed carbon content greater than 69% are classified by their volatile matter and fixed carbon values. Lower rank coals are differentiated according to their calorific value. The agglomerating characteristics are used to differentiate coals of similar rank” (Barranco, 2001). At the present time, the Economic Commission for Europe (ECE) Coal Committee “is working (in close co-operation with the ICCP, the International Committee for Coal Petrology) on an international classification of coals, which will cover the geological aspect of coal resources, coal mining and industrial uses” (Barranco, 2001).

2.2.1 Rank

“The degree of change undergone by a coal as it matures from peat to anthracite known as coalification has an important bearing on its physical and chemical properties and is referred to as the ‘rank’ of the coal.” (WCI, 2005) as shown in Figure 4. Additionally, carbon, hydrogen, oxygen and volatile matters are the four main constituents of coal, hence the heating value of the coal rank is determined by these elements (Ghosh & Prelas, 2009).

On the one hand, low rank coals are generally softer, friable materials with a dull, earthy appearance such as lignite and subbituminous coals. Additionally, they have a low content of energy because they are characterized by high moisture levels and low carbon content. In addition, higher rank coals are typically stronger and harder and often have a black, vitreous luster. Consequently, they produce more energy because they have a lower moisture content and contain more carbon. Anthracite, for instance, is at the top of the rank scale. It has a lower level of moisture and, correspondingly, a higher carbon and energy content(WCI, 2005).

The following factors, among others, are used to measure coal rank (degree of coalification) (Thomas & Fariborz, 2000) namely, the vitrinite reflectance (% R_o) (Williams et al., 2008): volatile matter content, carbon and water content, temperature of maximum hydrocarbon formation during heating (T_{max}), hydrocarbon indices and calorific value.



Source: WCI. (2005). *The coal resource: A comprehensive overview of coal (pp. 48).* London: World Coal Institute.

Figure 4. Types of coal.

"Vitrinite reflectance is commonly used due to its stability over a wide range of coal ranks, its abundance and independency on kerogen types or bitumen content. It is a measure of the percentage of light reflected from the vitrinite macerals at high magnification (×500) in oil immersion" (Achten & Hofmann, 2009). In other words, the rank is a metamorphism process undergone by coal when it matures from peat to anthracite, which in turn increases, while the burial pressure (Weaver & Wood, 1994) and heat do as well (KGS, 2013). The rank is important because, together with physical and chemical properties, it defines the end-use category and the economic viability of the coal. Ultimately the price of steam coal is mainly focused on its net calorific value (BGS, 2010).

2.2.2 Coal Petrography

"Coal petrology is the fundamental discipline that deals with the origin, occurrence, physical and chemical properties, and utilization of coal" (Speight, 2012). More specifically, coal petrology is the full study of the constituents of coal (inorganics and organics) and its transformation process through metamorphism. Equally, coal petrography as a branch of coal petrology is focused on the macerals analysis, rank and composition of coal.

According to Barranco (2001), petrography is a scientific discipline whose purpose is the systematic study of coal in terms of its discrete microscopic constituents as an organic sedimentary rock. The different petrographic constituents of coal may behave distinctively under various conditions of processing. Hence, petrography plays a significant role in predicting the behavior of coal and should be taken into consideration as a fundamental constituent of any coal analysis and testing program. In fact, the petrography is an instrument for the analysis of coal genesis and evolution processes on the basis of macerals analysis. In particular, "there is a good correlation between the petrography and morphological characteristics of macerals, their origin and physic-chemistry and the stage which they have reached in the evolutionary processes" (Durand, 1980).

2.2.2.1 Coal maceral composition

“Macerals are organic substances, or optically homogenous aggregates of organic substances, possessing distinctive physical and chemical properties, and occurring naturally in the sedimentary, metamorphic, and igneous materials of the earth” (Andrew C Scott, 2002). Macerals can also be defined as the complex of biological units represented by a forest tree which crashed into a watery swamp and there partly decomposed and was macerated in the process of coal formation, did not in that process become uniform throughout but still retains delimited regions optically differing under the microscope, which may or may not have different formulae and properties.

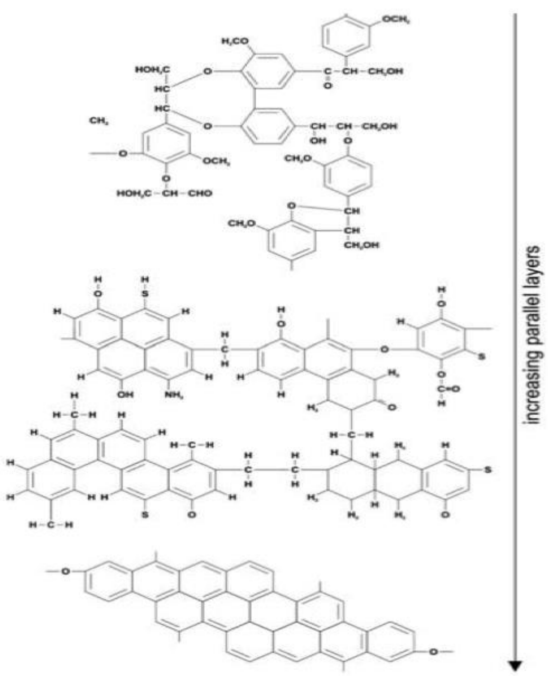
According to Achten (2009), three main families of macerals are identified in coal petrography, namely 1) Liptinite, which has a higher hydrogen-content compared to vitrinite, containing rich parts of higher plants and debris derived from lipid; 2) Vitrinite, which may be considered the standard coalification product of woody tissue, principally derived from the lignin cellulose walls of cells from higher plants; 3) Inertinite, which shows a lower hydrogen-content compared to vitrinite (Andrew C. Scott & Glasspool, 2007), and having, in general, the same origin as vitrinite but having been altered due to various reasons such as action of microorganisms, forest fires, or reworking.

2.2.3 Types of fossil organic matter

Kerogens chiefly represent about 90% of the fossil organic carbon in sediments. Additionally, they are formed by different sorts as follows: Type I is mainly formed by lipids from algal (hydrogen-rich) and of aliphatic nature; Type II is primarily derived from bacteria and marine plankton (both show a high oil and gas generating potential); Type III, the most common type of coal (humic coals, oxygen-rich), has organic matter formed from terrestrial higher plants and shows a mostly aromatic nature with low potential for oil generation. "After successive alteration stages of diagenesis, catagenesis and metagenesis, finally, a chemically uniform product (graphite) is generated" (Achten & Hofmann, 2009) as is presented in **Error! Reference source not found.**.

2.2.4 Coal Properties

“Coal is a natural occurring combustible material with varying composition and it is not surprising that the properties of coal vary considerably from coal type to coal type and even from sample within a specific coal types” (Speight, 2012). It is reasonable to assume that not only the coal composition but also the undergoing transformation over the years plays important roles in its properties.



Source: Achten, C., & Hofmann, T. (2009). Native polycyclic aromatic hydrocarbons (PAH) in coals - a hardly recognized source of environmental contamination. *Sci Total Environ, 407(8), 2461-2473.*

Figure 5. Small molecule sections of lignin (top) bituminous (middle) and anthracite (bottom).

According to Speight (2012), coal constituents can be separated into two main groups: 1) The organic fraction, which is commonly distinguished as ash after a combustion process; 2) the organic fraction, which in turn can be further subdivided into insoluble and soluble fractions as well as macerals that are microscopically recognizable. Due to this complex heterogeneity, it might be anticipated that the properties of coal can oscillate considerably, even within a specific rank of coal.

Besides, coals are separated into the following sorts depending on plastic properties and rank, namely:

- Hard coking coal, which is evaluated based on the yield, strength and size distribution of coke produced, depending on the plastic properties and rank of the coal; this coal is required for the production of strong coke.
- Weak coking or semisoft coking coals are utilized in the mixture of the coke, yet result in a coke of low quality with a possible increase in impurities; there is the possibility to interchange between semisoft coking coals and thermal coals.
- Coal used for pulverized coal injection decreases the consumption of coke per ton of pig iron as it substitutes coke as a source of heat.
- Thermal coal is principally utilized for the generation of electricity; the majority of thermal coal traded internationally is fired as pulverized fuel and oscillates in rank from subbituminous coal to bituminous coal.

Coal has several properties, including chemical as shown in Appendices (1-4) physical, mechanical and thermal, which are used in its evaluation. Nonetheless, in this research only chemical and physical properties will be considered.

2.2.4.1 Chemical properties of Coal

Coal is a sedimentary and combustible rock, which is generally characterized into subgroups known as lignite, subbituminous, bituminous and anthracite coal. From a geological standpoint lignite and anthracite are the youngest and oldest coals, respectively, with the rest of them in between. Additionally, coal is primarily formed by carbon, but also contains a low percentage of liquid, solid and gaseous hydrocarbons and/or other materials such as compounds of sulfur and nitrogen (Speight, 2012), which are important to take into account. Due to this fact, its properties change considerably from one coal to another. Coal undergoes several analyses in order to establish its main features such as its origin, composition, and rank, among others.

According to Barranco (2001), the coal classification systems are chiefly focused on two chemical analyses, proximate and ultimate. In addition, classification parameters have been introduced to characterize coal in different fields of utilization, including technological coal properties such as the fusibility of coal ash, calorific value, free swelling index and plasticity of coal, among others.

2.2.4.1.1 Proximate analysis

Proximate analysis is a process by which a determination of the "approximate" overall composition of a coal is carried out. It is described by ASTM Standard D3172(DOE, 2012) and shows the percentage of the fixed carbon by weight, moisture, volatiles, and ash content in coal (Blandon, 1999). The heating value of coal is directly proportional to the amount of fixed carbon and volatile combustible matter. Besides, the fixed carbon behaves as a principal generator of heat during the combustion process, while the high volatile matter assures easy fuel ignition. The content of the ash is also important to inform furnace grate design, volume of combustion, ash handling systems of a furnace and pollution control equipment.

2.2.4.1.2 Ultimate analysis

The ultimate analysis, which is described by ASTM Standard D3176, is used for calculations of coal combustion (DOE, 2012) and represents the absolute measurement of the elemental composition of coal excluding elements of ash. It provides (% by weight) the composition of coal by constituent elements (Cassel, Menard, Shelton, & Earnest, 2012). In particular, it determines the quantities of various chemical elements contained in coal such as carbon, hydrogen, nitrogen, and sulfur content in the coal, as well as the calculated oxygen content.

2.2.4.1.3 Atomic ratio

The ratios H/C and O/C determine the coal chemical analysis.

2.2.4.1.4 Elemental analysis

It is a measurement of the elements contained in coal, including elements of the ash.

2.2.4.1.5 Sulfur forms

It determines the sulfur forms chemically bonded in coal: organic, sulfate or sulfide.

2.2.4.2 Physical properties of Coal

"The physical properties and the behavior of coal play an important part in dictating the methods by which coal should be handled and utilized" (Speight, 2012). However, at first glance, there may appear to be little, if any, relationship between the chemical behavior and physical properties of coal yet it is totally opposite. For instance, a physical property of coal such as pore size is an essential factor in the chemical reactivity determination of the coal (Hower & Parekh, 2009). Moreover, chemical effects, which in turn result in the caking and swelling of coal have a considerable effect on the means by which coal should be "handled" either prior to or during an operation of conversion of coal (Speight, 2012).

2.2.4.2.1 Density (Specific gravity)

"The true density is usually determined by the displacement of a fluid, but because of the porous nature of coal and also because of physicochemical interactions the observed density data vary with the particular fluids employed" (Speight, 2012). Additionally, true density shows remarkable changes with the rank of the coal due to the content of carbon. This density is often called helium density because it is determined by the helium displacement, which is utilized due to its capability to penetrate into every single pore of coal without any chemical interaction.

2.2.4.2.2 Porosity and surface area

Because coal is a porous material, the surface area and porosity have a notable influence on the behavior of the coal during its mining, preparation and use. Even though porosity determines the rate at which methane can be released through the coal, there may also be some influence during preparation operation in terms of mineral removal; the major influence of the porous nature of coal is seen during the use of coal.

2.2.4.2.3 Reflectance

"The reflectance of coal is determined by the relative degree to which a beam of polarized light is reflected from a polished coal surface" (Speight, 2012). Moreover, coal may be examined in visible light by either transmission or reflectance,

> The former is a measure of light absorbance at various wavelengths and may be determined for thin sections of coal of finely divided coal pressed into a potassium bromide disk or solution of coal extracts in solvents such as pyridine of films of coal that have been deposited by evaporation of a dispersing liquid (Speight, 2012).

The reflectance of the coal is of great importance because it determines various properties of coal such as the carbonization temperature and several macerals content.

2.2.4.3 Coal Dust

The extraction, transportation and utilization of coal has generated the occurrence of coal dust in soils and sediments at or close to former coal handling facilities such as active and former mines, steel mills, foundries, power plants, rail yards and ports (Stout & Emsbo-Mattingly, 2008).

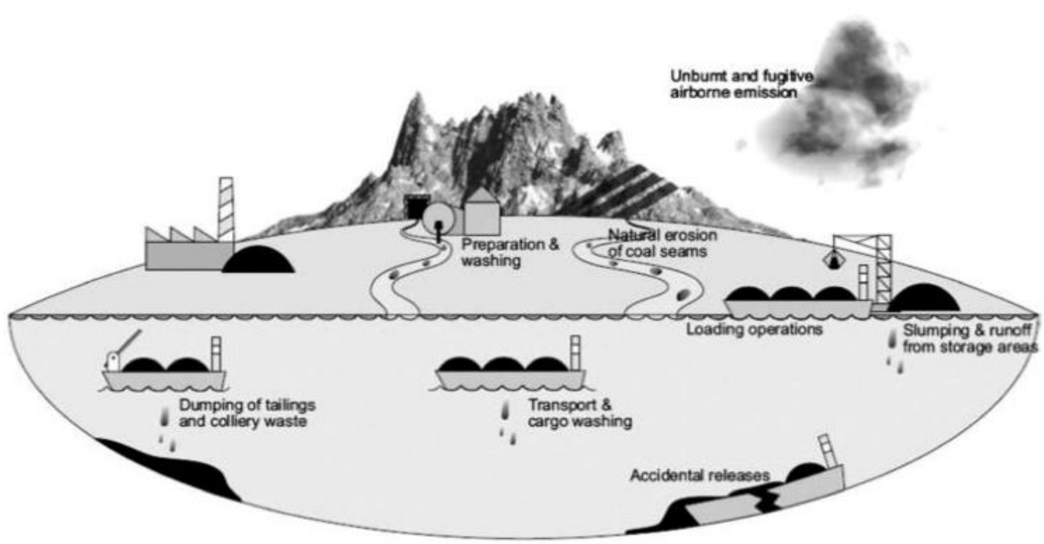
Bearing in mind that coal is a combustible rock, it should undergo various intense mechanical processes such as crushing, grinding and pulverizing in order to achieve its exploitation, transportation and use (Rohr et al., 2013). These processes produce a great deal of matter particles during mining activities called coal dust. According to Johnson et al. (2006), coal dust particles are measured between 53µm and 2360µm in size (Franco-Herrera, Grijalba-Bendeck, Ibáñez, & Daza, 2011)Moreover, coal dust is known to be highly susceptible to explosion, but this threat is managed with a low-silica limestone dust to prevent explosions.

According to WHO (1997) coal dust is a heterogeneous and complex mix having more than 50 distinct elements and their oxides. In addition, the content of minerals changes with the size of the dust particle and with coal seam. It is estimated that airborne breathable dust in underground coal mines is made up of 40-95% coal; the remaining portion consists of a variable mix of dust originating from fractured rock on the mine floor, roof or from within the coal seam.

In fact, a great many environmental concerns over the use of coal are because of the coal dust generation. Controlling the coal dust particles is quite difficult not only because they can spread easily, but also because they can be transported long distances. However, it is generally understood that coal dust contains several chemical elements and compounds such as traces of metals and polycyclic aromatic hydrocarbons (PAHs), which are dangerous to health, life and the environment, which will be explained in detail in section 2.3. Coal dust particles can reach the marine environment in so many different ways as shown in Figure 6.

2.3 Some impacts of coal on health and the environment

“Coal is an important fossil fuel used for energy generation. During coal extraction, large quantities of coal dust particles are emitted, contributing to environmental pollution” (Rohr et al., 2013). Coal, worldwide, is considered as a valuable natural resource. In addition, for its calorific value, large reserves and low cost, it is perhaps considered as a one of the most important sources of energy. However, there are also a lot of concerns about the potential effects that this material may have on life, health (Petsonk, Rose, & Cohen, 2013) and the environment. Risks usually occur by exposure during its exploitation, transport and use operations. “Extensive research has been conducted and reports written about the environmental problems associated with coal mining, processing, and combustion and related problems such as acid mine drainage, acid rain, smog, and greenhouse gas emissions” (Finkelmana et al., 2002). On the other hand, there is not much literature about human health impacts of coal use. Nevertheless, the majority of the literature has proved disturbing results related to the deterioration of health, quality of life and, as a result of many cases, death. As a consequence, it has been demonstrated on many occasions and with abundant evidence that there are health and environmental concerns due to the use of coal.



Source: Achten, C., & Hofmann, T. (2009). *Native polycyclic aromatic hydrocarbons (PAH) in coals - a hardly recognized source of environmental contamination. Sci Total Environ, 407(8), 2461-2473.*

Figure 6. Coal emission to the aquatic environment (modified after Ahrens & Morrisey, 2005).

For instance, according to Finkelmana et al. (2002), the development of lung disease in miners is a result of the inhalation of coal dust in mines. Additionally, coal dust deposited in lungs (WHO, 1997) has been associated with various diseases in exposed workers (Donbak, Rencuzogullari, Yavuz, & Topaktas, 2005). Furthermore, in US Appalachian regions elevated rates of kidney, heart and lung sickness are linked to coal mining (Hitt & Hendryx, 2010). Equally, another study has found a strong link between the risk of low-birth-weight and residence in coal mining areas (Ahern, Mullett, Mackay, & Hamilton, 2011). “Coal is also considered to be an environmental component in the multi-causal etiology of other common diseases besides cancer” (Tatu, Orem, Finkelman, & Feder, 1998).

Moreover, Balkan Endemic Nephropathy (BEN), which is an “irreversible kidney disease of unknown origin, geographically confined to several rural regions of Bosnia, Bulgaria, Croatia, Romania, and Serbia” (Finkelmana et al., 2002), has been hypothesized to be a result of long time exposure to Polycyclic Aromatic Hydrocarbons (PAHs) (Kuo et al., 2012) and other chemicals. In other words, toxic organic compounds in water, which constituents of coal probably cause this disease (Orem et al., 2007). For instance, PAHs "with two or more rings are a group of compounds of great environmental concern (Laumann et al., 2011) due to their immunotoxicity, genotoxicity, carcinogenicity, and reproductive toxicity" (Shen, Wang, Zhang, Zhang, & Wang, 2009). Therefore, "understanding the distribution, composition, and potential biological impacts is essential and important for appropriately managing PAHs levels in the environment" (Dong, Chen, & Chen, 2012).

Another study carried out in Colombia stated that “biota residing near coalmining activities in La Loma and La Jagua de Ibirico, Colombia, presents greater risk of DNA damage in blood cells than those living far from these sites (Cabarcas-Montalvo, Olivero-Verbel, & Corrales-Aldana, 2012). Likewise, rats that were exposed to coal dust underwent oxidative damage in lungs (Pinho et al., 2005).

In addition, it is now widely accepted that ecological integrity, which is defined as “the ability of environmental life support systems to sustain themselves in the face of human induced impacts” (Sieswerda, Soskolne, Newman, Schopflocher, & Smoyer, 2001), or an ecosystem, which ‘‘support(s) and maintain(s) a balanced, adaptive community of organisms having a species composition, diversity, and functional organization comparable to that of natural habitats within a region (Hitt & Hendryx, 2010) is considerably altered by coal mining as a large scale activity. This alteration affects, in the short and long term, the natural capability of the environment in the regions where it is developed because in most of the cases it threatens or endangers elements of biological diversity, such as populations, species, ecosystems, and landscapes. To exemplify, “coal mining was significantly associated with ecological disintegrity and higher cancer mortality” (Hitt & Hendryx, 2010).

One of the most surprising results was revealed in Pechorsk (Russia) where “an analysis of the actual data about the dynamics of the temperature mode of perennially frozen rocks over the territory of the Pechorsk coal basin showed changes of the average per year temperature and the depth of seasonal melting caused by various industrial factors, including pollution of the earth’s surface by coal dust” (Khilimonyuk, Pustovoit, & Filatova, 2011). The reason for this impact is the large amount of airborne coal dust because of the great mining activity. This particulate matter remains on the Earth's surface affecting the albedo on that area. Likewise, the albedo or "the ratio between the reflected part of radiation and the total of the incoming radiation to the Earth, is one of the most important parameters in the thermal balance of the Earth." Additionally, “The albedo may decrease two times or more due to pollution of a surface: snow cover, in particular, is affected by coal” (Khilimonyuk et al., 2011).

The preceding discussion indicates that coal can cause adverse health effects especially through the air and water. Similarly, the environment is also jeopardized by large scale mining (French, 1998). For instance, water quality is endangered by acid drainage, which is a natural process. Nevertheless, mining can trigger acid drainage processes. Acid drainage is a reaction that occurs with the elements in the rock (coal) on contact with air and rain (water). As a consequence, a change is caused in the characteristics of the water that drains off (INAP, 2014). More specifically, as coal contains sulphides (Chou, 2012), a natural acidification process happens in the water.

