



Metal Pollution and Ecological Risk Assessment in Sediment of Artificial Estuary: Case of Vridi Channel, Côte d'Ivoire

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ABSTRACT: This study focused on a yearly monitoring of sediment pollution in Cd, Co, Cu, Fe, Mg, Mn, Ni, Pb, Zn and the ecological incurred risks in Vridi channel. The results, expressed per dry weight, showed that the annual mean were 0.96 (\pm 0.16) mg/Kg for Cd, 22.36 (\pm 2.41) mg/kg for Co, 33.98 (\pm 4.61) for Cu, 31760.5 (\pm 5652.7) mg/kg for Fe, 981.2 (\pm 377.5) mg/kg for Mg, 302.9 (\pm 415.4) mg/kg for Mn, 42.53 (\pm 9.79) mg/kg for Ni, 83.37 (\pm 6.66) mg/kg for Pb and 27.11 (\pm 11.72) mg/kg for Zn. The measured oligo-elements (Fe, Mn, Mg, Zn) originated from natural sources and were away from accumulation, except from Fe which moderately accumulated. That hence the low sediment contamination by these metals. As for toxic trace metal (not essential) to living organisms (Co, Cu, Pb, Cd, Ni), they resulted from anthropogenic origin. These sediments were moderately contaminated in Co, Cu and Ni, significantly in Pb and strongly in Cd. All the studied trace metals were mainly from continental origin, except Cd which showed a marine origin. This estuary displayed a steady state of progressive deterioration and presented a very high ecological risk. © JASEM

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Vridi channel is the main connection of Ebrié lagoon system to Atlantic Ocean in front of Abidjan. It's known that industrial activities and major factories are located along Ebrié lagoon system, particularly in Abidjan district. Consequently, this estuary is subjected to many terrestrial and marine pollutants, as lagoon bays of Abidjan district (Inza *et al.*, 2014; N'Guessan, 2014; Yao *et al.*, 2009). Specifically, dumping of metal waste is suspected in fish collapse and eutrophication of the Ebrié lagoon. Some trace metals (Fe, Mg, Zn, Cu, etc.) are fundamental to the physiological development of living organisms. That could sustain the high productivity level in the Ebrié system. If harmfulness to those organisms appears with excessive concentrations (Habib *et al.*, 2016; Zhang *et al.*, 2016; Zheng *et al.*, 2010), many highly toxic metal (Hg, Cr, Cd, etc.), even at very low doses, are regularly measured near of this channel (Inza *et al.*, 2014; Yao *et al.*, 2009). These charges are transported through drains, meteoric waters runoff, atmospheric way, rivers, etc., in particulate and/or dissolved forms. Metal undergo irreversible sedimentation through the important mechanism of diagenesis (Lu *et al.*, 2014; Prajith *et al.*, 2016; Robbins *et al.*, 2015). However, the required time leads to remobilization by other processes, including bioturbation (He *et al.*, 2015; Remaili *et al.*, 2016). Indeed, the channel is subjected to periodic dredging, pipeline installations, daily passage of ships and other motorized vehicles. Furthermore, several parameters are involved in these processes, including pH, oxygen, salinity, hardness and organic carbon content, which are the most influential physical and

chemical parameters in this type of exchange in these entities (Blewett *et al.*, 2016; Kaplan and Cory, 2016; Lewis *et al.*, 2016; Ritchie and Mekjinda, 2016; Schijf and Zoll, 2011). These ways of contamination are likely to affecting all the entire food chain (Lu *et al.*, 2014; Pradit *et al.*, 2016); and organisms are exposed to many diseases and physiological disorders.

In the context of the sustainable development of Vridi channel, it is important to run monitoring of pollution level. This paper assessed metal pollution in this channel through analysis of concentrations in Cd, Cu, Co, Fe, Mg, Mn, Ni, Pb and Zn within three sedimentary fractions. Its ecological risk states were subsequently evaluated with regard to distribution of size of sediments.

