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POSSIBLE INFLUENCE OF SHIPPING OPERATIONS ON TRACE METALS GRADIENTS ALONG THE COMMODORE CHANNEL, LAGOS STATE, NIGERIA

[1]Ayoola Olubunmi Nubi, [2]Olu Timilehin Ayelagbe, [1]Olaiwola Falilu Adekunbi, [*1]Samuel Olatunde Popoola, [1]Otolorin Opeyemi Oyatola

[1]Department of Physical & Chemical Oceanography, Nigerian Institute for Oceanography and Marine Research, Lagos, Nigeria
[2]Department of Marine Science & Technology, Federal University of Technology Akure, Nigeria

*Corresponding Author Email Address: popoolaos@niomr.gov.ng

ABSTRACT
The impact of shipping operations on the level of trace metals along the Commodore Channel of the Lagos lagoon is a topic that requires careful consideration. Shipping activities can have a significant impact on the water quality of the lagoon, which in turn can affect the health of the flora and fauna that depend on it. This study attempts to assess the impact of shipping operations on the level of trace metals along the Commodore Channel of the Lagos lagoon. Concentrations of trace metals in the Lagos Lagoon specifically the Commodore channel were determined in March 2016, and the downstream variation was compared. Trace metals (Pb, Cd, Fe, Zn and Co) were determined using Atomic Absorption Spectroscopy (AAS). The concentration of trace metals were found to be beyond the permissible limits stipulated by World Health Organization (WHO) and European Union (EU). There exists an exception in the mean level of Zn (0.23±0.1107mg/L) in the harbor water which was lower than the WHO standard of 5mg/L as at the time of this study. The trace metals showed the decreasing order of Pb > Fe > Zn > Co > Cd with concentration of 1.0±0.6mg/L, 0.62±0.2mg/L. 0.23±0.1107, 0.14±0.12mg/L and 0.05±0.02mg/L respectively. The result of contamination factor showed the harbor water had very high degree of Pb and Cd contamination. This high CF can be caused by the shipping and vessel transportation route and gateway of the harbor into the country. Continuous monitoring is required to assess environmental quality and adopt suitable management techniques in order to prevent the negative impacts of shipping operations on trace metal occurrence in harbors.

Keywords: Shipping, Commodore Channel, Lagos Harbor, Trace metals, Contamination Factor

INTRODUCTION

Merchant goods worth billions of dollars are moved by marine transportation daily and accounts for > 90% of global trade (Walker, 2016). Nigeria being a coastal country with a maritime space of about 315,240 km^2, is a major player in world maritime trade and transportation. Regarding the volume of merchant shipping activities the Conference on Trade and Development (UNCTAD) ranked Nigeria highest among top 35 flags registration in 2021 (Adenigbo et al.,2023) and reported as supporting approximately 80% of maritime economy on the West African coast (Adenigbo et al.,2023). However, shipping activities have a detrimental environmental impact due to contribution to marine pollution. (Byrnolf et al., 2016). In recent years, significant attention has been paid to the problems of marine environmental contamination by a wide variety of pollutants from ship discharges, such as ballast water, sewage waste, scrubber washwater, oil spills, heavy metals and plastic litter (Gilliam 2023). Specifically, shipping processes has been reported to contribute about 11-12% of marine pollution arising from pipe failures, funnel gas emissions and garbage mismanagement in port facilities impacting water quality and having negative implications on human health (Bayazit and Kaptan 2023).

Heavy metals are metallic elements which have a high atomic weight and density much greater than that of water (Tam and Wong, 2000). They are highly toxic and can cause damaging effects even at very low concentration. They tend to accumulate in the food chain and in the body and can be stored in soft tissue (e.g. kidney) and hard tissues (Canli, 2003). Reducing the effect of contamination of marine ecosystems from heavy metals has been receiving global attention.

