Assessment of heavy metals distribution in a coastal environment of Versova coast, Mumbai, India

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The existence of heavy metals namely, copper, chromium, and cadmium was studied in coastal waters off Versova, Mumbai. Monthly sampling was carried out from October 2012 to March 2013 across 36 stations. Concentrations of Copper (Cu), Cadmium (Cd) and Chromium (Cr) were measured using the Atomic Absorption Spectrophotometry (AAS). The concentration of dissolved elements in surface water varied from 0.01 to 0.03 mg/l. Concentrations of dissolved elements in sub-surface waters were as follows: Cu **(**0.01 to 0.02 mg/l**)**, Cd **(**0.02 to 0.03 mg/l**)** and Cr **(**0.02 to 0.03 mg/l**)**. The concentrations of Cu, Cd and Cr in suspended solids of the surface water were 0.82 – 1.68, 5.22 – 10.24 and 3.26 – 16.03 mg/kg, respectively, while their concentrations in suspended solid obtained from the sub-surface water were 2.77 – 4.29, 3.24 – 10.10 and 1.91 – 5.67 mg/kg, respectively. The concentrations of Cu, Cd, and Cr in sediments were 74.52 – 112.81, 3.02 – 22.88 and 65.05 – 107.74 mg/kg, respectively. The physico-chemical parameters of water and sediment were analyzed to understand the temporal distribution of heavy metals.

[**Keywords**: Bio-accumulation, Heavy metal, Sediment, Water parameters]

Introduction

Certain heavy metals in trace concentrations perform a vital role in the physiology of aquatic plants and animals, but a slight increase of their concentration in the aquatic environment may show adverse effects and cause severe physiological disorders[1-3]. Rapid industrialization and economic development along coastal zone are driving anthropogenic contaminants including heavy metals into the aquatic environments, which have devastating effects on the inhabitant aquatic organisms. Due to their non-biodegradability, toxicity, persistence and bioaccumulation effects[4,5], the adverse effects of heavy metals are not only limited to the aquatic organisms; but they can affect human beings through the bioaccumulation of metal contaminants in the food web[6,7]. Heavy metals exist in the aquatic environment either in the water column in the dissolved form or attached to the suspended particulate matter and associated with the bottom sediments[8-13]. Heavy metals of both natural and anthropogenic sources can be readily transported from terrestrial region to coastal area by water[6]. Large proportion of free metal ions are incorporated into the sediment due to some complex mechanisms such as adsorption, hydrolysis and co-precipitation, etc. while a small portion of these ions remains in the water column in dissolved form[11]. Turbidity influences the disbursement of heavy metal in water coloumn[13]. In aquatic ecosystem, the heavy metals are adsorbed by suspended particulate matter present in water column and are finally deposited in the sediments through the process of flocculation and sedimentation[9]. Therefore, regular monitoring of heavy metal accumulation in water column sediments and associated biota is the best option to monitor their concentrations in the aquatic ecosystem[12,14]. India, being a developing country, effluent treatment plant facilities are limited to large-scale industries only, because important investments are needed which is not affordable by small and medium sized industries. Versova is located in the metropolitan city of Mumbai. Mumbai is densely populated and is the largest industrial centre in the country. It produces ample amount of domestic

sewage and industrial effluents, which are ultimately discharged into the Arabian Sea[7,15]. Earlier studies were profusely focused on the distribution pattern and accumulation of these heavy metals on the main channels of the estuaries or larger creeks of Mumbai region. A limited information is available on the heavy metal contamination and distribution along off Versova (Juhu-Bandra included) coast, Mumbai, India. Thus, this investigation was carried out with an aim to measure the distribution of cadmium, copper and chromium in the water column and in sediments off Versova coast, Mumbai, India.

