

# Geochemistry and Heavy Metal Levels in the Sediments of the Port of Santa Bárbara de Samana, Dominican Republic

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## Abstract

In the Port of Santa Bárbara de Samana, chemical residues, organic matter and heavy metals from domestic activities are deposited together in the waters and sediments. The analysis of the sediments by X-ray fluorescence of four extracted and sectioned cores showed that concentrations of trace metals such as Nickel, Chromium, Lead and Mercury were present at various depths, exceeding Limits of Toxicity (PEL) for marine sediments according to National Oceanic and Atmospheric Administration (NOAA) and Canadian Council of Ministers of the Environment (CCME). Cadmium presented values above the toxicity threshold (TEL) in its minimum values and in its maximum values they exceeded the PEL value. While the Zinc and Copper values were low in all sections and lower than TEL. The analysis of the loss by ignition and the dating with lead 210 due to excess of the C4 core, showed a sudden change in the organic matter content and sedimentation rate. The superficial sediments show that unlike the deeper ones, the heavy metal content is lower, as well as that they do not represent a risk to the ecosystem by not exceeding toxicity levels.

## Keywords

Sediment, Heavy Metal, Port of Samana, X-Ray Fluorescence, Mercury

## 1. Introduction

The degradation of coastal areas is of great international concern (Angulo et al., 2006). Activities carried out in the cities of the interior of the continent as well as

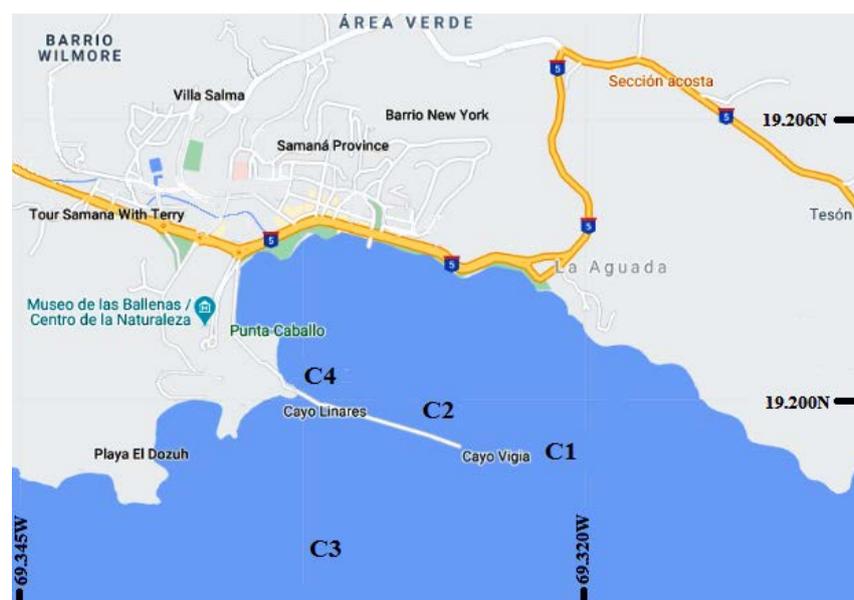
on the coasts, are affecting the coastal. These represent environmental assets that are being seriously affected (USAID-DSTA, 2006). The bay of Samana, specifically the Puerto Santa Bárbara de Samana, has been under pressure over time, decreasing its environmental quality due to wastewater and sediment contributions from the town of Samana and from the peninsula (Eptisa SYSMIN Program, 2004). Although it does not have large polluting industries, some artisan workshops could contribute to the contamination of the coastal zone together with domestic activities. The main economic sources in the region are tourism, fishing and agriculture; being its main ruble the cultivation of coconut. In the peninsula there are basaltic and karst rocks as well as some rocks with mineralogical compounds of Titanium, Magnesium and Iron (Hernaiz-Huerta, 2004); which by erosion and weathering by rains (Rodríguez-Vegas et al., 2013), especially during the presence of hurricanes and storms typical of tropical regions (Angeli et al., 2020), are deposited forming sediments in the port determining its geochemistry (Escuder-Virueite, 2008a, 2008b). Benthic animals that feed on nutrients (Valdés et al., 2014) in the sediments of the seabed (Landsea & Nicholls, 1996), can also ingest heavy metals that in many cases are toxic, inhibiting their development or reproduction (Ruelas-Inzunza et al., 2011). These heavy metals can also be bio-accumulated in the tissues and reach the humans through the food chain, which is harmful to health. The study of surface sediments gives us information (Loring & Rantala, 1992) of the heavy metal contributions associated with these that have recently been deposited (Fukue et al., 2006). The taking of cores, in addition to giving us recent information, gives us information on how the content of heavy metals has varied as measures have been deposited (Alonso-Hernández et al., 2016). To determine heavy metals in sediments, there are many techniques, the most common being Atomic Absorption Spectrophotometry (FAA) and X-Ray Fluorescence Spectrometry (XRF) (Marguí et al., 2011). Because XRF is simple and inexpensive, it is preferably used over other techniques that are normally used for these studies, such as Atomic Absorption Spectrophotometry (FAA) with a flame or Graphite furnace. If, in addition to the analysis of the metal content, the loss by ignition and the dating with excess lead 210 ( $^{210}\text{Pb}$ ) (Appleby & Oldfield, 1978), natural radio tracer (Muramat & Evans, 1977) with the which we can have information on how these have changed over time and their content of organic matter (Gaudette et al., 1974).