Accordingly, water increases the ability to leach other elements of the rock such as heavy metals. When the acid drainage reaches a body of water, it becomes polluted. Therefore, it endangers life, health and the environment. Regarding air pollution, the biggest concern occurs due to coal dust, which is generated because of different mechanical processes that coal undergoes. In addition, this problem occurs not only in the area of exploitation, storage and transport, but also in far distant places due to the action of the wind. A full discussion will be found later in chapter 4 regarding the impacts of coal on the marine environment.

3 AREA OF STUDY

3.1 Colombia

The Republic of Colombia is the fourth and fifth largest country of South America and Latin America, respectively. It measure approximately 1,138,910 square kilometers (including insular possessions and bodies of water), which is almost the same size as the United Kingdom, France, and Germany combined. Colombia is situated in the northwestern part of South America. It is bordered by the Caribbean Sea to the north and the Central Pacific Ocean to the west and shares international borders with five countries namely Ecuador, Peru, Brazil, Venezuela and Panama as shown in Figure 7. Furthermore, Colombia is the only country in South America with littorals along both the Pacific Ocean (1,448 kilometers) and the Caribbean Sea (1,760 kilometers), which represent a total of 3,208 kilometers of coastline. Colombia claims a 200-nautical-mile exclusive economic zone, a 12-nautical mile territorial sea, and jurisdiction over the continental shelf to a 200-meter depth or to the depth of resource exploitation (Hudson, 2010).

Source: *http://thecountrycolombia.blogspot.se*

Figure 7. Location of the Republic of Colombia.

The Andes is the most important geographical feature of Colombia. Additionally, it splits into three nearly parallel, trident-like cordilleras, which in turn divide the country from north to south between the coastal areas to the west and northeast and eastern Colombia. Owing to the fact, Colombia is divided into five main natural regions as follow: the Amazonian region, which is the tropical rainforest (selva); the llanos region, lying to the east of the Andes Mountains and bordered on the east by the Orinoco; the lowland Pacific region, which is located in the western side of the country; the Caribbean region situated in the northern part of Colombia and including the Archipiélago de San Andrés, Providencia y Santa Catalina; and the Andean region, which includes the high Andes Mountains, the inter-mountain high plateaus, and the fertile valleys that are traversed by the country's three principal rivers (Magdalena, Cauca and Caquetá).

Colombia has six major ports (San Andres, Santa Marta, Cartagena, Barranquilla, Puerto Bolivar and Tolú) on the Caribbean coast and two on the Pacific coast (Buenaventura and Tumaco) that perform port operations and maritime traffic, which transports chiefly general cargo, fuel oil, coal, passengers and fishing (INVEMAR., 2010). Besides, the risk of coal spilling into the marine environment has increased mainly due to two factors: 1) The inadequate transportation system of coal (i.e. use of barges), which has a potential to increase due to ocean atmosphere interaction, which causes strong winds, waves and currents in the Gulf of Salamanca (Colombian Caribbean Sea) defined as the study area, and 2) large amounts of this mineral mobilized daily. This was previously discussed in Chapter 1 (section 1.2).

3.2 Colombian Caribbean Coast

While the landmasses of Central and South America limit the Caribbean Sea in its western and southern borders respectively, it is also separated from the Atlantic Ocean by the Antilles Islands on its northern and eastern part. Due to that fact, it may be safe to say that the Caribbean Sea is a semi-enclosed basin. According to Andrade (2001), the Caribbean Sea consists of three main parts namely: 1) The Cayman Sea in the western part; 2) The basin of Venezuela on eastern side and; 3) The Colombia basin in the central and southwestern part as shown in Figure 8 Additionally, the Caribbean Sea is distinguished by westward currents flowing from the Lesser Antilles to the Gulf of Mexico (Alvera-Azcárate, Barth, & Weisberg, 2009). However, "the variability in circulation in the basin of Colombia is understood in its generality and a regional scale but little is known on seasonal scales, mesoscale or interannual" (C. Andrade, 2001).

Source: Andrade, C. (2001, Sep). Las corrientes superficiales en la cuenca de Colombia observadas con boyas de deriva. Rev. acad. colomb. cienc. exact. fis. nat., 25, 14.

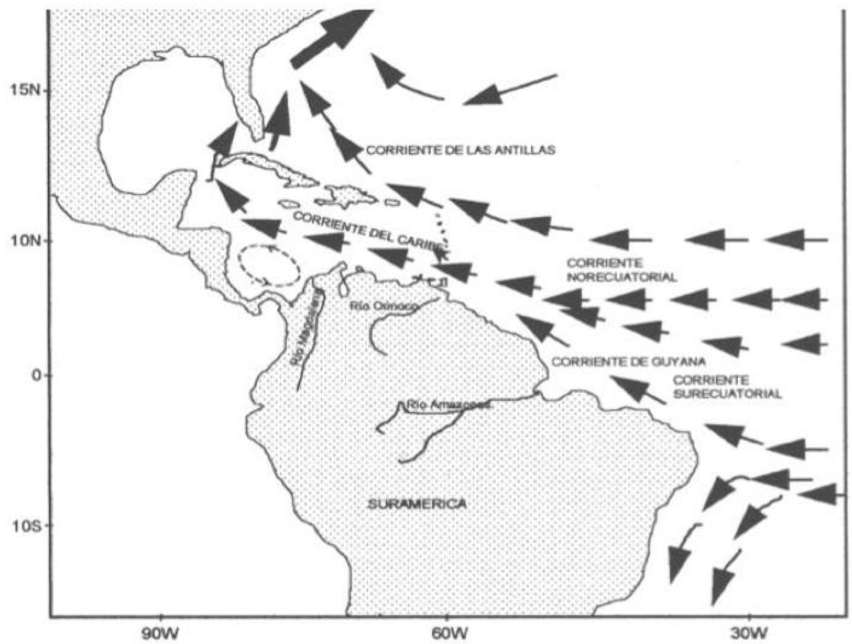
Figure 8. Caribbean Sea Basins.

In addition, although surface ocean currents in the basin of Colombia are governed by the Caribbean Current (Bernal, Poveda, Roldán, & Andrade, 2006) as shown in Figure 9, which flows northwestward to the Cayman Sea, the Southwestern Caribbean, as a semi-closed basin, presents a more complex surface circulation that seemingly is governed by a counterclockwise cyclonic direction.

Even though cyclonic and anticyclonic circulations are also observed in the Caribbean Sea, this investigation only will bear in mind the surface circulation that directly affects the study area (Gulf of Salamanca).

According to Andrade (2001), the Central Caribbean winds play an important role in the surface circulation in the Southwestern Caribbean, as they generate the force needed to cause enough stress on the surface circulation and contribute to the formation of the Gyre Panama-Colombia. For instance, Figure 10, which corresponds to November (i.e.

rainy season) of 2009, shows that as the Trade winds are weakened, the Panama-Colombia Countercurrent (Carlos Alberto Andrade, Barton, & Mooers, 2003) is diverted away from the Colombian coast in a northern direction. As a result, the cyclonic Gyre of Panama-Colombia is formed beside the Colombian coasts and reaches speeds as high as 6m/s (CIOH, 2009) at its superior side of the gyre.

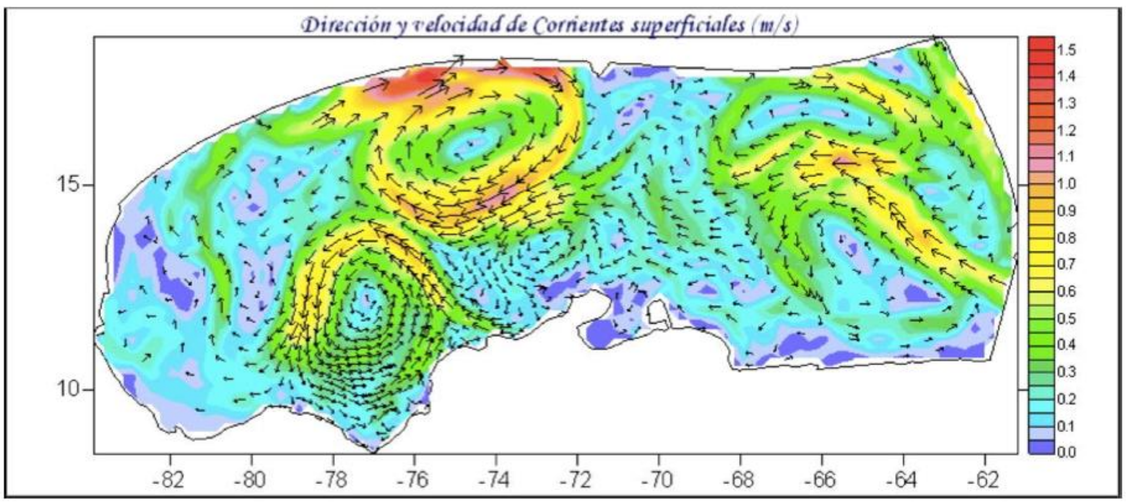


Source: Andrade, C. (2001, Sep). *Las corrientes superficiales en la cuenca de Colombia observadas con boyas de deriva. Rev. acad. colomb. cienc. exact. fis. nat., 25, 14.*

Figure 9. Surface currents in the tropical region of the Western Atlantic.

Conversely, Figure 11 shows an example of the circulation of the Caribbean Sea during the month of December in 2009 when the dry season begins (Carlos A Andrade & Barton, 2005). In particular, it can be seen that when Trade winds increase, the Panama-Colombia Gyre diverts from the Colombian coast and is confined to the

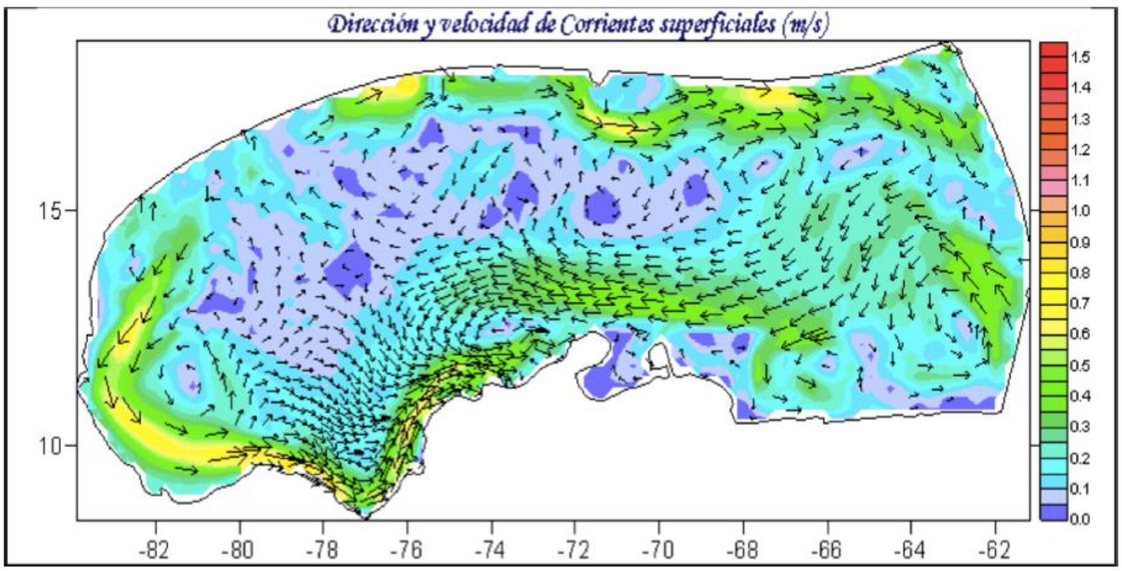
Southwest Caribbean side (Gulf of Mosquitos) (C. Andrade, 2001). As a result, the current (Countercurrent of Panama-Colombia) with an east-northeast direction reaches speeds between 0.2 to 0.4 m/s (CIOH, 2009) in front of the coasts of Panama and Colombia. This is because the masses of water are moved by strong winds and the continent acts as a barrier, which in turn obliges its movement in that direction. In fact, the circulation of the surface currents in the area of study (Gulf of Salamanca) is mainly governed by the Trade winds (Guzman-Alvis & DIAz, 1996), which cause the Panama-Colombia Countercurrent along these coasts. The local wind and current circulation are presented in Figure 12.



Source: CIOH. (2009). *Seguimiento de las condiciones meteorológicas y oceanográficas en el Caribe Colombiano 2009 (pp. 116)*. Cartagena, Colombia: Centro de Investigaciones Oceanográficas e Hidrográficas del Caribe (CIOH).

Figure 10. Behavior of the surface currents of the Caribbean Sea, November, 2009.

Additionally, the Colombian Caribbean coast is located in the northern part of the country and is approximately 1600 kilometers long (Leal, 2010), from Cabo Tiburón, in the department of Chocó at the eastern border of the Panamanian Republic, to Castilletes in the department of La Guajira on the western border of Venezuela as is presented in Figure 13. Moreover, "it is a relatively developed area with numerous small cities and five large commerce centres or ports" (Riohacha, Santa Marta, Barranquilla, Cartagena and Turbo). All the large and medium cities have the availability of land and air access from the interior of the country. This region as well has several islands of which the most important are the archipelago department of San Andres, Providencia and Santa Catalina Islands and the National Natural Park of Corales del Rosario and San Bernardo Islands, located approximately 100 kilometers southward of Cartagena.



Source: CIOH. (2009). *Seguimiento de las condiciones meteorológicas y oceanográficas en el Caribe Colombiano 2009 (pp. 116).* Cartagena, Colombia: Centro de Investigaciones Oceanográficas e Hidrográficas del Caribe (CIOH).

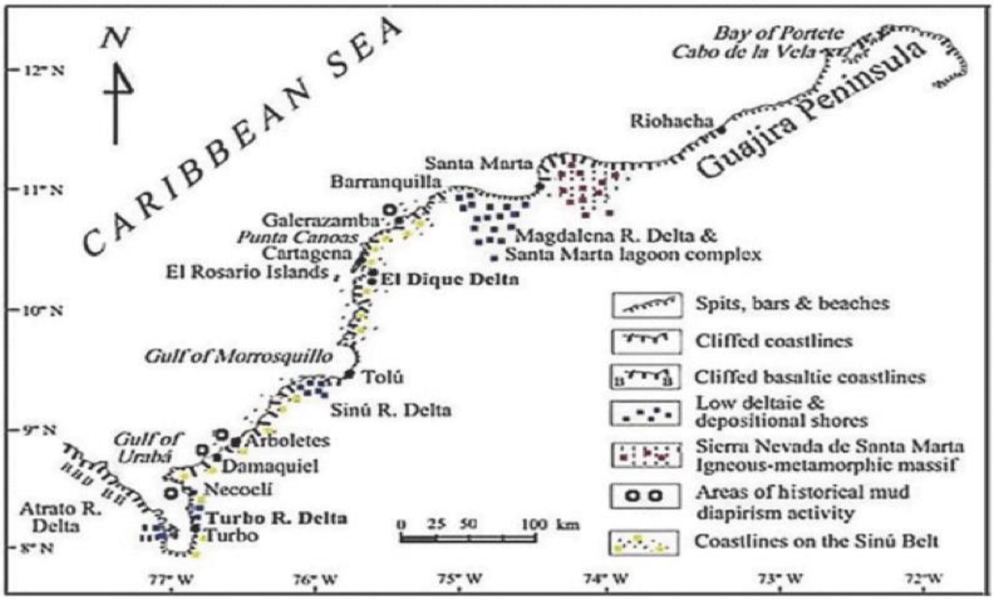
Figure 11. Behavior of the surface currents of the Caribbean Sea, December, 2009.

Besides, the Caribbean region is situated at the intersection between The Nazca, Caribbean and the South American plates. "The Caribbean coast of Colombia is a mosaic of geologic and physiographically varied units composed of both extensive low-relief plains and medium to high relief rocky massifs" (Correa & Morton, 2010). The Caribbean coastal zone is crossed by several active tectonic plaques that define its main morphostructural units and this area has been classified as an intermediate seismic risk zone.

Source: Franco-Herrera, A., Grijalba-Bendeck, L., Ibáñez, J., & Daza, J. (2011). *Carbón, clima, playas y peces. El caso de la zona costera del departamento del Magdalena. Universidad de Bogotá Jorge Tadeo Lozano, 2011*. Bogota, DC.

Figure 12. Summary of the antagonistic circulation tendency between of wind fields (green vectors) and surface currents (yellow vectors) in the coastal area of Magdalena Department, considering location of the coal ports (white arrows).

On the one hand, the climate of the Caribbean coast depends on the displacement of the Inter Tropical Convergence Zone (ITCZ) (C. Andrade, 2001) the high pressure center of the Azores (CIOH, 2009) and on particular orographic influences of the massif of the Sierra Nevada de Santa Marta. In general, there are two dry periods (December-April and July-September) and two rainy periods (April-May and October-November) (Correa & Morton, 2010).

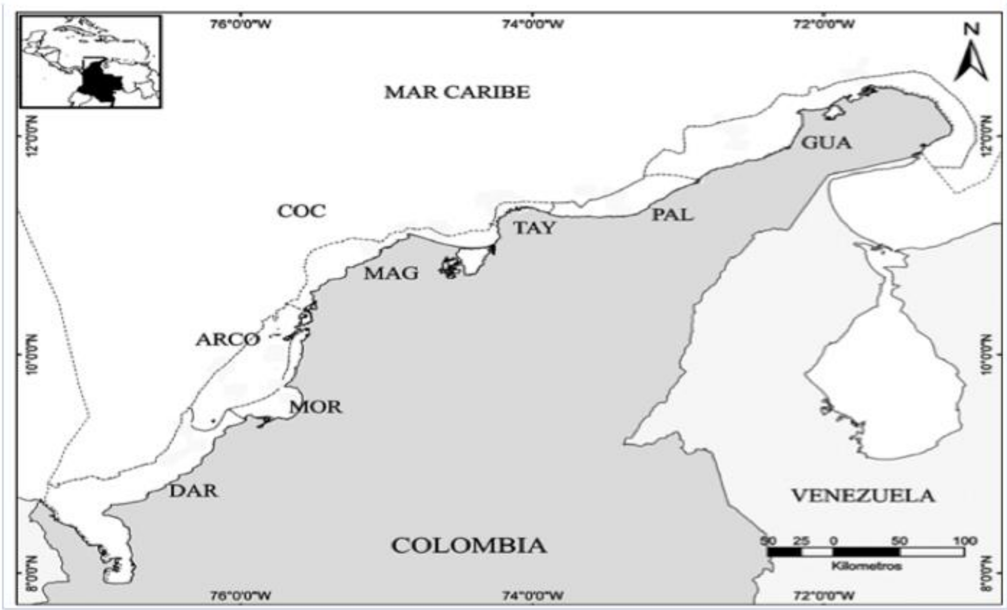


Source: Correa, I., & Morton, R. (2010). *Caribbean coast of Colombia Encyclopedia of the World's Coastal Landforms (pp. 259-264)*

Figure 13. Caribbean Coast of Colombia.

In addition, maximum values of annual precipitation for this region do not surpass 2.500 mm, where the maximum value occurs at the massif of the Sierra Nevada de Santa Marta (yearly mean 2.000 mm) and the minimum value is within the dessert region of the Guajira Peninsula. At the same time, average air temperatures for the Caribbean coast remain less than 24°C (Correa & Morton, 2010), which in fact shows that the temperature in this tropical part of the country does not change significantly throughout the year as in the subtropical stations (C. Andrade, 2001).

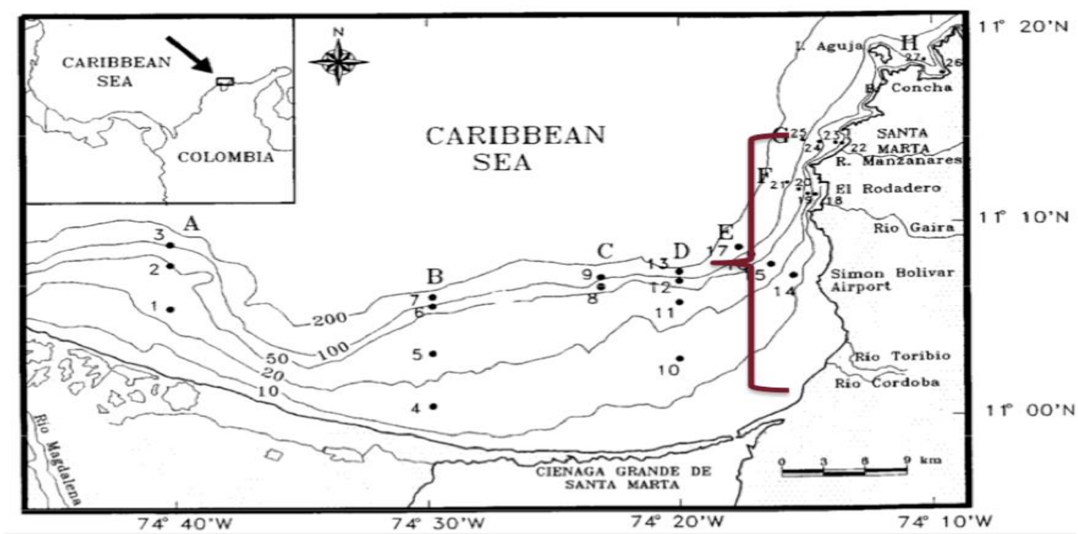
Furthermore, the Caribbean coast presents mixed semidiurnal tides, the maximum reached amplitudes of which are approximately 60 cm. Furthermore, trade winds predominate chiefly from the NE to SW, south of the Sierra Nevada de Santa Marta and from the east, north and northwest, at the Guajira Peninsula. As a consequence, the "net longshore drift along the Caribbean Coast of Colombia has a dominant southward component, minor reversals to the northeast occurring during the rainy periods when south winds become dominant in some sectors" (Correa & Morton, 2010).