Materials and Methods

Study area

Versova, Juhu and Bandra are parts of the metropolitan city of Mumbai, and are densely populated with several industries. These areas are margined with the Arabian Sea along the western side. Hence, the huge quantities of sewage and effluents generated in these areas finally discharged into the sea water. The area lies between 19°08'47.7" and 19°03'01.9" N, and 72°48'11.7" and 72°42'17.0" E was selected for the study. For the evaluation of physico-chemical parameters and heavy metals (Cd, Cr and Cu) concentrations a total of 36 samples were collected as of surface, sub-surface waters and from sediments from six sampling sites of the specified region from October 2012 to March 2013 using Marine Fishing Vessel Narmada of Central Institute of Fisheries Education, Mumbai. Permanently fixed Global Positioning System (GPS) in the fishing vessel was used to record the geo-references for sampling stations (Fig. 1).

Sample collection

Both surface and sub-surface water samples were collected in 500 ml polyethylene containers using a Niskin water sampler, transported to the laboratory in ice box and stored at 4 °C for further analysis. Sub-surface water was collected from an average depth of 15 m. Sediment samples were collected from the selected stations with the help of a Van Veen grab.

Phsico–chemical parameters analysis

The pH of water was analysed by a handheld digital pH meter (Eutech Instruments, India). Water temperature was also measured by using a mercury filled Celsius thermometer (G H Zeal Ltd., London, England). The Dissolved oxygen content of the water samples were estimated using Winkler's Method

(APHA 1998). For the estimation of total dissolved solid in the water, samples were taken in pre-weighed dried Petri plates and they were dried in hot air oven at 105 °C for 24 h. The dried samples were kept in desiccators to cool down and the weights of petri plates were noted. After subtracting the final weight of petri plates from the initial weight, the total dissolved solid result was estimated. The sediment pH and electrical conductivity (EC) were estimated by the pH meter and conductivity meter (Eutech Instruments, India) at 1:2.5 sediment and water ratio. The organic carbon content of the sediment was estimated by Walkley and Black, method (Walkley and Black, 1934).

Estimation of Cd, Cr and Cu in suspended particles

The water samples were filtered through 0.45 μm membrane filter paper under mild vacuum in laboratory with a Millipore filtration unit. The filter paper was dried in desiccators to attain constant weight and the weight of the filter paper was taken using an electric weighing balance with the accuracy of 0.01 mg (Sartorius, BSA224S-CW, and India). The dry weight of the suspended particles was determined by subtracting the initial weight of filter paper from
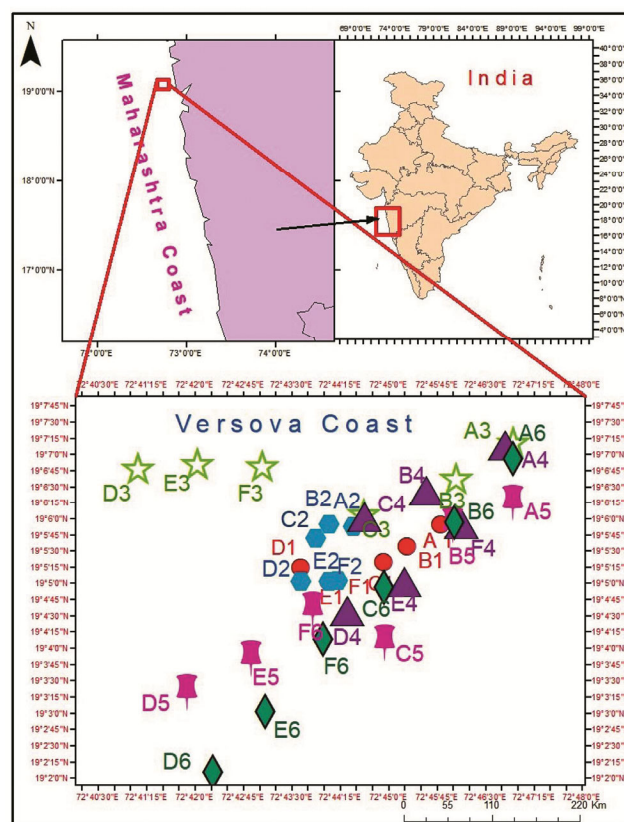

