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## Heavy Metal Pollution of the To–Lich and Kim–Nguu River in Hanoi City and the Industrial Source of the Pollutants

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The present study shows that stream water and sediment in the To–Lich and Kim–Nguu River are heavily polluted with heavy metals, and the metal concentrations all exceed the Vietnamese surface water standard. The metal concentrations in the water and sediment were indicated to be closely related to the type of manufacturing plants located along the rivers. The high concentration of Cu is due to discharges from textile manufactures. The metals such as Zn, Cr, and Ni were released from the battery factory located at Van–Dien area. Cadmium is derived from Dai–Kim plastic factory, and Pb can be attributed mainly to transportation activities.

*Keywords:* Heavy metals, streams, sediment, industry

### INTRODUCTION

Hanoi has experienced rapid economical growth and urban expansion in the last decades. However, inappropriate city planning and wastewater management for both industry and household has caused various environmental problems including the heavy metal pollution of surface water and sediment in rivers and lakes. In Hanoi City there are a great number of industries which could be the source of pollution: 274 enterprises and factories, 540 service establishments, 450 production cooperation and 3,350 production establishments. Most of them are concentrated in Thuong–Dinh industrial zone, and Van–Dien and Hai–Ba–Trung area (Environmental information office, 2001), and some are located in residential areas. Most manufacturers were established in the 1950s with assistance from China and the former Soviet Union. Their plants are old, and do not equip with appropriate wastewater treatment facilities. Exhaust emissions from motor vehicles are also a major source of pollutants. There are various environmental regulations and standards in Vietnam, but the implementation of these is lacking.

Heavy metals are harmful to human health because of their toxicity. Cadmium (Cd) is highly toxic and accumulative, and kidney in human and animals is targeted by cadmium toxicity. Other diseases include skeletal disorders such as *osteoporosis* or *osteomalacia* (softening of the bones) as well as the development of hypertension (high blood pressure) and heart disease (Brigden and Santillo, 2004). Lead (Pb) is one of the most toxic elements naturally occurring on Earth. High

concentration of lead can cause irreversible brain damage, seizure and coma, and death if not treated immediately. The kidney is also targeted by Lead toxicity and impaired at moderate to high level of lead concentrations. Other signs/symptoms of lead toxicity include gastrointestinal disturbances—abdominal pain cramps constipation anorexia, weight loss—immunosuppression, and slight liver impairment (Enhanced Oral Chelation, 2001)

The To–Lich and Kim–Nguu River are the source for irrigation to suburban agricultural land and for fish farming. The discharge of industrial wastewater into the rivers has adversely affected the quality of stream and sediments in the river system (Environmental Information Office, 2001). This affects not only farming and fish breeding, but also the health of general public in surrounding areas. Hence it is of importance to assess the water quality of streams and the extent of contamination in the sediment. In the present study we examined the chemical and physical properties, and heavy metal concentrations for streams and sediment, and discussed the relation of these to the industrial source of the pollutants.

### MATERIALS AND METHODS

#### Background of the study area

There are two rivers in Hanoi City (Fig. 1), the To–Lich and Kim–Nguu River. The To–Lich River with 17 km in length originating in West Lake flows through Thuong–Dinh industrial zone to Van–Dien, joining to the Kim–Nguu River. Industrial and non–industrial urban wastewater flowing into the To–Lich River amounts to 290,000 m<sup>3</sup>/day, which accounts for two third of the wastewater produced in the city (Environmental information office, 2001). The industry that discharges the wastewater includes 33 plants, and major ones are Gold–Star rubber, Thang–Long cigarette, Thang–Long cigarette, Dai–Kim plastic, and a soap plant. The waste-

