SEDIMENT HEAVY METAL POLLUTION OF AN URBAN RIVER IN VIETNAM

Ngoc Nguyen[1], Michael Daniels[1], Brian Majestic[1], Hung Duong[2]
[1]University of Denver, [2]Vietnam Academy of Science and Technology

Introduction

Nowadays, rapid urbanization, industrialization, and agricultural activities have released excessive waste products into the environment, directly affecting the urban hydrological systems. Urban rivers and lakes have become major city's wastewater pools when sewage and industrial treatment systems are overloaded (Ji et al., 2017). Among different types of hydrological pollution, heavy metal contamination has received great attention globally due to its toxicity and bio-persistence (Ji et al., 2017; Halder and Islam, 2015; Ahmad et al., 2010; Islam et al., 2014). To Lich River is the longest river in Hanoi city - the capital of Vietnam, and it is not an exception. Through atmospheric deposition and industrial/domestic wastewater, To Lich River has received a large amount of heavy metals with most of it settling in bottom sediments (Farkas et al., 2007). It is important to understand the heavy metal pollution dynamic as To Lich River's water has been frequently used to grow at-home and large-scale agricultural products. Nevertheless, there are very few studies evaluating the pollution level of To Lich River in the last 20 years. As a result, this research aims to measure the concentration of 7 typical heavy metals (Cr, Ni, Cu, Zn, As, Cd, and Pb) in surface sediments and use multivariate statistical analyses to evaluate the temporal and spatial river pollution dynamics.

Methodology

To Lich River

- Hanoi population has increased from 2 to 7 millions since 2000
- 17 km, run through 10/12 districts
- Receive 2/3 city wastewater (290,000 m^3/day) from 33 industrial plants
- July 20th, 2019 (7 a.m. – 6 p.m.): Collected samples at 19 sampling sites (C1-C19)



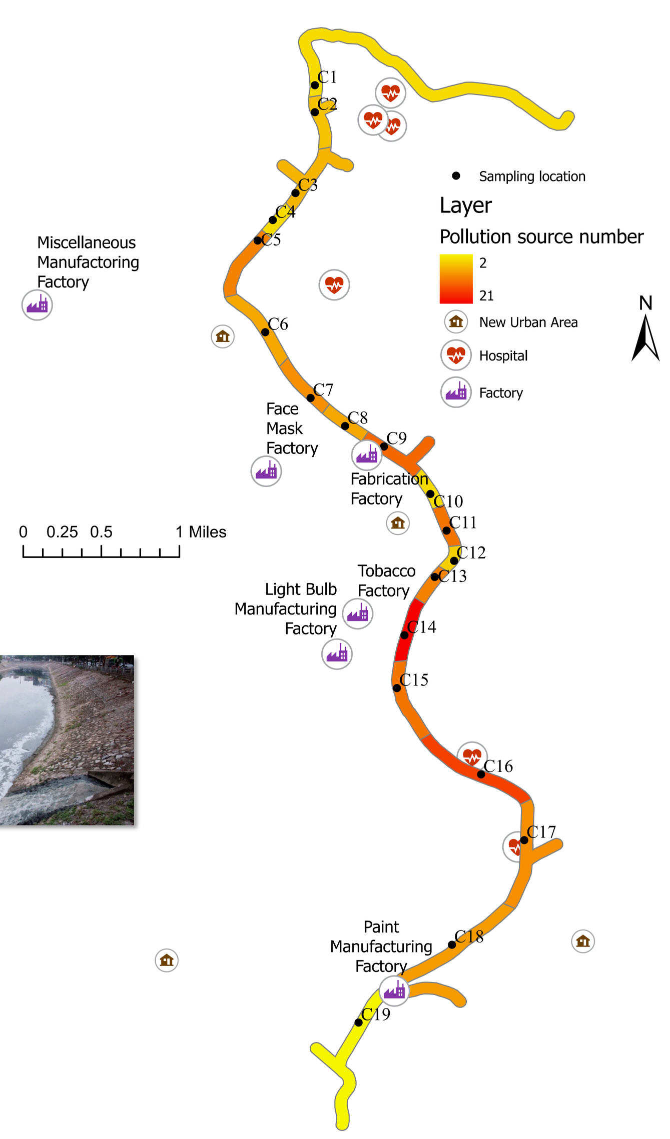

Fig. 1 Pollution source density of To Lich River and 19 sampling locations

Heavy Metal Analysis

1. Used a 2-meter PVC piston to take 0-20 cm sediments
2. Air-dried , ground, and sieve 19 samples to 0.154 mm in size
3. 0.2 g sample was microwave-digested with concentrated HCl and HNO_3
4. Digested solution was diluted with suspended solids removed
5. Heavy metal measurement was made by Perkin Elmer NexION 2000 ICP-MS