MATERIAL AND METHODS

Study area: Vridi Channel is a manmade estuary in the coastline near the locality of Vridi. It was realized from 1938 to 1950 during the creation of the autonomous harbour of Abidjan. This estuary is located between 4°0'50" west longitudes to the north latitude 5°15'23". Its 2.7 km long with depths ranging from 12 to 25 m. Draughts are estimated to reach 12 m, while her draft air of 11.8 m. Due to the presence of Atlantic Ocean, the watershed of this estuary is invaluable. However, its watershed on the continent is related to that of Ebrié system, which is 93600 km². Currents are important (about 1.5 m/s (Brenon *et al.*, 2008)) and generate two high tides and two low tides daily. At high tides, marine waters rise to Ebrié

system, while in low tides the opposite happens. Each of its phenomenons is observed for 5 hours during lagoon dry season, and 6 hours during lagoon flood season. These phenomenons occur successively 2 times a day with the observation of an equilibrium state of 1 hour between the marine and lagoon water. To avoid its rapid siltation, this estuary was oriented to the southeast (in the direction of the canyon) at north-west, accentuated by the construction of discarded and wing walls, but also by a carpet fascinage weighted riprap (Monde *et al.*, 2011). Vridi channel is at the intersection of Abidjan district (located on continental) and the department of Jacqueville (on the coast). Thus, the landscape is dominated by metropolis Abidjan on continental, while coastal areas is dominated by coniferous forests, coastal forests, coastal thickets, swampy forests, relics of mangroves that line Ebrié system. Climate is sub-equatorial characterized by four seasons: two dry seasons (December to March and July to September) and two rainy seasons (April to July and September to November). The atmospheric temperature varies between 27°C and 35°C. Temperatures are generally low during rainy season (May to July and November) and at the beginning of main dry season (December-January), and higher during dry seasons (January-April and September-October). Annual rainfall in the area varies between 1400 and 2500 mm. This estuary is subject to both marine seasons observed on the coast of Atlantic Ocean in front of Abidjan and Ebrié system seasons. The marine seasons are characterized by 2 dry seasons (little season (November-December) and great season (March to May)) and 2 cold seasons (little season (December-January) and great season (July-October)). Those of Ebrié system are characterized by a dry season (January-April), a rainy season (May-August) and a flood season (September-December). It is deduced Vridi channel seasons such as: dry season (February-April), rainy season (May-July), great cold season (August-September), flood season (October-November) and little cold season (December-January). The whole area from Ebrié system to Atlantic Ocean is experiences remarkable biodiversity. However, this biodiversity is highly threatened by the heavy pollution encountered by these ecosystems due to strong anthropogenic pressures. This pollution has many origins:

agriculture, industry, land, air, etc. Indeed, the real lack of sanitation infrastructure, the high population growth and the development of human activities in the district of Abidjan are responsible of that situation. Thus, these ecosystems hold receptacle place for pollutants without prior and/or weak treatments, particularly those of the industrial zone of Yopougon (about 30 Km from the Vridi channel) and industrial zone of autonomous harbor neighboring the estuary (Fig.1).

Samples Collection: This study was conducted over one year (April 2014-March 2015). Monthly sampling was done at three stations (Fig.2) and 36 samples were generated. These samples were collected upper 5 cm of the sediment-bed surface using a Wan-Veen type grab according to AFNOR X 31-100 (1992). Samples were collected in polyethylene bottles and stored in ice.

Samples Preparation: In laboratory, samples, and cleaned coarse elements, were firstly freeze-dried to constant weight according to the AFNOR NF EN ISO 16720 (2007). Then, they were screened through a sieve diameter equal to 2 mm according to AFNOR NF X 31-107 (2003). Sub-samples were put in dry and clean polyethylene bottled, finally stored in dark and cool (20°C) place for further analysis.

Samples analysis: Determination of size and distribution of sediments and their total content of Cd, Cu, Co, Fe, Mg, Mn, Ni, Pb and Zn was conducted. These measurements were made on three fractions of these sediments: fraction I (diameter > 250 µm), fraction II (0.63 µm < diameter < 250 µm) and fraction III (diameter < 0.63 µm). The determination of distribution of particle size was performed in accordance with AFNOR NF X 31-107 (2003). Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn were determined according to AFNOR NF T90-112 (1986), and Mg following AFNOR NF T 90-005 (1986). These analyzes were performed in triplicate. Metal concentrations were measured using an air-acetylene flame using atomic absorption spectrophotometer VARIAN AA 1275.