Dating with lead 210 (Considine et al., 2011) allows us to determine how the Sedimentary Accumulation Rate and the contributions of organic matter (Binford & Brenner, 1986) have varied for about 150 years and if it has been affected by climatic phenomena (Rozanski & Gonfiantini, 2004).  $^{210}\text{Pb}$  is a radioisotope as a result of Radio 226 decay, it can be determined by gamma, alpha or beta spectroscopy (Lozano et al., 2011). For the determination by beta spectroscopy, a Liquid Centello Counter (Mosqueda-Peña, 2010) can be used, measuring the beta activity of Bismuth 210 in secular equilibrium with  $^{210}\text{Pb}$  (Rodríguez et al., 1996). The gamma determination is carried out directly; while by alpha spectroscopy Polonium 210 (IAEA, 1992, 2016) is determined when it is in secular

equilibrium with  $^{210}\text{Pb}$  (Ruiz-Fernández & Sánchez-Cabeza, 2009), that is, when they are at the same level of radioactive emission. The TAS determined by dating with excess lead 210 ( $^{210}\text{Pb}$ ) (Sánchez-Cabeza & Ruiz-Fernández, 2012) can give us information if some measures adopted by the municipality have contributed to the decrease in the levels of heavy metals derived from human activities at any time or if there have been increases (Runnuw, 1999). As the Toxic Threshold Levels (TEL) and Permitted Toxic Levels (PEL) are above 2.0 mg/Kg in marine sediment (Buchman, 2008) in most heavy metals considered contaminants, the use of a technique to measure concentrations below this value, it is a waste of resources, in addition to being pollutants themselves, unlike XRF, which is a non-destructive technique, being able to use the sample for other analyzes or to be discarded more appropriately. The organic matter content by incineration of the sediment sample at 450 degrees Celsius is related to the loss of weight of the sample, this is known as loss by ignition (PPI) (Meyers & Teranes, 2001). Chemical elements in specific amounts are necessary for the development of living things, but higher values can be toxic, especially when this occurs in a very short period of time.

### Study Zone

The Port of Santa Bárbara de Samana is located north of the Bay of Samana (Figure 1), located north of the Dominican Republic; between the Samana peninsula and the Cordillera Oriental. The area of the port is 1.4 km<sup>2</sup> and its perimeter length is approximately 6.15 km. It is a port for small boats due to its low bathymetry. The Samana Peninsula, the place from which the natural sediments come to the port, is made up of Miocene-Pliocene siliciclastic rocks that have



**Figure 1.** Map of the Port of Santa Bárbara de Samana, Dominican Republic. Location of the cores collected in the Port of Samana; C1, C2 and C4 inside port and C3 behind the karst rock barrier.

been transformed. Quaternary marine terraces are also found, made up of stratified limestone composed of algae, mollusks and corals that are sometimes crystallized (Escuder-Viruete, 2008a, 2008b).

