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Original Research Paper

Heavy Metal Contamination in the Floodplains Along Mula River, Pune District, Maharashtra State, India



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Abstract

Pre-urban, urban and post-urban stretch of the Mula River in Pune District of Maharashtra (India) is examined for quantification of heavy metals (Cr, Co, Ni, Cu, Zn and Cd), calculation of the Pollution Load Index (PLI) and Contamination Factor (CF). They were estimated from the surface sediments (0-5 cm) at 10 sampling sites along the Mula river. High Cr anomaly (Max. 388.20 ppm) followed by Co (Max. 104.91 ppm), Ni (Max. 167.44 ppm), Cu (Max. 391.35 ppm), Zn (Max. 507.91 ppm) and Cd (Max. 2.38 ppm) is seen at various locations mostly encompassing the urban stretch. PLI is found to be high i.e., >1 in urban sites like Khadki, Kalyaninagar and Kharadi than the rural downstream sites. There is negligible mobility of the heavy metals and the urban floodplains are increasingly accumulating the heavy metals to a highly hazardous level.

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1 INTRODUCTION

Soil heavy metal (HM) contamination is a primary concern and severe disaster in many regions of the world. Studies pertaining to agricultural and urban soil contamination have received special consideration due to addition of heavy metals by both natural and anthropogenic sources (Song *et al.*, 2018; Stevanović *et al.*, 2018). However, the contribution of heavy metals in soils via anthropogenic inputs is much higher than that of natural sources (Adimalla and Wang, 2018; Adimalla, 2019). Heavy metal contamination has escalated due to their addition via industrial effluents, residential wastes, heavy usage of fertilizers and automobile exhaust emissions resulting from rapid expansion of agricultural and industrial development in the world (Song *et al.*, 2018; Zhong *et al.*, 2018; Adimalla, 2019). Heavy metal pollution of the natural environment is a universal problem. The studies of human exposure to heavy metals and the associated health risks have attracted attention of many researchers worldwide because of their potential toxicity (Zhang *et al.*, 2016, 2017). These

metals have a propensity to bioaccumulate and biomagnify (Pawar and Pawar, 2016). They are indestructible and most of them have toxic effects on living organisms when exceed in concentrations (Mmolawa *et al.*, 2011). Anthropogenic sources are responsible for the introduction of heavy metals in the rivers. Introduction of metals into the rivers is primarily due to rock weathering, soil erosion, and dissolution of water-soluble salts. Naturally occurring metals (especially the trace metals) move through aquatic environments independent of human activities and usually without any hazardous effects (Garbarino *et al.*, 1995; Opuene *et al.*, 2008). Anthropogenic pollutants are discharged into river water system via industrial, domestic and agricultural wastewater (Cheng *et al.*, 2014; Ho *et al.*, 2001; Priju *et al.*, 2007; Kumar and Pawar, 2011). Plants absorb heavy metals through soil which enter the food chain and become hazardous for living organisms (Biswal *et al.*, 1998).

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Sediments serve as sinks for most of the metals in aqueous phase (Klavins *et al.*, 1995). The concentrations of heavy metals in soils and sediments vary with the rate of particle sedimentation, the rate of heavy metals deposition, particle size and the presence or absence of organic matter in the soils (Saloman *et al.*, 1987). The urban and industrial areas are the sources of anthropogenic heavy metals and the rivers flowing from such areas often transport the heavy metal load downstream. These heavy metals are recycled during flooding and are re-deposited down streams. With this objective we attempted to examine the trend in heavy metal concentration in the flood plains of Mula River flowing rural upstream, urban and industrial area of Pune City and down streams (Figure 1).

Numerous ways can be adopted in order to assess the contamination of metals in sediments. Some of the most familiar ones are the index of geo-accumulation (I-geo) and Pollution Load Index (PLI). Contamination Factor (CF) has also been used to quantify pollution in the freshwater sediments (Singh *et al.*, 1997). PLI

represents the number of times by which the heavy metals concentrations in the sediment exceeds the background concentration, and give a collective estimate of the overall level of heavy metal toxicity in a particular sample (Priju *et al.*, 2006). PLI is thus a speedy tool used to compare the pollution status of sediments (Adebawale *et al.*, 2009). Although there is large amount of work done on contamination of sediments and soils by metals from various areas there is not much literature available in many parts of India. Therefore an attempt is made to study Pune Municipal Region, Maharashtra state from the heavy metal enrichment point of view. The main objective of this study was i) to assess the background levels of heavy metals in the soils and ii) to evaluate soil contamination if any using indices like CF and PLI. In order to achieve this objective surface elements were collected at 10 different sites along the banks of Mula River (Figure 3 a-f) and analyzed for 6 heavy metals (Cr, Co, Ni, Cu, Zn and Cd) concentration using Green shale (USGS) reference standards by X-ray fluorescence spectrometry (XRF).

