

Multivariate Analyses of Potentially Toxic Elements along an Industrialized Urban River in Northern Taiwan

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Abstract

The Ker-Ya River flows through the high-tech industrial park and urban residential areas of Hsin-Chu in northern Taiwan. Major and trace element concentrations of waste effluents, river water, and sediment samples collected during 2017 along the Ker-Ya River were analyzed to elucidate the distribution pattern of potential pollutants. Principal component analyses were applied, and four major contaminant associations were recognized: 1) Ce, Co, Fe, La, V, and Cr; 2) Cu and Ni associated with Hg, Ni, P, Ga, W, In, and Ti; 3) B, Li, Ba, Ca, and Ag; and 4) Sn with Zn, In, and Cd. All associations are considered to be mainly anthropogenic. Although the element associations recognized from the water samples are not exactly the same as those from the sediment samples but nevertheless, they are similar, suggesting that the short-term and long-term distribution patterns are consistent. The A association accounts for the most variance in the data and exhibits the widest distribution, suggesting the existence of contaminant sources in the upper and lower reaches, respectively. The sediments near the outlet of the city sewage plant also contain association A elements, signaling incomplete processing of the diverged waters sent to the plant at the river mouth. The B association (mainly Cu and Ni) appeared mainly in the upper and middle reaches, indicative of sources from industries in the upper reaches and the tributary Nan-Men Creek. The C association (B, Ba, Ca, and Li) was limited to the center part of the river, probably attributable to a nearby paper mill. The D association (primarily Sn, In, and Zn) was present in the top point of the middle reaches, suggesting the presence of other contaminant sources in the upper reaches. Although a total of four concomitant associations were recognized, none of the elements exceeded the drinking water standard, suggesting that there was no severe pollution present.

Keywords

Toxic Elements, Spatial Distribution, Principal Component Analysis, Point Sources

1. Introduction

Despite efforts advanced in sewage treatment, monitoring and law enforcement, pollution caused by wastewaters discharged from domestic, agriculture, and industry remains a dire and challenging problem in many cities [1]-[9]. This is also the case in certain cities in Taiwan [10] [11]. This paper uses a multivariate statistical method to investigate the element data of river water and surface sediment samples to determine contaminant distribution patterns and elucidate possible pollution sources in a densely populated, highly industrialized area, Hsin-Chu, in northern Taiwan.

Hsin-Chu has been developed as a major high-tech industrial area since 1980, and the related information technology (IT) industrial complex, also known as “Eastern Silicon Valley”, is clustered in the Hsinchu Science Park (HSP) and its environs. The Ker-Ya River is the single major river flowing through the industrialized urban complex. In the watershed, there exist more than 500 manufacturing factors, including plants of electroplating, computer chip manufacturing, packaging assembly, rubber processing, paper and pulp mills, glass factories, chemical plants, cement factories, biotechnology companies, fertilizer manufacturing, printing, dyeing, and metal processing. Indeed, more than 400 plants are located inside of the HSP, located to the north of the Ker-Ya River in its middle reaches. Along the upper reaches remain farms, possibly discharging agricultural wastes too.

Ever since the establishment of the HSP in 1980, waste management, regular monitoring, and law enforcement have been implemented. Yet, several major environmental events occurred in the late 1990s, including the pungent smell of the river water, abnormal statistics of blood test results of inhabitants in neighboring communities, and repetitive dead fish incidents in the Ker-Ya River [12], [13]. Currently, the Ker-Ya River itself is still the major receiving water body in the city of different kinds of contaminants discharged from various sources, including agricultural wastewater in the upper reaches, industrial and municipal runoff from the middle and lower reaches in the downtown area, and probably occasional illegal dumping of untreated wastewater from dispersed industries. Among the numerous pollutants, anthropogenic metals are highly mobile and bioavailable, and therefore can impart adverse effects on aquatic biota and human beings [14] [15].

Beginning from 2015, as a measure designed to improve the water quality of the Ker-Ya River running through the urban area of Hsin-Chu, the waters of small tributary creeks were intercepted at four sites before they enter the main

course of the Ker-Ya River. These waters have been sent via sub-ground conduits to a sewage plant located near the river mouth. The interception and processing have improved the river water quality significantly in the downtown area, as evidenced by the marked reduction of bulk organic deposits (BOD) from 9.0 mg/L to 6.6 mg/L. Nevertheless, a previous general survey of the sediments in the wetland and water mouth area during 2012-2016 by the Taiwan Environment Protection Administration (TEPA) showed that the concentrations of As, Cu, Hg, Ni, and Zn occasionally exceeded the lower limit of sediment quality prescribed by TEPA. Monitoring of the river water quality also identified relatively high concentrations of Pb, As, Cu, Zn, and Mn during 2016, although only Mn (0.234 mg/L) exceeded the quality standard value (not potable). All of these alarming findings called for a thorough study of the distribution of contaminants in the watershed of the Ker-Ya River. The present research investigated a total of 67 species of inorganic contaminants, which is far beyond the conventional nine elements (Cd, Pb, Cr, As, Hg, Cu, Zn, Mn, and Ag) required by current legislation in Taiwan. The purpose of such a markedly more comprehensive study is to attempt to recognize potential risks associated with new trace metals recently used in high-tech manufacturing and to identify other potential sources of pollutants.

This paper aims to examine the distribution patterns of major and trace elements measured from water and surface sediment samples in three batches collected during 2017 along the Ker-Ya River using multivariate analysis. The main purpose was to reveal the inter-relationship of various elements, and thus elucidate possible pollutant sources, as well as to map the distribution of such potential pollutants along the urban waterways in Hsin-Chu. The obtained results can shed new light on environmental forensics and contribute to optimal environment governance.