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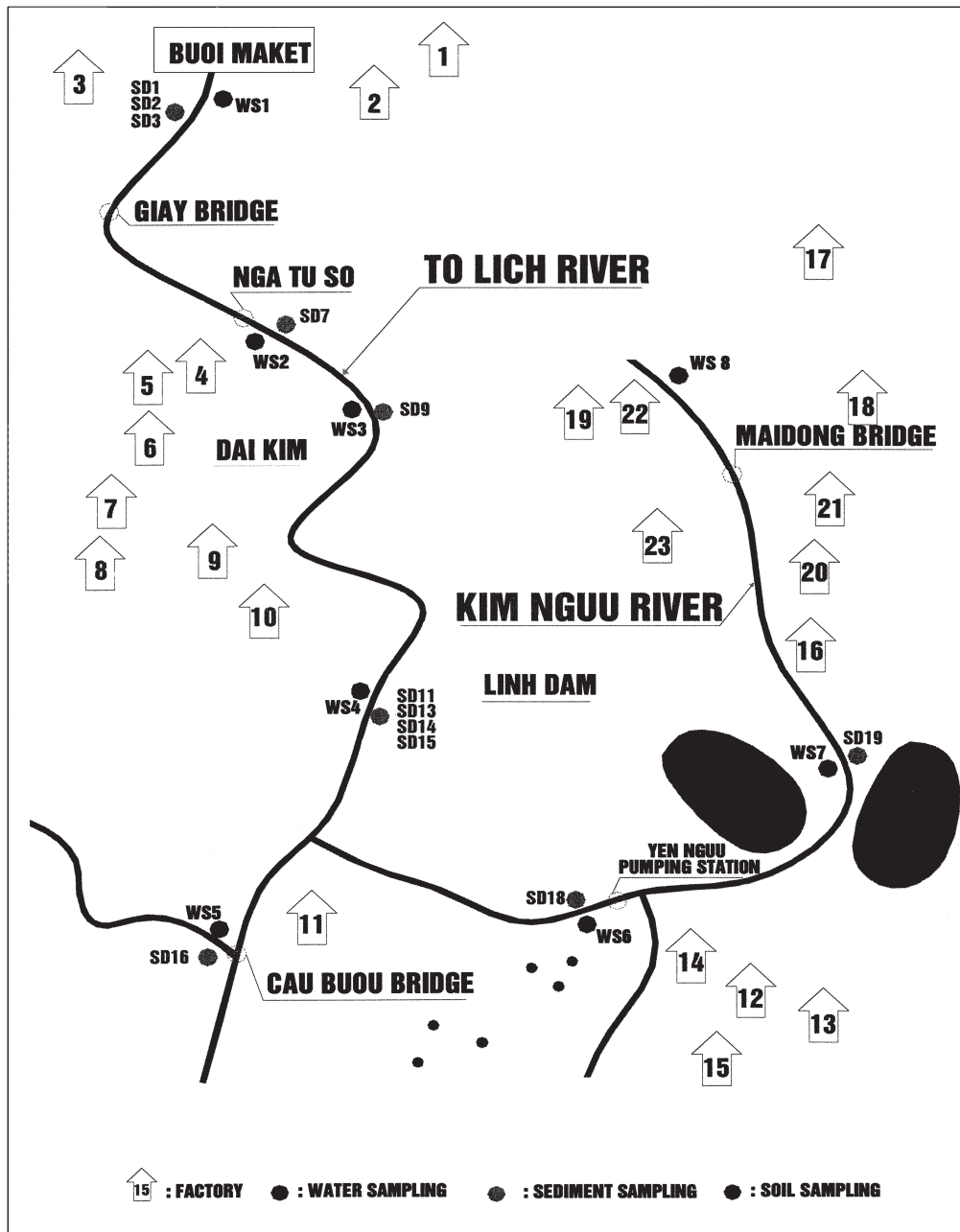


Fig. 1. Site sampling location.

water from these plants is being discharged without any appropriate treatment. The irrigation water from the To-Lich River covers 1,361 ha agricultural land in Yen-Hoa, Lang-Ha, and Nhan-Chinh (Cau-Giay) communes, My-Dinh (Tu-Liem), Thanh-Liet (Thanh-Xuan) and Dai-Kim (Thanh-Tri) communes.