Fig. 1 — Map showing sampling stations

the final weight. The dried suspended particles with the filter paper were acid-digested in a microwave digestion system. For microwave digestion, each sample was added with 5 ml concentrated nitric acid, 2 ml hydrochloric acid and 1 ml hydrofluoric acid. Then, the samples were capped and heated in microwave at 800 W to a temperature of 210 °C for 20 minutes at a pressure of 40 bars. The digested samples were diluted to 50 ml followed by analysis of the three metals (Cd, Cr and Cu) concentration by using the Atomic Absorption pectrophotometer (AAS) through the flame atomization mode (Analyst 800, Perkin Elmer, USA).

Estimation of Cd, Cr and Cu in water & sediment

Water samples were collected in polypropylene bottles. All the bottles were soaked in acidified water for 6 – 8 hours, followed by washing with metal-free distilled water and dried before use. Water samples were filtered with 0.45 µ filter paper to remove the suspended particles. The filtrate water samples (250 ml) was preserved using concentrated nitric acid (purity 65 %) (pH < 2). The preserved sample was concentrated by reducing the volume 1/50 times on a hot plate at the temperature of 80 ºC and again subjected to acid-digestion in the hot plate by adding concentrated nitric acid (10 ml), concentrated hydrochloric acid (4 ml) and concentrated hydrofluoric acid (2 ml). The digested samples were diluted to 50 ml each and subjected to analysis of Cu, Cd, and Cr by atomic absorption spectrophotometer using flame atomization.

The collected sediment was kept in transparent plastic bag and brought to laboratory. The samples were air dried, grinded to powdered form followed by sieving through 1 mm sieve. For acid digestion, 0.25 g sieved sediment was taken in a microwave reaction system along with 5 ml concentrated nitritic acid, 2 ml hydrochloric acid and 1 ml hydrofluoric acid (Multiwave 3000, Anton Parr, USA). The digestion was carried out in the microwave unit at 800 W to a temperature of 210 ºC for 20 minutes at a pressure of 40 bars. Again, after the digestion the digested samples were diluted to 50 ml each and were subjected to analysis of the three heavy metals by AAS.

Statistical analysis and instrumentation efficiency

All the statistical analyses were performed using SAS 9.3. The comparison of the metal concentrations in water and sediment was analysed by using one-way analysis of variance (ANOVA) at 5 % level of significance. The mean separation was carried out by Duncan Multiple Range Test. The efficiency of the analytical method and instrumentation was verified by the analysis of the reference materials obtained from the National Research Council of Canada for marine sediments (PACS-2), river water reference material for trace metals (SLRS-4) and Dog fish liver reference material (DOLT-3) using five replicates. The obtained percentage recovery for the metal in sediment reference ranged from 90.46 – 115.00.

Results

Analysis of heavy metals in surface, sub-surface water and sediments

The dissolved Cu (0.024 mg/l), Cd (0.032 mg/l) and Cr (0.030 mg/l) at the surface water reached at peak during December, January and February, respectively. After attending their peak concentration, these metals reduced to 0.011 (Cu), 0.024 (Cd) and 0.023(Cr) mg/l, respectively during March. The dissolved Cu was always lower than dissolved Cd and Cr. Similarly, dissolved Cr was lower than dissolved Cd during the observation period except February month. A clear pattern was observed for the distribution of dissolved Cu and Cd, where they decreased from October to March except in November for Cu and December for Cd (Fig. 2). It has been observed that Cd and Cr concentration in suspended solid present at surface water decreased from October to March except an increment in their concentration only during January. The concentration of Cr and Cd in the suspended solid of surface water were more than Cu.