## 2. Materials and Methods

### Methodology

**1) For the determination of the metals in the sediments, the following procedure was carried out:** Collection of 4 cores with Uwited gravity sampler (Table 1). Sectioning at 1 cm. Dried in a plastic sleeve at 45 degrees Celsius in an oven. Crushed sediments and sieved to 75 microns. Weighing 3 grams (UNEP/IOC/IAEA, 1995), compressed in a Specac press to make a tablet. Pellet analysis by XRF in Skyray Instrument EDX-36000B spectrometer. Use reference materials IAEA-356, BCR-277, SRM-1646a and SRM-1944. To determine the characteristics of the sediments, three cores were taken inside the Port and one outside with the objective of observing the variation in the composition of the majority elements and trace elements (Salamanca, 2003), especially those heavy metals toxic (Cadmium, Arsenic, Mercury, Lead, Zinc, Nickel and Copper) present in the sediments over time and to associate it with the development of the city of Santa Bárbara de Samana.

#### 2) Lost by Ignition

From the sediments already crushed and sieved, a gram was burned of the sample in Muffle at 450°C. The residue was weighed.  $\%LOI = (W_i - W_f) / W_i \times 100$   $W_i$  is the weigh initial and  $W_f$  is the weight final. The analysis of the organic matter content related to the loss of ignition was one of the analyzed carried out on the core that we consider to be the most significant, which was the C4 core (Figure 2).

#### 3) Determination of the activity of Lead 210 in Secular equilibrium with Bismuth 210 in Sediments

From the sediments already crushed and sieved digestion of 1 gram of sample with concentrated nitric and hydrochloric acid inside a 20 ml glass vial. If the carbonate content is high, it is recommended to do it in a 500 ml flask previously, adding hydrogen peroxide to the sample before adding the acids and then transferring it after reducing it by heating to 20 ml. Let stand in a dark place for 15 days. Place on the Liquid Scintillation Analysis vials for determination  $^{210}\text{Pb}$  in secular equilibrium with  $^{210}\text{Bi}$  with LSC Hidex-Triathler. The C4 core was dated with  $^{210}\text{Pb}$  to determine the Sedimentary Accumulation Rate (TAS) (Delanoy et al., 2020) at the site and thus be able to get an idea of how the sedimentation

**Table 1.** Coordinates of the cores taking places in the Port of Samana and its outside.

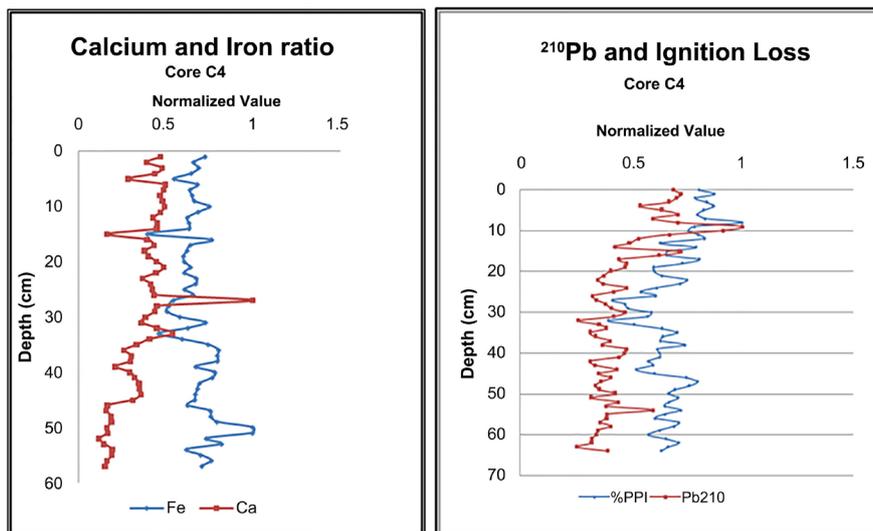
Station Code	Latitude (N)	Longitude (O)	Length core (cm)	Depth (m)
C1	19.1933	69.3198	58	5
C2	19.1960	69.3269	33	5
C3	19.1851	69.3312	14	15
C4	19.1980	69.3333	66	7

regime has changed over time and how this has been related to human activities or extraordinary natural events that have influenced the sedimentation of the port of Samana (Figure 2).