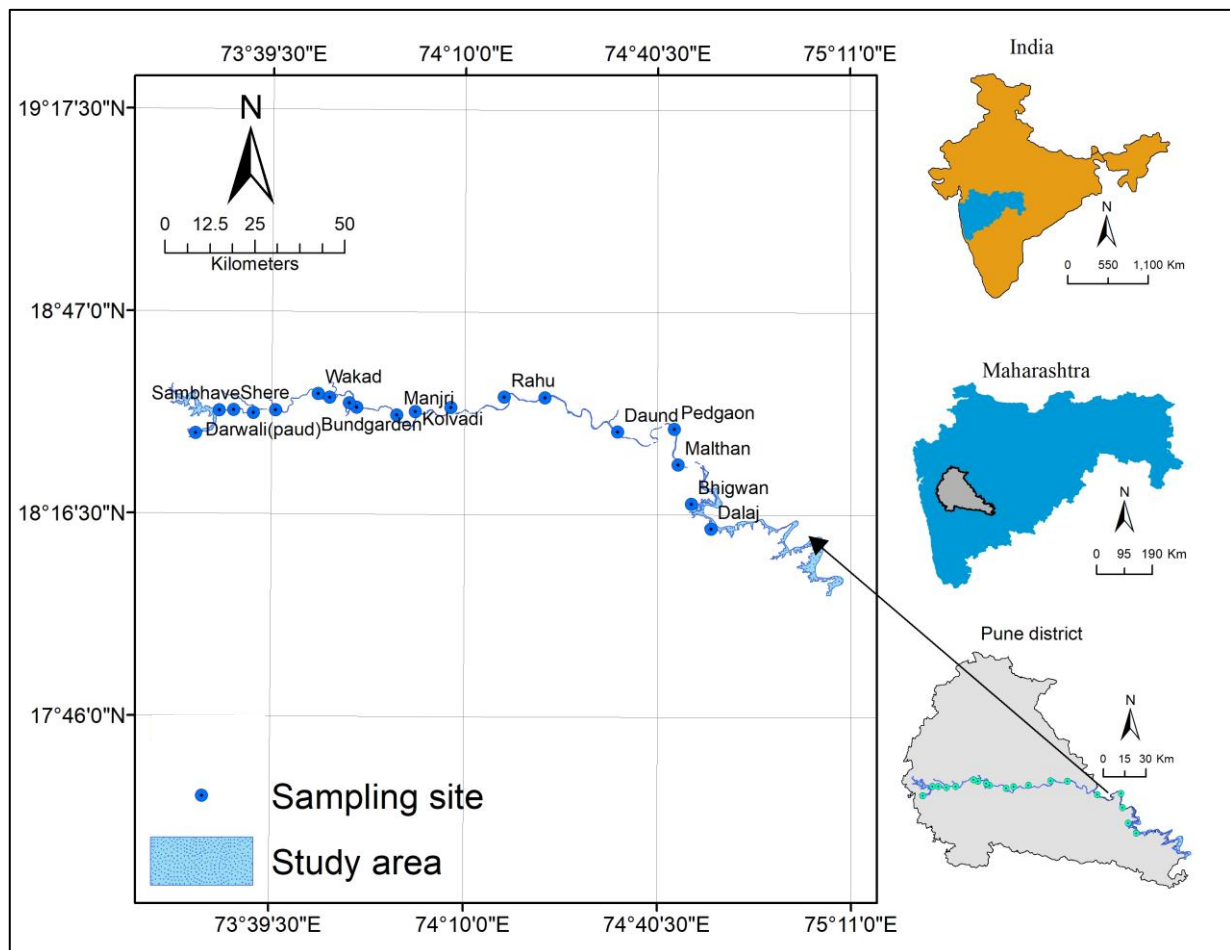


Figure 1. Study area with sample locations

2 STUDY AREA

Pune metropolis is situated on the confluence of Mula and Mutha rivers and their tributaries, Pavana and Indrayani (Figure 1) traversing through the north-western outskirts of the urban area. Geologically the area is characterized by simple as well as compound type lava flows. Based on lithological characteristics the flows from the study area have been classified by GSI (2001) into different units (Table 1; Figure 2). Chemostratigraphically the study area is characterized by Poladpur, Bhushe, Khandala and Thakurwadi formations (Cox *et al.*, 1985; Beane *et al.*, 1986). Poladpur formation is exposed to south of the study area along the Pune-Saswad road in the Dive Ghat. Ujjani reservoir falls in this formation. It bears fine to medium grained basalts typically bearing small phenocrysts of plagioclase and augite, or plagioclase, augite and occasionally olivine. Majority of the study area is covered by the Bhushe formation which is mainly

exposed in the central part of the study area. Sampling locations Mulshi, Wakad, Khadki, Sangamwadi, Kalyaninagar lie in this Bhushe formation. It comprises of coarse grained, altered and amygdaloidal, aphyric or sparsely plagioclase phyrlic, compound lava flows. Flows are simple with vesicular, oxidized tops. They are fine to medium-grained basalts with small phenocrysts of plagioclase, augite and olivine. Basaltic flows of the Khandala formation comprises essentially of simple flows generally columnar joints. It is encountered towards the east of the study area covering like Kharadi, Wagholi, Loni etc. Thakurwadi formation forms the youngest geological formation in the study area exposed in the NW region of the study area it consists of a thick sequence of coarse grained amygdaloidal, aphyric compound flows with well-developed lava flows and appears to be highly altered. Alluvial deposits are seen all along the valley portion and are of varying thicknesses.