Source: Florez-Romero, P., Montoya-Cadavid, E., Reyes-Forero, J., & Santodomingo, N. (2007). *Briozoos cheilostomados del Caribe colombiano. Bol. Invest. Mar. Cost., 36, 229-250.* (Arco)

Figure 14. Ecoregions at the Colombian Caribbean: Guajira (GUA), Palomino (PAL), Tayrona (TAY), Magdalena (MAG), Morrosquillo (MOR), Darien (DAR), Coral Archipelagos (ARCO), Oceanic Caribbean (COC).

According to Florez et al (2007), the Colombian Caribbean coast is divided into nine ecoregions, which were defined by geomorphology, ecology and coastal landscape, namely Guajira, Palomino, Tayrona, Magdalena, Darien Morrosquillo Archipelagos Reefs and Caribbean Oceanic as shown in Figure 14. Additionally, all these ecoregions extend from the shoreline to the isobath of 200m, except Morrosquillo, which extends up to 40m, and the ecoregion of the Oceanic Caribbean, which extends in front of all the other ecoregions (Florez-Romero, Montoya-Cadavid, Reyes-Forero, & Santodomingo, 2007). In other words, in the northern part are situated the Guajira and Palomino ecoregions respectively, which have as their main features a wide continental shelf, masses of highly energetic water and high productivity due to a seasonal upwelling. Tayrona is formed by the foothills of the Sierra Nevada de Santa Marta, which in turn has as its main features a narrow continental shelf, a sharp decline of the continental slope and several bays. The ecoregion of Magdalena, Morrosquillo and Darien, are characterized by many reef formations and are strongly influenced by inland swamps and river discharges. Several coral archipelagos are located in front of the Morrosquillo ecoregion, which is characterized by abundant reef formations (Florez-Romero et al., 2007).



Source: Guzman-Alvis, A. I., & DIAz, J. M. (1996). *Soft Bottom Marcobenthic Assemblages off Santa Marta, Caribbean Coast of Colombia. Caribbean Journal of Science, 32, 176-186.*

Figure 15. The area of study (western coastal zone, see the brown open bracket) in the Gulf of Salamanca (Colombian Caribbean Sea). Modified after Guzman-Aviz & Diaz, 1996.

3.3 Gulf of Salamanca (GoS)

The Gulf of Salamanca is located between 11°00' and 11°10' N and 74°12' and 74°40' W, in the Colombian Caribbean Sea (Guzmán-Alvis & Díaz, 1993) as shown in Figure 15**Error! Reference source not found.**. In addition, it is defined as the coastline between Bocas de Cenizas (Department of Atlántico) and Cabo de Agujas (Department of Magdalena). It is called Gulf of Salamanca due to the Salamanca Island, which is located in that area (Cortes & Campos, 1999). This zone is characterized by a narrow continental shelf, which is narrow at the beginning in front of Bocas de Cenizas (mouth of the Magdalena river) but widens, reaching its maximum amplitude in front of the Cienaga Grande de Santa Marta (16.5km) (Guzmán-Alvis & Díaz, 1993) and narrows again near the Sierra Nevada de Santa Marta. Additionally, this area is known for its high complexity and vulnerability to pollution due to anthropogenic factors. For example, this area includes the Parque Isla de Salamanca, the Sanctuary of Fauna and Flora Cienaga Grande de Santa Marta (CGSM) and Tayrona National Park (PNNT). The Gulf of Salamanca has rich marine fauna and flora, for instance, more than 120 fish species, more than 150 crustacean and mollusc species in the epifauna, more than 110 infauna families (amphipods, polychaetes, molluscs, etc.) (Luis Orlando Duarte & García, 1999), and the most important small pelagic fish is the Atlantic anchovy (Cetengraulis edentulum), which represents more than 55% of total landings (Luis O Duarte & Garcıa, 2004).

Furthermore, the PNNT is important due to its ecosystems of beaches, lagoons, mangroves, rocky coastline, coral formations, seagrass bed and algal congregations (PNNC, 2006). On the other hand, the CGSM is considered as a strategic ecosystem (C. B. Garcia, Duarte, & Von Schiller, 1999), which is formed of wetlands ecosystems, mangrove, swamps, rivers and streams, among others (INVEMAR, 2012). Besides, it is one of the most important wetland complexes in the country, not only in terms of its richness of flora and fauna, but also from a socio-economic standpoint (BRC, 2011) because the population of the region depends on its fishery resources and agricultural activities.

Source: Patiño, E. (2013, Dec). *La historia sucia del carbón. El Heraldo. Retrieved from http://www.elheraldo.co/economia/la-historia-sucia-del-carbon-137522*

Figure 16. Coal ports in the Gulf of Salamanca (Colombia).

In addition, its protected area together with the Salamanca Island are the nucleus areas of the Reserve of Biosphere declared by UNESCO (Severiche & Barreto, 2013) and Ramsar Wetland in Delta Estuary Cienaga Grande de Santa Marta (MAVDT, 2004). Nevertheless, between the CGSM and the PNNT, there are 4 coal ports (Viloria, 2006) as shown in Figure 16, which are defined as the area of study. By the above, it can be asserted that these ports could endanger all the ecosystems contained in this area.

4 IMPACTS OF COAL ON THE MARINE ENVIRONMENT

The 1982 United Nations Convention on the Law of the Sea (Article 1.1.4) defines marine pollution as “the introduction by man, directly or indirectly, of substances or energy into the marine environment, including estuaries, which results or is likely to result in such deleterious effects as harm to living resources and marine life, hazards to human health, hindrance to marine activities, including fishing and other legitimate uses of the sea, impairment of quality for use of sea water and reduction of amenities" (Nordquist & Nandan, 2011). Besides, “marine contamination changes the physical, chemical, and biological characteristics of the oceans and coastal zones, and potentially threatens marine organism, ecosystems, and biodiversity and affects thus the quality and productivity of marine ecosystems” (Wilhelmsson, Thompson, Holmström, Lindén, & Eriksson-Hägg, 2013). In this regard, the contamination causing damage or negative impact on marine ecosystems is called pollution. The final impact of pollution on marine resources depends on the intensity (acute or chronic), form and location of the contamination. Likewise, some species, ecosystems and marine environments are more sensitive to pollution than others.

“Coal is an organic sediment that contains inorganic constituents such as heavy metals, which can be very toxic to marine organisms” (Siboni, Fine, Bresler, & Loya, 2004). Therefore, it could be hypothesized that unburnt coal could be a marine pollutant. For example, a study carried out at the contiguous coal shipping terminal at the Lambert’s Point Docks in Norfolk, Virginia confirmed that “along with the particulate coal, arsenic associated with the coal is also enriched in these soils by 2 to 20 times over upper crustal abundances, and by ~five times over estimated background soil As concentrations” (Bounds & Johannesson, 2007). It has long been recognized that “arsenic is one of the most toxic elements and has serious effects on plants, animals and human health” (Kucuksezgin, Gonul, & Tasel, 2014). In addition, although coal dust was not toxic to the mangrove tree *Avicennia marina* (Naidoo & Naidoo, 2005), it "significantly reduced photosynthesis of upper and lower leaf surfaces by 17–39%" (Naidoo, 2004). In other words, coal dust does not allow that these mangroves reach an appropriate growth and development at Richards Bay Coal Terminal in South Africa compared to plants in environments free of coal dust. Appendix 5 contains a comprehensive background on unburnt coal effects, including leaching, on aquatic organisms.

There are several manners by which unburnt coal could reach the marine environment such as open pit mining, accident releasing coal, spill during coal loading or transport, among others as shown in Figure 6 (Achten & Hofmann, 2009). It is difficult based on the available scientific literature to establish exactly the extent of threat to different marine organisms unburnt coal may have. In fact, there is little hard evidence in the literature that ascertains that unburnt coal is a marine pollutant. Only a handful of studies have deeply addressed this problem. Actually, this issue requires full consideration, thus it should be approached from many different perspectives. From a physical point of view, for example, it is important to take into account turbidity as a direct effect and the change in the environment as an indirect effect when unburnt coal comes in contact with seawater. In contrast, from a chemical standpoint, there is no doubt that acidity generation, chemical oxygen demand, metal and metalloids and Polycyclic Aromatic Hydrocarbons (PAHs) (Eide, Berg, Thorvaldsen, Christensen, & et al., 2011), among others, play an important role. Even though there is an increasing tendency in the environmental literature that PAHs from coal are not bioavailable (Yunker, Perreault, & Lowe, 2012), there is no consensus in the scientific community (Deepthike et al., 2009).

4.1 Physical Impacts

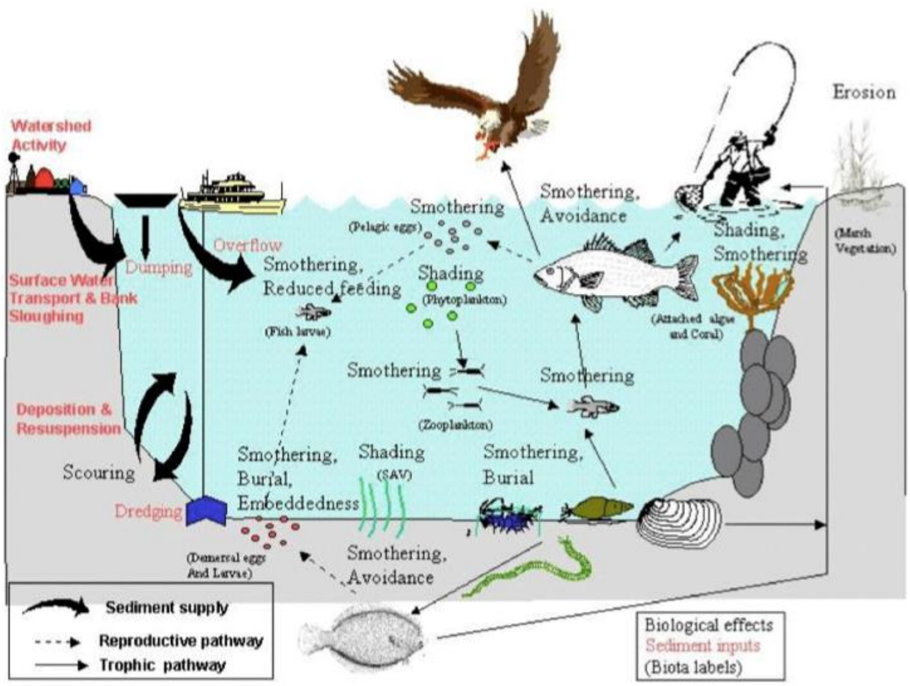
At first glance, physical impacts of unburnt coal on the marine environment may appear to be negligible. But in fact, the converse is very true. This mineral can produce significant impacts on many species in the marine environment, on which further discussion will be found later in this section dealing with coal's effects on the marine environment. For example, an experiment with Dungeness crabs during a 22 day period in seawater, which contained a mix of coal dust and sand, up to a maximum of 50% coal-to-sand by weight established that coal dust is not toxic to this species after that period. It could, however, be noted that a continuous increase of coal dust particles on gills to higher concentrations of coal, up to 50% by weight, could reduce the area available for breathing (Hillaby, 1981). Another example is that the coal dust, which is produced by several mechanical processes undergone by coal became the most abundant of the particulate pollutants in sediments at Severn Estuary in UK (Allen, 1987).

4.1.1 Coal as a Suspended and Bedded Sediment (SABS)

"SABS are defined as organic and inorganic particles that are suspended in, are carried by, or accumulate in water bodies" (EPA, 2006). A conceptual model of biological effects of SABS in estuaries is shown in Figure 17.

> "SABS can have effects in a wide range of habitats, including streams, rivers, lakes, estuaries, wetlands, coral reefs, and beaches. Excessive sediments in aquatic systems contribute to increased turbidity leading to altered light regimes which can directly impact primary productivity, species distribution, behavior, feeding, reproduction, and survival of aquatic biota. Reduced light can reduce production of phytoplankton, submerged aquatic vegetation, and the zooxanthellae in corals. Reduced light and increased turbidity can also affect

the feeding ability and movements of fish, especially larval fish" (Berry, Rubinstein, & Melzian, 2003).



Source: Berry, W., Rubinstein, N., & Melzian, B. (2003). *The biological effects of Suspended and Bedded Sediment (SABS) in aquatic systems: A review. Narragansett,* RI: United States Environmental Protetion Agency.

Figure 17. Conceptual model of biological of suspended and bedded sediments in estuaries.

Sediments require important attention not only because they affect all forms of life in water bodies, but also because they influence some abiotic factors such as turbidity, temperature and even in dissolved oxygen. Therefore, it is required that they maintain a proper balance so that changes that occur in the amount of sediment are properly assimilated by the aquatic environment and, in particular, by each inhabiting species. "Quantifying natural sedimentation rates and the susceptibility of macro fauna by functional groups is one key towards understanding environmental impacts" (Miller, Muir, & Hauser, 2002). For example, small changes in the amount of sediment could affect the penetration of light due to the absorption and scattering caused by particles of sediment to the light wave. In other words, the obstruction of the light could generate a reduction in primary production as a function of primary producer organisms, which essentially require the light in order to perform their photosynthesis and thus generate their own food (Robertson, Scruton, Gregory, & Clarke, 2006). Consequently, primary consumers are also affected due to reduction in primary production or decrease in biomass, which on the other hand replicates in primary consumers that are affected by the decrease in the population of primary producers and so on. The obstruction of light could also determine the distribution of primary producers in the water body. Phytoplankton for instance, usually moves to where it can find a better light source. As a consequence, primary consumers also move because they need to find their food (phytoplankton). Consequently, it is reasonable to assume that the distribution of species could be an indirect effect of the dynamics of sediment in water bodies. The different impacts caused by sediments to species basically depend on factors such as duration of exposure, severity, features of the particle (type, size, angularity, etc.), time of occurrence, magnitude or severity of the event, and strength of water currents, among others.

Coal particles in water perform very similarly to most of the suspended and deposited particles on the bottom (UJTL, 2013). It could be said its physical effect on marine organisms is quite similar to other sediments within the same medium (Ahrens & Morrisey, 2005).

“Because of its generally lower specific gravity, larger particles of coal will be transported further by a given current speed than particles of quartz sand, potentially producing greater abrasion” (Ahrens & Morrisey, 2005). Additionally, coal particles remain longer on the surface and within the water column than particles of sand, which means that organisms that live in these spaces would suffer more abrasion. In addition, “although the seawater renewal induces a dispersion of suspended particles, currents and waves are likely to make big coal chunks roll and thus erode, which would lead to a continuous production of fine suspended particles" (Jaffrennou et al., 2007b). For example, primary producers would be affected significantly because of turbidity, which causes absorption and scatter of light (UJTL, 2013). As a result, these organisms could not perform their photosynthesis. This scenario where they would not create their own food would of course endanger their survival. Primary consumers would be affected as well due to decrease in biomass (INVEMAR, 2013). It is because primary producers are the base of the trophic chain, meaning that, depending on the degree of damage to the base of the chain also higher levels would be affected.

A previous study (Hyslop & Davies, 1998; as cited by Ahrens & Morrisey, 2005), suggested that "coarse sediment acted as an abrasive and may have been responsible for the removal of components of the ephemeral algal flora of shores receiving colliery waste in northeast England." Furthermore, "turbidity in many coastal environments is caused mainly by resuspension of bottom sediments through wave action" (Anthony, Ridd, Orpin, Larcombe, & Lough, 2004).

According to Berry et al. (2003), it is recommended to divide this topic into taxonomic groups for better understanding.

4.1.1.1 Aquatic Plants

Aquatic plants generally suffer detrimental impacts due to coal. For instance, light penetration could be reduced by suspended particles from coal (J. A. Garcia & Ahrens, 2014). As a consequence, it would impede the growth of algae, which would also affect the fauna that depends on these algae (Jaffrennou et al., 2007b). Besides, "light availability affects both biomass and community structure of phytoplankton and submerged vegetation. Phytoplankton and macrophytes compete for solar energy not only with each other, but also with all the other light absorbing component of the water body" (Van Duin et al., 2001). In addition, according to Schiel et al. (2006), sediments have deleterious effects on microalgae. For example, a 100% in mortality of the *brown algae Hormosira* increased due to smothering by a thick layer of sediments.

Indeed, “even after a long time, a significant percentage of the light was still absorbed by the particles. As a consequence, in case of an accident occurring in an area where species sensitive to light live, the presence of suspended coal particles could have a detrimental effect on the flora and hence on the fauna” (Jaffrennou et al., 2007b).

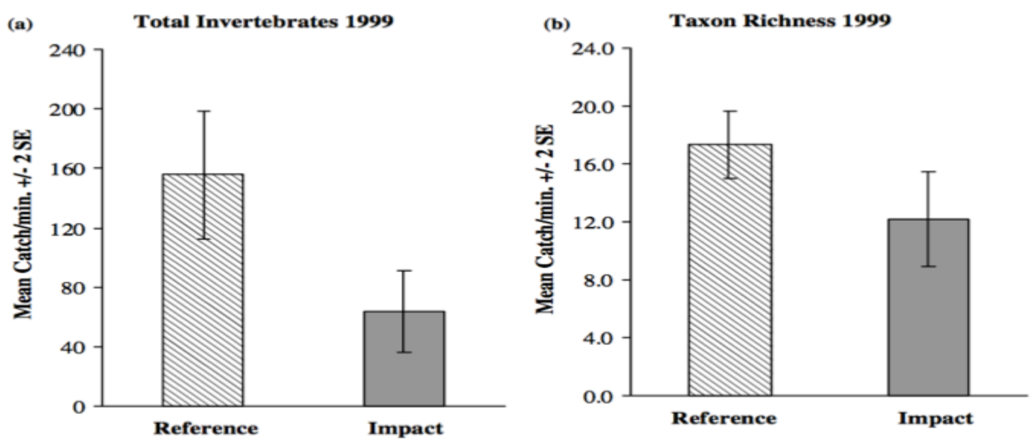
4.1.1.2 Benthic Invertebrates

Although there are very few published studies on the effect of coal on the marine environment, there is a substantial body of knowledge about impacts of sediments on benthic invertebrates, which is of great importance because coal particles in the water have quite similar behavior to SABS (UJTL, 2013).

> Elevated levels of SABS have been shown to have wide ranging effects on pelagic and benthic invertebrates. Effects can be classified as having a direct impact on the organism due to abrasion, clogging of filtration mechanisms thereby interfering with ingestion and respiration, and in extreme cases smothering and burial resulting in mortality. Indirect effects stem primarily from light attenuation leading to changes in feeding efficiency and behavior (i.e., drift and avoidance) and alteration of habitat stemming from changes in substrate composition, affecting the distribution of infaunal and epibenthic species (Berry et al., 2003).

In addition, catastrophic spills of hazardous materials can cause effects on aquatic environments in the short-term. For instance, it has been demonstrated that coal spills in streams result in reduction of food chains, decrease in fish populations, and decrease in both species abundance and aquatic invertebrate densities. These impacts have been generated by two different mechanisms. Firstly, physical perturbations, such as increased smothering of substrates (Alcaro et al., 2002) and turbidity (Grijalba & Franco, 2012) by coal can have deleterious effects on invertebrates with higher requirements of oxygen, exposed gills, or preference for of low-sediment environments. Secondly, chemical effects of coal reduce the quality of water because of increased Fe(OH)x levels and a decline in pH, which occur when coal is introduced into the water (D. S. Cherry, Larrick, Guthrie, Davis, & Sherberger, 1979). Consequently, it kills fungus and bacteria, negatively affecting the decomposition of detritus or biofilm where invertebrates feed, which are affected in an indirect manner (Harper & Peckarsky, 2005).

To exemplify, a previous study carried out in a small stream in New York, USA, investigated effects on invertebrate benthic community due to unburnt coal spillage. Even though the study does not demonstrate whether cleaning and channelization operations could have minimized or increased impacts, since first samples were collected after the coal was removed by bulldozer, results have shown that taxon richness and lower total invertebrate abundance were considerably reduced after the coal spilled into the stream as shown in Figure 18. Equally, the abundance of total invertebrate grazers was essentially reduced Figure 19. Furthermore, this study confirmed that invertebrate grazers underwent the worst impact. Basically, their mortality or migration was caused by smothering (direct impact) and / or changes in water quality due to contact with coal particles (indirect impact). Particularly, invertebrates such as mayflies, stoneflies and sedge-flies (*Ephemeroptera, Plecoptera*, and *Trichoptera*), are sensitive to turbidity. Therefore their presence in a water body has been used as an index of water quality (the EPT index) (Harper & Peckarsky, 2005), Figure 20. All in all, it can be noted that these communities and organisms suffer significantly harmful impacts because of coal.

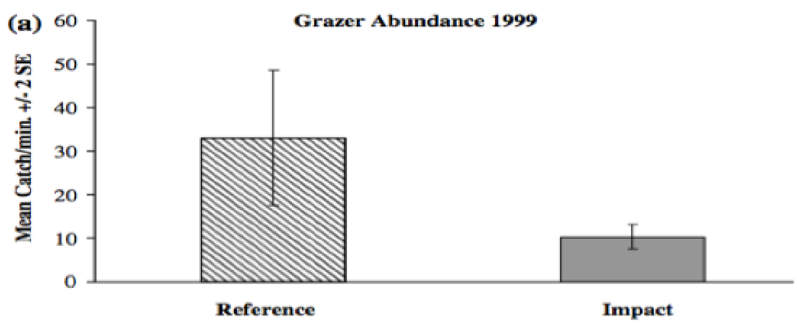


Mean abundance of total invertebrates and taxon richness (±2SE) at reference site (upstream) and impact site (downstream) of the coal spill in 1999. (a) Total abundance (Z1 = 2.32, df = 1, p = 0.020) and (b) taxon richness (Z1 = 2.49, df = 1, p = 0.013) were significantly reduced at the impact site of the coal spill in 1999.