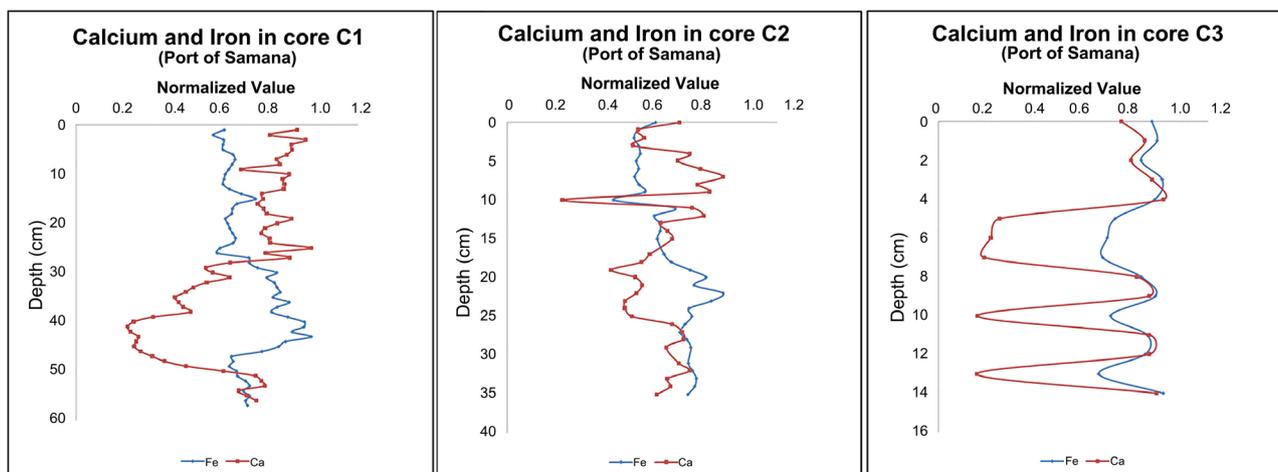
#### 4) Normalization of the Calcium, Iron, PPI and $^{210}\text{Pb}$ values to compare their behavior

Normalized value is equal to the quotient of the measure between the highest values of all the measures of the considered variable (Figure 2, Figure 3).

### 3. Results



**Figure 2.** The graph on the right shows the behavior of the loss by ignition (PPI) and  $^{210}\text{Pb}$ , these follow the same behavior, they experience similar changes in each section, the red arrows show abrupt changes due to the occurrence of meteorological phenomena extremes that change the enrichment factors of some elements (Birch, 2017). The figure on the left shows the changes occur at the same calcium and iron depths as the LOI. This occurs at 26 cm during storms Noel and Olga, 2007; 32 cm during Hurricane Jeanne, 2004; 43 cm Hurricane Klaus, 1990 (Delanoy et al., 2019).



**Figure 3.** Figures that relate the calcium and iron of the cores 1, 2 and 3. The cores 1 and 2 as well as the core C4 presents as the values of iron and calcium as one increases the other decreases, while in core 3 they have the same trend.

**Table 2.** Minimum and maximum values of heavy metals determined in three cores taken inside the Port of Samana and one outside; and the toxicity threshold values and limits according to the SquiRTs-NOAA\* and CCME\* table, in marine sediment.