The Kim-Nguu River with 11 km also flows through the densely populated area of Hanoi City. The wastewater from the area of 6 km<sup>2</sup> is flowing into this river, which amounts to 139,000 m<sup>3</sup>/day, being one third of the wastewater produced in the city (Environmental Information Office, 2001). The main industry that discharges wastewater is March-8 textile, Mai-Dong mechanical engineering, and Hanoi-Win. The irrigation

water from the Kim-Nguu River covers the agricultural land in Tran-Phu commune (Hai -Ba-Trung) and Yen-So Commune (Thanh-Tri); Tu-Hiep and Lien-Minh communes (Thanh-Tri).

#### Materials

Surface water samples were collected at eight representative locations on December 3 to 6 of 2005 (Fig. 1 and Table 1). Sediment samples were collected at eight locations from the top 20 cm of the sediment in the rivers. The sediment core samples were taken from the depth of 0 to 90 cm at the sites where sediment surface was exposed to the air.

**Table 1.** Water and sediment sample location

Sediment sample		Water sample	Location	Name of factories near sampling site	Number	Industrial Sector	Year of Establishment	Pollutants*
No	Depth (cm)							
SD 1	0–30	WS 1	Buoi Market	Thuy–Khe–Leather factory	1	Footwear	1950	Cu
SD 2	30–60			Hanoi Beer Manufactory	2	Foodstuff	1955	OM**
SD 3	60–90			Trang –An Food and Candy Factory	3	Foodstuff	1960s	OM
SD 7	0–20	WS 2	Nga–Tu –So	Hanoi Mechanical Company	4	Mechanical	1960s	Cu, Cr, Ni
				Gold Star Rubber Company	5	Chemical	1958	Zn, Pb
				Hanoi Soap Company	6	Chemical	1958	Zn, Cr, Ni
				Thang–Long Tobacco Factory	7	Tobacco	1958	Zn, Pb
				Rang–Dong Buld and Thermos Company	8	Chemical	1958	Cd, Ni
				Thuong –Dinh Footwear Factory	9	Footwear	1958	Cu
SD 9	0–20	WS 3	Dai–Kim	Dai–Kim Plastic Factory	10	Chemical	1960s	Zn, Pb
SD 11	0–20	WS 4	Linh–Dam		None			
SD 13	0–30							
SD 14	30–60							
SD 15	60–90							
SD16	0–20	WS 5	Cau –Buou	Painting company	11	Chemical	1984	Zn, Hg, Pb
SD 18	0–20	WS6	Yan–nguu Pump station	Van–Dien Phosphates Factory	12	Chemical	1957	Zn, Cu, Cd
				Van–Dien Battery Factory	13	Chemical	1958	Zn, Cd, Ni
				Van–Dien Mechanical Factory	14	Mechanical	1964	Cu, Cr, Ni
				Van–Dien Cemetery	15		1950s	OM
				Soldering Stick Factory	16	Mechanical	1950s	Fe, Zn
SD 19	0–20	WS7	Yen–So Lake	Hai–Chau Candy Factory	17	Foodstuff	1960s	OM
				Dong–Nam –A Beer Factory	18	Foodstuff	1998	OM
				Huu–Nghì Food Factory	19	Foodstuff	1960s	OM
				Hanoi Leather Factory	20	Footwear	1960s	Cu
				March–8 Textile Factory	21	Footwear	1960s	Cu
				Minh– Khai Lock Factory	22	Mechanical	1960s	Cu, Cr, Ni
				Mai –Dong Mechanical Engineering Factory	23	Mechanical	1960s	Cu, Cr, Ni
		WS 8	Mai– Dong bridge		None			

\* Sources of information: Environmental Information office (2001)