Table 1. Lithostratigraphic scheme proposed for western Maharashtra, GSI (2001)

Group	Sub-groups	Formations	Thickness (m)
North Sahyadri Group	Mahabaleshwar	Mahabaleshwar	400
		Purandargarh Formation	525
	Dive Ghat	Diveghat Formation	375
		Karla Formation	450
		Indrayani Formation	250
	Lonavala	Upper Ratangarh Formation	600
		Lower Ratangarh Formation	450
		Salher Formation (Base not seen)	+350

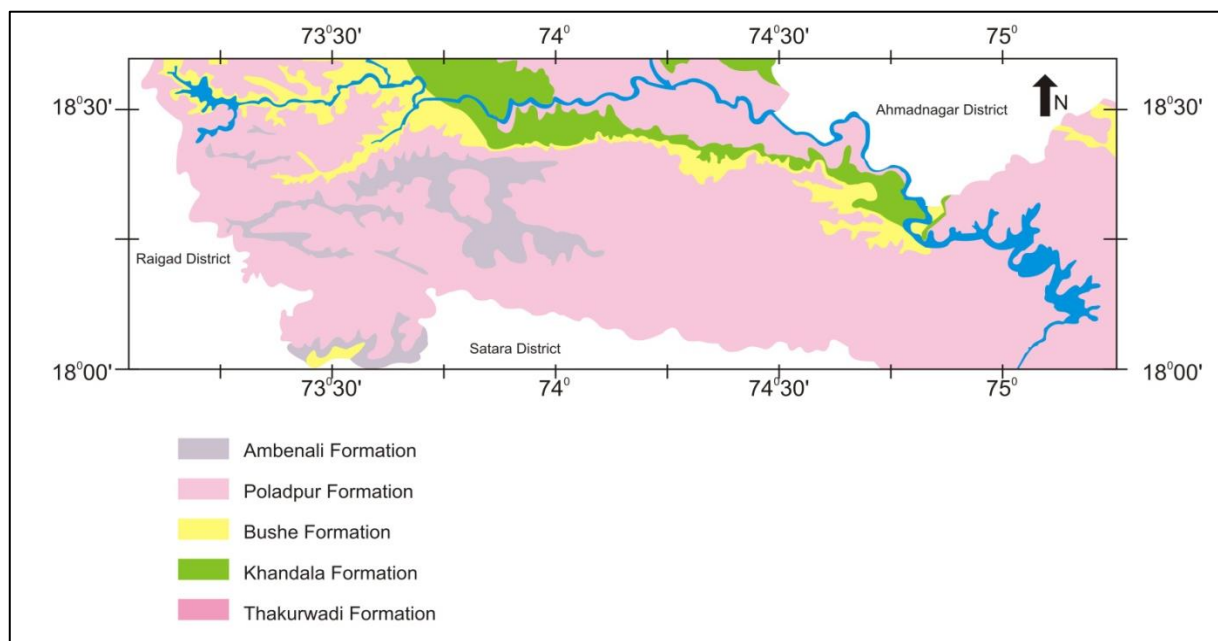


Figure 2. Geology

Inorganic chemistry plays a pivotal role in geology. The composition of rocks and minerals is vital in deciphering the chemical eminence of groundwater in general and heavy metals in particular. Since, the groundwater shows chemical interactions with the host rock to a considerable extent (Aravindan and Manivel, 2004). In view of this, information on chemostratigraphic classification of lava flows is imperative.

3 MATERIALS AND METHODS

3.1 Sampling

In the present study, amalgamation of both congenital as well as modern techniques for collection, analyses, processing and editing of geochemical data sets have been adopted for soil sampling and analytical techniques as well as using GIS tools. Total 10 soil samples were collected along the banks of Mula River from various locations. After removal of organic debris, trash, pebbles and stones, each soil sample was packed in self-locking polythene bags and were sealed in double bags to prevent cross contamination. Use of metal tool was strictly avoided and instead of a plastic spatula was used for sample collection.

Collected soil samples were dried for two days at 60°C until residual moisture was completely removed; these were then pulverized into a fine powder using US Standard in wooded mortar. Samples were further subjected to sieve analysis using a sieve of #240 mesh, 4 grams of the sieved samples was further subjected to XRF analysis (Table 2) for the determination of heavy metals in these soil. The samples were subjected to analysis on a SpectroXepos-EDXRF Model No. S/N-spectro-07004382 make XRF which is fully automatic, microprocessor controlled equipment with X-ray generator (detection limit 0.5 ppm). A palladium anode is used in the x-ray tube, reference materials, such as green shale issued by US Geological Survey were run along with the samples during the course of analysis.

3.2 Assessment of Metal Contamination

3.2.1 Contamination Factor (CF)

The contamination factor and degree of contamination are used to determine the contamination grade of the sediment in the present study. Contamination factor is calculated and considered as background concentration. $CF < 1$: low contamination factor; $1 \leq CF < 3$: moderate contamination factor; $3 \leq CF < 6$: considerable contamination factor; $CF \geq 6$: very high contamination factor.

Contamination factor (CF) is calculated (equation (1)) according to Thomilson et al. (1980) as:

$$CF = \frac{C_{ms}}{C_{mc}} \quad (1)$$

C_{ms} = metal concentration in a sample

C_{mc} = metal concentration in control sample

CFs for various metals were calculated (equation (1)) (table 3). Contamination Factor of samples collected in the urban sector like Khadki (4.60), Sangamwadi (3.75), Kalyaninagar (5.01) and Kharadi (5.52) indicate considerable contamination, whereas the downstream post urban stretches like Manjari (2.49), Daund (1.85), Malthan (2.94) and Ujjani (1.53) are moderately or less contaminated. CF of Co shows low contamination at all locations, except Khadki which indicates moderate contamination of 1.07. Ni exhibits low contamination. Cu indicates moderate contamination at all localities ranging from 1.02 to 2.29, except Daund which has lowest contamination of 0.78.