Source: Harper, M. P., & Peckarsky, B. L. (2005). *Effects of pulsed and pressed disturbances on the benthic invertebrate community following a coal spill in a small stream in northeastern USA. Hydrobiologia, 544(1), 241-247.*

Figure 18. Total invertebrates and taxon richness.

According to Johnson & Bustin (2006), benthos, made up of organisms inhabiting the sea bottom and in sediments, are the most greatly affected because of the perturbation of the bottom caused by deposition of particles of coal. Anoxic conditions, due to the depletion of oxygen during the degradation process of organic matter (including coal) results in the production of sulphides of hydrogen in the sediments. This is probably the most deleterious effect on the benthic fauna and flora. Additionally, bottom micro invertebrates carry out a very essential ecological contribution. For instance, herrings and juvenile salmon feed on benthic invertebrates. As a consequence, damage to the benthos not only causes major implications for invertebrate populations, but also for creatures that feed in the benthic environment. Another example can be observed because of the spilling of unburnt coal in the Gulf of Salamanca gulf (Colombia) in 2013, which in turn produced an extreme case of smothering and burial that resulted in mortality of benthic organisms, residing on the bottom of study area (Gulf of Salamanca) such as mollusks, crustaceans, and annelids. This situation as well would affect other species such as commercial fish, which mainly depend on these benthic organisms (INVEMAR, 2013).



Mean (±2SE) abundance of invertebrate grazers was significantly reduced at the impact site (Z1 = 2.81, df = 1, p = 0.005).

Source: Harper, M. P., & Peckarsky, B. L. (2005). *Effects of pulsed and pressed disturbances on the benthic invertebrate community following a coal spill in a small stream in northeastern USA. Hydrobiologia, 544(1), 241-247.*

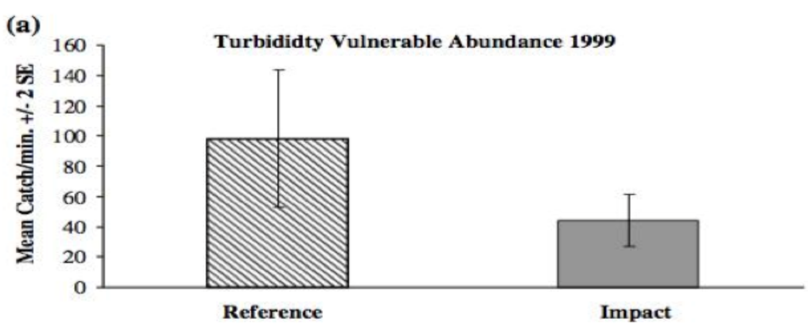
Figure 19. Grazer abundance

4.1.1.3 Fish

According to UJTL (2013), as soon as a coal spill occurs into the marine environment the fish swim migrate to other areas. However, there are of course situations when this is only partly true. It depends for instance, on such factors as the life stage of the fish (eggs and larvae are not very mobile), concentration, and time of exposure. The duration of exposure and concentration are two essential factors to consider in relation to effects caused by suspended sediments on fish and aquatic organisms. These effects are categorized depending on their severity of impact on fish and aquatic life as shown in Table 3 according to rank and impact.

According to Newcombe et al. (1991), effects are grouped into three classes, namely: lethal, sub-lethal and behavioral.

- Lethal effects kill individual fish, reducing the population and damaging the capability of the ecosystem to produce future individuals. This group as well includes reduction in size population due to behavioral and sub-lethal effects.
- Sub-lethal effects cause injury to an organism's physiology or its tissues, but without causing acute death. However, such damage may very well lead to mortality in a longer-term perspective.
- Behavioral effects are explained as changes in activity patterns compared with an organism in a not perturbed environment. Also behavioral effects may result in mortality due for example to decreased ability to find food/prey or affected ability to avoid predators.



The abundance of invertebrates belonging to orders vulnerable to turbidity (Trichoptera, Megaloptera, Ephemeroptera, and Isopoda) was significantly reduced at the impact site (Z1 = 2.00, df = 1, p = 0.045).

Source: Harper, M. P., & Peckarsky, B. L. (2005). *Effects of pulsed and pressed disturbances on the benthic invertebrate community following a coal spill in a small stream in northeastern USA. Hydrobiologia, 544(1), 241-247.*

Figure 20. Turbidity vulnerable abundance.

There is a wide range of information about several effects caused by suspended sediments on aquatic life. For example, the periphyton is highly affected by suspended sediments. (Periphyton is the term for the community of algae, bacteria and fungi that grow on various surfaces in the aquatic environment). In particular, the suspended sediments significantly reduce the penetration of light, thereby affecting its growth and biomass. As a result, many invertebrates and fish larvae and juveniles, which depend primarily on periphyton as food can be affected. For example, some benthic invertebrates may suffer not only impacts on producers (i.e. algae), but also considerable damage to their respiratory organs due to suspended sediments.

Table 3. Ranking of effects of suspended sediments on fish and aquatic life.

Source: Newcombe, C. P., & Macdonald, D. D. (1991). *Effects of Suspended Sediments on Aquatic Ecosystems. North American Journal of Fisheries Management, 11(1), 72-82.*

Rank	Description of effect
14	>80 to 100% mortality
13	>60 to 80% mortality
12	>40 to 60% mortality, severe habitat degradation
11	>20 to 40% mortality
10	0 to 20% mortality
9	Reduction in growth rates
8	Physiological stress and histological changes
7	Moderate habitat degradation
6	Poor condition of organism
5	Impaired homing
4	Reduction in feeding rates
3	Avoidance response, abandonment of cover
2	Alarm reaction, avoidance reaction
1	Increased coughing rate

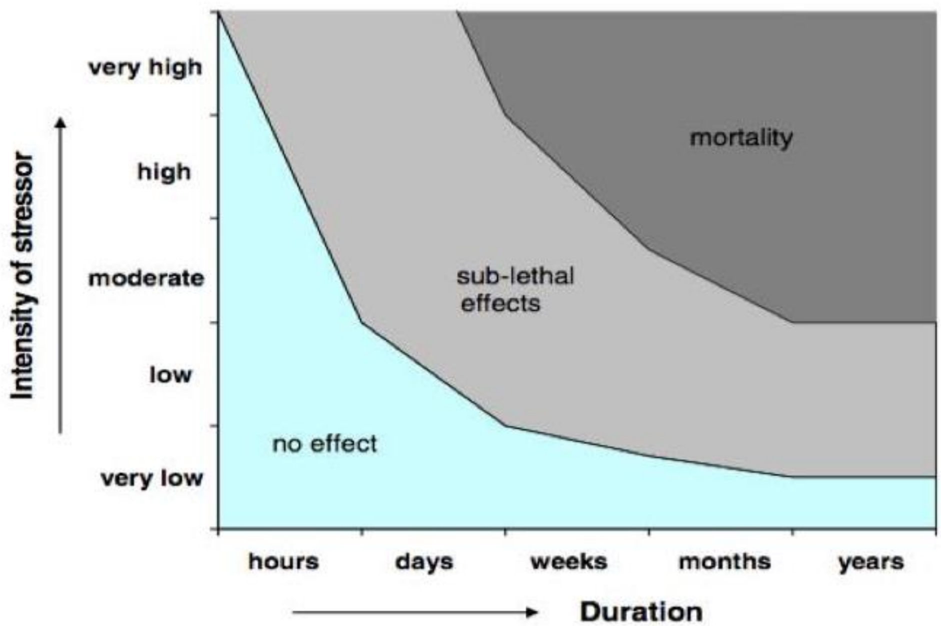
Filter feeder invertebrate organisms are also directly impacted by increased suspended sediment in water bodies (Schiel, Wood, Dunmore, & Taylor, 2006). These organisms suffer obstruction of feeding structures, which diminish their feeding efficiency. Consequently a decrease in growth rates, an increase in the level of stress and in some cases the death of these organisms may occur. There are many examples of the effects of suspended sediment on salmon, from reduced amount of food available to decreased growth rate (Araujo, 2011), and the ability to resist some diseases (Newcombe & Macdonald, 1991). It is equally true that growth and survival of juvenile salmonids can decrease by deposition of fine sediment, even at low concentrations (Suttle, Power, Levine, & McNeely, 2004). In addition, turbidity "is associated with a number of physiological effects in Pacific salmon. Physiological stress in fishes may decrease immunological competence, growth, and reproductive success" (Cara Berman & Bolton, 2001).

Franco-Herrera et al. (2011) also studied fish of commercial interests within the same research area (the coastal zone of the department of Magdalena). For this purpose a total of 294 individuals were collected, corresponding to 22 families (benthic, demersal and pelagic), 41 genuses and 49 species during five months of sampling (from February to June). The results confirmed the presence of coal particles greater than 10mm in size in the stomachs of only two individuals, which belonged to the species *Cynoscion jamaicensis* and *Lutjanus synagris*. These particles were easily identified by their characteristics. However, 245 of the 294 samples showed presence of some black particles that, by their size (less than 63µm), were classified as dust. These were found in hipoaxial muscles, gonads, liver, intestines, and stomach (Franco-Herrera et al., 2011). The study did not establish the potential impacts of coal particles, which were found inside the stomachs of the 2 individuals. Neither did it explain why it could not clear identify the black particles found in most of the investigated specimens or their potential effects on the health of the fishes.

4.1.1.4 Coral

According to Loiola et al., (2013) human activities have destroyed approximately 20% of the coral reefs in the world, while another 35% are threatened. Increasing the input of sediment and organic matter in marine systems has been indicated as the major cause of coral reef degradation worldwide. Increasing the concentration of sediment in the water may affect coral in various ways. Sediment particles and associated organic matter in suspension cause reduction of luminosity, which directly affects the photosynthetic performance of zooxanthellae associated with the coral polyp. The zooxanthellae exist in an endosymbiotic relationship with the coral animals and they are responsible for up to 90% of the nutrition supply to the coral (Loiola, Oliveira, & Kikuchi, 2013). Besides, "light is the primary resource for most of Earth's biological communities and provides the basis for the high productivity of tropical coral reefs" (Anthony et al., 2004). Therefore light reduction is one of the most important sediment related effects on coral. Light decreases exponentially with depth because of the process of attenuation, i.e. the scatter and absorption of light by particulate solids, dissolved matter and water molecules. Turbidity and sedimentation (Díaz-Pulido, Sánchez, Sven, Díaz, & Garzón-Ferreira, 2012) not only affect the reproductive success and probability of recruitment, as well as the survival and settlement of coral larvae but also influence the survival of adult corals" (Erftemeijer, Riegl, Hoeksema, & Todd, 2012). A conceptual relationship between the duration and intensity of a stress event on corals is shown in Figure 21. Likewise, Appendix 6 shows different responses of coral communities to sediments and turbidity. Moreover, inorganic sediments settling onto reef surfaces and suspended in the water column can determine the distribution and abundance of coral species through both sub-lethal and lethal effects. In the worst scenarios, settlement of inorganic particles onto live coral surfaces can provoke tissue necrosis and death because of the combined effects of smothering (Gleason, 1998). For instance, a study about the impacts of sediment on reefs was carried out in a small reef at Cahuita, Costa Rica. Results showed that sediment stress slows coral growth, and affects colony morphology and age distribution (Risk, 2014).

Another study was carried out by Florez et al. (2010) in the Tayrona National Park (Granate and Chengue bays) as shown in Figure 22, the main goal of which was to investigate the impacts of increases in sediments on the early development of *Dictyota spp*. and *Lobophora variegata* algae population in two bays (Granate and Chengue bays) of the Tayrona National Park. The results concluded a negative effect of sediments on the early stages of macroalgae and coral reefs through four main mechanisms: abrasion, nutrient access reduction, changes in substrate and smothering. As an example, an increase in sedimentation and its resulting mechanisms caused a reduction of the recruitment and growth of the *Dictyota* algae (Flórez-Leiva, Rangel-Campo, Díaz-Ruiz, Venera-Pontón, & Díaz-Pulido, 2010).



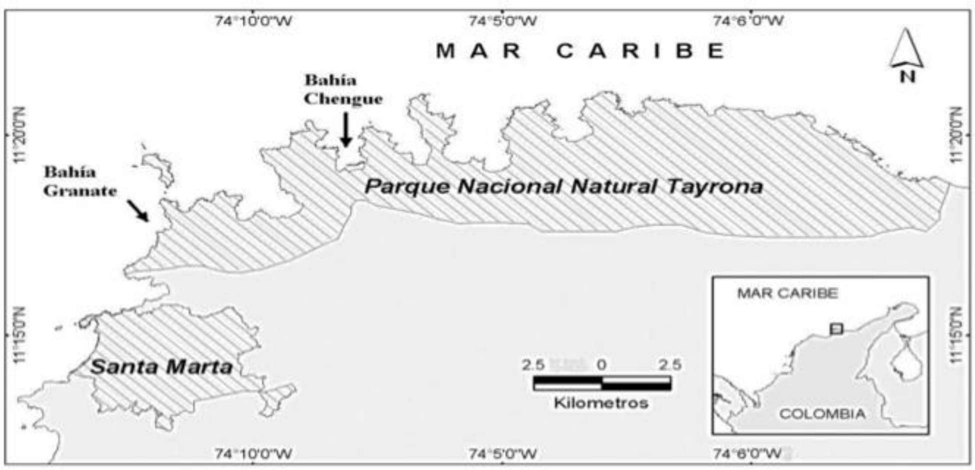
Conceptual relationship between the intensity and duration of a stress event and the risk of sublethal and lethal effects on corals. This graph shows the general relationship between the magnitude of an increase in turbidity or sedimentation above background levels (vertical axis), how long it lasts (horizontal axis) and the onset of (sub)lethal effects on corals. Actual thresholds will vary by location based on typical ambient conditions, sediment properties (e.g. grain-size) and the sensitivity of the coral species.

Source: Erftemeijer, P. L., Riegl, B., Hoeksema, B. W., & Todd, P. A. (2012). *Environmental impacts of dredging and other sediment disturbances on corals: A review. Mar Pollut Bull, 64(9), 1737-1765.*

Figure 21. Stress event on corals.

4.1.1.5 Aquatic-dependent Wildlife

There are just a few studies on the effect of sediments on aquatic-dependent wildlife. In addition, it is reasonable to assume that aquatic-dependent wildlife can evade more of the direct impacts of sediments. The main reason is because of its mobility capability. For instance, an eagle can move longer distances than an invertebrate or fish. Moreover, birds and mammals can choose clear water instead of turbid areas. Nevertheless, they can be affected by turbidity or high levels of water sediments. An example is the seabirds' migration due to lack of prey (food) due to turbidity. Although they can return, sediments can cause short-term impacts or even long-term impacts.



Source: Flórez-Leiva, L., Rangel-Campo, A., Díaz-Ruiz, M., Venera-Pontón, D., & Díaz-Pulido, G. (2010). *Efecto de la sedimentación en el reclutamiento de las macroalgas Dictyota spp. y Lobophora variegata: un estudio experimental en el Parque Nacional Natural Tayrona, Caribe colombiano. Bol. Invest. Mar. Cost. , 1, 41-56.*

Figure 22. Chengue and Granate Bays (Tayrona National Park).

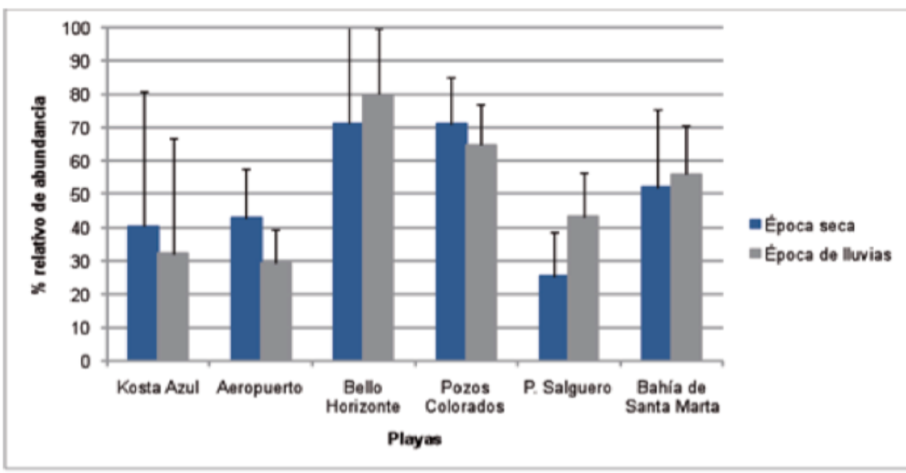
4.1.2 Coal Deposited on Beaches

“Just after coal immersion, a cloud made of fine coal particles will be carried away by the water flow, and this cloud could reach the shoreline, settling on beaches and creating some black stratum as it was observed on the San Lorenzo beach after the Castillo de Salas accident in Spain” (Jaffrennou et al., 2007b).

A mineralogical analysis of sediments in beach areas in the Magdalena department was conducted in 2009 using the densitometry method, and concluded that there was no presence of coal particles on monitored beaches. It is also important to note that all four coal ports of the Magdalena department are located within this area (Morales & Guzman, 2009). Additionally, a similar study carried out in 2010 in the same area revealed the presence of particles of coal in concentrations less than 0.1% by weight (Morales & Guzman, 2010). However, a previous study (INVEMAR, 2009a, and 2009b, cited by Morales et al., 2010), confirmed the presence of particles of coal between 0.2-0.9% in weight (Morales & Guzman, 2011). Furthermore, another study concluded that the particles of coal in the same area were less than 1% (Gamez-Ramirez, 2012).

A previous study (Nieves et al., 1992; cited by Franco-Herrera et al., 2011) confirmed that the accumulation of coal dust on the beaches of the coastal zone of the Magdalena Department is due to storage and shipment of coal, which negatively affects tourism in these areas. Due to a lack of appropriate port facilities for storing and transporting coal, a significant amount of coal dust particles are dumped into the environment (air and water), which represents an impairment in the quality of the beaches in the Magdalena Department (LIMCOL, 2014).

According to Franco-Herrera et al., (2011) in a study carried out in order to assess the levels of coal concentrations in the coastal area of the Magdalena Department (Colombia) in 2009, coal particles were found on all the beaches analyzed during both the dry season and the rainy season as shown in Figure 23. Furthermore, this research suggests that the coal found on the studied beaches probably has two origins: 1) coal operations performed on the docks which are located within the study area and/or; 2) bonfires, which are carried out by tourists and fishermen with some frequency on the beaches. However, the coal generated by barbequing is easy to distinguish from that from the ports because it is wood charcoal. This study confirmed that the concentrations of coal particles between 1000 and 250µm in size were above 20% during the dry season. In addition, the more remote beaches from the coal ports, that is, Bello Horizonte and Pozos Colorados were those that presented the highest relative abundance (in weight particle of coal / total weight of sediment x 100) with respective values of 71.25 +/- 32.17% and 71.12 +/- 13.95%. Similarly, the relative abundance in this size for the Santa Marta Bay beach was 51.99 +/- 23.7%, most of which corresponded to the bonfires mentioned above. Moreover, the beaches that presented results of relative abundance below 40% were Puerto Salguero, Kosta Azul and Airport (Franco-Herrera et al., 2011).

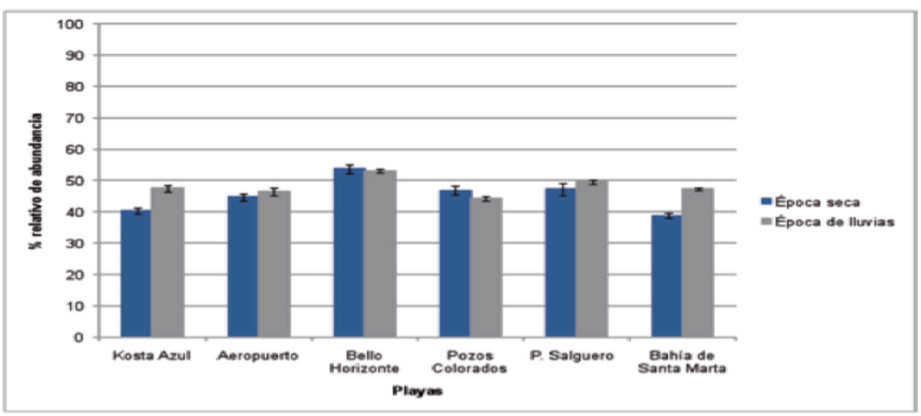


Source: Franco-Herrera, A., Grijalba-Bendeck, L., Ibáñez, J., & Daza, J. (2011). *Carbón, clima, playas y peces. El caso de la zona costera del departamento del Magdalena. Universidad de Bogotá Jorge Tadeo Lozano, 2011. Bogota, DC.*

Figure 23. The (y-axis) represents the relative percent of abundance (i.e. coal particles weight / total weight of sediment x 100) of coal particles between 1000-250µm in size. During dry (blue bars) and rainy (gray bars) seasons, in evaluated beaches (x-axis) Error bar: Standard deviation.

Therefore, this study shows that the beaches of Bello Horizonte (80.06 +/- 19.85%) and Pozos Colorados with (64.80 +/- 12.33%) are those that present the highest particle concentrations of coal between 1000 and 250µm in size. Moreover, the beach of Santa Marta has a very particular situation mentioned above and the rest of the beaches maintain levels of coal particles concentrations below 40%. According to the author, the beaches showed the same behavior during the wet season. Therefore, the study suggests that these results were due almost certainly to the slight difference between the sampled months during the development of this research (Franco-Herrera et al., 2011).

