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Trend analysis of heavy metals, Ni, Pb, Cd and As in marine sediments – A case study of ONGC Block (KG OSN 2009/2) in Krishna-Godavari Basin, Bay of Bengal

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Abstract

Heavy metals can be termed as conservative pollutants, introduce into the aquatic systems as a result of the weathering of soils and rocks, from under water volcanic eruption and other anthropogenic activities. Thereby it changes the natural concentration of metals in seawater resulting in a ten or even hundred fold increase near the source of an effluent discharge. While some metals like manganese (Mn), copper (Cu), iron (Fe) and zinc (Zn) are biologically important for marine life, others like Nickel (Ni), Lead (Pb), Cadmium (Cd), and Arsenic (As) are non-essential and become toxic at higher concentrations. Associated to particulate matters, heavy metals tends to stay in solution for a very long time, but they will end up in the sediments,

Therefore concentrations in the sediments are often higher than those in solution. In the sediments, these particles may form an important secondary source of contamination, even after the primary source has disappeared. Therefore, there is a need for timescale monitoring of the levels of these metals in all the marine resources, so as to establish the trends that could be linked to anthropogenic activities.

In this paper, the effect of E&P activities of ONGC Block (KG OSN 2009/2) in Krishna-Godavari Basin, Bay of Bengal is studied, by carrying out a trend analysis of heavy metal concentration (^{60}Ni, ^{208}Pb, ^{111}Cd, and ^{75}As) in the sediments from this block. Sediments samples were collected from the ONGC Block (KG OSN 2009/2) using OSPAR commission guidelines and the heavy metal concentration values averaged out. These average values are used to analyze the trend for a period extending from 2015 up to 2019.

In the years 2016, the pollution level recorded was minimum. Overall, from 2015 to 2019, ^{208}Pb shows a decreasing trend line, but ^{60}Ni, ^{111}Cd, and ^{75}As shows an increasing trend line. Albeit the increasing trend of ^{60}Ni, ^{111}Cd, and ^{75}As concentration are a matter of concern, but all the values are below the ERL (effects range low) set by the National Oceanographic and Atmospheric Administration (NOAA), USA. Hence, it can be concluded that the oil field activity of ONGC in the Eastern Offshore has not made any significant impact on the marine environment, in terms of heavy metal pollution.

A statistical analysis in terms of Relative Contamination Factors and Pollution Load Index has also been done in the paper.

Keywords: E&P Activities; Krishna-Godavari Basin; Sediment

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1. Introduction

Govt. of India started encouraging upstream hydrocarbon industry to surge the domestic oil and gas production to shrink import encumbrance. World-wide experiences with updating technology have proven that offshore regions have great potential for exploration and production (E&P) activities. These E&P activities, include exploration, development, production and transportation activities etc., may have adverse impact on marine environment. Oil and Natural Gas Corporation Limited (ONGC), accounts for two third of India's total oil and gas production, has an environment protection policy under which environmental monitoring study is carried out in its operational areas including exploratory blocks of the KG-PG Basin in Bay of Bengal. Present paper deals with the concentration of heavy metals in the sediments of shallow water block, KG-OSN-2009/2, in Krishna-Godavari Basin in Bay Bengal.

Marine environmental pollution is a worldwide problem and heavy metals belonging to the important pollutants. They are intrinsic, natural constituents of aquatic environment in small concentrations. In oceans, they originate from both natural processes and anthropogenic activities. Natural processes like soil erosion around mangrove forests, atmospheric inputs and Aeolian processes set the background values whereas anthropogenic inputs, rapid industrialization and urbanization in coastal regions, are the main sources of pollution in the marine environment. Heavy metals are also increasingly introduced to the coastal environments through oceanic dumping and riverine discharge where rivers that flow via high-populated urban areas may carry these substances to the downstream. It is difficult to remove them completely from the marine environment once they enter into it.

The study of heavy metals in the aquatic environment has attracted more attention in comparison with other pollutants due to their non-biodegradable nature, accumulative properties and long biological half-lives. They also pose potential threats to ecosystems because they could be concentrated and biomagnified at sufficient high concentrations, and partly converted to more toxic organic compounds. Many of these metals tend to remain in the ecosystem and eventually move from one compartment to the other within the food chain. Heavy metals from the aqueous phase eventually become deposited to sediment through various physical, chemical or biological mechanisms. Therefore, the distribution of metals in sediments might provide evidence for anthropological activities and their impact on ecosystems. Due to this, sediments are commonly chosen as environmental indicators of the quality and potential risks within aquatic systems.