2. Materials and Methods

Study Area and Sampling Design

The Ker-Ya River originates from the hilly Bao-Shan County to the east of the city at approximately a 100-m high altitude. It flows westerly through Hsin-Chu and enters the Taiwan Strait via a 24-km journey with a watershed of approximately 4560 ha. The upper reaches supply agriculture usage water, while the middle and lower reaches flow through the urban areas with a dense population (**Figure 1**). Geologically, the upper reaches eroded and carry sediments from Pliocene sandstone and mudstone, Quaternary table-land conglomerates, and alluvial deposits in the middle and lower reaches. The annual discharge of the Ker-Ya River is approximately 7830 km³, exhibiting a mild seasonal fluctuation with relatively high discharge during May – September. According to the permit registration of the Taiwan Environment Protection Administration (TEPA), the major sources of processed water discharges are the Hsinchu Science Park (HSP) (104,842 m³/d), Paper Mill A (2132 m³/d), and Glass Factory B (172 m³/d)

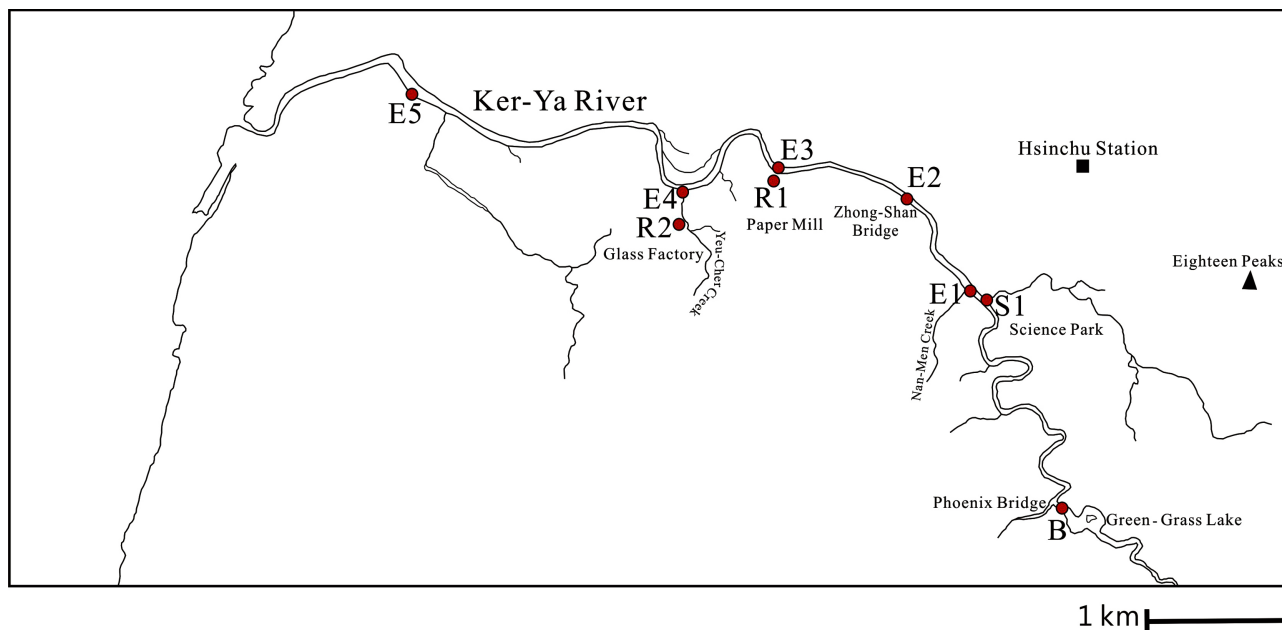


Figure 1. Location map of sampling sites (red dots) in the 2017 studied area along the middle and lower reaches of the Ker-Ya River, Hsinchu, northern Taiwan.

(see **Figure 1** for their locations).

Sampling points at 19 nodes along the Ker-Ya River were strategically chosen, mainly at the outlets of plants and confluence points of the river and creeks. A total of 35 water samples were collected in three batches on June 26-27, August 21-22, and October 10-12, respectively, during 2017. Meanwhile, a total of 20 surface sediment samples were taken at the same location or in the neighborhood of the water samples. Sample ID, collection dates, and coordinates of these samples are listed in **Table 1**. All of the sampling methods followed the procedures described in NIEA W102.51C (2005) and NIEA S104.32B (2016) issued by TEPA. Briefly, about 1 L river water was sampled *in situ* and HNO_3 solution was added immediately to make the $\text{pH} < 2$, stored at 4°C for further analyses. About 250 gm surface sediments (sub-depth 1 - 15 cm) were taken using an Ekman dredge, and then immediately stored in plastic bags and refrigerated at 4°C . All the NIEA guidelines (in Chinese) can be found on Internet Web.

A total of 67 major and trace metals were measured. Analytical methods followed the guideline NIEA M353.02C (2016) prescribed by TEPA. Briefly, water and sediment samples were first filtered through $0.45\ \mu\text{m}$ pore-size membrane filter paper (Whatman 5A), and then the filtered samples were put in H_2O_2 (30%, Suprapure, Merck) and HNO_3 solution (65%, Suprapure, Merck) with $\text{pH} < 2$ to convert the dissolved metal ions into nitrates. The nitrates were subsequently analyzed with inductively coupled plasma mass spectrometer (ICP/MS, Agilent 7500S) (following NIEA M353.02C, 2016).

Only concentrations of 46 elements (Ag, As, Au, B, Ba, Bi, Br, Ca, Cd, Ce, Co, Cr, Cs, Cu, Fe, Ga, Ge, Hf, Hg, I, In, K, La, Li, Mg, Mo, Nd, Ni, P, Pb, Pr, Rb, Sb, Sc, Si, Sm, Sn, Sr, Th, Ti, U, V, W, Y, Zn, and Zr) were reported and for statistical

Table 1. Sample list in the watershed of the Ker-Ya River.