Anthropogenic inputs contribute to the presence of pollutants that exhibit high toxicity into the marine ecological environment. The potential accumulation of waterborne heavy metals particularly Cadmium (Cd), Iron (Fe), Lead (Pb), Cobalt (Co) and Zinc (Zn) may have potential threat to marine communities and aggravate human health (Bryan and Langston, 1992). It should be noted that previous studies such as Chukwu and Akinyanmi (2018) and Basheeru et al. (2022) have survey the impact of pollutants from shipping operations in the past. However, the results of those studies may have been influenced by various other sources such as river runoffs and atmospheric depositions. Lagoons are known to be more susceptible to pollution, especially from heavy metals originating from industrial, agricultural, and urban activities compared to open seas (Bawa-Allah et al., 2018). Therefore, it is necessary to conduct location-specific studies to assess the contribution caused by shipping activities on metal occurrence in surface water around navigation channels. This is crucial in devising strategies to mitigate the impact of these pollutants. Coastal marine waters are usually enriched in trace metals compared with the open ocean (Kremling and Hydes, 1988; Kremling and Pohl, 1989). This enrichment results from the direct influence of rivers, submarine groundwater discharge (SGD), atmospheric dust deposition, natural weathering, or anthropogenic sources including shipping operations discharging along the coast (Ali et al., 2019). Therefore release of trace metals from anthropogenic activities is usually the major cause of the increase in concentrations that may result in alterations to their natural geochemical cycles. The influence of aerosol deposition may be exacerbated in some coastal environments such as harbours and bays, where industrial activities have concentrated since the industrial revolution, dumping large amounts of contaminants that accumulate in sediments. Shipping is one of the industrial activities that contribute to the increased in marine pollution (Lafabrie et al.,

2007; Garcia-Orellana et al., 2011; Moldanová et al., 2022).
This study focuses on the impacts of shipping operations on the concentration of selected trace metals in the surface waters of the Commodore channel, a shipping hub in Lagos, Nigeria, with the following objectives. (i) To investigate the concentrations of Cd, Co, Fe, Pb and Zn in the channel surface water. (ii), to determine the impact of shipping operation on the spatial distribution of the trace metals. (iii), to evaluate the degree of trace metals contamination in surface water around the Commodore channel.

Study Area
The Commodore channel is a navigational waterway along the bar beach of Lagos Nigeria West Africa, located between coordinates 3°23'51.46"E -3°21'31.04"E and 6°26'8.96"N -6°26'16.81"N (Badejo et al., 2020). The channel lies along Lagos Harbour where the Lagos lagoon opens to the Atlantic Ocean and contains ports and terminals facilities for bulk cargo clearing. At the entrance to the channel are two breakwaters, the East and West moles constructed to abate sedimentation due to longshore drift (Laibi et al., 2014) and fluvial processes (Rabiu et al., 2023) and to facilitate an unobstructed ship navigation. Nwilo et al. (2021) reported a consistent increase in average depth (11.67m) of the channel between 2012 and 2018 that is in connection to continuous dredging and its exposure to dynamic forces acting along the Lagos coast (Olusegun et al., 2017). The harbour waterway also host commercial offices of many shipping, clearing and transportation companies. It is one of the three main navigational channels in Lagos Nigeria; others include Elegbeta channel and the Apapa channel. It has a depositional nature with sand dredging being carried out on its sides. It is adjacent to the high wave energy waters of the Atlantic Ocean. The study site was chosen based on a preliminary survey to identify and locate low, medium and highly impacted sites by shipping operations. The channel was surveyed and partitioned into nine stations along its longitudinal axis, i.e. (CH 01, CH 02, CH 03, CH 04, CH 05, CH 06, CH 07, CH 08 and CH 09). and classified into, high, medium and low impacted areas based on shipping operations. The stations CH 01, CH 02, CH O3 are within the high impacted areas which include ship harbours, jetties, shipping lanes and dockyards. The areas around slums and industrial straits i.e stations CH 04,CH 05,and CH 06) are the medium impacted areas while Stations (CH 07, CH O8 and CH 09) around the opening to the Atlantic close to the harbour entrance experience low shipping impact.