Similarly, as shown in Figure 24 the percentages of relative abundance (numbers of coal particles / total number of particles x 100) for coal particles with sizes between 250 and less than 63µm did not show a significant variation between the beaches during the dry season. Nonetheless, the study established that the beaches of Bello Horizonte (52.94 +/- 0.57), Pozos Colorados (44.25 +/- 0.78) and the bay of Santa Marta (47.45 +/- 0.41%) stand again as the places with higher concentrations of coal particles of this size (Franco-Herrera et al., 2011).



Source: Franco-Herrera, A., Grijalba-Bendeck, L., Ibáñez, J., & Daza, J. (2011). *Carbón, clima, playas y peces. El caso de la zona costera del departamento del Magdalena. Universidad de Bogotá Jorge Tadeo Lozano, 2011. Bogota, DC.*

Figure 24. The (y-axis) represents the relative percent of abundance (i.e. coal particles weight / total weight of sediment x 100) of coal particles between 250 to < 63µm in size. During dry (blue bars) and rainy (gray bars) seasons, in evaluated beaches (x-axis). Error bar: Standard deviation.

The study shows that the beaches that have higher levels of concentration of carbon particles (Bello Horizonte and Pozos Colorados respectively), are not those that are closest to the carboniferous ports as could be reasonably assumed. In addition, this research also points out that the oceanographic and climatological factors are vectors for the transportation of coal dust into the water and sediment of the beaches. Therefore, that would explain the main reason why most of the coal particles do not settle on beaches closest to the coal ports. Nevertheless, this phenomenon in turn coincides with wind and current circulation patterns in the study area, which were previously shown in Figure 12 (Franco-Herrera et al., 2011). In other words, it can be observed in this figure that PRODECO and DRUMMOND docks are located southward of the mentioned beaches. Moreover, the surface currents flow in a northeast direction (countercurrent of Colombia and Panama) along the coast. As a result, it might be safe to say that the distribution of coal particles on the studied beaches is mainly governed by this phenomenon. However, the process of sedimentation of coal particles is quite complex; it depends not only on the ocean current but also on the size of the particles. Additionally, according to (Jaffrennou et al., 2007b), smaller particles travel longer distances and in turn take more much time to settle (Lucas & Planner, 2012). Additionally, wave agitation, turbulence and upwelling currents highly affect the sedimentation process of the coal particles (Johnson & Bustin, 2006).

A recent study was carried out in order to quantify the mineral coal on Colombian Caribbean beaches (Department of Magdalena). It is important to highlight two aspects: First, samples were collected before and after the spilling, which allowed calculation of impacts (if any) produced by the coal spill in the Gulf of Salamanca.

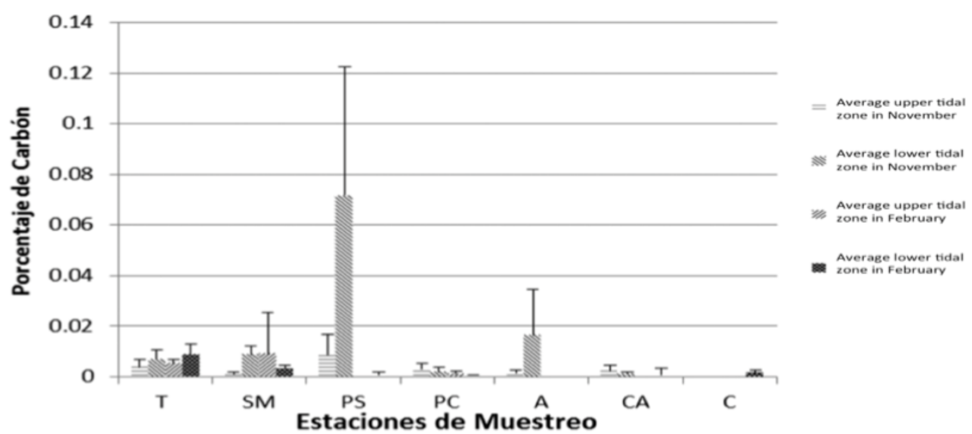
Second, the area of study is the same as that investigated by Franco et al. (2011) who obtained results of coal significantly higher in the interest area. The studied beaches as shown in Figure 25 are the same as those analyzed by Franco et al., 2011. Likewise, this investigation asserts that, when compared, the results of the November 2012 and February 2013 showed no significant differences in the percentages of coal on the beaches before and after the spill of 12 January 2013. In both, the percentage of coal sampled was below 0.02 % for all stations and the two tidal levels, except for Playa Salguero (November 2013 0.071%) as shown in Figure 26. By the above, it was concluded that the percentage of coal in the sampled beaches of the Magdalena department could not be greater than 0,071% (J. A. Garcia & Ahrens, 2014).

Source: Garcia, J. A., & Ahrens, M. (2014, Nov). *Cuantificación del carbón mineral en las playas del Caribe colombiano (Departamento del Magdalena). Acta Biologica Colombiana, 19, 101-112.*

Figure 25. Location of the sample stations (white stars) and main coal ports (red balloons). Coastal zone of Magdalena Department (Modified from Google Earth, 2012, Gulf of Salamanca).

Consequently, the dark material conforms to an inorganic mineral other than coal, which is poorly-combustible at 550 ^{o}C and heavier than coal (density greater than 3 $g.cm^{-3}$). Additionally, it was established that this mineral as a part of the sediment was found in high concentration in all of the sampled beaches. For instance, the beaches of Santa Marta and Cienaga were those that showed the highest percentages (regarding the total weight 78% and 63.2%) respectively. The other beaches had values less than

32% as shown in Figure 27. This study showed one of the most surprising results of less than 0.1% of coal in the beaches of the Magdalena department. Hence, this investigation questions the previous study carried out by Franco et al., (2011) who asserted that the same beaches presented up to 80% of coal based mainly on visual qualitative criteria. Nonetheless, according to Garcia et al. (2014), there are various possibilities to explain the low coal concentration on the studied beaches. Firstly, a coal particle can be transferred long distance basically due to its low density and small size; this movement in turn is governed by the weather conditions of the area (dry and rainy seasons). Secondly, the coal particle is composed of carbon, which is not easy to degrade during transportation. Therefore, it can be accumulated in a different area far away from its origin (J. A. Garcia & Ahrens, 2014).

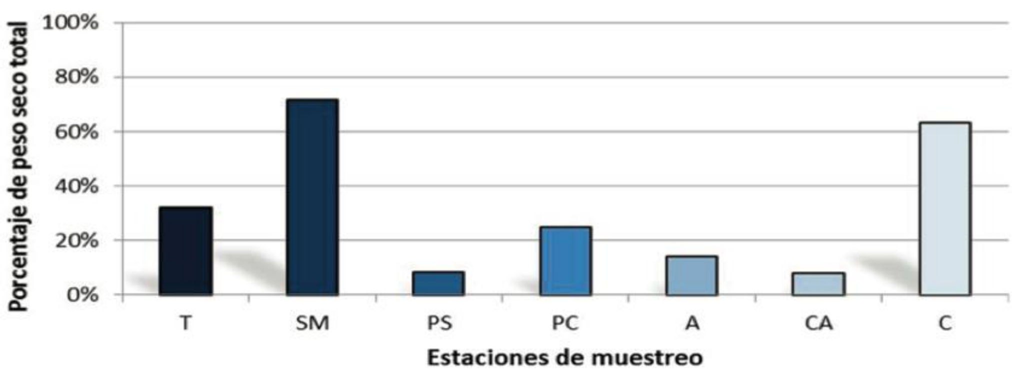


The (y-axis) Percentage of sediments of coal on the Magdalena Department beaches in November 2012 and February 2013. Error bars represent ± 1 standard deviation (n=3). (x-axis) Sampling stations: (T: Taganga; SM: Santa Marta; PS: Playa Salguero; PC: Pozos Colorados; A: Aeropuerto; CA: Costa Azul; C: Cienaga).

Source: Garcia, J. A., & Ahrens, M. (2014, Nov). *Cuantificación del carbón mineral en las playas del Caribe colombiano (Departamento del Magdalena). Acta Biologica Colombiana, 19, 101-112.*

Figure 26. Percentage of coal in the Department of Magdalena beaches.

Due to the high turbulence and hydrodynamic forces in that area, lighter particles as coal cannot settle. In other words, coal is lighter than other minerals on the beach such as ferromagnesian and quartz. As a result, it can be expected that coal particles have a much slower speed of sinking according to the Stokes' law, which states "velocity is proportional to the size of fragments and their density difference with water, divided by the viscosity of the medium" (J. A. Garcia & Ahrens, 2014). For example, the density of a coal particle is less than 2 g.cm-3, which represents a difference in density with seawater much smaller than that of a particle of quartz in the same medium (J. A. Garcia & Ahrens, 2014). As a consequence, the probability is increased that coal particles will remain in the water column or gradually settle on the bottom in deeper waters due to local currents. This study not only demonstrated that the dark materials found on the studied beaches are inorganic minerals of high density, poorly-combustible, other than coal, but also it proved that there was no increase in levels at the beaches due to the coal spilled in January 2013.



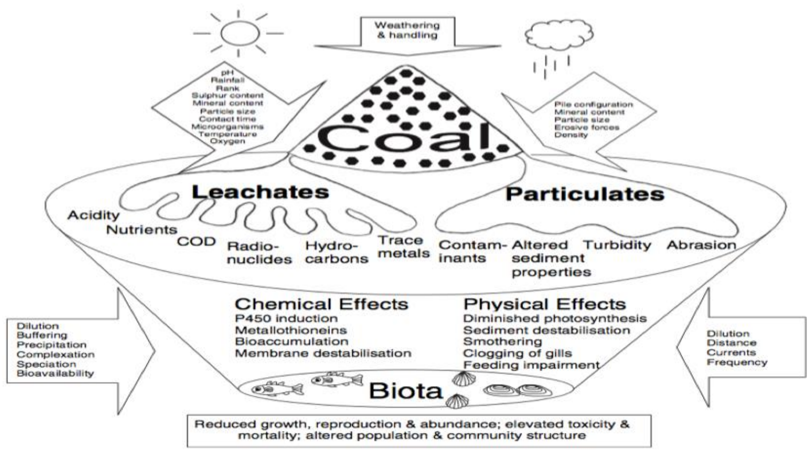
Percentage of total dry weight (y-axis) of minerals with dark appearance other than coal and density >3 g.cm-3 in sediments of beaches of Magdalena in November 2012 (T, SM, PS, PC, A, CA stations) and February 2013 (station C). Only one sample of each beach was analysed (T: Taganga, SM: Santa Marta PS: Playa Salguero, PC: Pozos Colorados, A: Aeropuerto, CA: Costa Azul, C: Cienaga).

Source: Garcia, J. A., & Ahrens, M. (2014, Nov). Cuantificación del carbón mineral en las playas del Caribe colombiano (Departamento del Magdalena). Acta Biologica Colombiana, 19, 101-112.

Figure 27. Percentage of minerals other than coal in Magdalena Department beaches.

4.2 Chemical Impacts

“Unburnt coal can be a significant source of acidity, salinity, trace metals, hydrocarbons, chemical oxygen demand and, potentially, macronutrients to aquatic environments, which pose potential hazards to aquatic organisms” (Ahrens & Morrisey, 2005). Unburnt coal contains organic and inorganic material, trace metal, metalloids and polycyclic aromatic hydrocarbons (PAHs) (C. Zhang, Zhang, Yang, & Liu, 2007). Hence, these constituents of coal could leach in contact with seawater as shown in Figure 28, which makes coal a potentially hazardous material. It could endanger the marine environment and its organisms. The leaching process depends on several factors, of which the most important are the specific chemical characteristics of the coaland oxidizing agents. Furthermore, acidification depends on the sulphur content of coal, which is why the chemical composition of coal plays an important role, which means that coals with high sulphur content are more likely to generate acid leachate.



Factors affecting behaiviour and effects of unburnt coal in the marine environment (COD=chemical oxygen demand). Influential factors in boxed arrows.

Source: Ahrens, M., & Morrisey, D. (2005). Biological effects of unburnt coal in the marine environment. *Oceanography and Marine Biology, 43, 69-122.*

Figure 28. Unburnt coal behavior in seawater.

4.2.1 Polycyclic Aromatic Hydrocarbons (PAHs)

“Coal is a mixture of a variety of chemicals, especially hydrocarbons, which can give rise to polycyclic aromatic hydrocarbons (PAHs)” (Rohr et al., 2013). Besides, “Polycyclic aromatic hydrocarbons (PAHs) are a type of organic contaminants chiefly derived from incomplete combustion (Mahler et al., 2012) of organic matter, such as fossil fuel, wood, and coal from forest fires, petroleum seeps and volcanic activities (Hu et al., 2011). In addition, there are more than 100 different PAH compounds and the health effects of the individual PAHs are not exactly alike" (ATSDR, 1995). Furthermore, “unburned coal is a significant source of hydrocarbons in marine coastal sediments” (Chapman, Downie, Maynard, & Taylor, 1996). Besides, “PAH contamination is a major hazard that is a concern for aquatic life in marine sediments, particularly in areas close to anthropogenic sources. Many PAHs are at the same time persistent, bioaccumulative, and toxic for humans and aquatic organism” (Tavakoly Sany et al., 2014). For instance, a brown bullhead catfish underwent physiological effects in brain, gills, and heart tissue due to PAH contaminant exposure (Beeson, Lewis, Powell, & DelWayne, 1998). Likewise, juvenile Chinook salmonids showed a reduction in size and alteration of physiological responses because of exposure to polycyclic aromatic hydrocarbons (PAHs). Furthermore the toxicity of PAHs (Jiao et al., 2012) causes a reduction in size and content of lipids, which are essential for salmonid survival. In addition, a critical period in the life cycle of salmonid happens during their first winter in a stream, marine environment or lake. For example, the availability of prey is reduced during the winter, thus they have to survive on their lipid reserves (Meador, Sommers, Ylitalo, & Sloan, 2006). The experiment revealed that coal dust contaminated seawater had a presence of several procarcinogens such as benzo(g,h,i)perylene, benzo(a)pyrene, indeno(1,2,3-cd), and dibenzo(a,h)anthracene. The study established that “coal dust has effects on the expression of several genes in juvenile chinook salmon. It is also possible that these sub-lethal effects may become manifest at higher levels of biological organization” (Campbell & Devlin 1997). In addition, a previous study (Herbert and Richards, 1963 as cited by Campbell & Devlin,

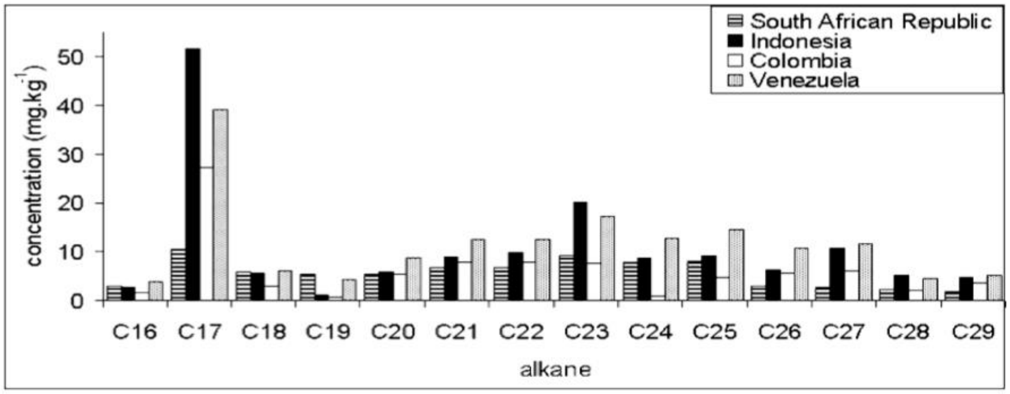
1997) states “coal byproducts and specific components found in coal dust leachate have been showed to reduce the growth rate of trout.”

Additionally, several experiments were carried out by (Jaffrennou et al., 2007a) where four kinds of coals from different countries were analyzed in order to determine contents of PAHs and their toxicity levels. The four different commercial coals were from Colombia (COL), Indonesia (IND), the South African Republic (SAR) and Venezuela (VEN) and were subjected to different experiments. The size fraction repartition from every sample is presented in Table 4. Additionally, most of the coal particles were bigger than 2 mm, which made up the greatest part of the samples (more than 60% in % weight).

Table 4. Size repartition of the four coal samples (% weight).

Source: Jaffrennou, C., Stephan, L., Giamarchi, P., Cabon, J. Y., Burel-Deschamps, L., & Bautin, F. (2007). Direct fluorescence monitoring of coal organic matter released in seawater. J Fluoresc, 17(5), 564-572.

Particle size range (mm)	Coal			
	Indonesia (IND)	Venezuela (VEN)	South African Republic (SAR)	Colombia (COL)
>25	8.6	23.1	24.2	61.8
10–25	26.5	24.8	20.9	13.8
2–10	48.6	29.0	32.1	15.0
1.6–2.0	8.6	2.7	3.8	2.3
1.0–1.6	6.9	4.7	6.6	4.5
0.5–1.0	0.7	5.7	7.1	2.1
0.25–0.50	0.1	4.1	3.3	0.4
0.10–0.25	0.0	4.8	1.9	0.1
0.063–0.100	0.0	0.9	0.1	0.0
0.050–0.063	0.0	0.2	0.0	0.0
<0.050	0.0	0.0	0.0	0.0



Source: Jaffrennou, C., Stephan, L., Giamarchi, P., Cabon, J. Y., Burel-Deschamps, L., & Bautin, F. (2007). Direct fluorescence monitoring of coal organic matter released in seawater. J Fluoresc, 17(5), 564-572.

Figure 29. Concentrations of Alkane in COL, IND, SAR and VEN coals.

As presented in Figure 29 the four coals showed a similar alkane distribution. Thus, no alkane trace was used as a fingerprint in order to identify the origin of the coals. Nonetheless, Of the C16 to C29 concentrations of alkane of the four different coals analyzed, C17 concentration was the most representative, reaching $50\ \mathrm{mg\ Kg^{-1}}$ and $40\ \mathrm{mg\ Kg^{-1}}$ for Indonesian and Venezuelan coals respectively. Although seven PAHs were recognized in the coal samples in Table 5, not all of them were detected in the four samples. But phenanthrene was almost always noticed (COL, IND and VEN samples). Furthermore, benzo(a)anthracene ($28.4\ \mathrm{mg\ Kg^{-1}}$) and anthracene ($6.0\ \mathrm{mg\ Kg^{-1}}$) were found in the highest amount in the SAR coals; and phenanthrene in the Venezuelan coal ($6.2\ \mathrm{mg\ Kg^{-1}}$). This study concluded that even though coals have PAHs, their potential release into the marine environment is not very strong. As a result, their concentrations are low (Cornelissen, Rigterink, Ferdinandy, & van Noort, 1998). On the other hand “coal releases humic and fulvic matter after immersion in seawater, which can induce an important increase of the organic content, depending on the coal origin and the size of the coal particles” (Jaffrennou et al., 2007a).

Table 5. Polycyclic aromatic compositions of the coal samples and of Zhao et.'s coals.

Source: Jaffrennou, C., Stephan, L., Giamarchi, P., Cabon, J. Y., Burel-Deschamps, L., & Bautin, F. (2007). Direct fluorescence monitoring of coal organic matter released in seawater. J Fluoresc, 17(5), 564-572.

Polycyclic aromatic hydrocarbon (mg kg^{-1})	SAR	IND	COL	VEN	Zhao a	Zhao b	Zhao c
Fluorene	1.8						
Fluoranthene			2.0				
Phenanthrene		0.7	2.9	6.2	0.09	0.14	1.46
Pyrene	1.5		1.0		0.12		
Naphthalene	0.1					0.08	2.78
Anthracene	6.0				0.19	0.06	
Benzo(a)anthracene	24.8						
Acenaphthene							1.36
Benzo(b)fluoranthene						0.05	0.78
Total PAHs	34.2	0.7	5.9	6.2	0.40	0.33	6.38

Although various countries have reported the presence of polycyclic aromatic hydrocarbons (PAHs) in hard coals, they have only taken into account qualitative results. Nevertheless, Table 6 shows a summary of the limited published quantitative information on PAHs from international large coal basins, which establishes that concentrations vary widely between 1 and 2500 mg/kg (Achten & Hofmann, 2009).

4.2.2 Metal and Metalloids

Coal is an organic sediment that has various inorganic constituents such as heavy metals (see Appendices 1-4), which can be very toxic to marine organisms (Siboni et al., 2004).

A study carried out with three different types of South African coal had as a goal the evaluation of the behavior of coal in seawater and the risks of trace metal pollution through the leaching processes. The three South African coals were prepared and certified by the Council or Mineral Technology (MINTEK) and will be referred to throughout this study as South African Reference Material (SARM) as follows: SARM 18 are a high volatile and low rank bituminous coals; SARM 19 are subbituminous to bituminous and usually very low rank coals; and SARM 20 are subbituminous to bituminous and normally low rank coals. In addition, the particle size of SARM coals was under 106 µm. Upon first glance, it is reasonable to assume that these coals have similar features, but it can be seen that they are quite different from each other as shown in Table 7 despite being from the same country. As seen above, it is important to bear in mind that the characteristics of coals change from one to another, even within the same country, as they are closely related to the formation process of the coal itself. This explains why behaviors of coals are so different from each other.

Table 6. Summary of total and 16 EPA PAHs concentrations in coals.

Source: Achten, C., & Hofmann, T. (2009). Native polycyclic aromatic hydrocarbons (PAH) in coals - a hardly recognized source of environmental contamination. *Sci Total* Environ, 407(8), 2461-2473.