In this paper, analysis of distribution of four non-essential heavy metals, ^{60}Ni, ^{208}Pb, ^{111}Cd, and ^{75}As, has been done in marine sediments of ONGC Block (KG OSN 2009/2) in Krishna-Godavari Basin, Bay of Bengal, from 2015 to 2019.

2. Study Area

Krishna-Godavari Basin in Bay of Bengal is considered significant address for oil and gas reserves. Subsequently, offshore E&P activities have been started on Indian east coast nearly two decades ago by public and private operators as well. The study area extends from 15.243ºN to 15.508ºN and 80.204ºE to 80.490ºE. In the study area, the depth of water column varies from 16-165 m.

Sr. No.	Block/Location	Latitude (˚N)	Longitude (˚E)	Depth (M)
1	KG OSN 2009/2	15.508 to 15.243	80.490 to 80.204	Varying between 16 to 165

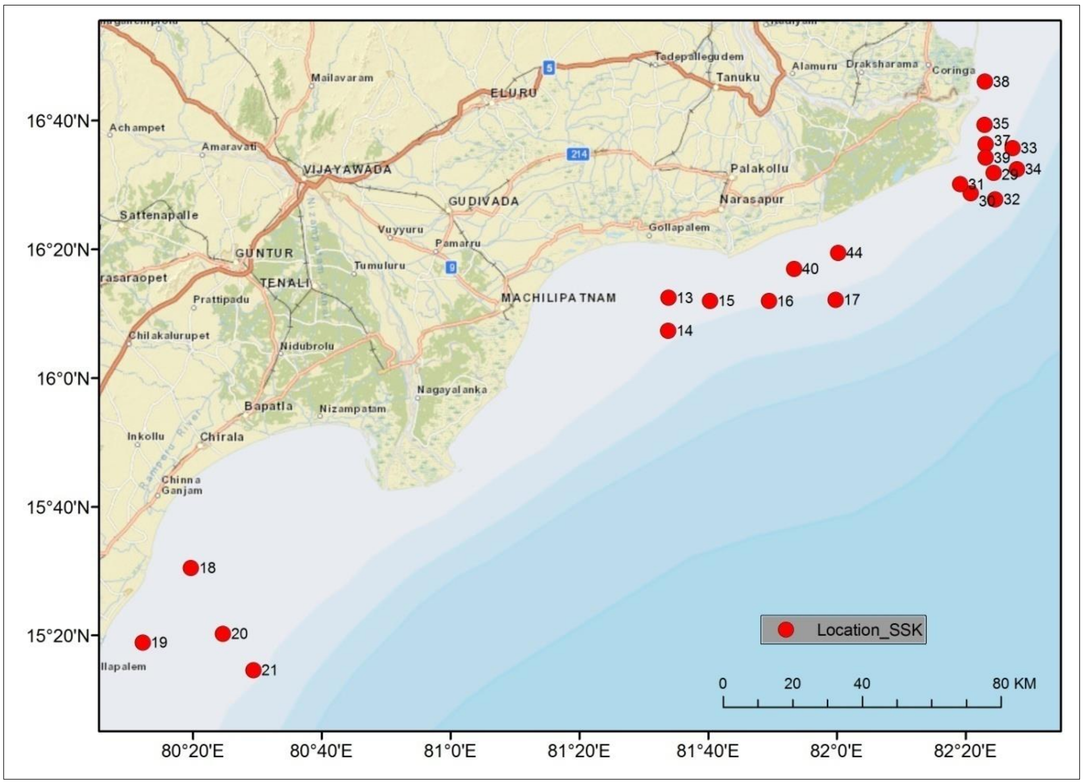

Figure 1 Map showing the location of sampling stations in the study area

3. Materials and Methods

3.1. Sample Collection and Pre-treatment

The box-corer available with CSIR-National institute of Oceanography (NIO)'s offshore going research vessel RV Sindhu Sankalp was operated for the collection of sediment samples from the block. Sediments of the upper 5 cm were collected with a plastic spoon and stored in clean vinyl bags to prevent the possible contamination. As soon as the field work was finished, sediment samples were carefully shipped and preserved at laboratory. From the bulk sediment, a representative subsample was transferred to an oven and dried at 50 ± 2 ^{0}C. The homogenized samples were then ground to powder in granite mortar with a pestle and kept in a pre-cleaned container for further analysis.