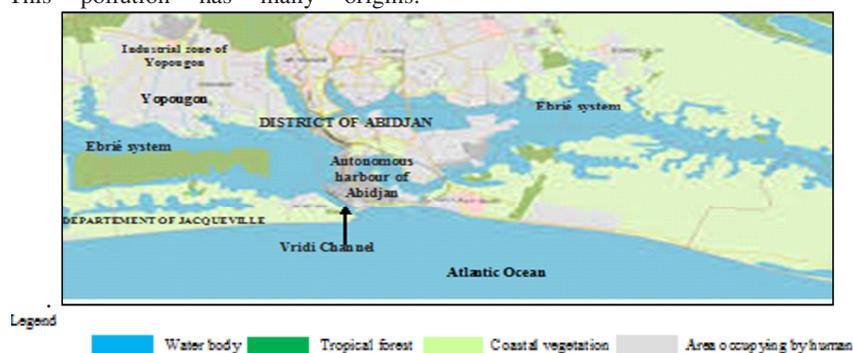


Fig.1: Presentation of study area



Fig. 2: Location of the sampling sites in Vridi channel

Data evaluation: The assessment of metal pollution level in sediments of Vridi channel was done taking into account 4 pollution indicators: the index of geo accumulation (I_{geo}), the contamination factor (CF), the enrichment factor (EF) and the pollution load index (PLI).

Regarding I_{geo}, it gives an estimate of accumulation level of trace metals in sediments (Ghani, 2015; Bøddeker *et al.*, 2017). Defined by Müller (1981), it is obtained using the following formula:

$$I_{geo} = \log 2 \left(\frac{C_m}{1.5 \times C_B} \right) \quad (I)$$

with:

- C_m, concentration of metals in sediment (mg/Kg);
- C_B, value of the geochemical background noise for the metal (mg/Kg);
- 1.5, constantly taking account of natural fluctuations in the content of a substance in environmental and anthropogenic variations.

Depending on the value of I_{geo}, it is defined the class and contamination level. This classification is as follows:

- Class (0) (I_{geo} < 0), uncontaminated;
- Class (1) (0 < I_{geo} < 1), uncontaminated to moderately contaminated;
- Class (2) (1 < I_{geo} < 2), moderately contaminated;
- Class (3) (2 < I_{geo} < 3), moderately contaminated to severely contaminated;
- Class (4) (3 < I_{geo} < 4), severely contaminated;
- Class (5) (4 < I_{geo} < 5), severely contaminated to extremely contaminated;
- Class (6) (I_{geo} < 5) extremely contaminated.

As regards the contamination factor (CF), it is possible to know metal contamination level of sediments (Nadem *et al.*, 2015, Ali *et al.*, 2016; Islam *et al.*, 2015). It is calculated from the following relationship:

$$CF = \frac{C_m}{C_B} \quad (II)$$

The different contamination levels based on CF values are defined as follows:

- CF < 1, low contamination;
- 1 ≤ CF ≤ 3, moderate contamination;
- 3 ≤ CF ≤ 6, significant contamination;
- CF ≥ 6, very high contamination.

As concern the enrichment factor (EF), it allows to distinguish anthropogenic origins of trace metals to their natural origins (Bøddeker *et al.*, 2017; Li *et al.*; 2017). Developed by Ackerman (1980), it is calculated according to the relation below:

$$EF = \frac{([X]/[R])_{sample}}{([X]/[R])_{reference\ material}} \quad (III)$$

With: [X], concentration of trace metal; and [R], concentration of normalizing element.

In this study, Fe was chosen as a reference material because it is mainly natural origin one hand, and it is not influenced by processes which can change its natural contents in sediments in second hand. EF values between 0.5 and 1.5 indicate a naturally occurring metal, while those above 1.5 are attributed to anthropogenic origins (Zheng *et al.*, 2010).