	Total PAHs [mg/kg]	EPA-PAHs [mg/kg]	References
High volatile bituminous coal A, Elmsworth gasfield, 10-11-71-11W6, Canada	2429.1	152.1	
High volatile bituminous coal A, Elmsworth gasfield, 10-03-70-10W6, Canada	2412.3	136.6	
Medium volatile bituminous coal, Ruhr basin, Osterfeld, Germany	1037.2	153.3	
Medium volatile bituminous coal, Ruhr basin, Hugo, Germany	933.8	123.6	
Low volatile bituminous coal, Ruhr basin, Westerholt, Germany	1200.7	163.9	
Low volatile bituminous coal, Ruhr basin, Blumenthal, Germany	786.5	155.4	Willsch and Radke (1995)
Low volatile bituminous coal, Elmsworth gasfield, 06-19-68-13W6, Canada	546.4	98.6	
Low volatile bituminous coal, Ruhr basin, Haard, Germany	567.7	154.8	
High volatile bituminous coal, Wealden Basin, Nesselberg, Germany	656.2	43.1	Radke et al. (1990)
High volatile bituminous coal, Wealden Basin, Barsinghausen, Germany	554.4	56.7	
High volatile bituminous coal, Saar, Ensdorf, Germany	165.9	50.5	
Medium volatile bituminous coal, Germany	68.0	22.4	Pies et al. (2007)
Bituminous coal, Germany	127.6	28.7	
Lignite A, Northern Great Plains, Beulah, USA	8.5[a]	1.2	
Lignite A, Northern Great Plains, Pust, USA	6.5[a]	1.0	
Sub-bituminous coal C, Northern Great Plains, Smith-Roland, USA	12.0[a]	0.1	
Sub-bituminous coal C, Gulf Coast, Bottom, USA	14.0[a]	1.6	
Sub-bituminous coal B, Northern Great Plaines, Dietz, USA	14.0[a]	0.8	
Sub-bituminous coal B, Northern Great Plaines, Wyodak, USA	5.4[a]	0.3	
Sub-bituminous coal A, Rocky Mountains, Deadman, USA	12.0[a]	1.5	
High volatile bituminous coal C, Rocky Mountains, Blue, USA	77.0[a]	5.3	
High volatile bituminous coal B, Eastern Coal, Ohio #4A, USA	60.0[a]	8.2	
High volatile bituminous coal A, Rocky Mountains, Blind Canyon, USA	78.0[a]	4.4	
High volatile bituminous coal A, Eastern Coal, Pittsburgh, USA	76.0[a]	11.0	Stout and Emsbo-Mattingly (2008)
Medium volatile bituminous coal, Rocky Mountains, Coal Basin M, USA	29.0[a]	1.8	
Low volatile bituminous coal, Eastern Coal, Pocahontas #3, USA	20.0[a]	3.8	
Semianthracite, Eastern Coal, PA Semi-Anth. C, USA	5.9[a]	2.1	
Anthracite, Eastern Coal, Lykens Valley #2, USA	0.2[a]	<0.1	
High volatile bituminous coal, Blind Canyon, USA	78.3	–	Stout et al. (2002b)
High volatile bituminous coal C-1, USA	7.5	0.5	
High volatile bituminous coal C-2, USA	3.4	0.4	
High volatile bituminous coal C-3, USA	2.4	0.3	
High volatile bituminous coal B-1, USA	1.6	0.3	
High volatile bituminous coal B-2, USA	12.7	2.4	
High volatile bituminous coal A-1, USA	13.7	5.4	Zhao et al. (2000)
High volatile bituminous coal A-2, USA	27.6	6.4	
Low volatile bituminous coal, USA	1.2	0.3	
Anthracite, China	2.5	1.8	Chen et al. (2004)
Bituminous coal, Brazil	13.0	–	Püttmann (1988)

[a] Sum of 43 PAHS.

The results of this study showed that chemical impacts of coal pollution on the marine environment through the leaching processes will be governed by several parameters such as physic-chemical properties and composition of coal, coal mass to seawater proportion, time contact and seawater agitation. According to Cabon et al. (2007), most hazardous trace metallic elements will not be leached from coal into seawater and, on the contrary, are probably to be released from seawater because of the presence of coal having high content of calcite. Although manganese (Mn) exhibits outstanding behavior because a high reactive fraction may be solubilized into seawater, which may cause a significant level of pollution higher than the limits of toxicity; the lowest concentration of Mn (10 µmL^{-1}) (World Health Organization, 2004) that could cause bioaccumulation and adverse impacts in a natural environment is still not reached (Jaffrennou et al., 2007b).

Table 7. Composition of SARM coals.

Source: Cabon, J. Y., Burel, L., Jaffrennou, C., Giamarchi, P., & Bautin, F. (2007). *Study of trace metal leaching from coals into seawater. Chemosphere, 69(7).*

Composition of SARM coals

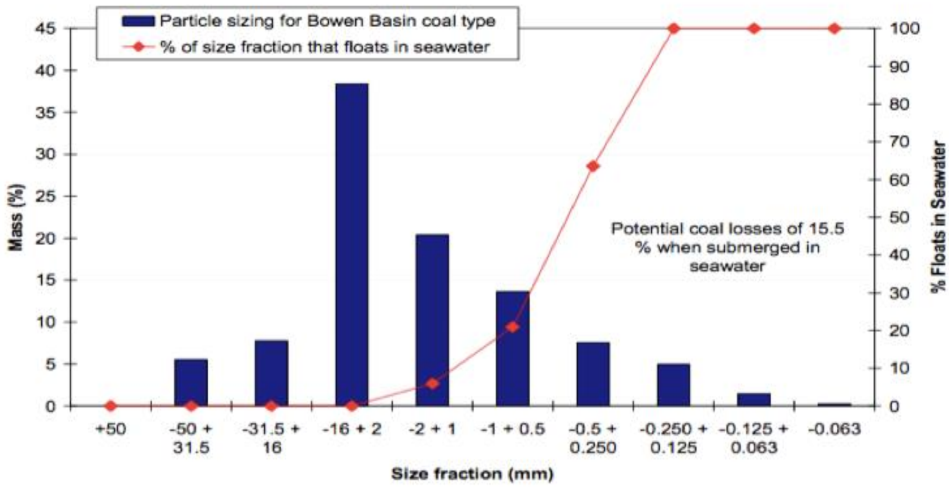
	SARM 18	SARM 19	SARM 20
Loss on ignition (%)	90.11	71.28	64.66
Al (%)	1.36	4.24	5.96
Ca (%)	0.13	0.99	1.34
Cr (µg g^{-1})	16	50	67
Cu (µg g^{-1})	5.9	13	18
Fe (%)	0.2	1.22	0.82
Mg (%)	0.066	0.12	0.26
Mn (µg g^{-1})	22	157	80
Na (%)	0.013	0.22	0.2
Ni (µg g^{-1})	10.8	16	25
Pb (µg g^{-1})	5	20	26
S (%)	0.56	1.49	0.51
Si (%)	2.9	7.01	8.26
Ti (%)	0.068	0.204	0.38
Zn (µg g^{-1})	5.5	12	17

The solubility of dissolvable sulfate minerals like gypsum mainly controls its leaching process from coal, but is reduced for coal that has a high content of calcite. More specifically, manganese transfer rate into seawater due to coal will be governed both by the renewal of seawater in contact with the coal and the seawater volume.

Additionally, this study also proved that the solubility of significant concentrations of trace metals because of coal in the seawater may be helped by the presence of strong chelating agents during periods of biological processes. Furthermore, it seems clear that the distribution between different mineral phases and the speciation of metals in coal govern the leaching processes. As a consequence, “the determination of total metal content in coal is not sufficient to predict trace metal pollution through leaching process into seawater and the knowledge of major mineral composition of coal is essential, particularly its gypsum and calcite content.” (Cabon et al., 2007).

During another experiment the effects of methanolic extract of coal dust on larvae of *Artemia franciscana* were studied. It was concluded that this extract is highly toxic because it killed the exposed larvae almost immediately. In addition, the study also suggested that the lethality of the product is probably due to the content of heavy metals in the coal dust (Pacheco, 2011). Nonetheless, it is important to highlight that there is still no study that demonstrates that the methanolic extract can be leachate when coal is introduced into seawater (Lucas & Planner, 2012).

A recent study calculated the potential of the leaching of trace elements of coal into seawater after the grounding of the bulk carrier “Sheng Neng” at Douglas Shoal, situated within the Great Barrier Reef in Queensland, Australia. The results of the floating test depend on the particle size and are presented in Figure 30. Approximately half of the total sample was composed of particles larger than 2 mm in size, which sank easily into the seawater during the flotation test. In addition, froth was formed on the surface of the seawater which consisted of coal particles smaller than 0.250 mm in size. These coal particles will be moved away from a grounded/submerged vessel or from a dumping point by the current. Additionally, some of the coal particles between -2 + 1mm and -1 + 0.5mm, and all of the coal particles smaller than 0.5 mm in size, are likely to stay in the water column and will also be transported by currents. In total it was estimated that approximately 15.5% of the total cargo, was transported away because of ocean currents (Lucas & Planner, 2012).



Source: Lucas, S. A., & Planner, J. (2012). Grounded or submerged bulk carrier: the potential for leaching of coal trace elements to seawater. *Mar Pollut Bull, 64(5), 1012-1017.*

Figure 30. Particle size distribution and associated percentage that floated in seawater.

The leaching test results are shown in Table 8 where the seawater used in the experiment is represented by the column "CONTROL" sample and the triplicate leaching results are represented by SW1A, SW1B and SW1C. Equally, the pre and post leaching differences in seawater are shown. The difference between pre and post leaching to seawater is also shown. No detectable concentrations of Cr, Se, Hg and Sn were observed in the experiment. However, there was a net removal of V, As and B from the seawater. This experiment shows that some elements contained in the coal have the ability to absorb some compounds from the seawater, thereby decreasing their concentration in the marine environment. Conversely, leaching processes from coal to seawater were noted for Cd, Cu, Pb, Mn, Mo, Ni and Zn. Equally, the leached quantity was calculated according to a mass balance approach which established the difference between trace elements found in the seawater leached and trace elements in the coal from Bowen Basin. For instance, if 10 Kg of coal has 15 mg/Kg Cu then in the test coal sample it means 150 mg (150.000 µg). If the initial concentration of the seawater was 3 µg/L (60 µg in 20L), thus it increased by 8 µg/L (160 µg in 20L). As a consequence, the leaching percentage (%) represents approximately 0.11% of the total Cu contained in the coal. The balances of mass of all trace elements leached from the coal into the seawater are given in Table 9.

Table 8. Leaching results-coal in seawater.

Source: Lucas, S. A., & Planner, J. (2012). Grounded or submerged bulk carrier: the potential for leaching of coal trace elements to seawater. *Mar Pollut Bull, 64(5), 1012-1017.*

	Units	LOR	CONTROL	SW1A	SW1B	SW1C	(Difference)			Trace elements leached from coal to seawater?
							SW1A	SW1B	SW1C	
Selenium (Se)	µg/L	2	<2	<2	<2	<2	0	0	0	No leaching
Chromium (Cr)	µg/L	0.5	<0.5	<0.5	<0.5	<0.5	0	0	0	No leaching
Tin (Sn)	µg/L	5	<5	<5	<5	<5	0	0	0	No leaching
Mercury (Hg)	µg/L	0.1	<0.1	<0.1	<0.1	<0.1	0	0	0	No leaching
Arsenic (As)	µg/L	0.5	2.3	1.2	1.2	1.4	−1.1	−1.1	−0.9	Net removal from seawater
Boron (B)	µg/L	100	5100	4500	4700	4700	−600	−400	−400	Net removal from seawater
Vanadium (V)	µg/L	0.5	1.6	0.5	0.5	0.5	−1.1	−1.1	−1.1	Net removal from seawater
Cadmium (Cd)	µg/L	0.2	0.4	0.6	0.8	0.6	0.2	0.4	0.2	Leaching
Copper (Cu)	µg/L	1	3	12	11	11	9	8	8	Leaching
Lead (Pb)	µg/L	0.2	0.4	0.9	0.8	0.8	0.5	0.4	0.4	Leaching
Manganese (Mn)	µg/L	0.5	1.8	37.1	36.5	37	35.3	34.7	35.2	Leaching
Molybdenum (Mo)	µg/L	0.1	13.8	17	16.8	16.7	3.2	3	2.9	Leaching
Nickel (Ni)	µg/L	0.5	0.6	5.6	5.9	6.2	5	5.3	5.6	Leaching
Zinc (Zn)	µg/L	5	5	23	27	54	18	22	49	Leaching

LOR = limit of reading.

Moreover, it may be noted that the range of leaching trace elements in the seawater was between 0.03% and 1.2% of the total trace elements content in the coal. "The relatively low amount of trace elements leached from unburnt coal suggests that many trace elements are strongly bound to mineral matrices, particularly when submerged in seawater with a high electrical conductivity and relatively high pH (~8.1)" (Lucas & Planner, 2012). Additionally, Table 10 shows the leaching result of the trace elements, making a comparison with the recommended levels according to the Water Quality guidelines of the Department of the Environment and Resource Management of Queensland, Australia. Although, two elements surpassed guideline values, the dilution would be expected to reduce the concentrations quickly in the open waters. Therefore, one would not expect any ecological effects because of Mn and Cu leaching from unburnt coal into the seawater (Jaffrennou et al., 2007a).

Table 9. Leaching results-coal in seawater.

Source: Lucas, S. A., & Planner, J. (2012). Grounded or submerged bulk carrier: the potential for leaching of coal trace elements to seawater. *Mar Pollut Bull, 64(5), 1012-1017.*

Element	Symbol	Degree of concern	Bowen Basin (top-size) (mg/kg)	In 10 kg of coal (µg)	Initial seawater concentration in 20 L (µg)	Increase after leach test (µg in 20 L)	% leached from total mass in coal
Cadmium	Cd	Major	0.05	500	8	6	1.20
Copper	Cu	Moderate	15	150,000	60	160	0.11
Lead	Pb	Major	5.3	53,000	8	16	0.03
Manganese	Mn	?	42	420,000	36	720	0.17
Molybdenum	Mo	Major	<2	20,000	276	62	0.31
Nickel	Ni	Moderate	2	20,000	12	106	0.53
Zinc	Zn	Moderate	18	180,000	100	620	0.34

? = "No concern". Mn is not considered an element of concern in the coal industry.

According to Lucas et al. (2012), the ecological resilience and the water quality are not jeopardized because of leached trace elements in the seawater. Any leaching of these elements is likely to dissolve and disperse rapidly in an open water accident.

Table 10. Comparison of water quality guidelines (recommended range) and leachate results (showing elements of concern in aquatic environments).

Source: Lucas, S. A., & Planner, J. (2012). Grounded or submerged bulk carrier: the potential for leaching of coal trace elements to seawater. *Mar Pollut Bull, 64(5), 1012-1017.*

Element	Recommended range QLD WQ Guidelines 2009 µg/L	Leach test Average µg/L	Less than Guideline?
As	<50	Net removal	Y
Cd	<3	0.7	Y
Cr	<100	No leaching	Y
Cu	<6	11	N
Mn	<10	37	N
Hg	<0.05	No leaching	Y
Ni	<40	5.9	Y
Sn	<1	<5[a]	?[a]
Zn	<200	35	Y

[a] Likely to be <1 but could not achieve desired limit of reading during analysis.

4.2.3 Physicochemical Parameters of Seawater Affected by Coal

4.2.3.1 Turbidity

Turbidity is defined as "the amount of small solid particles suspended in water as measured by the amount of scattering and absorption of light" (Anonymous, 2005). In addition, it makes the water opaque and blocks light penetration. Turbidity depends on the shape, size, color and concentration of suspended particles in the body of water. There are several units to measure turbidity, of which a very common measure is the Nephelometric Turbidity Units (NTU).

4.2.3.2 Dissolved Oxygen

Dissolved oxygen (DO) refers to the amount of oxygen gas that is dissolved into the water. Oxygen enters into the water mainly through two different mechanisms: aquatic plant photosynthesis and diffusion across the air-water barrier. Likewise, the amount of dissolved oxygen held into the water is governed by the temperature, salinity and pressure (Anonymous, 2005). Furthermore, generally warmer water holds less oxygen than cold water does.

4.2.3.3 pH

The pH is the measurement of the degree of alkalinity or acidity of a substance with a scale 0 to 14, where 7 represent neutrality. Likewise, higher values show alkalinity and lower values acidity (Anonymous, 2005).

An investigation was conducted by INVEMAR, which had as its main goal to establish the effects of coal spill into the marine environment by the barge TS-115 belonging to the American Port Company Drummond. The results showed that the depths in the 8 studied stations oscillated between 2.7 and 10.7m, while the visibility range was between 0.7 and 10.7m according to the Secchi disk showing the lowest value in the stations closest to the dock (red buoy). Furthermore, the average value of turbidity in surface water was 7.19 ± 4.81 NTU, Meanwhile on the bottom it stepped up to 10.78 ± 9.23 NTU. This situation was expected due to the process of sedimentation of coal particles. Likewise, the station ST10 presented the smallest value of turbidity (1.6 NTU), but the highest (23.0 NTU) was registered at the ST12 and ST19 stations. This behavior reasserts that there are more suspended particles of coal near the dock because of the permanent release of coal particles into the seawater by coal operations. As a consequence, there is less visibility in this area (INVEMAR, 2013).

The physicochemical parameters in situ are presented in Table 11. The values presented by the salinity conform to these kind of environments, which registered an average of 36.5 ± 0.12 on the bottom and 36.6 ± 0.37 on the surface. Meanwhile the temperature registered an average value of 28.5 ± 0.69 °C on the bottom and increased on the surface to 29.3 ± 0.53 °C. These behaviors are related to changes in density (INVEMAR, 2013).

Table 11. Results of physic-chemical parameters measure in situ (spilled area).

Zona = sampling area; Estacion = each sampled station; Temp = temperature (°C); Sal = salinity; pH = pH; O_2Disuelto = Dissolved oxygen in (mg * g-1); Saturacion O_2 = Dissolved oxygen in (%); Sup = surface; Fon = bottom.

Source: INVEMAR. (2013). *Efecto del derrame de carbón sobre el ecosistema marino, producido por la maniobra de rescate de la barcaza TS-115 de propiedad de la Compañía American Port Company INC (pp. 79).* Santa Marta, Colombia: Instituto de Investigaciones Marinas y Costeras.

Zona	Estación	Temp (°C)		Sal		pH		O_2 Disuelto ($mg*g^{-1}$)		Saturación O_2 (%)	
		Sup	Fon	Sup	Fon	Sup	Fon	Sup	Fon	Sup	Fon
Boya 23	ST01	29,0	28,0	36,6	36,5	8,18	8,24	5,78	5,80	92,3	89,1
	ST02	28,4	27,3	36,4	36,5	8,19	8,19	6,09	5,85	94,0	89,0
	ST04	29,1	28,2	36,4	36,3	8,22	8,24	6,05	5,91	98,0	95,4
	ST10	29,1	28,3	36,3	36,4	8,23	8,24	5,98	5,63	94,3	89,0
Boya Roja	ST12	29,6	28,9	36,7	36,7	8,18	8,16	5,62	5,27	90,0	82,0
	ST15	30,1	29,5	36,0	36,4	8,14	8,17	5,86	5,80	92,6	92,0
	ST16	29,8	28,8	37,0	36,4	8,17	8,17	5,88	5,34	95,7	88,6
	ST19	29,5	29,0	37,1	36,4	8,18	8,15	5,63	5,10	89,5	81,0
Histórico del Área (INVEMAR, 2013)		27,1 – 31,1		20,4 – 41,2		7,83 – 8,41		2,60 – 7,08		42,4 – 92,8	

On the other hand, the pH varied between 8.14 and 8.24, which complies with the requirements of the Colombian regulation of between 8.14 and 8.24 (INVEMAR, 2013). Likewise, values of pH registered on the surface water match with the values registered in the Network Quality Monitoring of marine and coastal waters of Colombia, which is called REDCAM (by its acronym in Spanish). By the above, it could be said that any change in the pH value was small, thus the ocean was able to recover by itself (INVEMAR, 2013).

According to INVEMAR (2013), the dissolved oxygen (DO) concentration and its corresponding percentage of saturation (% DO) were commensurate not only on the bottom (showed lower values) but also on the surface (higher values) of the water. Moreover, the study asserts that these values are in line with the historical values corresponding to that area. However, the first station (ST01) presented a higher value on the bottom than on the water surface.

According to INVEMAR (2013), sediments in the area of study presented a pH value between 6.99 and 7.97 as shown in Table 12. Likewise, in comparison with the values of the column water, a slightly acidic trend was established in the stations ST01 and ST10 (the closest stations to the spilling point), where the pH values are lower due to the deposited organic matter, which releases CO_2 causing a decrease in the pH, which might have an adverse impact on the diversity and productivity of the phytoplankton. As a consequence, this may result in a local impact on zooplankton (Geller, Schultze, Kleinmann, & Wolkersdorfer, 2012).

On the opposite side of the study area, the remaining stations maintained a slightly alkaline tendency in comparison to other investigations in similar areas of study (INVEMAR, 2013). In addition, the content of the volatile organic matter was high. For instance, "in the buoy 23 was reached the highest concentration values, 949.0 mg*g-1 (ST01) and 407.6 mg*g-1 (ST10), which reasserts the pH behavior in these stations, where according to the result of the microscopic evaluation of the samples there is preponderance of coal" (INVEMAR, 2013). Additionally, the "fat and oil concentrations, which were below the limit of detection of the analytical used technique (0.2 mg * g-1), except for the ST01 station where a value of 4.81 mg * g-1 was registered, showing adsorption of fatty compounds" (INVEMAR, 2013).