PVC piston + PE bag → Air-dried + Ground → Digested by acid → Removed suspended solids + Diluted with HNO_3 1% → ICP-MS

Statistical analyses

- Geo-accumulation Index (Igeo)
- Enrichment Factor (EF)
- Hierarchical Cluster Analysis & Principal Component Analysis

$$I_{geo} = log_2 \frac{C_{sample}}{1.5 \times C_{background}}$$

$$EF = \frac{(metal/Al)_{sample}}{(metal/Al)_{background}}$$

Results

Pollution Analyses

1. Geo-accumulation Index (I_{geo})

Table 1 I_{geo} statistics for seven heavy metals in 19 sampling locations

I_{geo}	Cr	Ni	Cu	Zn	As	Cd	Pb
Max	1.1	0.4	3.9	3.3	1.2	6.5	2.5
Min	-1.8	-8.0	-1.4	-0.3	-4.1	-0.4	-0.7
Mean	-0.5	-2.3	0.6	1.6	-0.9	2.5	0.8
Class 0 (%)	63.2	94.4	31.6	10.5	63.2	5.3	21.1
Class 1 (%)	31.6	5.6	31.6	21.1	31.6	10.5	42.1
Class 2 (%)	5.3	0.0	31.6	31.6	5.3	26.3	21.1
Class 3 (%)	0.0	0.0	0.0	31.6	0.0	36.8	15.8
Class 4 (%)	0.0	0.0	5.3	5.3	0.0	5.3	0.0
Class 5 (%)	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Class 6 (%)	0.0	0.0	0.0	0.0	0.0	15.8	0.0

Class 1 and lower:
- 95-100% for Cr, As, and Ni

Class 1 and higher:
- > 50% for Cd, Zn, Pb, and Cu

Class 2 or higher:
- Zn (68.5%) and Cd (78.9%)

Class	Value	Contamination level
0	≤ 0	None
1	$0-1$	None-moderate
2	$1-2$	Moderate
3	$2-3$	Moderate-heavy
4	$3-4$	Heavy
5	$4-5$	Heavily-extreme
6	> 5	Extreme

2. Enrichment Factor (EF)

Table 2 EF statistics for seven heavy metals in 19 sampling locations

Enrichment Factor	Cr	Ni	Cu	Zn	As	Cd	Pb
Max	8.8	2.4	35.1	41.2	7.8	304.0	21.8
Min	1.8	0.03	2.2	4.5	0.6	3.9	4.0
Mean	3.5	1.2	8.2	15.9	3.2	49.6	8.6
% No enrichment < 1	0.0	33.3	0.0	0.0	26.3	0.0	0.0
% Minor ≥ 1 & < 3	57.9	66.7	10.5	0.0	15.8	0.0	0.0
% Moderate ≥ 3 & < 5	26.3	0.0	26.3	5.3	42.1	5.3	15.8
% Moderately severe ≥ 5 & < 10	15.8	0.0	47.4	15.8	15.8	10.5	63.2
% Severe ≥ 10 & < 25	0.0	0.0	10.5	73.7	0.0	42.1	21.1
% Very severe ≥ 25 & < 50	0.0	0.0	5.3	5.3	0.0	21.1	0.0
% Extremely severe ≥ 50	0.0	0.0	0.0	0.0	0.0	21.1	0.0

Moderate enriched or higher:
- 89.5% (of samples) for Cu
- 100% for Zn, Cd, and Pb

Severely enriched or higher:
- 78.9% for Zn
- 84.2% for Cd

3. Sediment Quality Guidelines

Table 3 Heavy metal concentration in 19 samples (mg/kg) and SQG values

	Cr	Ni	Cu	Zn	As	Cd	Pb
Min	39.2	0.4	26.2	113.0	1.1	0.3	18.6
Max	279.7	137.3	1008.4	1378.7	44.2	40.9	166.5
Mean	111.8	35.7	149.5	529.3	16.0	6.6	64.1
Coefficient of variation (%)	60.2	90.7	143.6	63.6	77.6	184.3	67.2
TEC[a]	43.4	22.7	31.6	121	9.8	0.99	35.8
PEC[b]	111	48.6	149	459	33	4.98	128
< TEC (%)	5.3	33.3	10.5	5.3	36.8	15.8	31.6
>TEC <PEC (%)	52.6	38.9	68.4	47.4	52.6	68.4	57.9
>= PEC (%)	42.1	27.8	21.1	47.4	10.5	15.8	10.5

Threshold Effect Concentration (TEC): < TEC: absence of sediment toxicity
Probable Effect Concentration (PEC): > PEC: presence of toxicity to organisms living in sediments