ID	location	date	longitude	latitude	type
KYW01	Outlet of Paper Plant A (S3)	2017/6/26	120.946336	24.801126	water
KYW02	Outlet of Paper Plant A (S3)	2017/8/22	120.946336	24.801126	water
KYW03	Outlet of Paper Plant A (S3)	2017/10/12	120.946336	24.801126	water
KYW04	Original Waste Water of Paper Plant A (R1)	2017/6/26	120.946602	24.801186	water
KYW05	Original Waste Water of Paper Plant A (R1)	2017/8/22	120.946602	24.801186	water
KYW06	Original Waste Water of Paper Plant A (R1)	2017/10/12	120.946602	24.801186	water
KYW07	Phoenix Bridge (B)	2017/6/26	120.946602	24.801186	water
KYW08	Confluence of Paper Plant A Outlet (E3)	2017/6/26	120.946602	24.801186	water
KYW09	Urban effluence at Zhong-Shan Bridge (S2)	2017/6/27	120.946602	24.801186	water
KYW10	Urban effluence at Zhong-Shan Bridge (S2)	2017/8/21	120.946336	24.801126	water
KYW11	Confluence of Yeo-Che Creek (E4)	2017/6/27	120.946336	24.801126	water
KYW12	Confluence of Science Park Outlet (S1)	2017/6/27	120.946336	24.801126	water
KYW13	Confluence of Nan-Men Creek (E1)	2017/6/27	120.937817	24.799799	water
KYW14	Phoenix Bridge (B)	2017/8/21	120.937817	24.799799	water
KYW15	Confluence of Science Park Outlet (S1)	2017/8/21	120.937817	24.799799	water
KYW16	Confluence of Nan-Men Creek (E1)	2017/8/21	120.937817	24.799799	water
KYW17	Zhong-Shan Bridge (E2)	2017/6/26	120.937817	24.799799	water
KYW18	Zhong-Shan Bridge (E2)	2017/8/21	120.937817	24.799799	water
KYW19	Urban effluence at Zhong-Shan Bridge (S2)	2017/10/11	120.969668	24.775633	water
KYW20	Outlet of Glass Plant B (S4)	2017/6/27	120.969668	24.775633	water
KYW21	Confluence of Paper Plant A Outlet (E3)	2017/8/22	120.969668	24.775633	water
KYW22	Confluence of Yeo-Che Creek (E4)	2017/8/22	120.962542	24.792123	water
KYW23	River Mouth (E5)	2017/8/23	120.962542	24.792123	water
KYW24	Phoenix Bridge (B)	2017/10/11	120.962542	24.792123	water
KYW25	Confluence of Science Park Outlet (S1)	2017/10/11	120.962542	24.792123	water
KYW26	Confluence of Nan-Men Creek (E1)	2017/10/11	120.962542	24.792123	water
KYW27	Zhong-Shan Bridge (E2)	2017/10/11	120.962542	24.792123	water
KYW28	Outlet of Glass Plant B (S4)	2017/8/22	120.957347	24.799439	water
KYW29	Outlet of Glass Plant B (S4)	2017/10/12	120.957347	24.799439	water
KYW30	Outlet of Glass Plant B (S4)	2017/6/27	120.957347	24.799439	water
KYW31	Outlet of Glass Plant B (S4)	2017/8/22	120.957347	24.799439	water
KYW32	Original Waste Water of Glass Plant B (R2)	2017/10/12	120.957347	24.799439	water
KYW33	Confluence of Paper Plant A Outlet (E3)	2017/10/12	120.957347	24.799439	water
KYW34	Confluence of Yeo-Che Creek (E4)	2017/10/12	120.957347	24.799439	water
KYW35	River Mouth (E5)	2017/10/13	120.957347	24.799439	water
KYS01	Confluence of Paper Plant A Outlet (E3)	2017/6/26	120.957347	24.799439	sediment

Continued

KYS02	Confluence of Science Park Outlet (S1)	2017/6/27	120.918289	24.805433	sediment
KYS03	Confluence of Nan-Men Creek (E1)	2017/6/27	120.918289	24.805433	sediment
KYS04	Confluence of Nan-Men Creek (E1)	2017/8/21	120.918289	24.805433	sediment
KYS05	Confluence of Science Park Outlet (S1)	2017/8/21	120.918289	24.805433	sediment
KYS06	Confluence of Nan-Men Creek (E1)	2017/10/11	120.93795	24.79547	sediment
KYS07	Confluence of Paper Plant A Outlet (E3)	2017/8/22	120.93795	24.79547	sediment
KYS08	River Mouth (E5)	2017/8/23	120.93795	24.79547	sediment
KYS09	Confluence of Science Park Outlet (S1)	2017/10/11	120.93795	24.79547	sediment
KYS10	Confluence of Yeo-Che Creek (E4)	2017/6/27	120.93795	24.79547	sediment
KYS11	Confluence of Yeo-Che Creek (E4)	2017/8/22	120.93795	24.79547	sediment
KYS12	Confluence of Paper Plant A Outlet (E3)	2017/10/12	120.963876	24.791712	sediment
KYS13	Confluence of Yeo-Che Creek (E4)	2017/10/12	120.963876	24.791712	sediment
KYS14	River Mouth (E5)	2017/10/13	120.963876	24.791712	sediment
KYS15	Phoenix Bridge (B)	2017/6/26	120.963876	24.791712	sediment
KYS16	Phoenix Bridge (B)	2017/8/21	120.963876	24.791712	sediment
KYS17	Phoenix Bridge (B)	2017/10/11	120.963876	24.791712	sediment
KYS18	Zhong-Shan Bridge (E2)	2017/6/26	120.969668	24.775633	sediment
KYS19	Zhong-Shan Bridge (E2)	2017/8/21	120.969668	24.775633	sediment
KYS20	Zhong-Shan Bridge (E2)	2017/10/11	120.969668	24.775633	sediment

analyses because most of the other elements were usually below the detection limits at the ppb level.

A substantial body of literature has demonstrated that multivariate analyses could easily yield meaningful results in recognizing significant parameters and identifying pollution sources [2] [3] [16]-[22]. The element data of waters and sediments were subjected to a series of principal component analyses (PCA) separately. Mathematically, each principal component (PC) is a linear combination of the original variables, and all the principle components are not correlated with one another. The purposes of PCA are three-fold: 1) reducing the dimensionality, while retaining the most variance in the data with a few principal components (PCs); 2) forming several linear combinations (associations) of individual elements, while the coefficients or correlations of the elements with the PCs are indicative of the relevance among the various elements; and 3) calculating the scores of each sample on the principal components, and thus categorizing the samples into groups in terms of different element associations. Since the concentrations of major and trace elements vary greatly in several orders, in order to avoid the scale effect on the PCA, we used a correlation matrix among the 46 elements initially for preliminary PCA analyses and data evaluation using the software Past 4.02 [23]. Some of the elements that exhibit extremely low concentration and thereby high variability in the correlation matrix were removed from

analysis because they tended to make particular samples become statistical outliers and to result in spurious PCA solutions. After several runs of iterative PCA analyses, eventually only 24 elements from the water analyses (**Table 2**) and 25 elements (**Table 3**) from sediments, respectively, were retained for the final eigenfunction and eigenvalue calculation, and the final resolved PCA patterns were eventually stabilized.