Table 12. Results of physic-chemical parameters in sediments collected in situ (spilled area).

Zona = sampling area; Estacion = each sampled station; pH = pH; M.O.Vol.1 = Volatile organic matter in (mg* g-1); G y A.2= Fats and oils in (mg* g-1).

Source: INVEMAR. (2013). *Efecto del derrame de carbón sobre el ecosistema marino, producido por la maniobra de rescate de la barcaza TS-115 de propiedad de la Compañía American Port Company INC (pp. 79).* Santa Marta, Colombia: Instituto de Investigaciones Marinas y Costeras.

Zona	Estación	pH	M.O. Vol.[1] $(mg*g^{-1})$	G y A[2] $(mg*g^{-1})$
Boya 23	ST01	6,99	949,0	4,81
Boya Roja	ST02	7,60	344,2	<0,2
	ST04	7,05	205,5	<0,2
	ST10	6,99	407,6	<0,2
	ST12	7,44	345,5	<0,2
	ST15	7,15	303,0	<0,2
	ST16	7,74	275,6	<0,2
	ST19	7,97	291,7	<0,2
Otros estudios (INVEMAR, 2012; GÓMEZ, et al., 2011)		7,57 – 7,86	40,6 – 85,9	- - -

[1] Materia orgánica Volátil, [2] Grasas y Aceites,

5 CHAPTER CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

At first consideration, it is reasonable to assume that coal is a marine pollutant, which is in accordance with the fact that it is a significant source of inorganic constituents such as heavy metals (Siboni et al., 2004; Ahrens & Morrisey, 2005; Cabon, 2007; Cabarcas-Montalvo et al., 2012) and many different complex organic substances such as Polycyclic Aromatic Hydrocarbons (PAHs), organic sulphur compounds and humic acids (WHO, 1997; Jaffrennou et al., 2007a; Hu, 2011; Rohr, 2013). These organic and inorganic constituents of coal are a great concern when it comes to human health and therefore it is natural to also carefully consider their impacts on the marine environment. For these reasons the spills of coal to the marine environment is an issue that requires full consideration. Accordingly, it should be addressed from diverse perspectives.

From a chemical standpoint the research shows that even though coal is a great source of organic and inorganic elements and compounds potentially polluting as described above, the probability of significant release of trace metals and Polycyclic Aromatic Hydrocarbons (PAHs) to the marine environment in connection with the loss of coal for example as a result of an accident at sea is quite low for the following reasons:

Regarding the release of trace metals from coal, this process depends on multiple factors such as the composition of the coal, the physicochemical properties of each metal contained in the coal, the contact time and agitation of the seawater in which the coal is contained, and the coal mass to seawater ratio. A factor which is important to consider is the buffering capacity of seawater, which does not help the dissolution of the metals (Cabon et al., 2007; Lucas et al, 2012). Under normal cases it seem reasonable to assume that the quantities of metals mobilized into the ecosystem from coal would be insignificant. This assumption seems to be supported by the few field studies that have been carried out to study this particular phenomenon. On the contrary, these elements seem more likely to be removed from the seawater especially in the presence of coal with high calcite content (Cabon et al., 2007) such as South African coals. Many trace elements contained in unburned coal are strongly bound to mineral matrices especially when they are immersed in seawater with normal pH and conductivity. As a consequence, it is highly probable that any dissolved metals would be diluted and / or dispersed by ocean currents. However, if an accident occurs in a semi-enclosed basin levels could be higher and there could be cumulative impacts due to other forms of pollution (Lucas & Planner, 2012).

In regard to the PAHs, studies demonstrate that "Sampling, analysis, and interpretation of PAHs in sediments from such sources as coal remain problematic" (Chapman et al, 1996). However, recent studies show that the amounts released by coal into the seawater are too low to be detectable (Jaffrennou et al., 2007a; Jaffrennou et al., 2007b). Therefore it is not likely that they will have any significant impact on the ecosystem. For instance, the South Wales coalfields, UK, remains in contact with the seawater all the time, but the marine ecosystem is dynamic and healthy (Cleal, 2007). Several studies asserted some time ago that polycyclic aromatic hydrocarbons (PAHs) present in Prince William Sound Alaska were due to the coal that remains in contact with seawater in that area. However, a further investigation proved that these PAH's had an origin other than coal. They were linked to the Exxon Valdez (Deepthike et al., 2009) shipwreck, which occurred in 1989.

On the other hand, from a physical point of view, studies demonstrate that particles of coal in seawater behave quite similarly to other sediments (Ahrens & Morrisey, 2005; UJTL, 2013). As a result, the main impacts to take into account due to coal spillage are:

Decrease in photosynthesis, which occurs due to turbidity in the water column caused by coal particles. This phenomenon in turn directly affects primary producers, which essentially depend on light to get their own food (Berry et al., 2003; Robertson et al., 2006; INVEMAR, 2013). Consequently, deleterious impacts may occur at different levels of the trophic chain because primary producers are at the first level (Robertson, 2006; Jaffrennou et al., 2007; UJTL, 2013). Additionally, coal particles suspended in the water column can cause abrasion mainly in respiratory organs such as gills of the organisms that remain in the water column (Hillabi, 1989; Ahrens& Morrisey, 2005; Franco-Herrera et al., 2011).

Smothering and burial, although probably only a local issue, is considered the greatest impact that directly affects benthic organisms (Harper et al, 2005; Jaffrennou et al., 2007; INVEMAR, 2013; UJTL, 2013). Such smothering can cause total mortality of species present on the seabed, depending on the amount of coal particles spilled. Likewise, changes may occur on the substrate, (Franco-Herrera et al, 2011; INVEMAR, 2013; UJTL, 2013) which could be colonized by new species, thus changing the ecology of the area.

Accumulation of carbon particles on beaches depends on the prevailing dynamics of ocean currents in the area (Ahrens& Morrisey, 2005; Jaffrennou et al., 2007b; Franco-Herrera et al., 2011; Garcia & Ahrens, 2014). Although this does not represent a threat, it could deteriorate the quality of beaches and seawater, which in turn would affect tourism in the area.

In the particular case of the spilling of coal in the Gulf of Salamanca (Colombia) in 2013, it caused not only smothering and burial but also mortality of benthic organisms, which could affect higher levels of the trophic chain since many species depend on benthic organisms. Additionally, the affected area is characterized by soft bottom substrates with a rich community of organisms. Therefore, the presence of fragments of coal, which are thicker and heavier than the normal sediment in the area, can alter the ecology of the environment. In addition, sediment is essential for benthic communities not only because it provides suitable habitats for relevant biological processes but also provides a significant link between biological and chemical processes (X. Zhang, Jiang, & Zhang, 2013).

As a consequence, it would affect the establishment and distribution of infaunal species, especially because this is an important variable, which defines the spatial distribution of organisms in soft bottom ecosystems (INVEMAR, 2013). Although the results of the study showed that the concentration of organic matter is linked to the presence of coal, the physicochemical parameters evaluated in the sediment did not permit to establish whether its quality was affected by the coal spilling. It should be said that Colombia does not have any regulation and/or standard (INVEMAR, 2013) to establish a comparison with referenced values. It is reasonable to assume that impacts may have occurred in phytoplankton during the acute phase but these were not detected because the samples were collected 67 days after the incident. As a consequence, diversity, richness, composition and abundance in the study area were normal at the time of the investigation (UJTL, 2013). It may be pointed out that the life cycle of many phytoplankton is very fast and even a major impact on these organisms in the open sea would rapidly disappear as a result of reproduction of new plankton, mixing and dilution (INVEMAR, 2013).

To conclude, this type of accident will provoke physical impacts with potential biological perturbations due to the dispersion of fine particles on the sea floor and beaches, by the darkening of the water column and by the smothering of benthic life around the area where the release of the coal took place (Jaffrennou et al., 2007b). Additionally, coal particles produce an increase in turbidity and smothering, which are physical impacts that on some occasions are more deleterious than the toxicity caused by the coal/water mix (D. Cherry, Guthrie, Sherberger, & Larrick, 1979). Moreover, if sedimentation surpasses natural thresholds, as occurred in the Gulf of Salamanca (Colombian case), then probably the impacts will involve the loss of parts of or the total community and succeeding colonization by pioneer species and be driven by an entirely different suite of ecological processes, which might result in a significant alteration of benthic communities (Miller et al., 2002). Accordingly, it could so far be suggested that coal in the marine environment behaves as a physical contaminant rather than a chemical pollutant (Chapman et al., 1986).

5.2 Recommendations

Perform physicochemical analysis of all types of existing coal in Colombia, in order to know their characteristics and create a database, which in turn will serve as a reference tool.

Conduct an environmental impact assessment as soon as an incident occurs. For example, despite the great effort made by INVEMAR in 2013 to collect samples in order to establish the impacts on phytoplankton in the Gulf of Salamanca, the samples were taken 67 days after the incident occurred (INVEMAR, 2013). Hence, this led to speculation about the results of these studies, which most likely did not reflect the actual impacts during the acute phase.

Carry out more comprehensive studies of beaches and on the seabed, particularly in deeper areas near point sources such as coal ports in order to determine where the coal particles are deposited. Coal particles reach the marine environment by different means such as transport and cargo washing, loading operations, slumping and runoff from storage areas, and accidental releases (Ahrens & Morrisey, 2005; Achten & Hofmann, 2009). Nonetheless, existing studies on beaches (Morales & Guzman, 2009; Morales & Guzman, 2010; Morales & Guzman, 2011; Gamez-Ramirez, 2012, Garcia & Ahrens, 2014) show the percentage of coal (by weight) was insignificant. These results suggest that the most important sedimentation area may be occurring elsewhere.

Perform analyses of living organisms in the areas where coal has been lost in order to provide more information particularly regarding species of commercial interest (fish and shellfish). Equally, appropriate techniques should be used, which allow determination of the presence of coal particles in these species. For instance, thanks to the great effort made by Franco-Herrera et al., in 2011, it was possible to identify coal particles in two individuals of 294 analyzed. Nevertheless, 245 contained black particles (Franco-Herrera et al., 2011), which could not be identified probably due to the technique used.

Develop and implement standardized techniques in order to assess the quality of marine sediments. Colombia does not have any sediment standard (INVEMAR, 2013) by which the level of impact of sediments due to pollution and sedimentation such as from the spillage of coal can be determined.

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APPENDICES

Appendix 1: Inorganic chemical properties of particulate coal.

Cont. Appendix 1

Ge	ppm	2–80			1.2–2	0.10–6.0	1–43	0.1–3.0	<0.3–30		0.07–7.8	0.05–0.5		
Hg	ppm	0.03–2.0	0.1–1.4	0.02–1.3		0.05–0.47	0.03–1.6	0.02–6.3	0.026–0.40	0.26–29	0.12–0.56	0.19–0.24	0.15	1
Mn	ppm	1–1600	55, 68	2–600	40–86	2.4–61	6–210	1.4–220	2.5–900		1.3–2.8	7–63		
Mo	ppm	0.1–20	6–30	0.4–13	0.6–32	0.10–22	0.3–29	0.10–30	<0.3–6		<0.02–0.42	0.12–0.76		
Ni	ppm	3–60	15–95	2–38	8–33	6.3–28	7.6–68	1.5–18	0.8–70		0.6–27.5	2.9–11.0	21	52
P	ppm	<10–1000	40–1240	45–5200	68–275	15–1500	10–340	10–510	30–4000		<1.6–29.3	<2.2–9.4		
Pb	ppm	1–900	0.1–390	1.8–53	5–21	1.0–18	0.8–220	0.7–9	1.5–60		0.3–18.0	1.3–16.0	50	220
Sb	ppm	1–10	0.14–5.0	0.1–16	0.7–3.2					1.7–210	<0.04–3.7	<0.05–0.29	2	25
Se	ppm	0.3–5.1	0.6–5.5	<0.1–8.0	0.5–1.6	1.1–8.1	0.4–7.7	0.4–2.7	0.21–2.5					
Sn	ppm	0.3–75	3.6, 3.9	2–15	0.9–2.3	0.2–8.0	0.2–51	0.1–15	<0.9–15		0.14–7.5	0.52–17.5		
Th	ppm	0.7–6.7	1.6–4.4	0.1–9	2–6									
Tl	ppm	0.6–1.7	0.01–0.72		0.20–0.39	1.8–9.0	0.71–51	0.62–5.7	<0.2–8		<0.004–6.7	<0.005		
U	ppm	1.1–3.0	0.3–2.2	0.4–12	0.9–26	0.40–2.9	0.31–4.6	0.3–2.5	0.4–5					
V	ppm	3–150	31–179	3.4–200	14–76	14–73	11–90	4.8–43	4–90		0.68–13.8	1.3–18.5		
Zn	ppm	3–7000	14–1742	2.0–62	35–95	2–120	10–5300	0.3–17	12–73		0.7–27.5	1.0–55.5	200	410
Reference		1 and 2	2	2	3	4 in 5 and 6	4 in 5 and 7	4 in 5 and 7	8 in 5	9	10, 11 and 12	11 and 12	13	13

Abbreviations: Empty cells = not analysed; ISQG = interim sediment quality guideline, L = lignite, SB =sub-bituminous, B = bituminous, A = anthracite, * = concentrations calculated from original data (ash) by multiplying by ash fraction

References: 1 Francis 1961, 2 Swaine & Goodarzi 1995, 3 Querol et al 1996, 4 Gluskoter et al. 1977, 5 Ward 1984, 6 Fendinger et al. 1989, 7 Davis & Boegly 1981b, 8 Swaine 1977, 9 Ding et al 2001, 10 Solid Energy, New Zealand Ltd. 2002, 11 Soong & Berrow 1979, 12 Sim 1977, 13 ANZECC 2000

Appendix 2. Organic chemical properties of particulate coal.

Organic chemical properties of particulate coal (all concentrations in ppm (= μg g-1) dry weight).

Source: Ahrens, M., & Morrisey, D. (2005). Biological effects of unburnt coal in the marine environment. Oceanography and Marine Biology, 43, 69-122.

Name	Rank	Total aliphatics	Total aromatics	Total PAHs	ANT	NAP	PHE	BaP	BaA	BbF	CHR	FL	FLT	PYR	Reference
'U.S. coal'	B	670–960	200–2160												1
W Washington coal	L, SB, B, A	0.2–3350[a]													2
Coal or coke particle	B				1.43	2.74	4.94	1.27	1.46	1.32	1.53	1.53	1.62	1.65	3
Pennsylvania and Maryland coals	B	3.4–29.9	17.6–62.4			0.34–0.65	0.08–0.46				0.25–1.17	0.12–0.36		0.04–0.41	4
Virginia coal				1081.8	2.571	3.268	26.803	0.535	1.978	6.281	15.332[b]	7.218	9.190	7.051	5
ANZECC & NOAA ISQG – Low = ERL				4	0.085	0.16	0.24	0.43			0.384		0.6	0.665	6, 7
ANZECC & NOAA ISQG – High = ERM				45	1.1	2.1	1.5	1.6			2.8		5.1	2.6	6, 7
MOEE LEL							0.56	0.37			0.34		0.75	0.49	pers. commun.

Abbreviations: Quotation marks = geographical origin not specified; empty cells = not analysed; [a] = total n-alkanes in μg g^{-1} of organic carbon; [b] = sum of chrysene and triphenylene; L = lignite; SB = sub-bituminous; B = bituminous; A = anthracite; ERL = effects range low; ERM = effects range mean; ISQG = interim sediment quality guideline; LEL = lowest effects level; ANT = anthracene, NAP = naphthalene; PHE = phenanthrene; BaP = benzo(a)pyrene; BaA = benz(a)anthracene; BbF = benzo(b)fluoranthene; CHR = chrysene; FL = fluorene; FLT = fluoranthene; PYR = pyrene; ANZECC = Australian and New Zealand Guidelines for Fresh and Marine Water Quality; NOAA = NOAA Screening Quick Reference Table for Organics; MOEE = Ministry of the Environment and Energy guideline (Ontario, Canada) for particulate bound PAH, as personal comunication Kim Irvine (16 June 2004).

References: 1 Tripp et al. 1981, 2 Barrick et al. 1984, 3 Chapman et al. 1996a, 4 Fendinger et al. 1989, 5 Bender et al. 1987, 6 ANZECC 2000, 7 Buchman 1999

Appendix 3. Inorganic physicochemical properties of coal leachates.

Source: Ahrens, M., & Morrisey, D. (2005). Biological effects of unburnt coal in the marine environment. Oceanography and Marine Biology, 43, 69-122.

Type of leachate	Coal type and origin	Sulphur % dw	Condi-tion	TSS mg l⁻¹	TDS mg l⁻¹	Filter pore µm	pH	EC µS cm⁻¹	SO_4 mg l⁻¹	Al mg l⁻¹	As µg l⁻¹	Cd µg l⁻¹	Cr µg l⁻¹	Cu µg l⁻¹	Fe mg l⁻¹	Hg µg l⁻¹	Ni µg l⁻¹	Pb µg l⁻¹	Se µg l⁻¹	Zn µg l⁻¹	Ref.
Coal leachate	B E U.S.	4.6	Lab			0.45	2.1–3.8	187–4320	213–4060				0.18–55	n.a.	6–1470		n.a.	n.a.		n.a.	1
Coal leachate	SB W U.S.	1.1	Lab			0.45	4.6–8.3	27–670	35–189				0.16–49	n.a.	<0.10		n.a.	n.a.		n.a.	1
Stockpile runoff	n.a.	n.a.	Field Canada			Unfilt	3.1–4.6	122–1716	100–1640				n.a.	500–2500	1.0–71.0					200–3100	2
Stockpile runoff	n.a.	1–3	Field U.S.	8–2300 (470)	2500–1600 (7900)	?	2.3–3.1 (2.79)		1800–9600 (5160)	66–440 (260)	5–600 (170)	<1	<5–11 (7)	430–1400 (860)	240–1800 (940)	<0.2–2.5 (0.4)	740–4500 (2590)		<1–30 (6)	2300–16,000 (6680)	3 in 4
Stockpile runoff	n.a.	>3	Field U.S.	38–2500 (420)	1200–7500 (3150)	?	2.5–3.1 (2.65)		870–5500 (5080)	22–60 (43.3)	6–46 (20)	<1–3 (2)	<5–11 (7)	10–460 (230)	62–480 (265)	3–7 (4)	240–460 (330)		<1–1 (1)	1100–3700 (2180)	3 in 4
Stockpile runoff	n.a.	n.a	Field Canada	2188 ± 3402		Unfilt				3.2 ± 3.4		1.9 ± 1.5	24 ± 24	35 ± 28	15.5± 14.4		50 ± 30	22 ± 18		280± 300	5
Stockpile runoff	Coal from 11 power plants	n.a	Field U.S.		247–44,050 (12,600)	?	2.1–7.8		133–21920 (6880)				0–15.7 (2.74)	1600–3400 (2100)	0.06–93,000 (10,800)					6–23,000 (5890)	6 in 4
Stockpile runoff	?	?	Field, U.S.		9330–14,900 (11,700)	?	2.2–5.8						100–750 (260)	100–6100 (1690)	10–5250 (1140)					2400–26,000 (5900)	7 in 4
Stockpile runoff	?	?	Field Canada		4600–11,600 (6500)	?	2.4–2.9 (2.7)		1100–6900 (4100)	48–75 (62)					150–1000 (420)						8 in 4
Ground-water under coal pile	E U.S.	Sulphur-rich	Field, U.S.		>10,000	?	2.2	Up to 8480	Up to 22,200	Up to 1100					Up to 9560						9, 10
Simulated runoff	E. U.S.	2–5	Lab	322–3300		?	1.7–3.2	3300–24,000													11
Stockpile runoff	E U.S.	2–5	Field U.S.			?	1.9–2.0	2800–19,000													11
Coal leachate	SB U.S.	'Low'	Lab			0.45	7.0–7.7	15–350	40–120			<0.2–0.8	0.2–0.5	0.1–0.6	0.0017–0.0025			<0.5		0.4–2.1	12
Coal leachate	SB & B Spain	2.2–9.5	Lab			Centri-fuged	n.a.			0–1851	0–345	7–52	0–700	100–2100	1–7900		100–21,000	0–6	1–180	100–42,000	13

Cont. Appendix 3.