- Most locations have their metal concentrations between TEC and PEC values
- High coefficient of variation
- > PEC: Cr (42.1% of samples); Zn (47.4% of samples)

Correlation Analyses

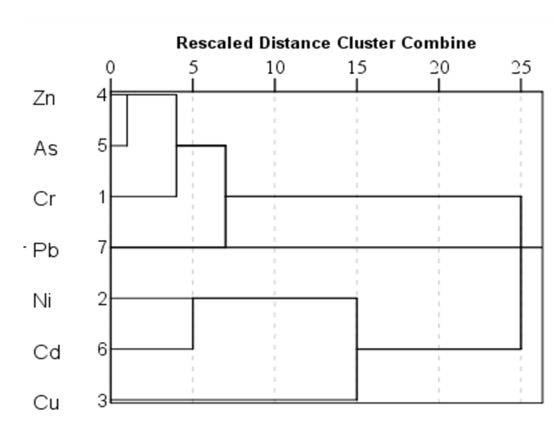

Fig. 2 Dendrogram for seven heavy metals in To Lich River's sediments.

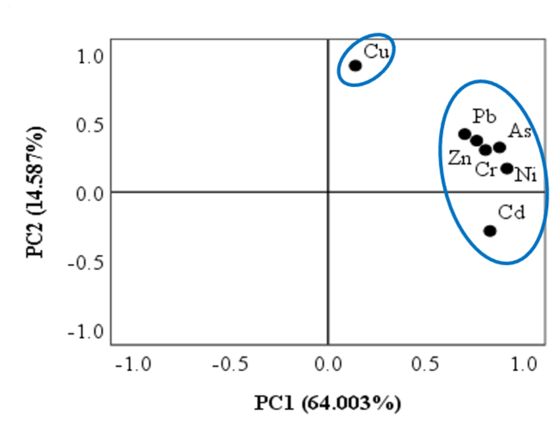

Fig. 3 Principal Component Analysis for seven heavy metals in To Lich River's sediments

- 3 possible clusters : (Ni, Cd) > (Zn, As, Cr, Pb) > Cu (ranked by order of significance) (Seeing Fig 5 for visualization purposes)
- Linkage between Zn, As, Cr, Pb, Ni, and Cd
- Cu behaves differently from the other metals

Comparison to other studies

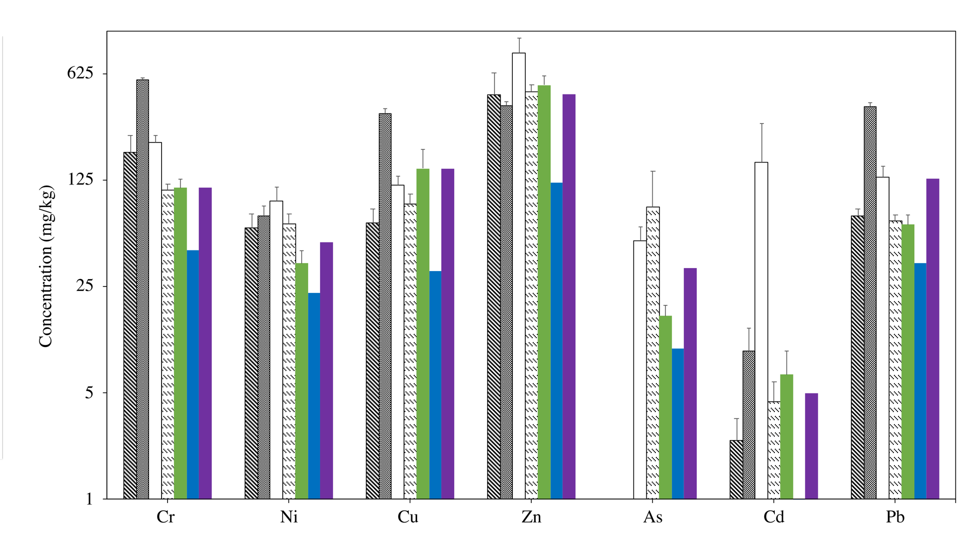

Fig. 4 Mean heavy metal concentration (mg/kg) between five different studies of To Lich River and the TEC-PEC Sediment Quality Guideline.