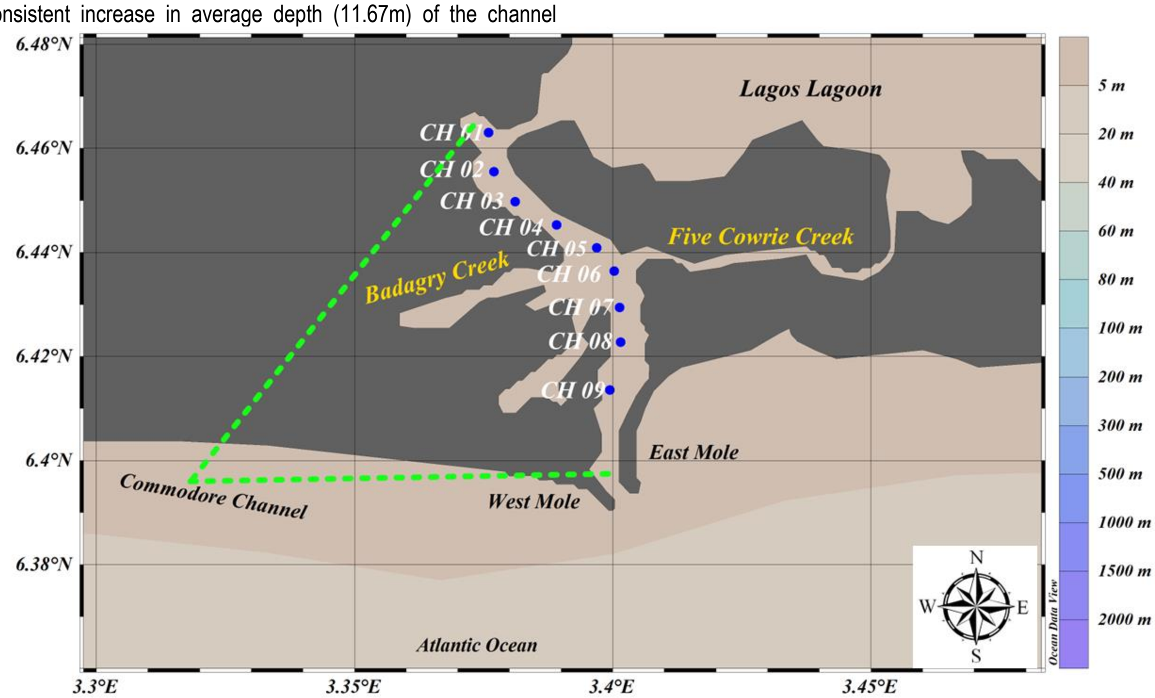

Figure 1: Map of Commodore Channel and associated sites in the Lagos Harbour

MATERIALS AND METHODS
Collection and analyses of water samples
Surface water samples for heavy metals were collected during a survey in March 2016 along a longitudinal transect at nine locations (Figure 1). Samples were collected at 0.5 meters depth with plastic bottles soaked overnight with nitric acid and rinsed with de-ionized water. The collected water sample was used to rinse bottles thrice before taking samples and labelled immediately. Samples were kept at a temperature of 4 ºC and laboratory analysis was done within three days.
Samples were further pre-treated by adding 5 ml of nitric acid (HNO_3) to ensure that the respective ions remain in solution pending analysis. Sample digestion was done following the procedure by Charles et al. (2018), using standard digestion procedure according to American Public Health Association, (APHA, 1998). Water samples were subjected to standards according to the World Health Organization standard (World Health Organization, 2006).Analytical grade reagents were used in all analyses and conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society (Keith et al., 1983).The digested samples were analysed for heavy metals (Pb, Cd, Fe, Zn and Co) concentrations from the nine stations with Agillent 200 A model, Atomic Absorption Spectrophotometer (AAS).

Pollution indices

The contamination factor depicts the level of the anthropogenic metal contamination, and is calculated by the ratio of metal content at a given station to the background concentration levels. The degree of trace contamination in surface water of the Commodore Channel was evaluated according to Popoola et al. (2015).

$$C_F = C_{metal}/C_{background}$$

Where;

C_F = mean concentration of trace metal in water;

$C_{background}$ = pre-industrial concentration of the trace metal

RESULTS

Trace metals concentration in surface water samples

Mean concentration of the investigated trace metals in the channel and the permissible limits are shown in Table 1. Lead had the highest concentration while Cd showed the lowest occurrence. The mean concentration followed decreasing order; Pb>Fe>Zn>Co>Cd. The mean concentrations of trace metals were compared to their permissible limits by WHO and EU as reported by Mahmud et al. (2016) and Popoola et al. (2015) Table 1. Cadmium, Co, Fe, and Pb all had mean concentration 0.05±0.02 mg/L, 0.14±0.12 mg/L, 0.62±0.16mg/L and 1.00±0.60mg/L which were respectively above permissible limit by WHO (2004) and US EPA (1999). The mean Zinc (0.23±0.11 mg/L) level in the water of the channel was below the permissible limits set by WHO and the US EPA..