Cont. Physicochemical properties leachates. Inorganic

Coal leachate	W U.S.	Low	Lab			?					0–0.1	0.05–0.08	0–0.1	0.10–1.8			0–20.5	0–0.30	0–0.95	0.1–1.9	14
Coal leachate	W U.S.	Low	Lab pH 7.3			?	Adjust. to 7.3				0.5–2.35	0–0.18	0.01–0.95	0.7–4.2			1.6–7.9	0.4–1.9	2.4–3.5	0.7–4.2	14
Coal leachate	W U.S.	Low	Lab pH 4.8			?	Adjust to 4.8				1.76–6.08	0.02–0.57	0–0.22	0.9–3.5			2.9–21.1	0–0.5	1–0–1.2	0–5.0	14
Coal leachate	W U.S. No. 2	Low	Lab			?	7.48–8.30				0.05–0.95	0.1–0.7	0.09–0.27	1.50–6.27		0.06–0.51	0–6.0	0–0.41	0–2.1	1–13.5	14
Coal leachate	E U.S.	High	Lab			?	3.08–3.90				0–1.9	2.30–4.79	0.43–1.95	6.44–63.9		0.29–0.42	180–323	0.01–0.22	0–2.2	65–220	14
Coal leachate	MW U.S.	0.6	Lab			?	5.94		598						0.32						15
Coal leachate	MW U.S.	2.9	Lab			?	2.22		33,766						15,700						15
Stockpile runoff	E U.S.	2.7–4.1	Field U.S.	1.3–17.0	0.002–6.49	?	1.4–3.1	1050–20,000	796–13,625	19.9–1872	<1–16,240				954–83,536	25–<100				3820–19,4350	16
Guidelines																					
CWQG (FW)							FW 6.0–9.0 SW 7.0–8.7			0.005–0.1	5.0	FW 0.017 SW 0.12	FW 1.0–8.9* SW 1.5–56*	2–4	0.3	0.1	25–150	1–7	1	30	17
ANZECC (FW)							6–9	n.e.	n.e.	0.055	13–24*	0.2	1.0	1.4	n.e.	0.6	11	3.4	11	8	18
ANZECC (SW)							n.e.	n.e.	n.e.	n.e.	n.e.	5.5	4.4–27.4*	1.3	n.e.	0.4	70	4.4	n.e.	15	18
NOAA SQuiRT acute							n.e.	n.e.	n.e.	FW 0.75 SW n.e.	FW 340 SW 69	FW 4.3 SW 42	FW 16–570* SW 1100–10,300*	FW 13 SW 4.8	n.e.	FW 1.4 SW 1.8	FW 470 SW 74	FW 65 SW 210	FW 13–186 SW 290	FW 120 SW 90	19
NOAA SQuiRT chronic							n.e.	n.e.	n.e.	FW 0.087 SW n.e.	FW 150 SW 36	FW 2.2 SW 9.3	FW 11–74* SW 50	FW 9 SW 3.1	FW 1 SW n.e.	FW 0.77 SW 0.94	FW 52 SW 8.2	FW 2.5 SW 8.1	FW 5 SW 71	FW 120 SW 81	19

Abbreviations: n.e. = not established; n.a. = not analysed; ? = no information available; B = bituminous; SB = sub-bituminous; unfilt = unfiltered; ± = mean ± standard deviation; (parentheses) = mean; TSS = total suspended solids; TDS = total dissolved solids; E = eastern; W = western; MW = midwestern; FW = freshwater; SW = sea water; EC = electrical conductivity; * = trigger value depends on speciation of element; CWGQ = Canadian Water Quality Guideline for Protection of Aquatic Life; ANZECC = Australian and New Zealand Guidelines for Fresh and Marine Water Quality (2000); trigger level for protection of 95% of species; NOAA SQuiRT = NOAA Screening Quick Reference Tables for Inorganics in Water; quotation marks = concentration not specified.

References: 1 Davis & Boegly 1981b, 2 Scullion & Edwards 1980, 3 Cox et al. 1977, 4 Davis & Boegly 1981a, 5 Curran et al. 2000, 6 Nichols 1974, 7 Anderson & Youngstrom 1976, 8 Featherby & Dodd 1977, 9 Carlson 1990, 10 Carlson & Carlson 1994, 11 Fendinger et al. 1989, 12 Gerhart et al. 1980, 13 Querol et al. 1996, 14 Coward et al. 1978, 15 Cook & Fritz 2002, 16 Swift 1985, 17 Environment Canada 2002, 18 ANZECC 2000, 19 Buchman 1999

Appendix 4. Organic physicochemical properties of coal leachates.

Source: Ahrens, M., & Morrisey, D. (2005). Biological effects of unburnt coal in the marine environment. Oceanography and Marine Biology, 43, 69-122.

Type of leachate	Coal type or origin	Sulphur % dw	Study location	Suspended solids mg l^{-1}	Filtration procedure	ACE $\mu g\ l^{-1}$	BaA $\mu g\ l^{-1}$	BaP $\mu g\ l^{-1}$	BkF $\mu g\ l^{-1}$	CHR $\mu g\ l^{-1}$	FLT $\mu g\ l^{-1}$	FL $\mu g\ l^{-1}$	PHE $\mu g\ l^{-1}$	NAP $\mu g\ l^{-1}$	PYR $\mu g\ l^{-1}$	DOC mg l^{-1}	Σ Arom $\mu g\ l^{-1}$	Ref.
Stockpile runoff	n.a.	n.a	Field Canada	2188 ± 3402	Unfiltered			71 ± 85[a]		47 ± 49[a]	208 ± 254[a]		284 ± 339[a]		140± 173[a]			1
Stockpile runoff	n.a	n.a	Field Canada	dissolved	Whatman #1			0.9 ± 0.2		0.7 ± 0.2	4.5 ± 2.1		6.1 ± 3.3		3.1 ± 1.4			1
Simulated rain runoff	B Illinois #6	>2%	Lab	extracted 1 kg coal	Glass wool	1	2	0.6	0.6	1	3	5	40–48	20–33	4			2
Simulated rain runoff	B Kentucky	>2%	Lab	extracted 1 kg coal	Glass wool								11	8				2
Simulated rain runoff	SB Nerco Montana	<2%	Lab	extracted 1 kg coal	Glass wool								0.7–6					2
Simulated rain runoff	L Texas	1–3%	Lab	extracted 1 kg coal	Glass wool								0.6–1.2					2
Simulated rain runoff	? Montana	?	Lab	extracted 9 kg coal	n.a.	15					16	14						3 in 2
Simulated rain runoff	Pennsylvania & Maryland	2–5%	Lab	extracted 6.8 kg coal	Whatman GFC	0.06–0.47						0.15–0.29	0.06–0.19	0.04–0.97	0.01–0.33	1–28	0.9–16.7	4
Simulated rain runoff	Pennsylvania & Maryland	2–5%	Lab		Suspended	0.08–2.26				0.12–11.20	0.5–5.76	0.10–2.78	0.05–3.58	0.07–5.22	0.10–5.15		0.4–323	4
Stockpile runoff	Pennsylvania & Maryland	2–5%	Field U.S.		Filtered											29	34–95	4
Stockpile runoff	Pennsylvania & Maryland	2–5%	Field U.S.		Suspended												5–42	4

Cont. Appendix 4.

Cont. Organic physicochemical properties leachates.

Stockpile runoff	Canada		Field Canada	100	Settled SW leachate		0.285	0.233	0.417[c]	0.466[b]	0.353	0.28	2.037	0.408	0.373		5
Simulated runoff	SB	Low	Lab	0.8% w/w	0.45 µm											13–27	6
SW leachate	Virginia	n.a.	Lab	1–10 mg l^{-1}	Filtered							<0.001	0.2	0.1			7
Guidelines																	
MOEE				10				144		46	102		95		85		in 1
ANZECC														FW 16 SW 70			8
CWQG						5.8	0.018	0.015	n.r.		0.04	3	0.4	FW 1.1 SW 1.4	0.025		9
NOAA SQuiRT–acute, SW						FW 1700 SW 970	300	300	300	300	FW 3980 SW 40	300	FW 30 SW 7.7	FW 2300 SW 2350	300		10

Abbreviations: n.a. = not analysed; ? = no information available; [a] = total concentration in µg g^{-1} organic carbon; [b] = including triphenylene; [c] = sum of benzo(b)fluoranthene and benzo(k)fluoranthene; B = bituminous; L = lignite; SB = sub–bituminous; ± = mean ± standard deviation; FW = fresh water; SW = sea water; FLT = fluoranthene; PHE = phenanthrene; BaP = benzo(a)pyrene; PYR = pyrene; CHR = chrysene; NAP = naphthalene; FL = fluorene; BaA= benz(a)anthracene; BkF = benzo(k)fluoranthene; ACE = acenaphthene; DOC = dissolved organic carbon; Σ Arom. = total aromatic hydrocarbons; MOEE = Ministry of the Environment and Energy guideline (Ontario, Canada) for particulate bound PAH; taken from Curran et al. (2000), with corrected units; ANZECC = Australian and New Zealand Guidelines for Fresh and Marine Water Quality (2000); trigger level for protection of 95% of species; CWQG = Canadian Water Quality Guidelines for the Protection of Aquatic Life (2002); NOAA SQuiRT = NOAA Screening Quick Reference Tables for Organics.

References: 1 Curran et al. 2000, 2 Stahl et al. 1984, 3 Wachter & Blackwood 1978, 4 Fendinger et al. 1989, 5 Campbell & Devlin 1997, 6 Gerhart et al. 1980, 7 Bender et al. 1987, 8 ANZECC 2000, 9 Environment Canada 2002, 10 Buchman 1999

Appendix 5. Effects of unburnt coal, including leachates, on aquatic organisms.

Source: Ahrens, M., & Morrisey, D. (2005). Biological effects of unburnt coal in the marine environment. Oceanography and Marine Biology, 43, 69-122.

Species	Experiment type	Exposure condition	Coal type	Coal concentration	Assumed stressor	Observed effect	Reference
Freshwater algae	Lab	Centrifuged leachate	Sub-bituminous, Montana, U.S.	3–20% v/v	Volatile organic compounds	Stimulation of algal growth by coal leachates and changes in species composition. Growth inhibition by coal distillates in closed containers, which disappeared upon aerating containers, possibly due to removal of volatiles. In field mesocosms, 1–20% v/v distillate concentrations increased algal and bacterial numbers and killed zooplankton	Gerhart et al. 1980
Green alga (*Ulva lactuca*)	Lab	Suspended colliery waste	NE England, U.K.	29% by weight in waste, 1 g l^{-1} suspended waste	Abrasion by particulates	Reduced growth in presence of waste and water movement but increased growth with waste under still conditions	Hyslop & Davies 1998
Duckweed (*Lemna minor*) (freshwater)	Lab & field	Unfiltered slurry	Western Coal No. 1, U.S.	16.6–83.3 g l^{-1}	Metals, suspensoids	Similar growth over 16 d compared to controls; greater bioaccumulation of some metals (Ba, Co, Cu, Zn).	Coward et al. 1978
Mangrove (*Avicennia marina*), South Africa	Field	Airborne coal	n.d	n.d.	Light reduction	Reduced CO_2 exchange by 17–39%, decreased photosynthetic performance	Naidoo & Chirkoot 2004
Deposit-feeding polychaete (*Arenicola marina*), NE England	Field	Deposited colliery waste	NE England, U.K.	11% of sediment by weight	Physical destabilisation of sediment by particulates	Worms avoided ingesting coal particles during deposit feeding (possibly on the basis of particle size); avoidance of contaminated sediments in choice tests; reduced abundance	Hyslop & Davies 1999
Crab (*Cancer magister*)	Lab	Deposited (and suspended?) coal	n.d.	Up to 50% of sediment by weight	Smothering of gills by particulates	Accumulation of coal in gills at higher concentrations	Pearce & McBride 1977

Cont. 1 Effects of unburnt coal, including leachates, on aquatic organisms.

Crab (*Cancer magister*)	Lab	Deposited (and suspended?) coal	n.d.	Up to 75% of sediment by volume	Smothering of gills by particulates	No measurable difference in ventilation and oxygen consumption over 21 d relative to controls	Hillaby 1981
Marine predatory snail (*Hexaplex trunculus*), Israel	Lab & field	Coal sediment	n.d.	n.d.	Cd from direct contact	Snails from coal–impacted site had 1.8 times higher Cd concentrations in hepatopancreas, up to 3.6 times increased epithelial permeability, reduced lysosome transport and 3 times higher metallothionein levels than coal–free controls	Siboni et al. 2004
Oyster (*Crassostrea virginica*)	Lab	Suspended coal dust including leachate (pre-equilibrated for 2 weeks)	<40 um	0, 1 and 10 mg l^{-1}	PAH	No significant adverse effect on oyster survival, shell growth or pumping activity after 28 d, but clams in highest treatment had slightly reduced shell growth (non-significance due to large variance). No significant accumulation of PAHs in tissues of depurated oysters, despite observable ingestion of coal. However, note again high variance in tissue levels after 28d.	Bender et al. 1987
Deposit–feeding bivalve (*Macoma balthica*), Alaska	Field	Coal in sediments	Erosion of exposed coal seams, Kachemak Bay, Alaska, U.S.	n.d.	Saturated and unsaturated hydrocarbons	Animals from naturally coal-contaminated site contained an array of hydrocarbons characteristic of the coal in the sediment, but animals were not depurated prior to analysis, so ingestion and assimilation could not be distinguished	Shaw & Wiggs 1980
Intertidal assemblages of rocky and sandy shores, NE England	Field	Deposited colliery waste	NE England, U.K.	27% of sediment by weight	Physical abrasion, destabilisation of sediment by particulates	Reduced number of macroalgal species on contaminated rocky shores, and of macroinvertebrates on sandy shores	Hyslop et al. 1997

Cont. 2. Effects of unburnt coal, including leachates, on aquatic organisms.

Species	Experiment type	Exposure condition	Coal type	Coal concentration	Assumed stressor	Observed effect	Reference
Benthic faunal assemblages, NE U.K.	Field	Colliery waste dumped on the shore	NE England, U.K.	n.d.	Suspended and deposited particulates	Infilling of crevice habitats of crabs and lobsters, reduced abundance and diversity of soft–sediment assemblages, with only mobile polychaetes, amphipods and ophiuroids present around one of the larger beach dumpsites	Shelton 1973
Subtidal soft-sediment benthic assemblages, NE England	Field	Colliery waste dumped on sea bed	NE England, U.K.	Up to 20% in waste, and waste represents >70% of sediment	Suspended and deposited particulates	Reduced diversity and abundance at sites with large amounts of waste present, but effects of colliery waste confounded by disposal of dredge spoil at same site and by differences in water depth. No evidence of uptake of metals by commercially harvested fish and crustaceans	Norton 1985
Subtidal soft-sediment benthic assemblages, NE England	Field	Colliery waste dumped on sea bed	NE England, U.K.	1.8–5.7% of sediment by weight	Suspended and deposited particulates	Reduced abundance and diversity at former waste disposal sites compared with control site, with variable evidence of recovery among impacted sites, but one impacted site had higher diversity than the control (6 months after cessation of dumping)	Johnson & Frid 1995
Intertidal soft-sediment benthic assemblages, NE England	Field	Colliery waste dumped on shore	NE England, U.K.	Up to 20% in waste, no data given on concentration in sediment	Suspended and deposited particulates	Reduced abundance and diversity at former waste disposal sites compared with control site and undumped site with nearby, natural source of coal, with variable evidence of recovery among impacted sites	Barnes & Frid 1999

Cont. 3. Effects of unburnt coal, including leachates, on aquatic organisms.

Intertidal soft-sediment benthic assemblages, British Columbia, Canada	Field	Coal in sediments	Bituminous coal from wrecked collier	4.35% of sediment (as TOC)	Deposited particulates	Changes in benthic assemblage at sites where coal present, attributed to grain-size effects rather than the toxicity of coal-derived PAH (which showed little correspondence with sediment toxicity)	Chapman et al. 1996a
Benthic faunal assemblages, Svalbard	Field	Coal in sediments	Svalbard	n.d.	Fine sediment	High concentrations of PAH present in sediments, presumed to be derived from runoff from coal stores and general industrial activity. Low faunal diversity and dominance by species characteristic of organically enriched areas attributed to effects from deposition of fine-grained glacial sediments, untreated sewage inputs and garbage dump leachate.	Holte et al. 1996
Stream invertebrate assemblages, South Wales, U.K. (freshwater)	Field	Suspended and deposited stockpile runoff	South Wales, U.K.	n.d.	Siltation by coal particulates, low pH, trace metals	Reduced faunal abundance and diversity in both pH-affected and sediment-affected stretches of the stream, with variable susceptibility among taxa, with Ephemeroptera, Plecoptera and Trichoptera most susceptible and burrowers, e.g., chironomid larvae and oligochaetes least	Scullion & Edwards 1980
Stream invertebrate assemblages, eastern U.S. (freshwater)	Field	Coal-pile runoff	Eastern U.S.	n.d.	Trace metals, low pH	Reduced faunal diversity attributed to combination of effects of periodic drought and coal-pile runoff	Swift 1985

Species	Experiment type	Exposure condition	Coal type	Coal concentration	Assumed stressor	Observed effect	Reference
Fathead minnow (*Pimephales promelas*)	Lab	Suspended coal, spiked with phenanthrene	Sub-bituminous, Decker, Montana, U.S.	10–20 mg l^{-1}	Abrasion	No changes to gut and gill epithelium and no changes to growth rate over a 14-d period; pronounced mucus and coal accumulation in gut, but rapid gut clearance after exposure; no difference in phenanthrene uptake between coal treatments and particle-free controls	Gerhart et al. 1981
Fathead minnow (*Pimephales promelas*)	Lab	Centrifuged and uncentrifuged leachates	Sub-bituminous, Montana, U.S.	6.3 g l^{-1} centrifuged; 25 g l^{-1} uncentrifuged	PAHs	100% mortality in uncentrifuged leachate after 96 h. No increased mortality of juveniles or adults exposed to centrifuged leachate for 3–24 weeks; growth rate similar to controls, but onset of maturity delayed; 36% spawning success in leachates vs. 90% in controls; Some qualitative differences in GC analyses of tissue extracts	Carlson et al. 1979
Bullhead catfish, rainbow trout (*Ictalurus nebulosus* and *Oncorhynchus mykiss gairdneri*)	Lab	Coal heavy distillate and derived fractions	Mixed with water	10 mg l^{-1}	Hydrocarbons	Pathological responses (hyperplasia and engorgement of blood vessels of gill tissue, changes to mitochondria and rough endoplasmic reticulum), particularly in rainbow trout	Stoker et al. 1985
Rainbow trout (*Oncorhynchus mykiss gairdneri*)	Lab	Suspended coal		120–600 mg l^{-1}	Mechanical irritation	Cough rate increased twofold	Hughes 1975

Cont. 5. Effects of unburnt coal, including leachates, on aquatic organisms.

Rainbow trout (*Oncorhynchus mykiss gairdnerii*)	Lab	Suspended coal washings	Nottinghamshire, U.K., coal washings	200 mg l^{-1}	Mechanical irritation	No toxic effects but reduced growth over a 10-month period	Herbert & Richards 1963
Rainbow trout (*Oncorhynchus mykiss gairdneri*)	Lab	Centrifuged leachate	Sub-bituminous, Montana, U.S.	6.3 g l^{-1} centrifuged;	PAHs	No pronounced differences in liver parameters: liver weight, hepatic microsomal protein, DNA content and AHH activity after 28 d; no consistent increase in hepatic AHH activity and cytochrome P450 content over 21 d upon exposure to coal steam distillates	Carlson et al. 1979
Chinook salmon (*Oncorhynchus tshawytscha*)	Lab	Suspended coal	n.d.	60–500 mg l^{-1}	PAHs	Increased CYP1A1 and ribosomal protein L5 expression in liver	Campbell & Devlin 1997
Steelhead and cutthroat trout (*Oncorhynchus mykiss* and *O. clarkii*), eastern U.S. (freshwater)	Field	Suspended coal	Washington, U.S.	22.5 g l^{-1} (?)	Mechanical irritation by particulates	Mortality after 0.5–2.5 h exposures to suspended coal washing in a stream	Pautzke 1937
Eight fish species, including brown trout (*Salmo trutta*) South Wales, U.K. (freshwater)	Field	Suspended coal washings	SE Wales, U.K.	TSS up to 1530 mg l^{-1}	Suspended solids	Fish densities of all species except trout declined downstream of discharge; no spawning in main trunk of river; poor growth of trout	Williams & Harcup 1974

n.d. = no data.

Appendix 6. Coral responses to turbidity and sediment.

Schematic cause-effect pathway for the response of corals and coral communities to sedimentation and turbidity. Level of stress increasing from top to bottom (adapted from Gilmour et al., 2006).

Source: Erftemeijer, P. L., Riegl, B., Hoeksema, B. W., & Todd, P. A. (2012). Environmental impacts of dredging and other sediment disturbances on corals: A review. Mar Pollut Bull, 64(9), 1737-1765.

	Sedimentation	Turbidity
Stress		
Photophysiological stress	• Reduced photosynthetic efficiency of zooxanthellae and autotrophic nutrition to coral	• Reduced photosynthetic efficiency of zooxanthellae and autotrophic nutrition to coral; switch to heterotrophic feeding, ingestion of sediment particles
Changes in polyp activity	• Extrusion of mesenterial filaments following severe stress • Increased ciliary or polyp activity, and tissue expansion in some species, to remove sediment	• Increased ciliary or polyp activity to feed
Mucus production	• Increased mucus production or sheeting to remove sediment	• Evidence of mucus production
Severe stress		
Sediment accumulation	• Accumulation of sediment on tissue of susceptible growth forms due to failure of mechanisms of rejection	
Change in coral colour	• Change in coral colour arising from changes in the density of zooxanthellae and photosynthetic pigments • Paling of coral due to partial bleaching	• Change in coral colour arising from changes in the density of zooxanthellae and photosynthetic pigments • Darkening of coral in response to reduced light due to photoacclimation
Bleaching	• Considerable whitening of corals due to the expulsion of a large proportion of zooxanthellae from the colony	• Not known
Partial mortality	• Injury to coral tissue, loss of polyps and partial mortality of the colony • Decrease in (live) coral cover	• Injury to coral tissue, loss of polyps and partial mortality of the colony • Decrease in (live) coral cover
Mortality	• Mortality of small-sized colonies and partial mortality of large corals • Mortality of susceptible species and size classes. • Decreased density, diversity and coral cover • Changes in community structure • Wide-spread mortality of corals • Major decreases in density, diversity and coral cover • Dramatic changes in community structure, and shifts towards the dominance of non-coral species, such as sponges and algae	• Mortality of susceptible species and size classes • Decreased density, diversity and coral cover • Changes in community structure • Wide-spread mortality of corals • Major decreases in density, diversity and coral cover • Dramatic changes in community structure, and shifts towards the dominance of non-coral species, such as sponges and algae