\*\* OM: organic matter

## Methodology

### Chemical properties of water

The pH of water was measured with a pH meter (HM 30 G Horiba). Electric conductivity (EC) was determined using conductivity meter (CM 20S TOA). Dissolved oxygen (DO) was measured with Yellow Spring YS1 58 58 dissolved oxygen analyzed with an YSI 5730 electrode. Chemical oxygen demand (COD) was determined by Kali Manganates methods (KMnO<sub>4</sub>). For total suspended solid (TSS), original water samples were filtered using glass filtering paper, and then the solid was dried at 100 °C and weighed. Cation and anion concentrations in water were measured for filtered water samples with ion chromatograph (DIONEX DX–100). Water-soluble and total heavy metal concentrations were determined for filtered and non-filtered water samples, respectively. The metals in the water samples were analyzed after adding 1 M HNO<sub>3</sub> with atomic absorption spectrophotometer (AAS–Solar S2 Thermo electronic cooperation).

### Chemical and physical properties of sediment

The pH was measured using soil suspension with soil/water ratio of 1/25. Organic matter content was determined by the Tyurin method. Particle size distribution was determined by the pipette method (Khoa, *et al.*, 1996). Cation exchange capacity (CEC) was measured by the method proposed by Muramoto *et al.* (1992). For total metal concentration, heavy metals in the sediment was digested with 1 M HNO<sub>3</sub> at 96 °C for an hour and centrifuged, and the dissolved metals in the supernatant were analyzed by atomic absorption spectrophotometer (Committee of Soil standard methods for Analyses and Measurement, 1986).

## RESULTS AND DISCUSSIONS

### Water quality

The water quality determined is summarized in Table 2. The pH ranged between 6.8 and 11. The pH for WS 2, 3, and 6 was much higher than that (pH 5.5–9) of

**Table 2.** Chemical properties of water of To–Lich and Kim–Nguu river system

No	pH	EC (ms/cm)	DO (mg/L)	COD (mg/L)	TSS (mg/L)	Cation (mg/L)				Anion (mg/L)					
						Ca	Mg	K	Na	F	Cl	Br	NO <sub>3</sub>	SO <sub>4</sub>	PO <sub>4</sub>
WS 1	7.1	0.66	0.7	120	250	11.2	45.4	45.4	24.8	–	109	–	23.2	1.0	71.1
WS 2	11.4	0.75	0.4	136	350	13.4	39.0	39.0	25.7	–	97	–	20.8	1.3	27.2
WS 3	10	0.75	0.3	152	350	15.7	42.1	52.1	32.5	–	166	0.32	4.5	5.1	52.2
WS 4	7.8	0.75	0.1	184	300	14.5	39.7	39.7	21.6	–	87	–	3.2	0.5	34.1
WS 5	8.0	0.76	0.4	156	350	10.1	30.0	33.0	21.8	–	60	–	2.5	1.6	42.8
WS 6	10	0.76	0.2	164	210	11.1	36.5	36.5	19.0	21	122	0.65	4.6	1.4	12.7
WS 7	8.0	0.75	0.5	120	200	12.9	33.6	33.6	20.0	15	95	1.59	7.4	5.4	14.7
WS 8	6.8	0.78	0.6	106	250	22.8	49.6	39.6	24.9	90	–	–	4.1	4.7	47.7
TCV	5.5		> =2	< 35	80					1.5			15		
N	–9														

\* TCVN 5942–1995 B: Category B: applied to surface water used for purpose other than domestic water supply

Vietnamese standard for surface water, which would be due to effluents from Gold–Star rubber and the soap factory. The EC ranged from 0.65 to 0.78 mS/cm. The DO exhibited extremely low values of 0.1 to 0.7 mg/L, which exceed the Vietnamese Requirement ( $> = 2$  mg/L) for surface water. The COD and TSS were in the range of 106 to 184 mg/L and 200 to 350 mg/L, respectively, which exceed the limitation B of standard TCVN (5942–1995) by 3 to 5 times. The cation concentrations were 10.1 to 22.8 mg/L for Ca, 30.0 to 49.6 mg/L for Mg, 33.7 to 45.4 mg/L for K, and 19.0 to 32.5 mg/L for Na. For anions, F in all water samples measured exceeds the F standard discharge concentration. The NO<sub>3</sub> concentration for WS 1 and 2 exceed the standard of irrigation water. Other anions ranged 60 to 166 mg/L for Cl, 0.5 to 5.1 mg/L for SO<sub>4</sub>, and 12.7 to 71.2 mg/L for PO<sub>4</sub>.