3.2. Laboratory Analysis

Trace metal extraction is carried out following the standard method EPA 3052. Approximately 200 mg of homogeneous sediment sample was digested with 6 mL of nitric acid and 3 mL of perchloric acid in Teflon vessels for 50 minutes using a closed microwave reaction system (Perkin Elmer, Titan MPS). After cooling the vessel completely, dissolved samples were then filtered through Whatman filter paper and diluted to 25 mL with milli Q water. The extract was stored in polythene bottles at 4°C till the analysis of trace metals. Similarly, duplicate samples were digested following the slight diverse method for mercury analysis and stored in glass bottles at 4°C for mercury analysis.

In order to obtain more accurate data, all the glassware and Teflon sample cups in this study were soaked with 5% nitric acid, rinsed with milli-Q water, and dried to eliminate potential contamination. An inductively coupled plasma mass spectrometer (ICP-MS; model Agilent 7700) was used for determination of trace metals concentration. Background correction and matrix interference were monitored throughout the analysis. The accuracy was examined by analyzing all samples in duplicate. The analytical concentrations of the selected metals of our interest were listed in Table 1.

OSPAR (Oslo and Paris) Commission Guidelines [2] have been followed, as shown in Figure 2.

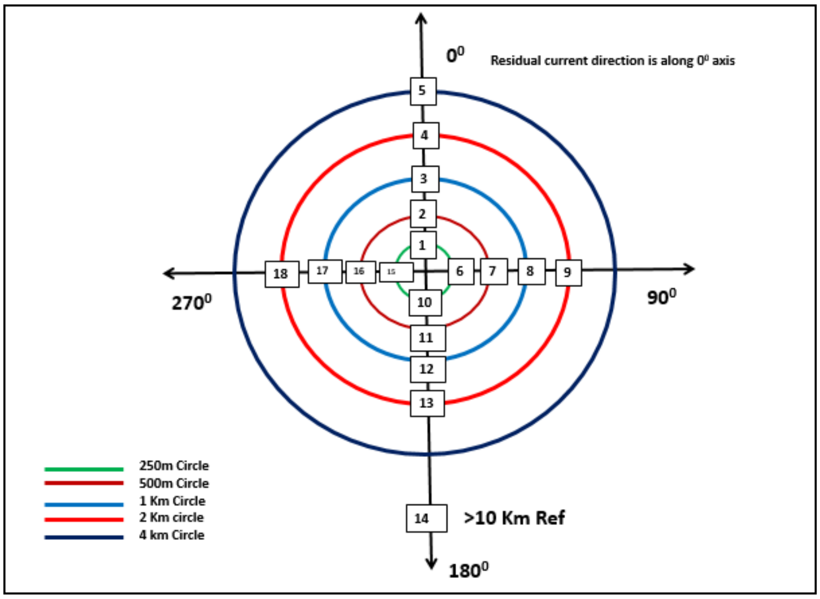

Figure 2 OSPAR Commission Sampling Strategy

During the oceanic cruise onboard RV *Sindhu Sankalp* sediment sample was collected using a large Van Veen Grab Sampler (0.4 m^2) and a spade corer. In the case of sampling in the shelf and slope region using the mechanized boat, a relatively small Van Veen Grab Sampler (0.04 m^2) was used. Immediately after collecting the sediment samples, the physical appearance of the sediments (as per OSPAR convention) and visual details of the sediment surface (e.g. presence of drill cuttings, debris, and empty shells) were noted. The sediment samples were then imaged with a high quality field camera. Presence/absence of large and/or conspicuous fauna were recorded. Sediment colour based on Munsell Soil Colour Chart System and sediment smell (e.g. H_2S, Oil) were recorded. Sub-samples for all chemical and biological parameters were collected from the sediments collected using the Van Veen Grab samplers and the box corer.

4. Results and Discussion

The distribution of Ni, Pb, Cd and As, over the ONGC Block (KG OSN 2009/2) in Krishna-Godavari Basin, Bay of Bengal, was determined annually from 2015 to 2019. For each year, the values were averaged out for each metals (^{60}Ni, ^{208}Pb, ^{111}Cd, and ^{75}As). The average concentration of these elements in the ONGC Block (KG OSN 2009/2) in Krishna-Godavari Basin, Bay of Bengal have been tabulated year-wise in Table 1.

Also, added to the table are values of ERL (Effects Range Low) and ERM (Effects Range Medium), of the respective elements, set by NOAA (National Oceanographic & Atmospheric Administration, US) [3].