The analysis of dissolved concentration of Cu, Cd and Cr in sub-surface water revealed increasing trend from October to December, and afterward a decreasing trend was noted. A clear pattern was observed in the case for the distribution of Cr concentration in suspended solid, where it decreased continuously from October (8.45 mg/kg) to March (1.91 mg/kg). The Cd concentration in suspended solids increased at initial period from November to February, but it decreased drastically during March. Therefore, the lowest concentration for all three metals (Cu, Cd and Cr) were observed during March (Table 1). Cadmium concentration at sediment was much lower than that of copper and chromium. Maximum copper concentration was reported in the month of January and lowest in November.
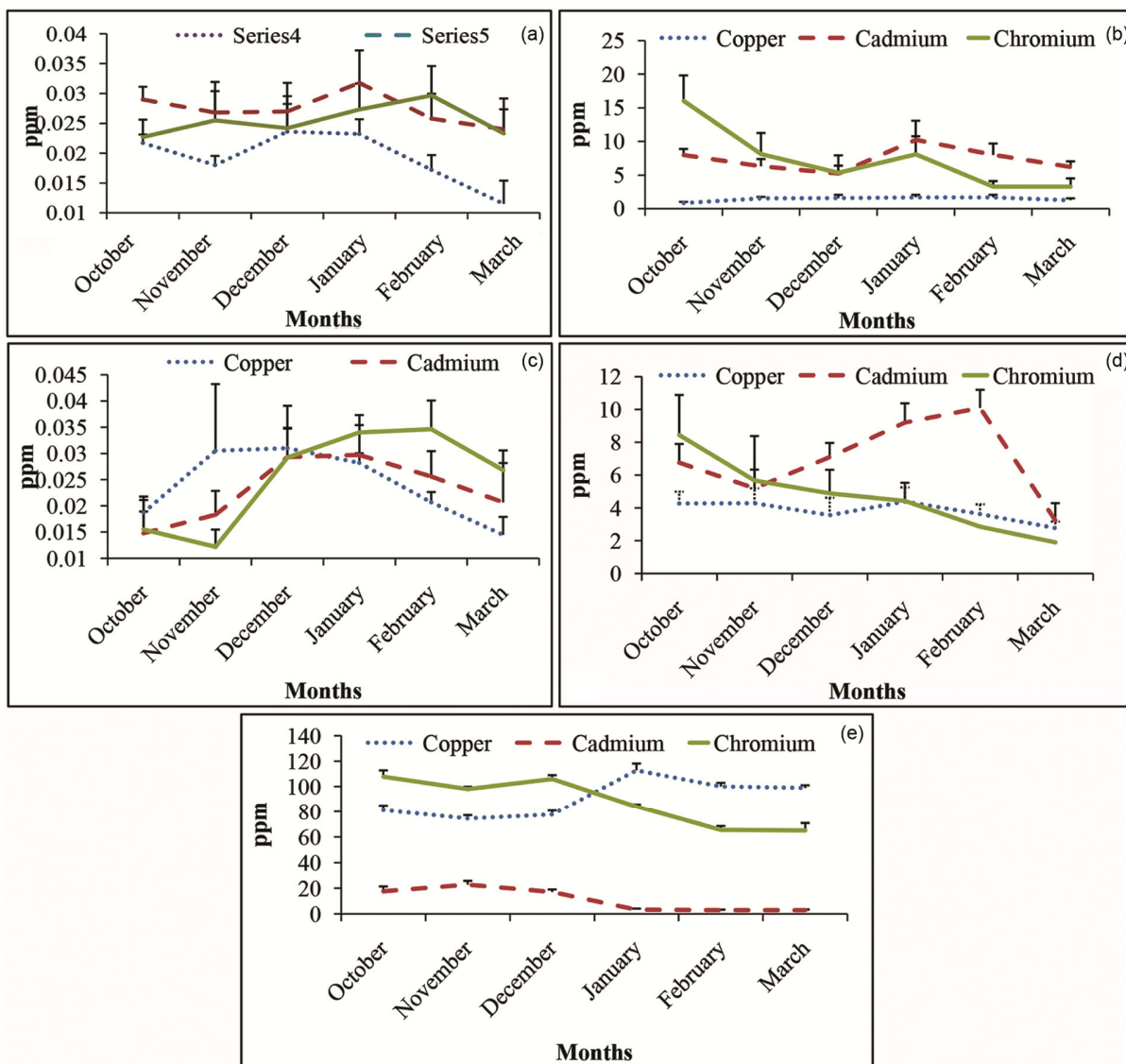
Fig. 2 — Heavy metal Distribution: A) surface water, B) suspended solid at surface water, C) dissolved at sub-surface water, D) suspended solid at sub-surface water, and E) sediments