Trace metals spatial distribution

The distribution of trace metals along the longitudinal axis of the Commodore channel is shown in Figure 2. Cadmium ranged from 0.03 to 0.08 mg/L in the surface waters of the stations (Figure 2a). Cobalt concentration ranged from 0.03 to 0.4 mg/L. It showed its lowest (0.03 mg/L) and highest (0.4 mg/L) concentrations in stations CH 05 and CH 09 respectively (Figure 2b). The concentration of Fe in surface water of the Commodore

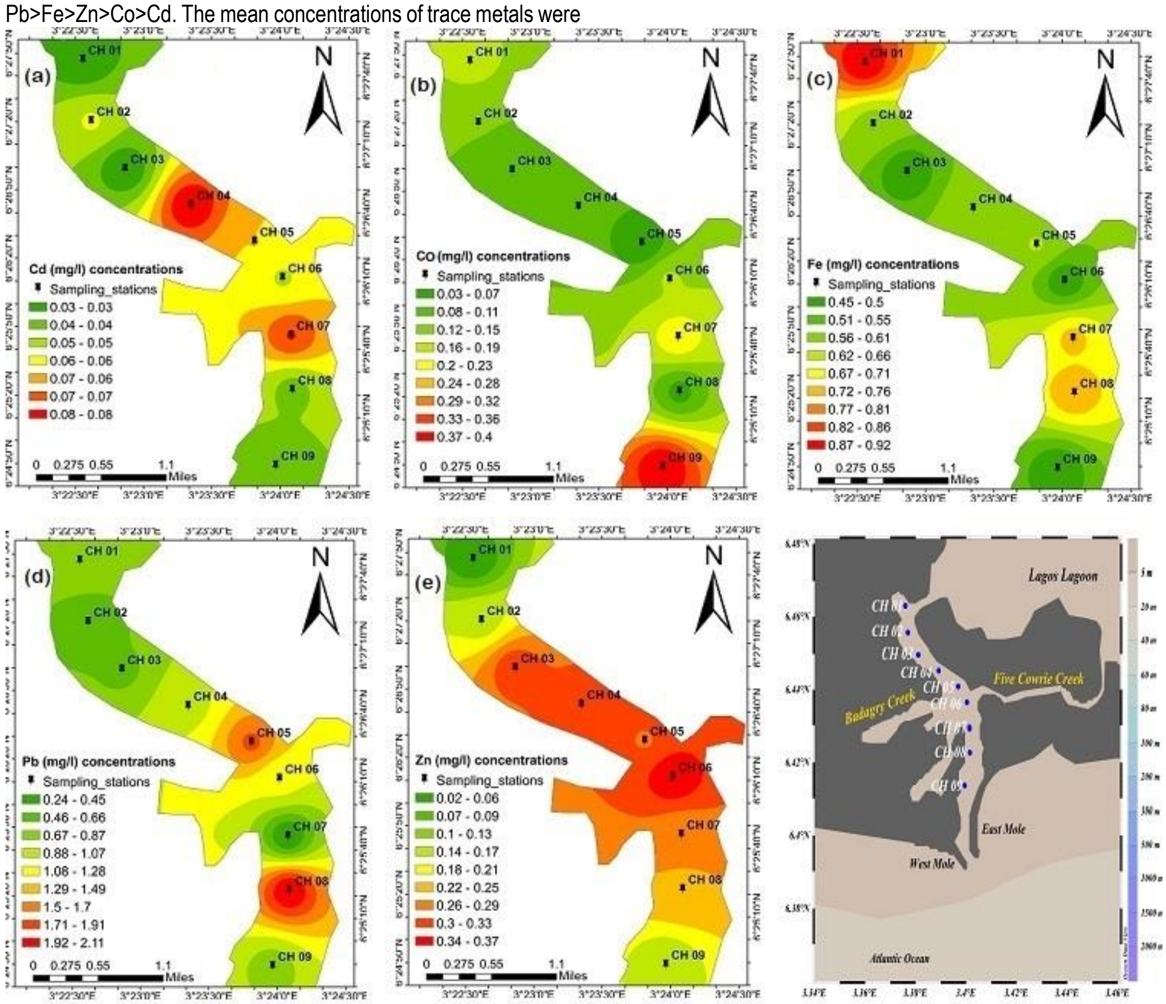

Figure 3: Distribution of trace metals along the Commodore Channel

channel ranged from 0.5 to 1.0 mg/L (Figure 2c) Station CH 01 demonstrated the highest concentration in Fe content which is in the high impacted harbour area. Lead showed the highest occurrence in the trace metals distribution in the surface water in the Commodore channel. It ranged from 0.2 mg/L in station CH 07 to 2.1 mg/L in station CH 08 (Figure 2d). It exhibited the highest concentration of all the trace metals distributed in the channel. Zinc concentration ranged from 0.01 to 0.4 mg/L. It showed its lowest concentration in station CH 01 which is a high impact region of the

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ship harbour.