Table 2. Correlation coefficients of elements with the first four PCs of the water samples. The second row lists the variance explained by the first four principal components (PCs), respectively. The remaining lines list the correlation coefficients of elements with the four PCs. Significantly high correlation coefficients are marked with bold-face.

	PC1	PC2	PC3	PC4
Variance explained	33.60%	19.90%	14.10%	8.40%
As	0.45	0.76	0.03	-0.01
B	0.42	-0.45	0.64	-0.26
Ba	0.06	-0.55	0.68	0.01
Ca	0.58	0.03	0.62	-0.45
Cd	0.11	-0.28	-0.02	0.3
Ce	-0.93	0.16	0.03	-0.09
Co	-0.83	0.08	0.46	-0.25
Cr	-0.81	0.30	0.39	0.12
Cu	0.31	0.90	0.13	0.11
Fe	-0.92	0.16	0.22	0.04
Hg	0.49	0.83	-0.08	-0.03
In	0.22	0.06	0.34	0.77
La	-0.94	0.09	0.05	-0.06
Li	-0.07	-0.10	0.82	0.39
Mg	0.72	-0.35	0.36	0.33
Mo	0.78	0.04	0.54	0.11
Ni	-0.12	0.93	0.21	0.01
P	0.45	0.87	-0.02	-0.01
Si	0.87	0.24	0.17	0.27
Sn	0.20	-0.18	0.22	0.79
Sr	0.88	-0.10	0.37	0.05
V	-0.94	0.19	0.23	-0.02
W	0.51	0.81	-0.15	-0.05
Zn	-0.06	-0.15	0.04	0.45

Table 3. Correlation table of elements with the first four PCs of the sediment samples. The second row lists the variance explained by the first four principal components (PCs), respectively. The remaining lines list the correlation coefficients of elements with these four PCs. Significantly high correlation coefficients are marked with bold-face.

	PC1	PC2	PC3	PC4
Variance explained	43.2%	20.6%	16.7%	5.10%
Ag	0.30	-0.60	0.69	0.1
B	0.41	-0.57	0.66	0.02
Ba	-0.24	-0.42	0.81	0.02
Br	0.90	0.26	0.11	-0.12
Ca	0.67	-0.28	0.65	0.03
Cd	0.04	-0.09	-0.36	0.61
Ce	-0.84	0.28	0.14	-0.34
Co	-0.84	0.25	0.46	0.03
Cr	-0.76	0.48	0.29	0.23
Cu	0.52	0.77	-0.00	0.08
Fe	-0.86	0.34	0.23	0.2
Ga	-0.09	0.80	0.40	0.02
Hg	0.81	0.49	-0.10	-0.18
In	0.31	0.77	0.06	0.22
K	0.85	0.44	0.01	-0.08
La	-0.87	0.21	0.15	-0.34
Li	0.06	0.04	0.91	0.16
Mg	0.87	-0.21	0.37	-0.01
Mo	0.87	0.16	0.44	0.07
Ni	0.34	0.88	0.16	0.07
Si	0.95	0.14	0.08	0.07
Sr	0.85	-0.28	0.42	0.02
Ti	0.43	0.75	0.05	0.08
V	-0.87	0.38	0.28	-0.04
Zn	0.28	0.29	0.22	0.76

3. Results and Discussion

3.1. PCA Results of Water Samples

A scree plot of the variance associated with each principal component of the water samples shows that starting from the principal component 5 and the succeeding ones account for only incrementally small amounts, and therefore only

the first four principal components were retained for further interpretation. In total, these four principal components (PCs) account for 76% of the variance (**Table 2**). Four major contaminant associations were recognized accordingly: 1) V, La, Ce, Fe, Co, Cr, and La with significant negative correlation coefficients with PC1; 2) As, Cu, Hg, Ni, P, and W with high correlation with PC2; 3) B, Ba, Ca, and Li with high correlation with PC3; and 4) In, Sn, and Zn, with high correlation with PC4. The listed elements in the four associations are mainly characteristic of anthropogenic origin.

3.2. PCA Results of Sediment Samples

Four PCs were retained for the sediment samples, accounting for 85.6% of the variance in total (**Table 3**). Corresponding to PC1 – PC4, four-element assemblages were recognized: 1) Ce, Co, Fe, La, and V; 2) Cu, Ga, In, Ni, and Ti; 3) Ag, B, Ba, Ca, and Li; and 4) Cd and Sn. It is expected that the associations recognized from sediments do not necessarily correspond to the overlying water because potentially toxic elements in the Ke-Ya River are mainly bounded with fine-sized (<25 μm) sediments, and each element has its own speciation pattern; in general, potentially toxic elements are preferentially bonded with organic matters [9] [15]. Generally, the water samples constitute a snap-shot of chemicals in the water, while surface sediments retain longer-term records.

3.3. Integrative Interpretations of PCs

For a thorough interpretation of the PCA results of both water and sediment samples, we discuss contaminant associations one-by-one below. The scatter plots showing the scores of water and sediments are presented in juxtaposition. **Table 4** summarizes the integrative results in listing samples that have extreme (positive or negative) scores in both water and sediment samples. The locations of the listed samples are presented in a simplified flow chart in **Figure 2**.

3.4. Contaminant Association A—PC1

In the water sample set, the elements with high positive correlation coefficients ($r > 0.7$) with PC1 are considered to be general, background ones, likely to be the crust origin (Mg, Mo, Si, and Sr), whereas, the elements with significantly high negative loadings (V, La, Ce, Fe, Co, Cr, and La) constitute a contrast against the general background elements, and represent potential pollutants.

Association A is the most significant contaminant association in the water samples of the Ker-Ya River. These contaminant elements appear in the original effluents of Glass Factory B in the lower reaches area (**Figures 1-3**). Not surprisingly, these elements are also present in the sediment samples at the confluence of the Yeu-Che Creek where the outlet of the Glass Factory flows in (**Figure 1**, **Figure 2**, **Figure 4**, and **Table 4**). Nevertheless, these elements also occurred in the water samples of upper reaches, including W07 at the Phoenix Bridge, W13 at the confluence of Nan-Men (South Gate) Creek, and in the urban effluent

Table 4. Samples with relatively high concentrations in the four contaminant associations recognized by principal component analyses in both water and sediment samples of the Ker-Ya River. The elements exhibiting relatively higher correlation coefficients are bold-faced.