Table 1 — Sampling stations during the study period

Sampling months	Sampling stations
October	A1, B1, C1, D1, E1 and F1
November	A2, B2, C2, D2, E2 and F2
December	A3, B3, C3, D3, E3 and F3
January	A4, B4, C4, D4, E4 and F4
February	A5, B5, C5, D5, E5 and F5
March	A6, B6, C6, D6, E6 and F6

Subsequently, the peak value was reported for chromium concentration in the month of October and lowest in March (Fig. 2).

Physico-chemical parameters of water and sediment

Dissolved oxygen (DO) in surface water (7.60 – 9.98 ppm) was higher than that of sub-surface water (4.36 – 7.87 ppm). In case of both surface and sub-surface water, DO was recorded to be lowest in November. Temperature of water column decreased with depth and also temperature pattern was similar for both surface and sub-surface water column. In this study, a sharp decline in water temperature was observed from October to January and afterwards temperature again started to rise during succeeding month *i.e.* February. pH of surface water (7.53 – 8.58) was comparatively higher than sub-surface water (7.43 – 8.47). Total dissolved solids (TDS) in sub-surface water (38.49 – 41.18 ppm) was higher than surface water (35.74 – 39.37 ppm). The summarized values of all the water quality parameters are illustrated in Figure 3.
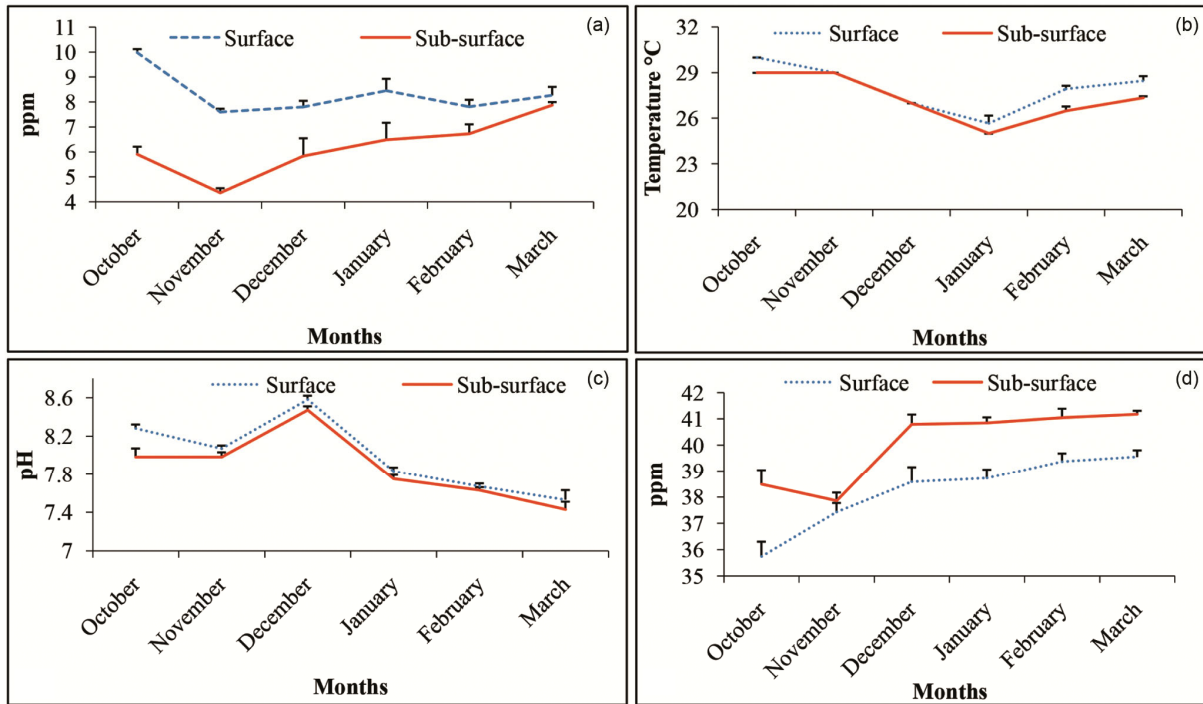
Fig. 3 — Distribution of environmental parameters at surface and sub-surface waters: A) Dissolved Oxygen, B) Temperature, C) pH, and D) Total dissolve solids