Table 1 Concentration of Ni, Pb, Cd and As in sediments from 2015- 2019

Year	**Concentration in *ppm***			
	Nickel (^{60}Ni)	**Lead (^{208}Pb)**	**Cadmium (^{111}Cd)**	**Arsenic (^{75}As)**
2015	14.70	6.82	0.09	2.33
2016	13.67	5.94	0.06	0.82
2017	22.23	6.25	0.20	3.56
2018	19.61	7.94	0.08	5.26
2019	17.25	5.87	0.12	2.15
ERL	20.90	46.70	1.20	8.20
ERM	51.60	218.00	9.60	70.00

4.1. Graphical Representation

Data from Table 1 has been graphically plotted in Figure 3, 4, 5 and 6.

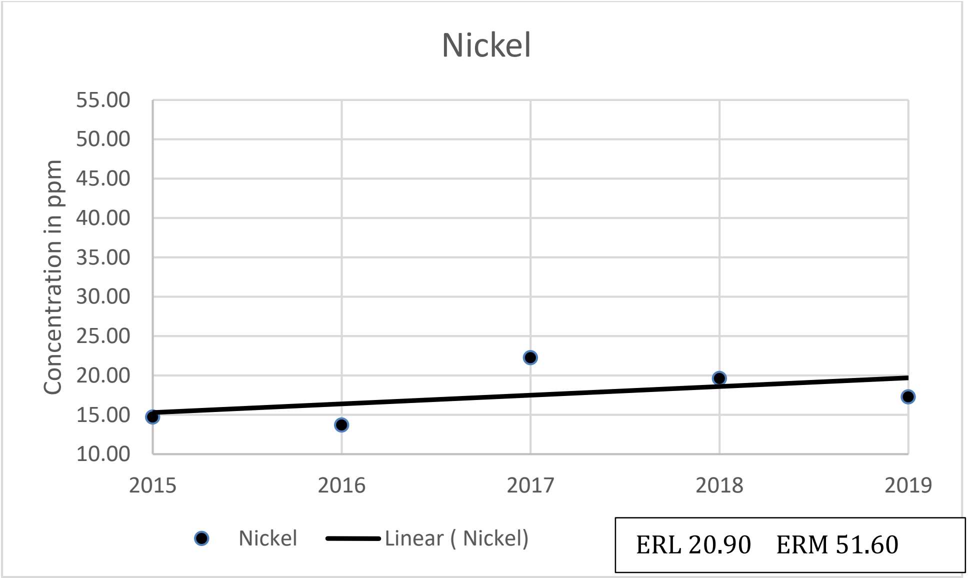

Figure 3 Concentration of ^{60}Ni in sediments from 2015- 2019

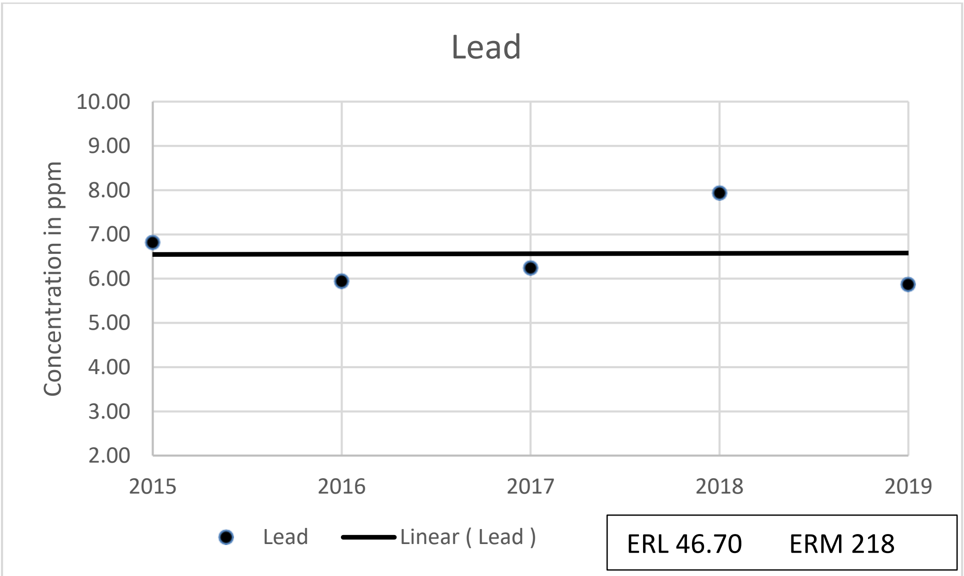

Figure 4 Concentration of ^{208}Pb in sediments from 2015- 2019

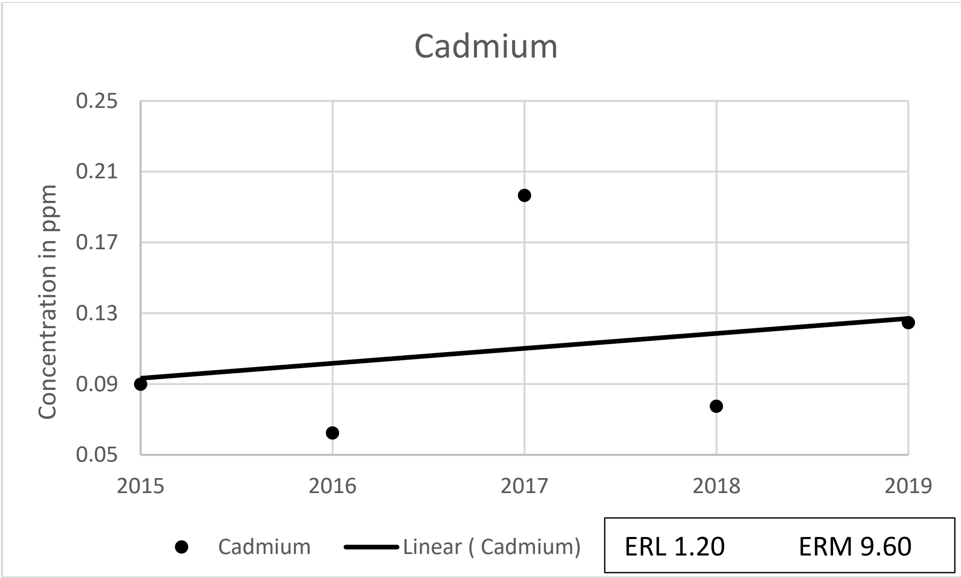

Figure 5 Concentration of ^{111}Cd in sediments from 2015- 2019