Water samples	Sediment samples
PC1 (Ce, Co, Cr, Fe, La, V)	PC1 (Ce, Co, Cr, Fe, La, V)
W30 Wastewater of Glass Plant (R2) 06/27	S14 River Mouth (E5) 10/13
W31 Wastewater of Glass Plant (R2) 08/22	S13 Entrance of Yeu-Che Creek (E4) 10/12
W07 Phoenix Bridge (B) 06/26	S04 Entrance of Nan-Men Creek (E1) 08/21
W32 Wastewater of Glass Plant (R2) 10/12	
W13 Entrance of Nan-Men Creek (E1) 06/27	
W19 Urban effluents at Zhong-Shan Bridge (S2) 10/11	
PC2 (As, Cu, Hg, Ni, P, W)	PC2 (Br, Cu, Ga, In, Ni, Ti)
W27 Zhong-Shan Bridge (E2) 10/11	S17 Phoenix Bridge (B) 10/11
PC3 (B, Ba, Ca, Li)	PC3 (Ag, B, Ba, Ca, Li)
W04 Wastewater of Paper Plant (R1) 06/26	S07 Entrance of Paper Mill effluents (E3) 8/22
W05 Wastewater of Paper Mill (R1) 08/22	
PC4 (In, Sn)	PC4 (Zn, Cd)
W24 Phoenix Bridge (B) 10/11	S04 Entrance of Nan-Men Creek (E1) 8/21
W25 Entrance of Science Park effluents (S1) 10/11	

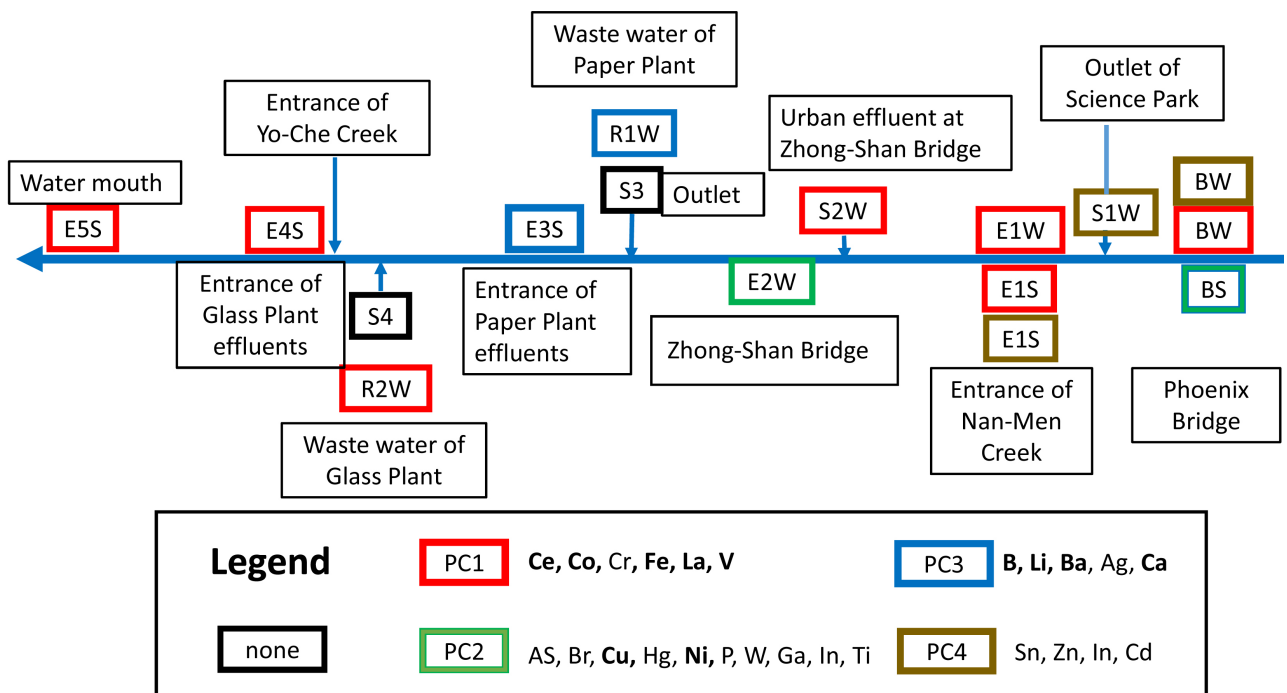


Figure 2. Simplified flow chart showing sample sites and PC1 - PC4 contaminant associations coded in color along the Ker-Ya River. The letter W in the rectangle indicates water samples, while S denotes sediment samples. In each associations, the common elements in both water and sediments are bold-faced. It is worth noting that the associations recognized from water samples do not necessarily correspond to those of surface sediment samples.

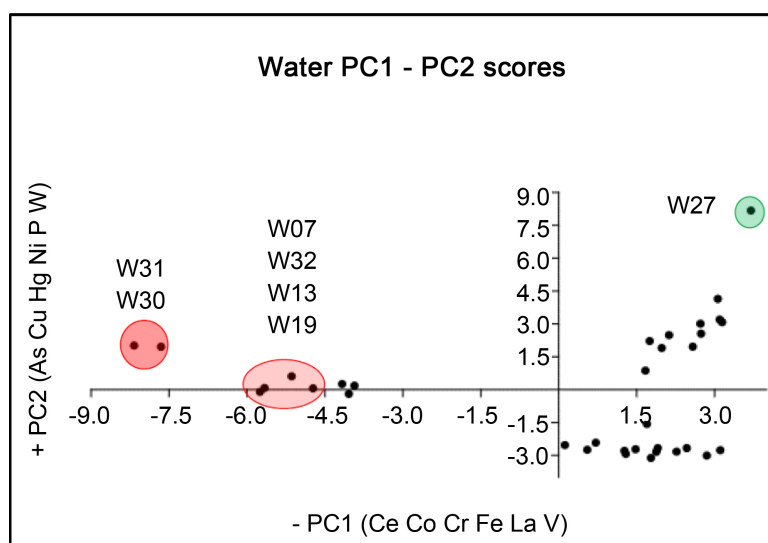


Figure 3. Scatter plot of scores of water samples on the plane of PC1 and PC2. Three groups of water samples containing relatively high concentrations of elements were recognized. The red ellipses mark samples of high concentrations in contaminant association A (PC1: Ce, Co, Cr, Fe, La, and V), while the green circle marks those of association B (PC2: As, Cu, Hg, Ni, P, and W).