Table 3 shows the water soluble and total heavy metal concentrations in water samples. The water soluble metal concentration was determined for the samples after removing suspended solid by filtering. The total heavy metal concentration was measured on the samples with suspended solid. The total heavy metal concentrations exceed the standard (TCVN 5942–1995 B) for Pb and Cd in all the samples and for Cu in WS 2, 3, 5, and 7. The Ni and Zn concentrations were below the

standard level.

### Sediment quality

The chemical and physical properties of the sediment samples are shown in Table 4. The pH was in a range of 7.10 to 7.80. The organic matter content varied 3.36 to 7.97%. The highest organic matter content in SD 19 (Fig. 1) suggests the inflow of organic wastes from the factories such as Huu–Nghi food, Hai–Chau candy, Dong–Nam–A beer, open markets, and residence (Fig. 1). The cation exchange capacity (CEC) ranged between 9.26 and 20.32 cmol/kg. The highest value of CEC in SD 19 can be attributed to the high organic matter content.

All the sediment samples have relatively low clay content, ranging between 3.33 and 10.3%. For SD 11, 13, 14, and 15 the predominant fraction was silt and fine sand while was coarse and fine sand, and silt for the other samples.

The total heavy metal concentration varied considerably among the samples: 220 to 475 mg/kg for Cu, 260 to 665 mg/kg for Pb, 250 to 535 mg/kg for Zn, 2.5 to 40 mg/kg for Cd, 505 to 655 mg/kg for Cr, and 48 to 165 mg/kg for Ni. The metal concentrations of sediments in the rivers were also determined by Ho (2000).

**Table 3.** Heavy metal concentration in water

No	Water soluble heavy metal concentration (mg/L)						Total heavy metal concentration (mg/L)					
	Cu	Pb	Zn	Cd	Cr	Ni	Cu	Pb	Zn	Cd	Cr	Ni
WS 1	0.34	0.31	0.29	0.09	4.17	0.24	0.92	0.82	0.74	0.09	4.8	0.25
WS 2	0.49	0.6	0.24	0.09	3.79	0.25	1.66	1.56	0.88	0.10	4.89	0.38
WS 3	0.31	0.35	0.24	1.01	3.85	0.23	1.42	0.87	1.05	1.03	4.77	0.27
WS 4	0.32	0.34	0.27	0.09	3.68	0.21	0.98	0.9	0.79	0.10	5.04	0.31
WS 5	0.27	0.5	0.23	0.09	4.43	0.22	1.03	1.24	0.88	0.09	5.77	0.26
WS 6	0.41	0.22	0.37	0.09	3.79	0.24	1	0.91	1.87	0.09	5.36	0.29
WS 7	0.55	0.76	0.38	0.09	4.71	0.23	1.07	1.74	1.25	0.09	5.96	0.3
WS 8	0.34	0.27	0.24	0.08	3.53	0.2	0.91	0.65	0.74	0.08	4.2	0.25
	TCVN 5942–1995 B						1	0.1	2	0.02	1	1

\* TCVN 5942–1995 B: Category B: applied to surface water used for purpose other than domestic water supply