CF of Zn indicates considerable values at Mulshi (3.90), Wakad (3.05), Sangamwadi (3.64), Malthan (3.05) and Ujjani (3.14) indicate a considerable contamination; whereas Khadki (8.21), Kalyaninagar (11.98) and Kharadi (10.27) indicate very high contamination CF of Cd for all sites from Mulshi to Ujjani fall under low contamination ranging from 0.04 to 0.13.

3.2.2 Pollution Load Index (PLI)

PLI is obtained as CF, this CF is the quotient obtained by dividing the concentration of each metal with its control value. The PLI of the place are calculated by obtaining the n-root from the n-CFs that was obtained for all the metals. Generally, PLI (equation (2)) as Tomlinson et al., (1980) as:

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \dots \times CF_n} \quad (2)$$

where,

CF = contamination factor, n = number of metals

The PLI value of > 1 is polluted, whereas < 1 indicates no pollution (Harikumar et al., 2009).

In order to effectively measure of degree of overall contamination, the PLI was calculated using equation (2), for each sample as presented in table 3. Mulshi, Wakad, Sangamwadi, Manjari, Daund, Malthan and Ujjani were comparatively unpolluted with Contamination Factor < 1 whereas the sites in the urban stretch viz Khadki (1.30), Kalyaninagar (1.29) and Kharadi (1.35) are polluted and the pollution can be attributed to anthropogenic influences and or the unscientific disposal of non-treated industrial waste discharged and agricultural runoff into the river.

4 RESULTS AND DISCUSSIONS

A study of the soil quality indicates that most of the toxic elements accumulation depending upon pollution status of sampling location. The results show that concentrations of heavy metals are more in urban areas like Khadki, Kalyaninagar and Kharadi, as compared to rural area in the source and sink regions namely Mulshi, Daund, Malthan and Ujjani. In urban areas anthropogenic impact is more evident due to discharge of industrial effluent and disposal of municipal waste. Soils were assessed using Cr, Co, Ni, Cu, Zn and Cd.

The CF were observed generally indicates low, moderate in pre urban stretches and considerable to very high contamination by heavy metals in the urban and occasionally post urban regions. The mean heavy metal concentrations (in ppm) of 10 soils the samples along the bank of Mula River using XRF analysis is presented

(Table 2) as 245.53 for Cr, 74.10 for Co, 127.187 for Ni, 260.41 for Cu, 222.803 for Zn and 2.10 for Cd. Amongst these the mean concentration of Cu is more and Cd is least. Figure 3 (a-f) presents the GIS plots of the elemental concentration variation at each location.

Table 2. XRF analysis

Location	Cr	Co	Ni	Cu	Zn	Cd
	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)	(ppm)
Mulshi	244.92	3.18	167.44	302.82	165.22	2.12
Wakad	263.69	88.43	138.11	198.51	129.34	2.28
Khadki	323.30	104.91	142.70	364.34	347.88	2.32
Sangamwadi	263.82	78.33	145.40	238.04	154.47	2.18
Kalyaninagar	352.41	62.15	138.19	386.69	507.91	2.37
Kharadi	388.20	95.35	135.00	391.35	435.51	2.10
Manjari	175.19	86.06	113.93	185.04	119.33	0.74
Daund	129.73	67.12	100.74	133.53	105.73	2.38
Malthan	206.55	76.09	105.46	173.47	129.47	2.18
Ujjani	107.47	79.40	84.80	230.32	133.07	2.35
Mean	245.53	74.10	127.18	260.41	222.79	2.10

Table 3. Contamination Factor (CF) and Pollution Load Index (PLI)

Location	CF Cr	CF Co	CF Ni	CF Cu	CF Zn	CF Cd	Multiplication of all CF	PLI
Mulshi	3.48	0.03	0.50	1.78	3.90	0.12	0.05	0.60
Wakad	3.75	0.90	0.41	1.16	3.05	0.13	0.63	0.93
Khadki	4.60	1.07	0.42	2.14	8.21	0.13	4.74	1.30
Sangamwadi	3.75	0.80	0.43	1.40	3.64	0.12	0.80	0.96
Kalyaninagar	5.01	0.63	0.41	2.27	11.98	0.13	4.70	1.29
Kharadi	5.52	0.97	0.40	2.29	10.27	0.12	5.96	1.35
Manjari	2.49	0.88	0.34	1.08	2.82	0.04	0.09	0.67
Daund	1.85	0.68	0.30	0.78	2.49	0.13	0.10	0.68
Malthan	2.94	0.77	0.31	1.02	3.05	0.12	0.27	0.80
Ujjani	1.53	0.81	0.25	1.35	3.14	0.13	0.17	0.75
							Standard Deviation	0.28
							Standard Error	0.09