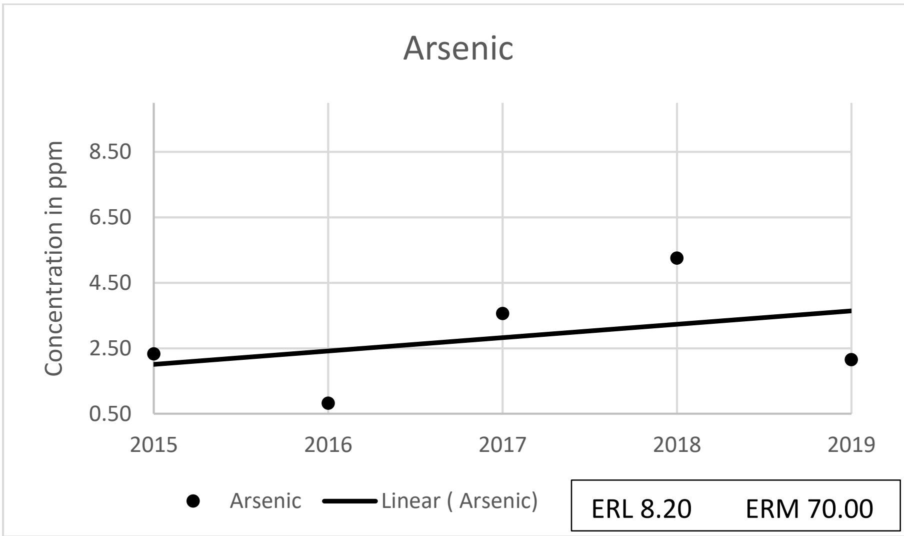

Figure 6 Concentration of ^{75}As in sediments from 2015- 2019

4.2. Trend Analysis

4.2.1. Nickel (^{60}Ni)

Average values of Nickel in sediments fluctuate from 13.67 to 22.23 ppm during the years 2015-2019, the highest being in 2017 and lowest in 2016 (Table 1).

Considering concentration of Nickel from around the overall study areas, a trend analysis has been made from 2015 to 2019 as shown in Figure 3.

The trend line has a positive slope, and hence the concentration of Ni is showing a increasing trend with time.

However, the trend line and all average concentrations are well below the ERL set by NOAA.

4.2.2. Lead (^{208}Pb)

Average values of Lead in sediments fluctuate from 5.87 to 7.94 ppm during the years 2015-2019, the highest being in 2018 and lowest in 2019 (Table 1).