Table 2: Summary of trace metals concentrations (mg/L) in Commodore Channel and the permissible limits of trace metals in water (Mahmud et al., 2016; Popoola et al., 2015)

Trace metal		**Permisssible Limit (mg/L)**	
	Mean±SD (mg/L)	WHO	US EPA
Cd	0.05±0.02	0.005	0.005
Co	0.14±0.12	0.05	
Fe	0.62±0.16	0.6	-
Pb	1.00±0.60	0.005	0.015
Zn	0.23±0.11	5.0	5,0

Degree of trace metals contamination
Contamination factor of trace metals in Commodore Channel was analysed to ascertain the degree of contamination (Figure 3). Contamination factor of an aquatic system value is categorized into four classes. Class 1, low contamination factor CF<1; Class 2 moderate contamination factor 1≤CF<3; Class 3 considerable contamination factor; 3≤CF≤6 and Class 4 very high contamination factor CF<6 (Roy et al., 2021). The contamination factor of the trace metals can be arranged in descending order; Pb > Cd > Co > Fe > Zn. Accordingly, Zn fall in Class 1 which means it showed low contamination, Co is categorised in Class 2 i.e. of moderate contamination while Pb and Cd both fall in Class 4 which is very high contamination factor and (Figure 3).

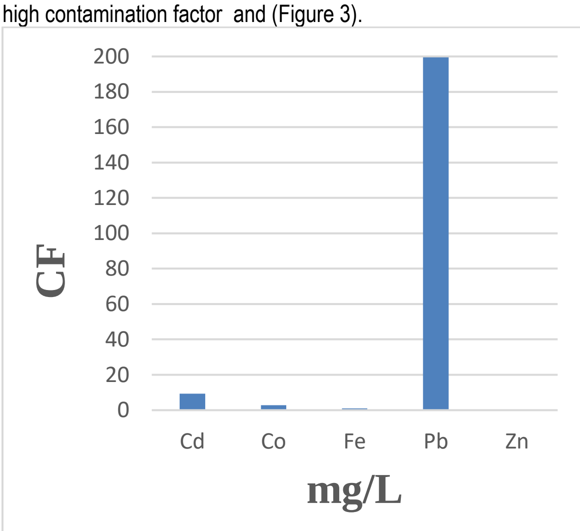

Figure 4: Contamination factor of trace metals in Commodore Channel

DISCUSSION
With the exception of zinc, the research results reveal that the concentrations of the four other trace metals (Pb, Cd, Fe, Zn) investigated in this study are above the WHO acceptable limits for drinking and fishing (Table 1 and 2). This signifies that the concentration of trace metals in the surface water in the harbour area is relatively high, suggesting a direct impact of shipping which is a predominant activity observed. Previous studies in the Lagos harbour concentrated on the presence of heavy metals in sediments and as well as in surface waters. Ihenyen (1991) observed that the part of the harbour where shipping activity was most intensive had low levels of heavy metal pollution, whereas the area around the harbour entrance and the northwest sections, associated with effluent release from industries had medium and high levels of pollution respectively. However, in a recent study, Basheeru et al. (2022) investigated the health risk of potentially toxic elements (PTEs) in surface water of the Lagos harbor. The authors found variable amounts of Pb, Cd, Cr, and Ni in the harbour's water, with the greatest quantities found in industrial zones and shipping lanes. These metals were also found to be beyond the international allowable limits for drinking and industrial water quality. In the present study, the level of the metals is found to be highest in the high and intermediate impact zones, demonstrating a link between the shipping operation and the level of the metals.

Cadmium
The high level of cadmium observed in the high impact zones could be indirectly attributable to this activity since certain cadmium-containing items and materials may be carried by ships. Furthermore, Cadmium levels in the water could also be enhanced as it does not react with water hence its high values. Cadmium levels are observed to be concentrated in the region. Stations CH03 and CH09 have low pollution levels because there is no active or stationary pollution. This demonstrates that the effect is strongly related to the waterways influenced by shipping operations.