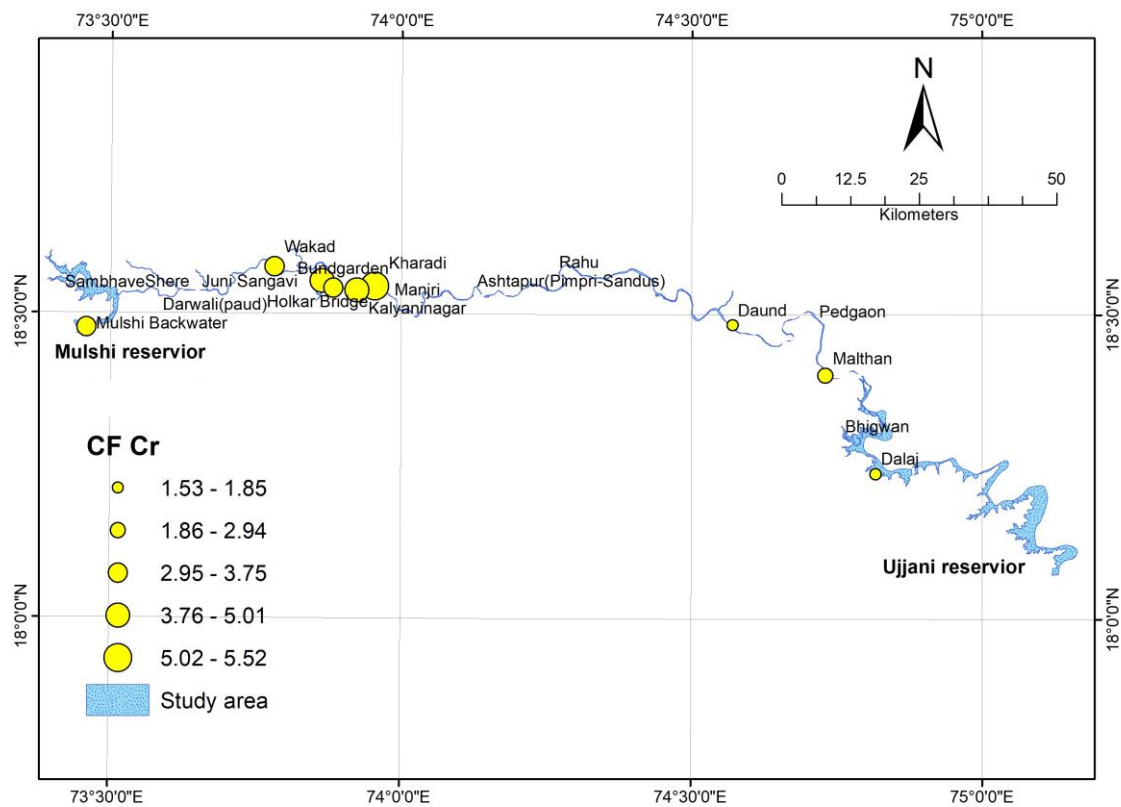


Figure 3(a). Concentration of Cr

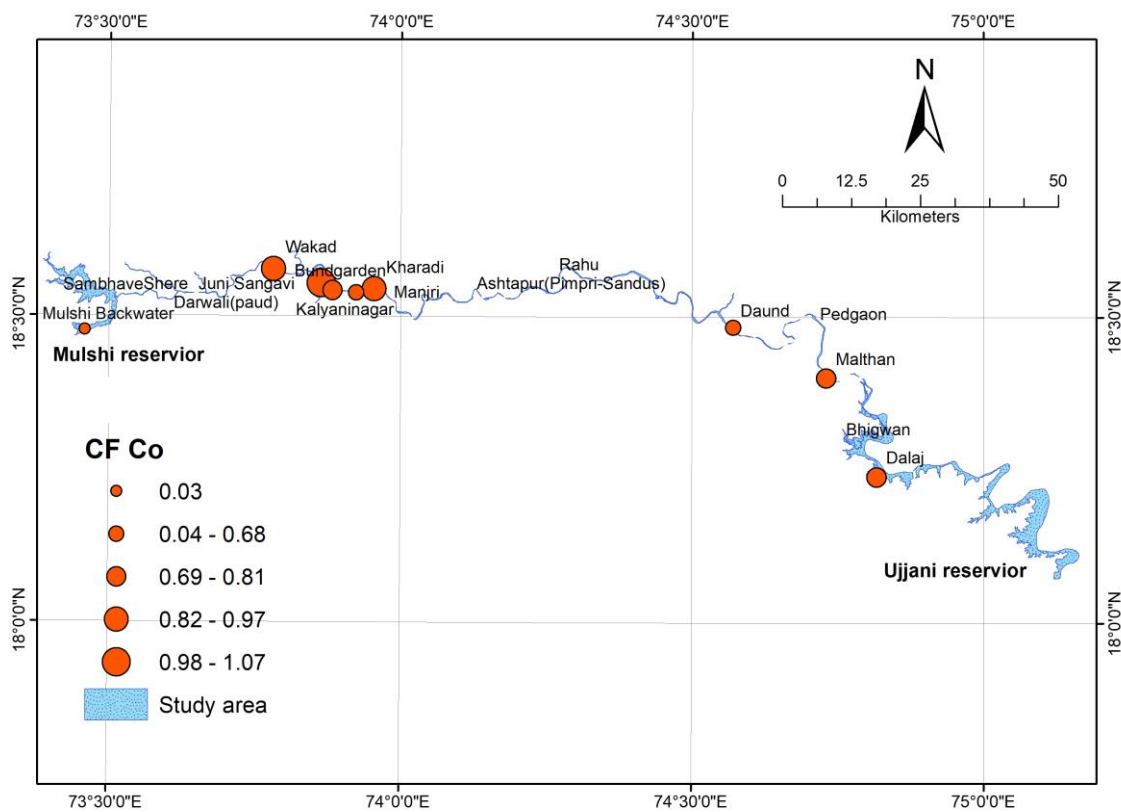


Figure 3(b). Concentration of Co

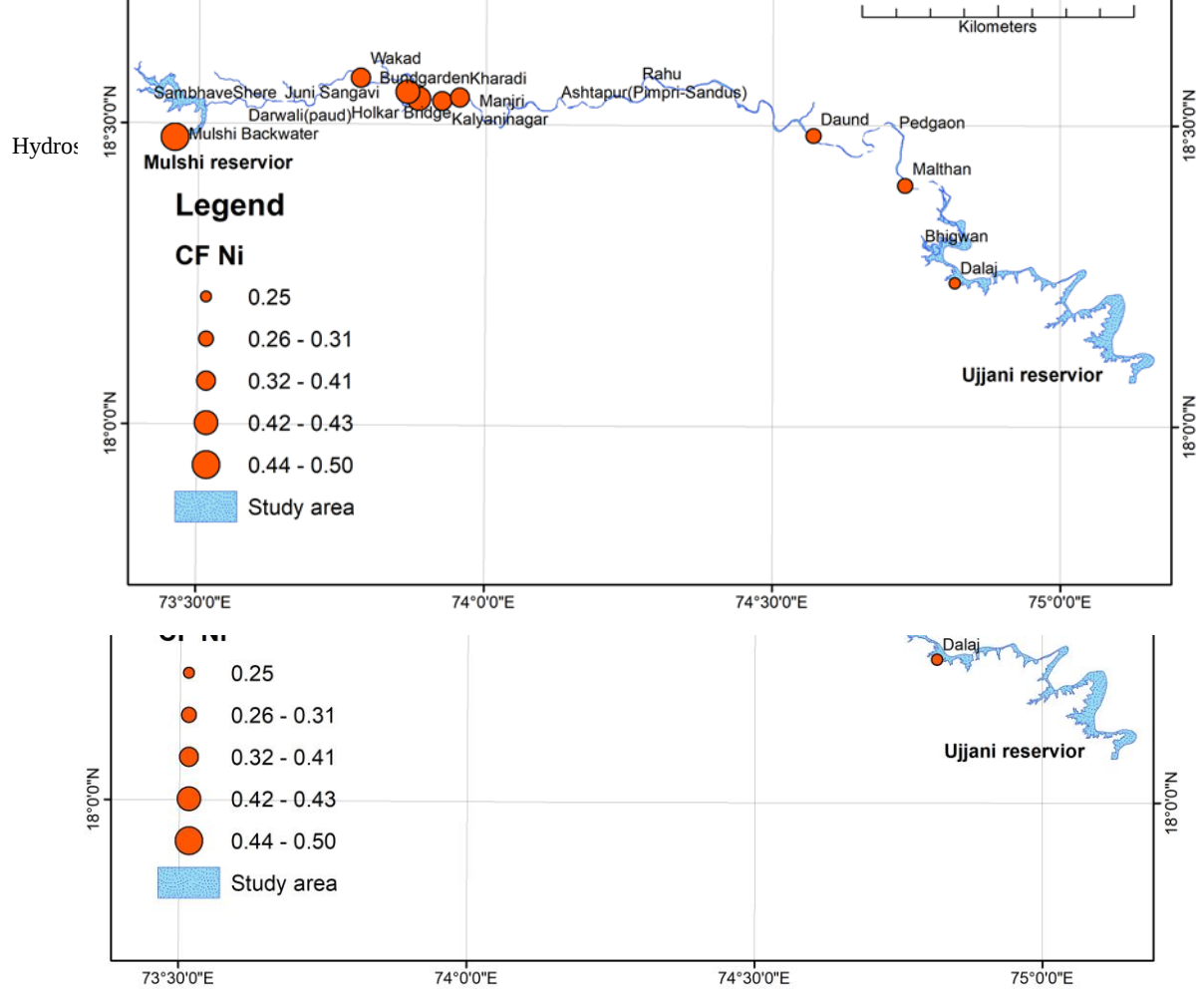


Figure 3(c). Concentration of Ni

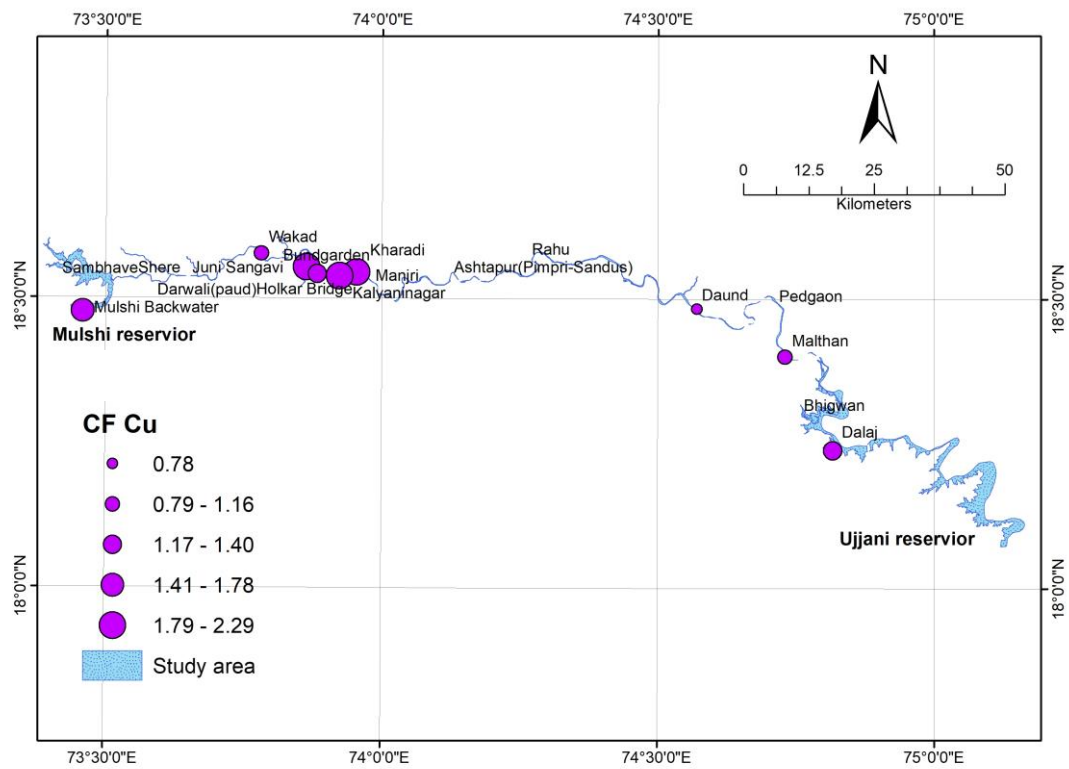


Figure 3(d). Concentration of Cu

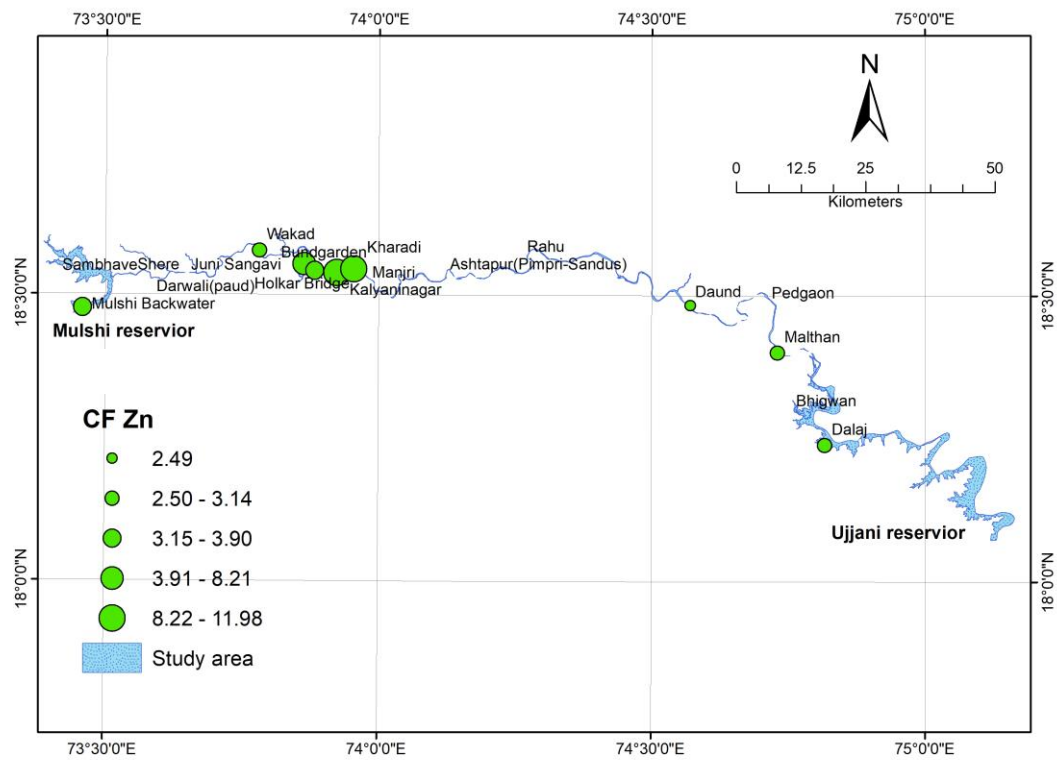


Figure 3(e). Concentration of Zn

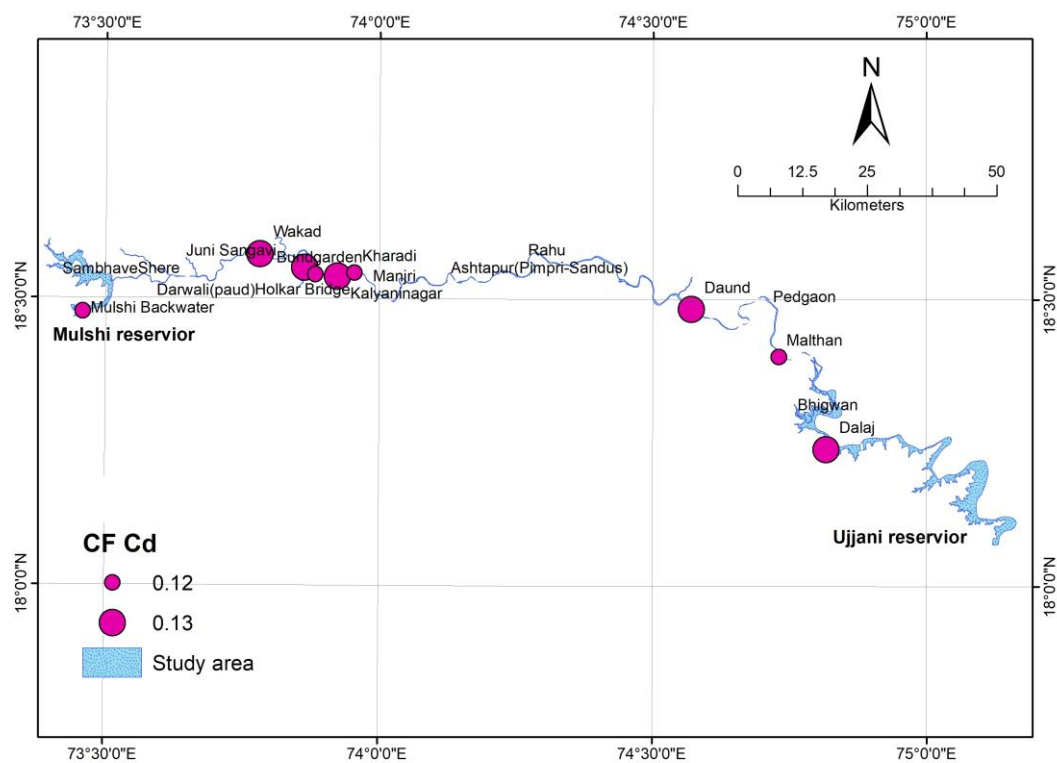


Figure 3(f). Concentration of Cd

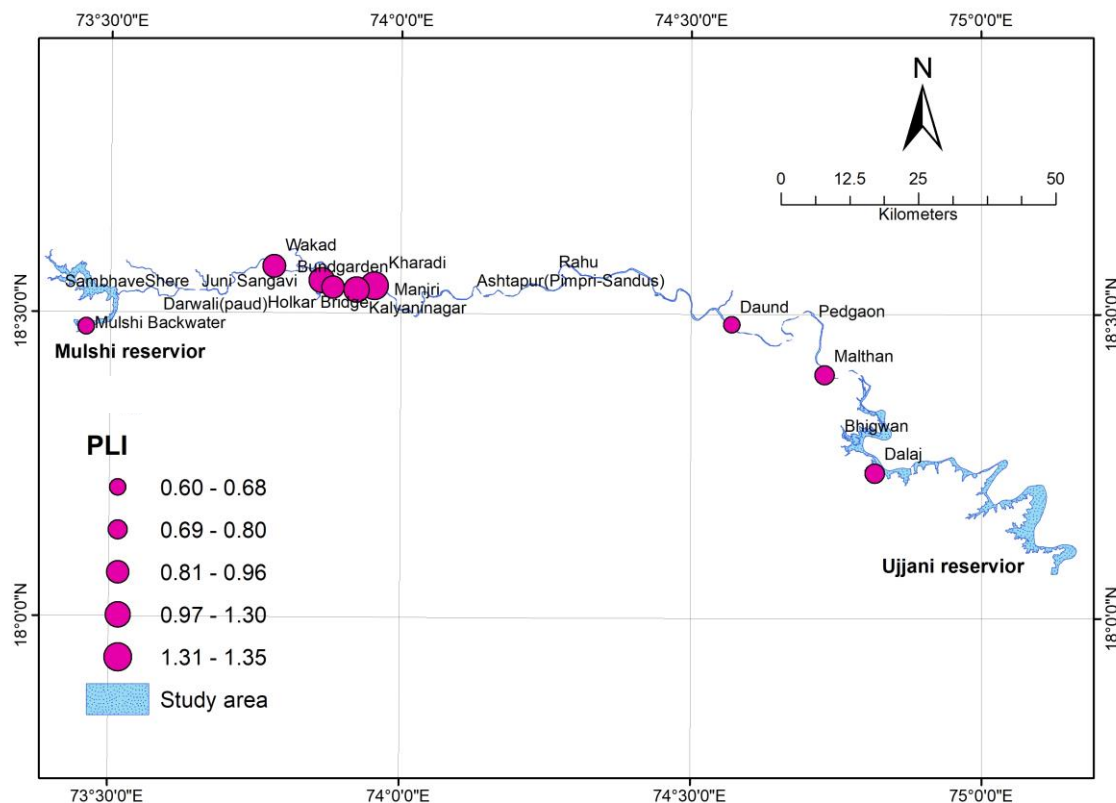


Figure 4. Variation in Pollution Load Index (PLI)

5 CONCLUSIONS

In the urban domain the values are higher and the transfer of heavy metals to downstream is not linear. Rather a major break can be observed at the margin where the Mula River enters the rural domain. Majority of the elements show this trend while others do not show such kink, neither do they show any decreasing/increasing trend. The floodplains of the Mula River in urban domain are encroached and thus display a competitive nature. Whereas the floodplains become wider as the river enters into rural domain. This prompted us to suggest two hypotheses as: 1) the downstream decrease in PLI in the rural domain is because of the settling of heavy metals within urban domain restricting its transport. The confined floodplains in the urban domain cause erratic flooding and rapid downstream flow of water and the sediments are not transported effectively further restricting the heavy metals within the floodplains. 2) The river shows a change from confined to unconfined nature from urban to rural domain. As a result the heavy metal loaded sediments/suspension is distributed over wider area depleting the concentration due to dilution. However, in any case we observe increasing heavy metal concentration and the PLI in the urban domains hazardous to the population.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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ABBREVIATIONS

CF: Contamination Factor; **GSI:** Geological Survey of India; **HM:** Heavy Metal HM; **PLI:** Pollution Load Index; **USGS:** United States Geological Survey; **XRF:** X-Ray Fluorescence Spectrometry.

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