The load index of pollution (PLI) was used as the overall index for the general assessment of metal pollution in sediments of Vridi channel. This index, defined by Tomlinson and *al.*, (1980), is obtained according to (IV):

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

with: CF_i, the contamination factor for trace metal i.

Thus, according to the value of the PLI, it is noted:

- PLI = 0, no damage;
- PLI = 1, only the reference levels of pollutants are present;
- PLI > 1 indicates a gradual deterioration of the estuary.

In the lack of a guide on the contents of these trace metals before the pre-industrial era in Ivoirian surface waters and even on the Gulf of Guinea, the different metal background values (reference) were taken from those provided by Wedepohl (1995) for the upper continental crust.

The ecological risk assessment was evaluated by the potential ecological risk index (PERI). Developed by Håkanson (1980), it is defined by:

$$\text{PERI} = \sum \text{Er}^i \text{ (V)}$$

$$\text{Er}^i = \text{Tr}^i \times \text{CF}^i \text{ (VI)}$$

with:

- Er^i , is the monomial potential ecological risk factor;
- TR^i is the toxic-response factor for a given substance (Cu=Pb=Ni=5, Zn=1, Cd=30);
- CF^i , obtained following (II).

According PERI value, it is obtained the potential ecological risk of the sediment. So, if:

- $\text{PERI} < 150$, low ecological risk for the sediment;
- $150 \leq \text{PERI} < 300$, moderate ecological risk for the sediment;
- $300 \leq \text{PERI} < 600$, considerable ecological risk for sediment;
- $\text{PERI} \geq 600$, very high ecological risk for the sediment.

This index is calculated with trace metals which have anthropogenic origin (Effendia *et al.*, 2016; Nadem *et al.*, 2015; Ali *et al.* 2016).

RESULTS AND DISCUSSION

Sediments have a decreasing particle size distribution from the station S1 to the station S3 (Fig.3). Sediments of the station S1 compounds were: (2.99 ± 1.51) % of rudites, (92.19 ± 12.50) % of sand and (4.82 ± 0.41) % of silt. Those in the station S2 were: (5.43 ± 2.72) % of rudites, (79.90 ± 8.09) % of sand and (14.67 ± 0.50) % of silt. As regards the sediments of the station S3, their compositions were: (0.77 ± 0.39) % of rudites, (52.43 ± 4.38) % of sand and (46.80 ± 1.05) % of silt. So, sediments of Vridi channel are sandy texture. Qualitative analysis of sediments in the estuary highlighted its slow siltation as designed in its realization. Indeed, it was noted an almost non mixing marine sediments (mainly sand Marine 50 Quaternary (sandy texture of very rough and coarse) (Wagner, 2002)) to the station S1 with lagoon sediments (coarse sand and silt from meteorites contributions, wastewater discharges, organic matter from detritus terrigenous particles and/or plant debris) to stations S2 and S3. Due to its orientation, the contribution of marine sediments from Atlantic Ocean are most hampered by the canyon and finally stopped by discarded and wing walls just after the station S1; while those from

continental will first settle in the lagoon area of the harbor and later stopped (mostly in the form of coarse and medium sands) by discarded and wing walls at the station S2. This would explain the decrease in distribution of the particle size from the station S1 to the station S3.

Results from trace metals studies are presented in Table 1. Fe showed the highest annual mean value and Cd the lowest annual mean value at all stations and within various fractions. In the different sampling stations, the decreasing order of annual mean values of trace metals evaluated was:

$$\text{Fe} > \text{Mg} > \text{Mn} > \text{Pb} > \text{Ni} > \text{Cu} > \text{Zn} > \text{Co} > \text{Cd}$$

Most of these trace metals exhibited their high annual mean value in the station S3, except those of Cd in the station S1, Mn and Fe in the station S2. Annual variations were marked ($\text{VC} > 50\%$) for Cd, Cu, Mn in all the sampling stations, Mg and Co in stations S2 and S3, and Fe in the station S1. Except Cd, which has a relatively low variation of annual mean values from one station to another (< 0.1 mg/kg dry weight), those of other trace metals were relatively higher. For fractions considered in this study, the decreasing order of annual mean values of trace metals evaluated as follows:

- Fraction I: $\text{Fe} > \text{Mg} > \text{Mn} > \text{Pb} > \text{Cu} > \text{Ni} > \text{Zn} > \text{Co} > \text{Cd}$;
- Fraction II: $\text{Fe} > \text{Mg} > \text{Mn} > \text{Pb} > \text{Ni} > \text{Co} > \text{Cu} > \text{Zn} > \text{Cd}$;
- Fraction III: $\text{Fe} > \text{Mg} > \text{Mn} > \text{Pb} > \text{Zn} > \text{Ni} > \text{Cu} > \text{Co} > \text{Cd}$.

Fe, Mn and Cu showed their maximum annual mean value in the fraction I and that of Ni in the fraction II. As concerned Cd, Zn, Pb, Mg and Co, their maximum annual mean value was observed in fraction III. Annual variations are important ($\text{VC} > 50\%$) for Cd and Mn in the fraction I, for Mn in fraction II, for Cd, Ni and Mg in the fraction III. Variations of annual mean values for these trace metals were relatively important. Referring to the Müller criteria (1981), it is noted that only Cd accumulated moderately ($1 < \text{Igeo} < 2$) within the sediments of Vridi channel; while Co, Pb, Ni, Cu and Fe tend to accumulate moderately ($0 < \text{Igeo} < 1$). Mg, Mn and Zn didn't accumulate ($\text{Igeo} < 0$). Contamination of these sediments in Cd ($\text{CF} \geq 6$) was extremely important and those of Pb, considerable ($3 \leq \text{FC} \leq 6$) in all sampling stations. These sediments were moderately contaminated ($1 \leq \text{CF} \leq 3$) in Ni, Cu, Co within all sampling sites, and by Fe in the station 2. As regard that binds to Mg, Mn, Zn in all sampling stations and Fe in stations S2 and S3, it is moderate. As concerned EF values obtained for these trace metals, it deduces that Cd, Pb, Ni, Co have anthropogenic origin ($\text{EF} > 1.5$) and Mn, Mg, Fe Zn

natural origin. All values of PLI and PLI' obtained in all sampling station are greater than 1 (Table 2). So, this estuary is in a gradual degradation state. The mean value of PERI in Vridi channel is 828.2, with that of stations S1, S2 and S3 of 812.3, 741.6 and 930.3 respectively. Therefore sediments Vridi channel has a very high environmental risk referring classification established by Håkanson (1980).

Thus, Vridi channel is subjected to a relatively low contamination by these trace metals, except those for Cd and Pb. The anthropogenic pressures on the estuary would be relatively less important. This seems contradictory when we know the strong anthropogenic pressures on Ebrié system and Atlantic Ocean coasts, especially in front of the district of Abidjan. For illustration, the mean values of trace metals, obtained in Abidjan lagoon bays by Yao *et al.*, (2009) and Inza *et al.*, (2014), are significantly higher than those obtained in this study. Bathymetry and the hydrodynamics of the estuary would explain this contradictory fact. Indeed, the shallow depth and low hydrodynamics of the Ébrié system would favor trace metals accumulation, in addition to physical and chemical environmental conditions that contribute to it. However, the high depth and strong hydrodynamics in Vridi channel, compared to that of Ebrié system, disadvantage trace metal accumulation. That would also favor the desorption of trace metals in sediments, as shown by Nan *et al.*, (2016). Except Cd and Mn which exhibited their highest annual mean values in stations S1 and S2 respectively, all other trace metals studied have theirs in the station S3. This reflects a relatively strong continental contribution compared to that of Atlantic Ocean. The high annual mean values of Fe, Mg and Mn in all stations and fractions illustrate their abundance in the upper crust (Wedepohl, 1995), especially in the continental shelf, the sedimentary basin and the coast of Gulf of Guinea. These trace metals are transported by meteorites continental contributions via Ebrié system in the form of coarse and medium coarse sands. As for the strong presence of Pb, observed after those of Fe, Mn and Mg in all fractions and stations, it is explained by its strong industrial use, especially in that of the oil industry next to the autonomous harbour of Abidjan. It also comes from the oil and gas wharf installed within this estuary. The strong presence of Zn, Cd and Co in sediments in