Element	TEL* (µg/g)	PEL* (µg/g)	Level Range in each Core (µg/g)							
			C1		C2		C3		C4	
			Min	Max	Min	Max	Min	Max	Min	Max
As	7.24	41.6	5.8	7.3	3.9	6.6	2.0	3.1	4.5	7.2
Cr	52.30	160.0	9.6	<b>168.1</b>	3.7	<b>164.6</b>	5.7	49.0	86.1	<b>549.7</b>
Cu	18.70	108.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Pb	30.20	112.0	12.8	<b>66.6</b>	11.9	<b>43.7</b>	8.3	37.2	12.3	<b>50.4</b>
Hg	0.13	0.7	2	<b>2.5</b>	<b>2.2</b>	<b>8.2</b>	<b>2.6</b>	<b>3.4</b>	<b>2.0</b>	<b>4.2</b>
Zn	124.00	271.0	13.2	53.9	3.0	31.0	0.0	0.0	13.2	75.9
Ni	15.90	42.8	<b>37.4</b>	<b>243.7</b>	<b>66.1</b>	<b>242.0</b>	5.5	<b>132.9</b>	<b>44.3</b>	<b>246.2</b>
Cd	0.7	4.2	<b>2.8</b>	<b>6.2</b>	<b>2.2</b>	<b>13.5</b>	<b>4.0</b>	<b>6.8</b>	<b>2.3</b>	<b>16.6</b>
			Level Range in each Core (%)							
Mn			0.01	0.07	0.05	0.07	0.04	0.05	0.02	0.07
Fe			2.8	4.8	2.1	2.7	0.9	1.0	1.8	4.6
Ca			0.09	4.4	5.7	8.0	9.5	16.3	0.9	7.3
Ti			0.2	0.6	0.2	0.2	0.05	0.08	0.07	0.4

Source: \*Canadian Council of Ministers of the Environment (CCME); \*National Oceanic and Atmospheric Administration (NOAA); \*Screening Quick Reference Tables (SquiRTs); \*Threshold Effect Level (TEL); \*Probable Effect Levels (PEL).

**Table 3.** Concentration levels of the main and trace elements in the surface sediments of nuclei C1, C2, C3 and C4. Port of Santa Bárbara Samana in 2017.

Core	Depth (cm)	Majority Elements (%)					Traces Elements (mg/kg)					
		Ca	Ti	Mn	Fe	Cr	Ni	Zn	As	Cd	Hg	Pb
C1	0	4.1	0.3	0.1	3.0		150.1	29.5	6.6	6.2		25.7
	1	3.6	0.3	0.1	2.8	52.0	94.5	13.4	6.8			47.1
	2	4.3	0.2	0.1	3.0	45.1	144.0	19.9	6.5			38.5
	3	4.0	0.2	0.1	3.0	16.7	157.2	16.6	6.3			66.6
	4	4.0	0.2	0.0	3.0	75.4	112.4	16.3	6.8			26.7
	<b>Average</b>	<b>4.0</b>	<b>0.3</b>	<b>0.1</b>	<b>3.0</b>	<b>47.3</b>	<b>131.6</b>	<b>19.1</b>	<b>6.6</b>	<b>6.2</b>		<b>40.9</b>
C2	0	7.4	0.2	0.1	2.3	68.0	115.0	19.7	6.5	3.1		32.3
	1	6.8	0.2	0.0	2.3	58.2	144.7		4.5	13.5		28.1
	2	6.9	0.2	0.1	2.2	53.4	182.1	3.0	5.5	3.3		40.4
	3	6.7	0.2	0.1	2.3	59.7	117.7	21.7	6.4	3.3		35.6
	4	7.5	0.2	0.0	2.3	43.0	112.8	3.8	6.3			18.4
	<b>Average</b>	<b>7.1</b>	<b>0.2</b>	<b>0.1</b>	<b>2.3</b>	<b>56.5</b>	<b>134.5</b>	<b>12.1</b>	<b>5.8</b>	<b>5.8</b>		<b>31.0</b>
C3	0	14.8	0.1	0.0	1.0	34.8	94.2					16.5
	1	15.6	0.1	0.0	1.0	26.7	47.7				3.4	37.2

## Continued

<b>C3</b>	2	15.1	0.1	0.0	0.9	41.0	91.1		2.7		8.3
	3	15.9	0.1	0.0	1.0	11.4	104.8			4.3	12.3
	4	16.3	0.1	0.0	1.0	24.4	5.5				2.6 25.7
	<b>Average</b>	<b>15.5</b>	<b>0.1</b>	<b>0.0</b>	<b>1.0</b>	<b>27.7</b>	<b>68.7</b>				<b>20.0</b>
	0	3.4	0.3	0.0	3.3	232.6	51.7	44.5	5.7		48.6
	1	2.9	0.3	0.1	3.0	283.5	135.7	40.5	6.6		24.8
<b>C4</b>	2	3.5	0.3	0.1	3.2	144.7	103.0	61.7	6.6	2.9	22.3
	3	3.2	0.2	0.1	3.0	198.0	195.7	47.4	6.3		2.8 20.0
	4	2.1	0.2	0.0	2.5	203.9	159.8	46.8	6.6	2.3	37.1
	<b>Average</b>	<b>3.0</b>	<b>0.3</b>	<b>0.0</b>	<b>3.0</b>	<b>212.5</b>	<b>129.2</b>	<b>48.2</b>	<b>6.4</b>	<b>2.6</b>	<b>30.6</b>