- Coefficient of Variation between five studies: Cr (70.9%), Ni (27.7%), Cu (64.7%), Zn (30.6%), As (55.3%), Cd (169.4%), Pb (84.8%)
- All studies exceed the TEC threshold for every metal
- A major of them exceed PEC values for Cr, Ni, Zn, Cd

Spatial dynamics of pollutions

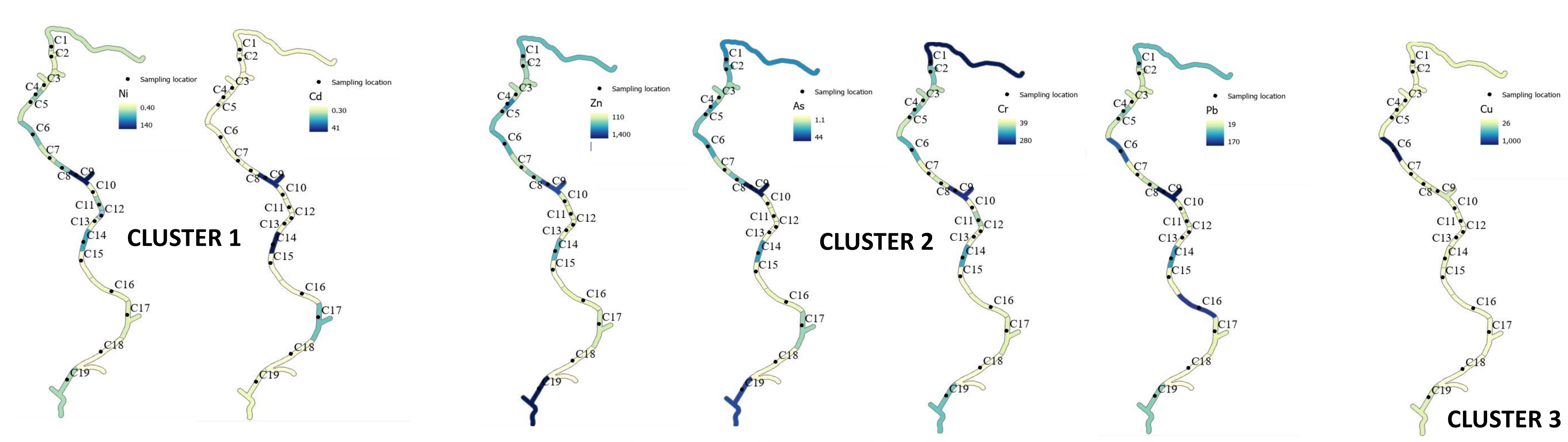

Fig. 5 Heavy Metal Distribution in To Lich River

Dangerous locations that exceed PEC (toxic) and have I_{geo} > 0 (contaminated):

Ni: 9
Cd: 9, 14, 17
Zn: 1, 2, 4, 5, 6, 8, 9, 14, 19
As: 9, 19
Cr: 1, 2, 3, 4, 9, 14, 19
Pb: 9, 16
Cu: 4, 6, 9, 19

Pollution source: higher frequency in the middle of the river; factories concentrates in the middle of the river

C9: Highly polluted in terms of 7/7 metals; In a high pollution source density
C14: Middle-range pollution levels of most metals
C19: High in As and Zn; location is next to a paint factory
C1: High in Cr, As, Zn, Pb (highest in terms of Cr)

Discussion

Pollution Analyses

- Ranking for both I_{geo} and EF indices: Cd > Zn > Pb > Cu > Cr > As > Ni
- Using Al as the Normalizing element may have made the EF scale higher than I_{geo} scale, although they yield the same ranking order
- There is a great level of dispersion around the mean value, and samples vary significantly between locations in terms of these heavy metal concentrations
- While I_{geo} and EF indicate most samples are low-polluted in terms of Cr, 42.1% of them are seen as toxic for organisms
- Most of the locations are not free of toxicity in terms of seven studied heavy metals → Questioning the practice of using river water to irrigate self-planted vegetables near the riverside

Correlation Analyses and spatial dynamics

- It is still unclear why Cu behaves differently from the other metals
- Metal clusters might be the consequences of different factories yielding different type of pollution combination
- Factory locations play an important role in pollution spatial dynamics

Comparison to other studies

- Dec-05 study yields much higher values (3 to 5 times) compared to the other four studies (Ex: Cr, Cu, and Pb)
- Cu has moved from class 1 to class 2 Igeo level. As has moved from class 3 to class 0 compared to study from Mar-2011
- Difference in sampling size and limited number of studies are accountable for the high coefficient of variation between five studies

Conclusion

- Pollution and Anthropogenic-Influenced ranking:
  Cd > Zn > Pb > Cu > Cr > As > Ni
- There is a significant difference between results from the five studies (difference in sampling size)
- Comparing to the latest study in Mar-2011, there is no significant difference in terms of Cd, Zn, Pb, Cr, and Ni concentrations; Samples become more contaminated in terms of Cu and less contaminated in terms of As
- Locations C1, C9, C14, C19 show a high number of nearby manufacturing factories as well as a high pollution level
- Most of the locations are not free of toxicity in terms of all heavy metals. On average, river sediment has been toxicated during the last 20 years

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