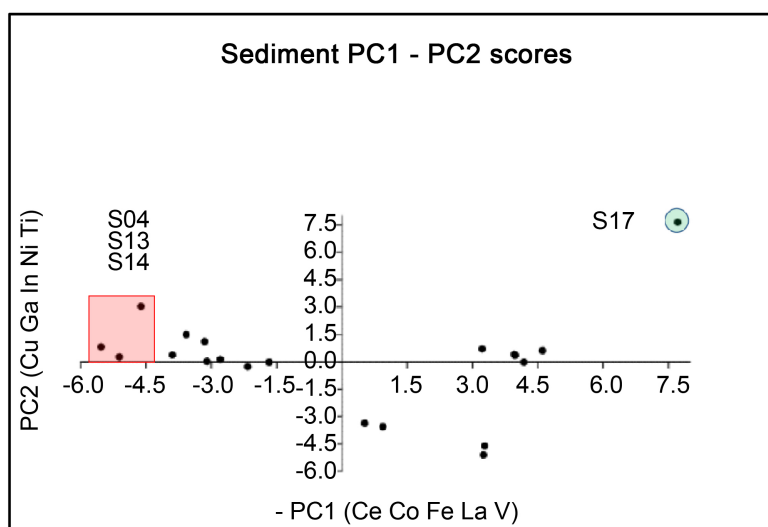


Figure 4. Scatter plot of scores of sediment samples on the plane of PC1 and PC2. The red rectangle marks samples of high concentrations in association A (PC1: Ce, Co, Fe, La, and V), while the green circle marks sample S17 with relatively high element concentrations in association B (PC2: Br, Cu, Ga, Ni, and Ti).

discharge into the Ker-Ya River at Zhong-Shan Bridge (**Figure 2**, **Figure 3**, and **Table 4**), suggesting that there were sources in the upper reach and tributary creeks other than Glass Factory B. Consistently, sediment samples also signal the occurrence of association A in S14 (River Mouth), S13 (entrance of Yeu-Che Creek), and S04 (entrance of Nan-Men Creek) (**Figure 2**, **Figure 4**, and **Table 4**). Overall, elements of assemblage A were present in water and surface sedi-

ments both in the middle and lower reaches.

3.5. Contaminant Association B—PC2

The second PC of water samples, accounting for 19.9% of the variance, is basically an association of Ni, Cu, P, Hg, W, and As (in descending order of correlation coefficients, see **Table 2**). Only one water sample (W27 collected on 2017/10/11 at Zhong-Shan Bridge, **Figure 3**) contains a high concentration of these elements (**Table 2, Figure 3**). For sediments, association B is characterized by Br, Cu, Ga, In, Ni, and Ti (**Table 4**). Only Cu and Ni are common in the contaminant associations of water and sediments (**Table 4**). W27 (Zhong-Shan Bridge (E2) 10/11) and S17 (Phoenix Bridge (B) 10/11) are the two samples showing high scores (**Figure 3** and **Figure 4**).

3.6. Contaminant Association C—PC3

The third PC represents an association of Li, Ba, B, and Ca (**Tables 2-4**) for both water and sediment sets. These elements are characteristic of the original waste water (W4, W5) of the Paper Mill (**Figure 5**). They were also present in the surface sediment S07 at the entrance of Paper Mill effluences (**Figure 6**). We consider that this association of elements is closely related to the Paper Mill (**Table 4**).

3.7. Contaminant Association D—PC4

The PC4 recognized from water samples has a high correlation with In and Sn, but the sediment's PC4 is correlated mainly with Zn and Cd (**Table 4**). According to the loading matrices, PC4 is not a well-defined association, and is only roughly correlated with Zn, Cd, In, and Sn. Those elements occurred primarily

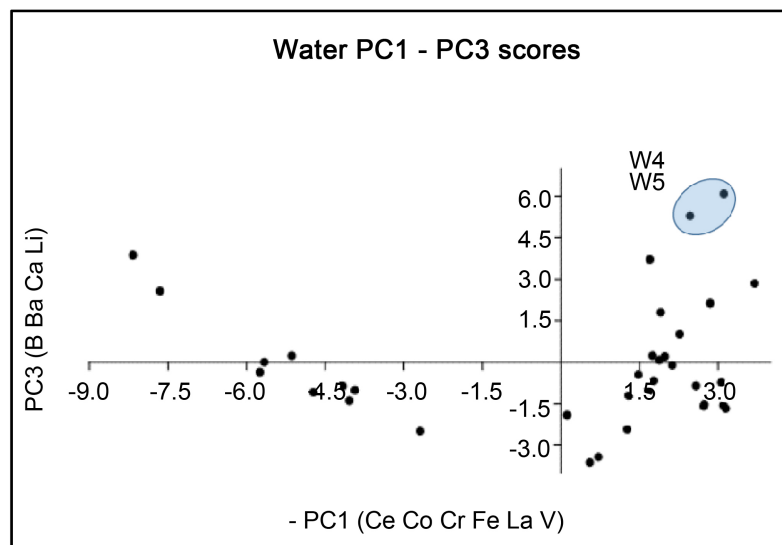


Figure 5. Scatter plot of scores of water samples on the plane of PC1 and PC3. The blue ellipse marks samples of high concentrations in contaminant association C (PC3: B, Ba, Ca, and Li).

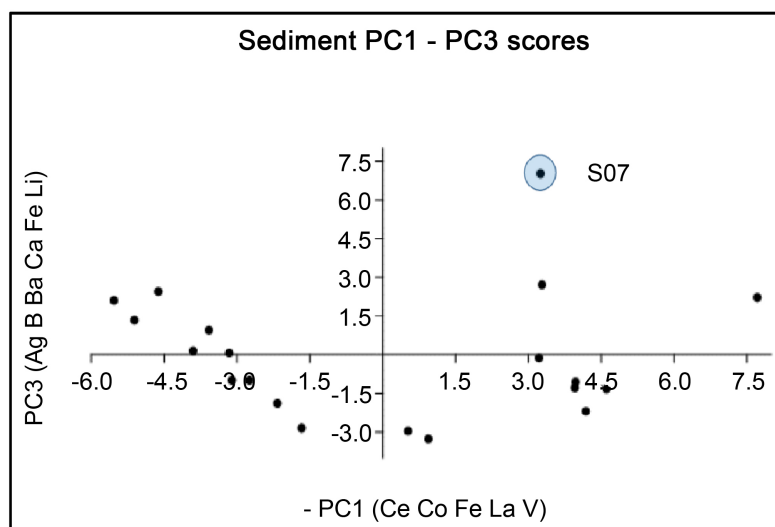


Figure 6. Scatter plot of scores of sediment samples on the plane of PC1 and PC3. The blue circle marks sample S07 which has high concentrations in contaminant association C (PC3: Ag, B, Ba, Ca, and Li).