the form of slits (Fraction III) show that they would come from the organic matter decomposition linked to anthropogenic wastes. This fact seemed to be of particular importance in the lagoon area of the harbour for Zn and Co (strong presence at the station S3), and for Cd (strong presence at the station S1) to the coasts of Atlantic Ocean in front of Abidjan. The strong presence of Cu in the coarse sand (fraction I) and that of Ni in coarse and medium sands (fraction II) would show that they come from industrial sources, including those of harbour industrial zone if it is referred their importance to the station S3.

The progressive degradation of this estuary, shown by PLI values in all stations, is mainly due to the strong human pressure exerted on this estuary. This fact was mentioned by Ali *et al.*, (2016), Effendia *et al.*, (2016), Mashiatullah *et al.*, (2013) and Nadem *et al.*, (2015). The strong values of PLI' testify to the strong involvement of industrial discharges in this situation, especially those of industrial zone of the harbour. This is illustrated by the observation of the highest values of PLI and PLI' to the station S3. The immediate consequence is a very high ecological risk presented by this channel, especially its sediments; as specified by the high values of PERI in the sampling station. This state of advanced deterioration of this channel would show those of Ebrié system and the coasts of Atlantic Ocean in front of Abidjan, as shown by Yao *et al.*, (2009) in the specific case of Abidjan lagoon bays.

Conclusion: This work has shown that Vridi channel presents an advanced state of degradation with very high ecological risk, bound to metal pollution particularly by Pb and Cd. This fact is essentially due to anthropogenic pressures, especially wastes coming from to harbour industrial zone. This situation seemed to be lessened by its strong hydrodynamic and high depth.

If no precautions are taken, the ecological future of this estuary will darken further with regard to population growth and human activities in Abidjan district. This study should be extended to other types of pollutants for a real diagnosis of its pollution state. In the future, it would be necessary to lead important political involvements for safeguarding of this estuary for its sustainable development.

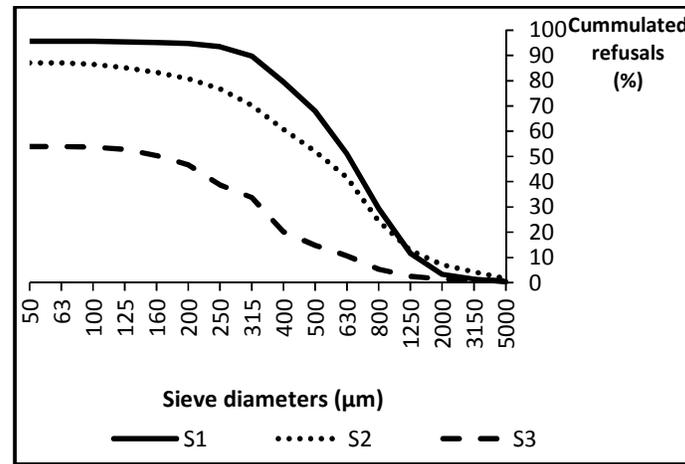


Fig.3: Size distribution of sediments in sampling sites

Table 1: Annual means (\pm SD) of trace metals concentration in fractions and sampling sites