Table 2 — Physico-chemical parameters of sediment

Parameters		October	November	December	January	February	March
pH	Range	8.0-8.0	8.1-8.4	7.8-7.8	7.6-7.7	7.4-7.5	7.4-7.8
	Mean	8.0	8.2	7.8	7.6	7.3	7.5
Electric conductivity (µs)	Range	32.10-36.60	30.60-38.10	29.60-39.40	23.10-25.40	18.00-22.10	14.43-26.20
	Mean	33.58 ± 0.65^c	34.47 ± 1.36^c	34.10 ± 1.66^c	24.42 ± 0.37^b	19.36 ± 0.60^a	20.65 ± 1.64^a
Organic carbon (%)	Range	5.16-5.57	4.80-5.72	5.54-5.84	4.38-6.14	5.61-6.49	4.90-5.89
	Mean	5.35 ± 0.06^a	5.43 ± 0.13^a	5.69 ± 0.05^a	5.54 ± 0.26^a	6.14 ± 0.14^b	5.37 ± 0.15^a

*Values with different superscripts along the row vary significantly ($p < 0.05$) at 5 % level of probability

The maximum and minimum pH values of sediment were observed in the months of November (8.2) and February (7.3), respectively. The ANOVA outcomes showed significant difference ($p < 0.05$) in mean electric conductivity (EC) of sediments analysed on monthly basis. Therefore, EC was found to be maximum in November and Lowest in the month of February. Data analysis shows that the maximum organic carbon content was reported in the month of February and lowest in October (Table 2).

Discussion

This study provides the information on physico-chemical parameters and distribution of Cu, Cr, and Cd in water and sediment off Versova coast, Mumbai for the period from October 12 to March 13. A sharp decline of water temperature was observed in the month of January[16]. Temperature of sub-surface sea water was slightly lower than surface water. Further, it was recorded that pH of surface water was higher compared to sub-surface water. Though, dissolved oxygen level in sub-surface water was comparatively lesser than that of surface water, still higher than 4 ppm. Dissolved oxygen concentration has an inverse relationship with temperature and it is also varied due to variation in temperature with respect to time[17]. A high DO content in water was recorded during study period may be due to accelerated photosynthesis in phytoplankton, lower temperature and high waves, turbulence and currents, whereby increased interaction between atmospheric oxygen and water. Even though a slight changes in total suspended solids (TDS) during December to March at both surface and sub-surface water, and the different values of heavy