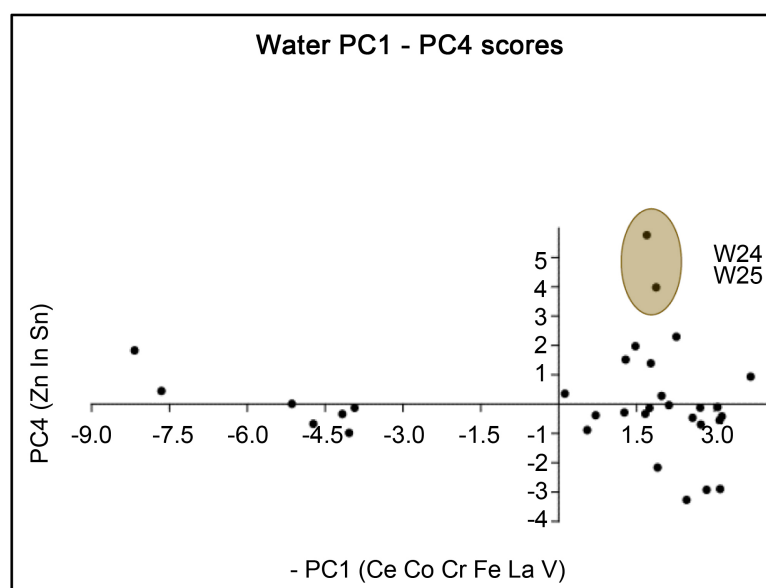


Figure 7. Scatter plot of scores of water samples on the plane of PC1 and PC4. The brownish ellipse marks samples of high concentrations in contaminant association D (PC4: In and Sn).

in the top area of the middle reaches in both water and surface sediments (W24 and W25 in **Figure 7**; S04 in **Figure 8**, see **Figure 2** for their locations).

3.8. Potential Pollutants and Pollution Sources

Samples exhibiting high positive or negative scores of the four principal components are listed in **Figure 9**. A total of 21 elements that exhibit high correlation values with the associated principal components are evaluated against the standard high-limit concentrations prescribed by the drinking water guidelines issued

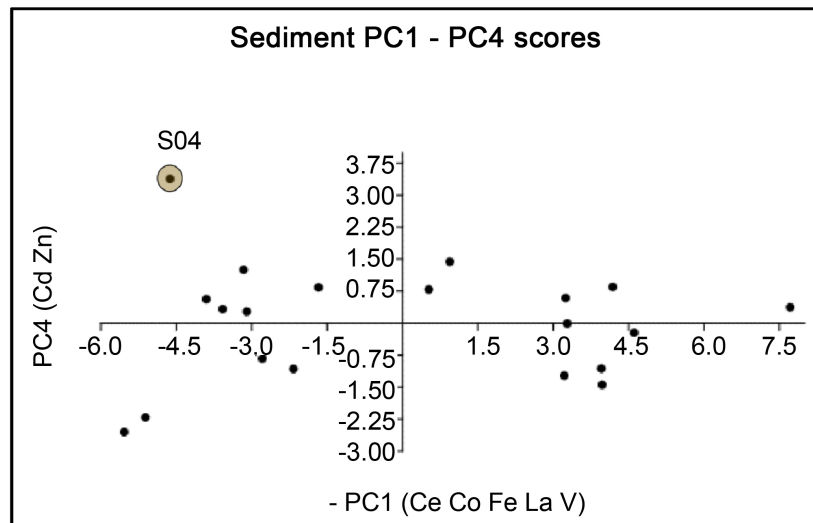


Figure 8. Scatter plot of scores of sediment samples on the plane of PC1 and PC4. The brownish circle marks sample S04 which has high concentrations in contaminant association D (PC4: Cd and Zn).

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(<https://oaout.epa.gov.tw/law/EngLawContent.aspx?lan=E&id=171&KW=drinking+water>). Notably only one water sample (KYR27) that has relatively high concentration of arsenic (As, 0.0148 mg/L), slightly exceeding the prescribed standard value of water quality (0.01 mg/L), may cause minor health impact. On the other hand, quite a few samples exhibit high concentration of iron (Fe), however, it may only cause aesthetic, cosmetic, and/or technical effects.

4. Conclusions

Industrial effluents, domestic sewage, and agriculture are the major anthropogenic sources of potential toxic contamination along the studied Ker-Ya River in northern Taiwan. PCA analyses of element concentrations measured from water and sediment samples recognized four element associations. The association A, mainly led by Ce, Co, Fe and La, exhibits the most dispersed distribution in water and sediments in both middle and lower reaches. The sources of these contaminants are markedly diverse geographically, and thus Glass Plant B in the low reaches of the Ker-Ya River in the downtown area of the city is not the only possible source that is responsible for their presence. The second association, comprising Cu, Ni, and other associated elements (As, Hg, P, W, Ga, In, and Ti), appears to be contributed from industries from the upper reaches and manufacturers to the south of the Ker-Ya River, instead of the Hsinchu Science Park (HSP), a conventional target that has been blamed due to its poor practice legacy in early years. Instead, the HSP should be responsible for the presence of association D (Sn, Zn, Cd, and In) in water and sediments at the top of the middle reaches. Paper Mill A appears to be responsible for the presence of association C (B, Li, Ba, and Ca) in the sediment sample of the middle reaches.