	Stations			Fractions of sediments			Annual mean
	S1	S2	S3	I	II	III	
Cd (mg/Kg per dry weight)	1.04 \pm 0.95 (90.92%)	0.89 \pm 0.89 (99.37%)	0.93 \pm 0.96 (102.68%)	0.47 \pm 0.29 (62.14%)	0.37 \pm 0.02 (5.03%)	2.03 \pm 0.01 (0.45%)	0.96 \pm 0.16 (16.64%)
Zn (mg/Kg per dry weight)	25.05 \pm 12.16 (48.56%)	23.14 \pm 23.17 (100.16%)	33.09 \pm 38.34 (115.86%)	17.84 \pm 12.94 (62.92%)	10.60 \pm 4.51 (42.51%)	52.89 \pm 27.65 (52.34%)	27.11 \pm 11.72 (43.21%)
Pb (mg/Kg per dry weight)	82.21 \pm 17.63 (21.44%)	76.34 \pm 12.47 (16.33%)	91.57 \pm 22.07 (24.10%)	74.28 \pm 1.87 (2.52%)	84.20 \pm 10.6 (11.94%)	91.64 \pm 15.08 (16.45%)	83.37 \pm 6.66 (7.99%)
Ni (mg/Kg per dry weight)	41.71 \pm 8.67 (20.79%)	34.12 \pm 9.48 (27.77%)	51.76 \pm 10.88 (21.02%)	39.95 \pm 5.21 (13.04%)	47.29 \pm 2.14 (4.52%)	40.35 \pm 20.42 (50.60%)	42.53 \pm 9.79 (23.02%)
Cu (mg/Kg per dry weight)	32.29 \pm 17.16 (53.15%)	32.52 \pm 19.66 (60.46%)	37.14 \pm 19.95 (53.72%)	50.52 \pm 5.21 (13.04%)	13.91 \pm 1.24 (8.90%)	37.11 \pm 10.44 (28.12%)	33.98 \pm 4.61 (13.58%)
Mn (mg/Kg per dry weight)	259.1 \pm 158.5 (61.2%)	346.2 \pm 209.5 (60.5%)	303.5 \pm 283.1 (93.2%)	371.5 \pm 790.9 (212.9%)	353.2 \pm 662.9 (187.7%)	184.1 \pm 15.9 (8.6%)	302.9 \pm 415.4 (137.1%)
Mg (mg/Kg per dry weight)	793.1 \pm 254.1 (32.1%)	1025.3 \pm 639.5 (63.4%)	1125.1 \pm 915.9 (81.4%)	465.4 \pm 230.7 (49.5%)	840.8 \pm 87.8 (10.5%)	1637.3 \pm 801.3 (52.6%)	981.2 \pm 377.5 (38.5%)
Co (mg/Kg per dry weight)	21.28 \pm 0.83 (3.89%)	19.43 \pm 9.80 (50.45%)	26.37 \pm 18.37 (69.62%)	15.42 \pm 5.24 (34.01%)	18.92 \pm 1.73 (9.18%)	32.76 \pm 0.64 (1.95%)	22.36 \pm 2.41 (10.75%)
Fe (mg/Kg per dry weight)	26903.2 \pm 16385.8 (60.9%)	35201.8 \pm 14657.3 (41.6%)	33176.4 \pm 13031.1 (39.3%)	40559.3 \pm 15757.7 (38.8%)	20773.8 \pm 4454.5 (21.5%)	33948.4 \pm 9911.9 (29.2%)	31760.5 \pm 5652.7 (17.8%)

*in bracket, the variation coefficient (VC)

Table 2: Pollution index evaluated in all sampling sites

		Cd	Zn	Pb	Ni	Cu	Mn	Mg	Co	Fe
Igeo	S1	1.14	-0.19	0.81	0.48	0.48	-0.18	-1.11	0.39	0.06
	S2	1.07	-0.23	0.78	0.39	0.48	-0.06	-0.99	0.35	0.18
	S3	1.09	-0.07	0.86	0.57	0.54	-0.11	-0.95	0.53	0.16
CF	S1	10.24	0.48	4.85	2.24	2.26	0.49	0.06	1.83	0.87
	S2	8.77	0.44	4.49	1.83	2.27	0.66	0.08	1.68	1.14
	S3	9.14	0.67	5.39	2.78	2.60	0.58	0.08	2.53	1.07
EF	S1	11.76	0.55	5.55	2.57	2.59	0.56	0.07	2.11	
	S2	7.70	0.39	3.94	1.61	1.99	0.58	0.07	1.47	
	S3	8.51	0.59	5.02	2.59	2.42	0.54	0.08	2.36	
PLI	S1					1.21				
	S2					1.24				
	S3					1.46				
*PLI'	S1					21.45				
	S2					16.59				
	S3					30.02				

*calculated with trace metals from anthropogenic origin

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