**Table 4.** Chemical and physical properties of sediment

No	pH H <sub>2</sub> O	pH KCl	OM (%)	CEC (cmolc/kg)	Particle size distribution (%)				Total heavy metal concentration (mg kg <sup>-1</sup> )					
					Clay (< 2µm)	Silt (2–20µm)	Fine sand (20–200µm)	Coarse sand (200–1000µm)	Cu	Pb	Zn	Cd	Cr	Ni
SD 1	7.58	7.99	4.13	10.52	4.33	24.33	30.54	40.65	260	368	250	4.4	540	65
SD 2	7.71	7.85	4.28	11.01	4.00	24.00	49.43	22.57	320	395	441	5.3	550	63
SD 3	7.83	7.87	4.45	12.49	4.33	24.33	48.65	22.69	345	425	345	5.2	525	48
SD 7	7.56	7.86	6.55	10.87	3.33	25.00	44.42	27.25	472	490	478	20.0	505	165
SD 9	7.45	7.73	5.60	12.86	4.00	35.30	55.47	5.23	445	450	490	40.0	517	108
SD 11	7.80	7.66	3.54	10.60	7.33	57.33	30.34	5.23	357	348	422	2.7	638	57
SD 13	7.26	7.10	3.54	9.52	7.33	53.33	36.08	3.26	340	280	395	2.5	637	52
SD 14	7.10	6.70	3.36	9.69	8.51	54.23	30.12	7.44	220	260	370	3.7	615	58
SD 15	7.25	6.67	3.84	9.26	10.3	59.00	25.45	4.77	240	370	325	2.7	605	50
SD 16	7.45	7.91	4.54	10.46	5.67	25.33	54.10	14.90	401	435	324	8.5	560	64
SD 18	7.14	7.54	4.94	12.84	4.33	19.76	58.21	17.46	415	430	535	17.0	655	142
SD 19	7.17	7.29	7.97	20.32	5.00	19.33	64.78	11.35	475	665	520	3.5	585	151

Compared with those, the metal concentrations determined in this study (Table 4) were almost the same for Ni and Cd, slightly lower for Zn, and higher for Cu, Cr, and Pb.

#### Impact of industrial activity on the quality of water and sediment in the To-Lich and Kim Nguu River

The relationship between the type of industry and heavy metal concentration in water and sediment is

shown in Table 5. The extremely high Cd concentrations of 1.03 mg/L and 40 mg/kg were observed in WS 3 and SD 9, respectively, which would be due to effluents from Dai-Kim plastic and Hanoi-Mechanical factories. The highest Cr concentrations were found in SD 18 (142 mg/kg) and WS 7 (5.96 mg/L), which would be attributed to the effluents from Van-Dien mechanical engineering and Mai-Dong mechanical factory. In Van-Dien area, the wastewater of 100 m<sup>3</sup> per day is being released from mechanical engineering factories to

**Table 5.** Relationship of types industry and metal concentration in the water and sediment

Sediment sample	Water sample	Types of factories	Industrial sector	Volume of wastewater (m <sup>3</sup> /day)	Stream conc. (mg/L)	Sediment conc. (mg kg <sup>-1</sup> S)
SD 1	WS 1	Thuy Khe- Leather factory				
SD 2		Hanoi Beer Manufactory				
SD 3		Trang-An Food and Candy Factory				
SD 7	WS 2	Hanoi Mechanical Company	Mechanical	4,907	Ni (0.38) Cu (1.66)	Pb (665) Ni (165) Cu (472)
		Gold Star Rubber Company	Construction	54		
		Hanoi Soap Company	Textile and shoes	1,015		
		Thang-Long Tobacco Factory	Foodstuff and tobacco other	22,114		
		Rong-Dong Buld and Thermos Company		95		
		Thuong-Dinh Footwear Factory	Total	28,165		
SD 9	WS 3	Dai-Kim Plastic Factory			Cd (1.03)	Cd(40)
SD 16	WS 5	Painting company				
SD 18	WS 6	Van-Dien Phosphates Factory	Mechanical	100	Zn (1.87)	Zn (535) Ni (142) Cr (142)
		Van-Dien Battery Factory	Construction	329		
		Van-Dien Mechanical Factory	Office	1,003		
		Van-Dien Cemetery	Total	1,432		
SD 19	WS 7	Soldering Stick Factory				
		Hai-Chau Candy Factory	Mechanical	296.9		
		Dong-Nam-A Beer Factory	Construction			
		Huu-Nghi Food Factory	Textile Garment	18,243	Cu (1.07)	
		Hanoi Leather Factory	Office	750	Pb(1.74)	Cu (475)
		March-8 Textile Factory	Total	2,106	Cr (5.96)	
		Minh-Khai Lock Factory				
		Mai-Dong Mechanical Engineering Factory				

the To-Lich and Kim-Nguu River, which is mainly responsible for high Cr concentrations (Environmental Information Office, 2001).