Sample	ID	Location	Date	PC1							PC2							PC3							PC4						
				As	Ce	Co	Cr	Fe	La	V	Cu	Ga	Hg	Ni	Ti	W	B	Ba	Ca	Li	Cd	In	Sn	Zn							
KYR04		Waste water of Paper Plant(R1)	06/26	0.0050	0.0004	0.0048	0.0065	1.00	0.0003	0.0004	0.0103	0.0030	0.0001	0.012	0.005	0.002	1.650	0.215	375.00	0.025	0.0005	0.0006	0.0025	0.018							
KYR05		Waste water of Paper Plant(R1)	08/22	0.0036	0.0002	0.0043	0.0045	0.75	0.0001	0.0003	0.0105	0.0054	0.0003	0.008	0.003	0.003	1.100	0.145	320.00	0.023	0.0006	0.0001	0.0014	0.043							
KYR07		Phoenix Bridge (B)	06/26	0.0030	0.0225	0.0056	0.0165	12.45	0.0105	0.020	0.0044	0.0038	0.0001	0.011	0.027	0.000	0.002	0.047	0.74	0.011	0.0002	0.0001	0.0001	0.020							
KYR13		Entrance of Nan-Men Creek (E1)	06/27	0.0023	0.0240	0.0066	0.0180	15.00	0.0108	0.018	0.0102	0.0051	0.0002	0.017	0.017	0.000	0.004	0.075	1.95	0.014	0.0005	0.0004	0.0002	0.036							
KYR19		Urban water effluents (S2)	10/11	0.0013	0.0195	0.0041	0.0150	10.65	0.0090	0.015	0.0122	0.0038	0.0001	0.012	0.026	0.000	0.007	0.038	0.78	0.012	0.0005	0.0004	0.0012	0.029							
KYR24		Phoenix Bridge (B)	10/11	0.0045	0.0012	0.0009	0.0160	2.08	0.0015	0.005	0.0203	0.0021	0.0001	0.007	0.023	0.001	0.750	0.113	42.50	0.038	0.0010	0.00035	0.0850	0.058							
KYR25		Outlet of Science Park (S1)	10/11	0.0022	0.0003	0.0004	0.0024	0.65	0.0002	0.001	0.0070	0.0017	0.0000	0.004	0.004	0.001	0.340	0.085	36.00	0.021	0.0008	0.00027	0.0800	0.055							
KYR27		Zhong-Shan Bridge (E2)	10/11	0.0148	0.0030	0.0016	0.0145	0.58	0.0001	0.005	0.0500	0.0118	0.0080	0.058	0.028	0.275	1.118	0.013	170.00	0.020	0.0003	0.00015	0.0140	0.028							
KYR30		Waste water of Glass Plant (R2)06/27		0.0050	0.0180	0.0089	0.0405	34.50	0.0089	0.029	0.0165	0.0065	0.0001	0.029	0.035	0.000	0.003	0.054	3.00	0.030	0.0008	0.0003	0.0004	0.056							
KYR31		Waste water of Glass Plant (R2)08/22		0.0029	0.0165	0.0081	0.0375	31.50	0.0075	0.026	0.0150	0.0077	0.0001	0.036	0.038	0.001	0.004	0.069	5.70	0.033	0.0007	0.0008	0.0125	0.050							
KYR32		Waste water of Glass Plant (R2)10/12		0.0021	0.0126	0.0051	0.0255	19.50	0.0057	0.020	0.0129	0.0053	0.0001	0.026	0.023	0.001	0.002	0.042	4.35	0.020	0.0004	0.0003	0.0014	0.044							
KYS04		Entrance of Nan-Men Creek (E1)	8/21	0.0036	0.0141	0.0083	0.0390	30.00	0.0062	0.024	0.0195	0.0060	0.0003	0.029	0.027	0.002	0.004	0.065	7.80	0.026	0.0009	0.0005	0.0047	0.056							
KYS04		Entrance of Nan-Men Creek (E1)	8/21	0.0036	0.0141	0.0083	0.0390	30.00	0.0062	0.024	0.0195	0.0060	0.0003	0.029	0.027	0.002	0.004	0.065	7.80	0.026	0.0009	0.0005	0.0047	0.056							
KYS07		Outlet of Paper Plant (E3)	8/22	0.0036	0.0002	0.0041	0.0048	1.05	0.0001	0.004	0.0080	0.0027	0.0002	0.013	0.004	0.002	1.500	0.170	360.00	0.029	0.0005	0.0001	0.0015	0.024							
KYS13		Entrance of Yiu-Che Creek(E4)	10/12	0.0032	0.0330	0.0077	0.0195	16.50	0.0146	0.023	0.0066	0.0048	0.0001	0.014	0.017	0.000	0.004	0.065	3.30	0.015	0.0004	0.0002	0.0001	0.024							
KYS14		River Mouth (E5)	10/13	0.0035	0.0300	0.0075	0.0210	16.50	0.0134	0.026	0.0060	0.0060	0.0001	0.014	0.027	0.000	0.006	0.087	3.75	0.018	0.0005	0.0002	0.0001	0.023							
KYS17		Phoenix Bridge (B)	10/11	0.0165	0.0048	0.0017	0.0103	0.80	0.0001	0.006	0.0600	0.0138	0.00078	0.063	0.050	0.250	0.123	0.020	165.00	0.020	0.0006	0.00016	0.0073	0.038							
Taiwan EPA drinking water quality guidelines, 2020				0.01			0.05	0.3		1.0		0.001	0.1			2.0				0.005	0.07		5.0								

Figure 9. Element concentrations (mg/L) in samples categorized in terms of four principal components (PCs). Boldfaced numbers are those exceeding the values prescribed by Taiwan EPA drinking water guidelines (2020)

<https://oatout.epa.gov.tw/LawContent.aspx?id=FL015512>.

Although four major associations of contaminants were recognized, a close examination of the element concentrations in the water and sediments demonstrates that the Ker-Ya River is not heavily polluted, because only As in the W27 sample (0.0148 mg/L) slightly exceeded the limit value (0.01 mg/L) of drinking water quality standards issued by the Taiwan Environmental Protection Administration (TEPA). In addition, relatively high concentrations of Fe (ranging from 0.58 to 34.50 mg/L) in all of the listed water samples in **Figure 9** may cause aesthetic, cosmetic, and/or technical effects when in use, but are not considered to be seriously polluted.

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Availability of Data

All of the analyzed data were taken from the report entitled “Sediment Characteristics (Rivers, Lakes, Reservoirs) Contaminants Identified Technology Development” (1/2) available from the Government Research Bulletin at <https://www.grb.gov.tw/search/planDetail?id=12337429>.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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