metal concentration might be attributed with anthropogenic input sources of municipal waste, catchment runoff and industrial effluents[18,19]. The variations in quantity of suspended solids concentration in coastal water depend on natural decaying process and riverine transport[20]. The findings illustrated that TDS in sub-surface water was higher than that of surface water. The finding illustrated that sub surface water was having more dissolved solids than the surface water. In this study, a close association between pH of sediment and DO content of sub-surface water was observed, where sediment pH decreases with rightward shifting of DO of sub-surface water. A higher average organic carbon (5.35 – 6.14 %) in sediment off Versova coast may be due to huge disposal of domestic sewage, wastewater drainage and freshwater flow from nearby land-based plants and sewage treatment plant into Versova creek. Anandan *et al.*[24], has recorded 83.08 mg/l organic matter in water of Versova coast due to directly discharge of concentrated pollutants into the coastal area[21]. A large discharge of industrial waste, sewage, runoff, aerosol deposition, freshwater discharges and boat traffic may be responsible factor for the dissimilar values of Cu, Cd and Cr concentration in water and sediment[22-24]. Results indicated that dissolved Cu content was lower in the water samples than its suspended solids, and both dissolved and suspended solid Cu level increased with depth of seawater column. Generally, Copper coexists in dissolved form in seawater with several chemical compounds such as free hydrated cations, organic and inorganic complexes, whereas copper in suspended solid is associated with various minerals and organic matters and also change in water quality parameters affects its availability in seawater[25]. An increasing pattern of dissolved Cr in surface and sub-surface water was observed from November onwards. But naturally chromium does not persist long term in aquatic environment in dissolved condition, it tends to precipitate or suspended in water column[26]. A decreasing pattern of Cr in particulate matter of both surface and subsurface water must be accounted towards continuously lowering of its concentration at sediments. The pattern of dissolved and particulate Cd was similar for surface and sub surface water during the study period. This indicates the close association between dissolved and suspended Cd in sea water. Balkis *et al.*[20], has also reported the higher concentration of Cu than Cd in surface water, could

be due to their more stable complexes with amorphous iron oxides and clay minerals present in the sediment[20]. Heavy metal concentration in surface aquatic environments depends on point and non-point sources, which carry heavy metals along with[27,28]. Therefore, the pattern of occurrence of dissolved Cu, Cd and Cr in sub-surface water was closely associated with their concentration in surface water. Further, higher concentration of this heavy metal in the suspended solid of sea water might be due to dominance of heavy metal in particulate form than the dissolved fraction, as metal ion and suspended solids possess strong linkage[29]. It is reported that in slightly alkaline water with high oxygen content, poorly soluble forms of metal ions are adsorbed by suspended matter in the water column[30]. High organic carbon content in sediment must have tied up with high Cu and Cr concentration available at sediment. In sediment, the weak bond between the Cd and organic compound might have resulted for more Cd concentration in water[32]. The mobility of heavy metals in aquatic systems depends on absorption of heavy metals to constituents of sediment[33]. In sediment, availability of Cr and Cu has strong affinity with organic carbon content. A combined effect of high pH and organic carbon content might be the major factor for higher concentration of Cu in sediment compare to dissolved and suspended solid in the water column[34]. The current study opined that the concentration of Cu, Cd and Cr in the suspended solids and sediments was higher compared to their concentration in dissolved form in water. The temporal variations in these metals may depend on physico-chemical properties of sea water and anthropogenic sources. Further, study can be carried out to access the bioaccumulation and bio magnification of these heavy metal and their impact on the organisms living in the same ecosystem.

Conclusion

In the present study, the assessment of distribution of Copper (Cu), Cadmium (Cd) and Chromium (Cr) showed that their concentration was more in suspended particles than the dissolved form in sea water, simultaneously their concentration is found to be increased towards sediments. Analysis of water quality parameters indicated that the dissolved oxygen, pH and total dissolved solids were higher in surface and sub-surface water, respectively. The more organic carbon content and heavy metals in the

sediments off Versova coast must have associated with high discharge of the domestic sewage and industrial wastes. Therefore, regular monitoring and enforcement of regulations are essentially required on discharge of effluents from domestic and sewage treatment plants to prevent the aquatic ecosystems getting contaminated from heavy metals so as to ensure healthier ecosystem for the aquatic organisms.

Acknowledgements

Conflict of Interest

The authors declare that they have no competing interests.

Author Contributions

PRB: Investigation, writing the original draft; VB: writing original draft, review and editing; SKA: review, editing; CSP: conceptualization, review, editing; & AV: review, editing.

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