Cobalt
The above average permissible levels of Cobalt (0.14±0.12 mg/L) at stations CH 09, CH 07 and CH 01 with the lowest observed at Stations CH 05 and CH 08 may be related to its usage in the production of ships and local fishing boats. Cobalt is used in paints to produce blue colour and to produce wear resistant and high strength alloys (Mark Winter, 2016). This explains the high level encountered in locations 9, 7 and 1. Pure cobalt does not react with water, but its compound does (Friedrich Stromeyer, 2016) hence the low level observed in the shipping lane. Its non-reactivity makes it absent in the effluent being discharged at location 8, hence a low level observed there.

Iron
The highest level of Fe (0.61562±0.1569) above the permissible levels for drinking waters by the world health organization is observed at stations CH 01, CH 07 and CH 08 with the lowest observed at stations CH 09, CH 06 and CH 03 may be attributed to its application in the production and maintenance of ships. The high concentrations observed in locations CH 01, CH 07 and CH 08 can be attributed to the high corrosive nature of iron in the presence of water and air. This is further explained as these locations are highly involved in the use of iron. Just like the cobalt and cadmium areas in which carriers of this metal are not stationary are seen to have low levels suggesting that they are localized. The point that the effect of the iron is localized is affirmed in its standard deviation of 0.1569 which represent a low value as compared to the mean of the iron levels observed.

Lead
The high concentration of Pb (1.0±0.6 mg/L) than the permissible limit by international standards for drinking water at stations CH 08 and CH 05 with the lowest observed at stations CH 07, CH 09 and CH 02 (Figure 3d) can be attributed to its usage as a bye-product

of combustion. Pb is found to be highest around shipping lanes signifying their presence owing to the combustion of the ship engines and lowest at the parking lot or harbours of the ships wherein there is no engine operation. This points out to the fact that shipping operations affect the level of the trace metals. The concentration is a little evenly dispersed signifying that there are other source of input of this pollutant into the waterways. This means that the effect of shipping operations is not confined to an area.

Zinc
The enriched concentration of Zn (0.14±0.12 mg/L) than the stipulated permissible limit is attributed to corrosion of galvanized metal. When galvanized metal is exposed to an acidic water, zinc is dissolved from the exposed surface, along with iron and trace amounts of lead and cadmium (Bird et al., 1996). The highest level is observed at Station CH 06 and CH 03 with the lowest observed at stations CH 01 and CH 09 (Figure 3e), and increase seaward suggesting an offshore source . In addition, the contamination factor of class 4 exhibited by Pb and Cd indicates the harbour water is highly contaminated by these metals. On the other hand Zn exhibited contamination factor of class 1, an indication that this metal possess low degree of contamination in the harbour environment.

Conclusion
The various observations in this study has shown that shipping operation can be attributed to trace metals pollution levels in the waterways. The result showed high level of the pollutants above international standards in high impact delineated area. This high level also spreads down to other zones delineated medium and low. For some of the pollutants the effect could be suggested to be localized and in some areas regional. The influence on trace metals varies, with cobalt and zinc not localized in any particular order, but cadmium, cobalt, and iron are limited to areas of significant impact. By analyzing the trace metal content in Lagos's Commodore Channel, this study attained its goals and objectives. The findings indicate that the Commodore Channel is of medium to highly-contaminated by trace metals. The metals have considerable potential for adverse impacts on the local ecosystem. As a result, these metals must be checked to ensure that their levels are lowered.
To achieve this, public awareness must be raised through mass media because stakeholders in the maritime sector need to be sensitized to the damage that shipping activities poses on the marine environment. In order to provide a clean and safe environment, frequent data on water quality throughout shipping operations should be collected and compiled.

Recommendation
The key trace metals analyzed are present in such high amounts that they cannot be supplied only from shipping activities, as evidenced by the results and concentrations gathered. This region should be investigated further, and any sources of contamination should be discovered. Another transect might be investigated starting at the mouth of the ocean to see other point source and direction of pollution. Several authors have proposed that pH, salinity, temperature, and redox potential all influence metal absorption and retention in sediments. This component should be researched more in order to completely understand metals occurrence in this environment.

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