#### 4. Discussion

Heavy metals nickel exceeded the Threshold Toxicity Level (TEL) and the Limit Toxicity Level (PEL), according to the SQuRTs table for marine sediment. This occurred in most sections of cores 1, 2 and 4 (Table 2), taken inside the port; not so in core 3 which was mined outside the port and separated by the barrier of karst rocks. In the superficial sediments of the C1, C2 and C4 cores, Nickel exceeded the PEL value. Chromium except in core 3 in many of the sections of the other cores exceeded the PEL (Table 2), while in core 3 the values did not exceed TEL. Indicating that the karst rock barrier retains the spread of sediment (Cattani & Lamour, 2016) and therefore of the chrome towards the bay of Samana, which are confined in the port. For the same reason, Copper, Zinc and Lead are in very low concentrations. Two of these heavy metals, Copper and Zinc, in the superficial sediments of the sampled points do not reach the TEL value; while lead was found close to its TEL value in cores C1, C2 and C4. As for the surface levels of Chromium only in core C4, this was determined above the PEL, the other sampling points barely approached the TEL (Table 3). Cadmium was found in some sections and exceeded the TEL and PEL values, possibly due to its high solubility it can be dispersed through water. At the surface level, Cadmium exceeded cores to PEL except in core C3 (Table 3). Mercury was found in some sections; could be as a result of maritime activities in the area or due to mobility during storm surges or human activities (García, 1979). In the superficial sediments of the C3 and C4 cores, a higher concentration of mercury was found than the PEL; while in the C1 and C2 cores there was no presence. Arsenic, Copper and Zinc had values below TEL and PEL values in all cores; In other words, these three elements do not represent any contamination hazard in the port, much less on the outskirts near the port. The same happened in the superficial sediments. In general, it can be observed that the superficial sediments contained heavy metal levels below the maximum values determined, as determined in cores C1, C2, C3, these values were below the TEL. Fe and Ca concentration levels have opposite tendencies in cores 1, 2 and 4 (Figure 2 and Figure

3); when one increases the other decreases. While in the core C3 both have the same tendency. These changes are related to temporary meteorological events (Delanoy et al., 2019).

## 5. Conclusion

Nickel levels in the Port of Samana are above toxicity levels according to the SQiRTs table NOAA-USEPA and the CCME in marine sediments (Table 2). This element throughout the region in soil and sediment is generally found to be exceeding these values. Reason why we consider that it's content in the sediments is not the product of polluting sources; therefore it is not possible to adopt a remediation measure in relation to this element. The surface sections of the C4 core contained Cadmium levels that exceeded the toxicity level (Table 3), the same step with the other cores. As for Chromium, the cores taken inside the port of Samana exceeded the levels of toxicity in most of the sections. In the core C3 taken outside the port, however, the levels did not exceed the TEL, indicating that this heavy metal originates from human activities. In other pollutants such as Arsenic, Copper and Zinc, their levels are below the TEL values, so the port of Samana does not require a remediation measure in relation to these trace elements. The presence of Mercury in some sections with values higher than the TEL and PEL refers to sporadic activities, since in the first 12 centimeters of the surface of the Core C4 it was only determined in one section and in the entire core in 4 sections; so it is not an element of concern. In the case of Lead, some values exceeded the TEL, reason for which it is necessary to take some surveillance measures to avoid its increase and reach the PEL. The major elements in the sediments of the Port of Samana can be considered normal since these are basically due to the mineralogical compositions of the rocks in the region. Heavy metal concentrations at the surface are generally below the maximum values of the cores; indicative of a recent improvement in the health of the ecosystem of the port of Santa Bárbara de Samana, compared to other episodes.

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## Conflicts of Interest

All authors declare no conflicts of interest in this paper.

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