The highest Cu and Pb concentrations were found in SD 7 (Cu = 472 mg/kg) and SD 19 (Cu = 475 mg/kg and Pb = 665 mg/kg) as well as in WS 2 (Cu = 1.66 mg/kg) and WS 7 (Cu = 1.07 mg/L and Pb = 1.74 mg/L). These samples were taken at the sites into which wastewater from Thuong-Dinh and Hai-Ba-Trung industrial zones is flowing. The Cu accumulated in sediment is derived mainly from textile and shoes industrial sectors (Environmental Information Office, 2001). Hence the high Cu concentrations for SD 7 and WS 2 can be ascribed to wastewater from the factories such as Hanoi leather, March-8 textile (Hai-Ba-Trung industrial zone), and Thuong-Dinh footwear (Thuong-Dinh industrial zone).

According to the survey of industrial wastewater (Table 5), 28,165 m<sup>3</sup> wastewater is being produced in the Thuong-Dinh industrial zone, and 24% of that amount is domestic and 76% is industrial origin. The water used in this zone is mostly for cooling and washing. The water quality of the To-Lich River including biological, chemical, and physical properties have been degraded by the effluents from this industrial zone containing high organic matter and various toxic substances such as cuprous salt, chrome salt and cyanide (Environmental Information Office, 2001).

The source of Pb in water and sediment is present in the pollutants discharged from transportation activities as well as manufacturing processes. The particulates on the street contaminated with Pb due to emission from increasing number of motor vehicles are still the main source of Pb in Hanoi City, though Pb emission has been reduced drastically by phasing out of tetra-ethyl lead as a fuel additive. The Pb in storm water derived from exhaust emissions and Pb-based paint accounts for more than 1.2% of chemicals in the storm water (Birth, 1996).

The SD 18 exhibited high concentrations for Ni (142 mg/kg) and Zn (535 mg/kg), which would be due to effluents from Van-Dien battery factory, Van-Dien engineering and Van-Dien phosphate factory (Van-Dien area). Brigden and Santillo (2006) indicated that Cd, Co, and Ni are used in a battery manufacturing process, and water and sediment in a drain are heavily contaminated with those heavy metals. In battery manufacturers Zn and Hg are used in a manufacturing process; hence the high Zn concentrations for WS 6 (1.87 mg/L) and SD 18 (535 mg/kg) can be ascribed to effluents from Van-Dien battery factory.

## CONCLUSIONS AND RECOMMENDATION

Stream water and sediment in the To-Lich and Kim-Nguu River are heavily polluted with Pb, Cu, Zn, Cr, Cd, and Ni. The heavy metal concentrations determined all exceed the Vietnamese surface water quality standard (CVN 5942-1995 B).

A wide variation in the extent of pollution of water and sediment is the result of accumulation of contaminants from different sources. The main source of Cu is effluents from textile and garment industry sectors of the Thuong-Dinh and Hai-Ba-Trung industrial zones. The high concentrations of Zn, Cr, and Ni result from effluents from battery and mechanical factories at Van-Dien area. Extremely high Cd concentrations in water and sediment can be attributed to wastewater from Dai-Kim plastic factory. The Pb accumulated in water and sediment is derived from both manufacturing processes and exhaust emissions from motor vehicles.

To reduce the pollutants discharged from plants, countermeasures by the government and the technological improvement of wastewater treatment in manufacturing processes are needed.

For further study, we need to evaluate the leachability of heavy metals in sediment and assess the effects of heavy metals in irrigation water on the contamination of agricultural soil and metal accumulation in farm products.

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