Considering concentration of Lead from around the overall study areas, a trend analysis has been made from 2008 to 2018 as shown in Figure 4.

The trend line has a negative slope, and hence the concentration of Pb is showing a decreasing trend with time.

However, the trend line and all average concentrations are well below the ERL set by NOAA.

4.2.3. Cadmium (^{111}Cd)

Average values of Cadmium in sediments fluctuate from 0.06 to 0.20 ppm during the years 2015-2019, the highest being in 2017 and lowest in 2016 (Table 1).

Considering concentration of Cadmium from around the overall study areas, a trend analysis has been made from 2015 to 2019 as shown in Figure 5.

The trend line has a positive slope, and hence the concentration of Cd is showing a increasing trend with time.

However, the trend line and all average concentrations are well below the ERL set by NOAA.

4.2.4. Arsenic (^{75}As)

Average values of Arsenic in sediments fluctuate from 0.82 to 5.26 ppm during the years 2015-2019, the highest being in 2018 and lowest in 2016 (Table 1).

Considering concentration of Arsenic from around the overall study areas, a trend analysis has been made from 2015 to 2019 as shown in Figure 6.

The trend line has a positive slope, and hence the concentration of As is showing a increasing trend with time. However, the trend line and all average concentrations are well below the ERL set by NOAA.

4.3. Statistical Analysis

Sediment quality can be assessed in terms of Contamination Factor (CF) and Pollution Load Index (PLI). CF_{metals} is the ratio between the content of each metal to the background values.

i.e., $CF_{metals} = C_{metal}/C_{background}$

CF can be classified into four grades for monitoring the pollution of one single metal over a period of time: low degree (CF < 1), moderate degree (1 ≤ CF < 3), considerable degree (3 ≤ CF < 6), and very high degree (CF ≥ 6). Thus, the CF values can monitor the enrichment of one given metal in sediments over a period of time.

The PLI is defined as the nth root of the multi-plications of the contamination factor of metals

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n)^{1/n}$$

PLI value of zero indicates excellence, a value of one indicates the presence of only baseline level of pollutants and values above one indicate progressive deterioration of the site and estuarine quality [4].

Taking values of 2015 as baseline, CF and PLI has been calculated for 2016-2019.

$$CF_{metal} = C_{metal\ in\ required\ year}/C_{metal\ in\ 2015}$$

$$PLI = (CF_{Ni} \times CF_{Pb} \times CF_{Cd} \times CF_{As})^{1/4}$$

Table 2 Statistical Analysis of Sediment Quality

Year	CF_{Ni}	CF_{Pb}	CF_{Cd}	CF_{As}	PLI
2016	0.93	0.87	0.69	0.35	0.67
2017	1.51	1.92	2.19	1.53	1.47
2018	1.33	1.16	0.86	2.26	1.32
2019	1.17	0.86	1.39	0.92	1.07

4.3.1. Nickel (^{60}Ni)

CF is more than 1, indicating low degree of Ni contamination, relative to values recorded in 2015.

4.3.2. Lead (^{208}Pb)

CF is near to 1 indicating very low degree of Pb contamination, relative to values recorded in 2015.

4.3.3. Cadmium (^{111}Cd)

CF is near to1, indicating low degree of Cd contamination, relative to values recorded in 2015.

4.3.4. Arsenic (^{75}As)

CF is more than 1 indicating low degree of Pb contamination, relative to values recorded in 2015.

PLI values are more than1, indicating progressive deterioration of the site and estuarine quality.

5. Conclusion

The trend analysis (2015-2019) of contamination of sea sediments around the study area reveals that concentration of ^{208}Pb is decreasing whereas concentration of ^{60}Ni, ^{111}Cd, and ^{75}As are observed to be increasing. Nonetheless all values are well within toxicity range, either below ERL.

From the statistical analysis it is clear that CFs are near to 1 and hence there is low to moderate contamination of sediments by ^{60}Ni, ^{208}Pb, ^{111}Cd, and ^{75}As. PLI values are around more than 1, indicating that the sediment quality is deteriorating, in terms of ^{60}Ni, ^{208}Pb, ^{111}Cd, and ^{75}As content.

It is evident that offshore E&P activities of ONGC has not alarmingly polluted the marine ecosystem. However, the increasing trend in the metal concentrations needs to be arrested. The future E&P activities have to be planned, keeping in mind sustainability of the marine life.

Compliance with ethical standards

Acknowledgments

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Disclosure of conflict of interest

The authors declare no conflict of interest.

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