Source apportionment of metal elements in a river by using an effective variance chemical mass balance model: a feasibility study

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1 **Source apportionment of metal elements in a river by using an**
2 **effective variance chemical mass balance model: a feasibility study**

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10

11 **Abstract**

12 This technical report aimed to determine the sources of water pollution in a major

13 river in northern Taiwan by using the characteristics of actual industrial wastewater

14 and the effective variance chemical mass balance (EV-CMB) model. River water

15 samples from 9 sampling sites and 14 profiles of potential sources were collected and

16 a total of 52 metal elements were analyzed. To monitor the levels of industrial

17 pollutants in the water samples, the metal index (MI) is used. The model results

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identified the major sources of river pollution and may suggest the existence of unknown sources. This study demonstrates the feasibility of applying the receptor model in the strategic investigation of river pollution and highlights the need for a comprehensive source profile database.

Keywords: river pollution, source profile, source apportionment, spatial variation

Article Highlights

- Feasibility of applying EV-CMB to investigate pollution sources of river water is demonstrated.
- Industrial sources showed different contribution patterns in terms of the total mass concentration and metal index.
- Conducting a comprehensive view of effluent regulations on semi-conductors and bare printed circuit boards manufacturing is recommended.

1. Introduction

River pollution has caused serious concerns due to its long-term influence on the environment and human health. Rivers usually have complex compositions that include materials such as metal pollutants (Akbal et al., 2011; Ismail et al., 2016; Kumar et al., 2019; Li et al., 2015; Shil and Singh, 2019; Simeonov et al., 2003; Vu, 2017). To reduce water pollution and its potential hazardous impact, identifying the sources of pollutants and estimating their contribution to river pollution are essential.

The heavy metal pollution of river water is usually coming from discharge of industrial wastewater in modern city. In order to evaluate the risk level of metal pollution in the river water, monitoring the metal elements is crucial (Abdo and El-Nasharty, 2010; Fishar and Ali, 2005). A metal index (MI) with regard to maximum allowable concentration (MAC) has been used to evaluate the water quality (Goher et al., 2014; Tamasi and Cini, 2004). The MAC of each element is adapted to local conditions and usually the MAC is set to protect human health and ecological environment.

Multivariate statistical techniques, such as absolute principal component scores–multivariate linear regression and positive matrix factorization, have been widely applied for the source apportionment of environmental pollution (Jiang et al., 2019; Kowalkowski et al., 2006; Li et al., 2015; Palma et al., 2010; Soonthornnonda and

51 Christensen, 2008; Zanotti et al., 2019; Zhou et al., 2007). The factor profiles retrieved
52 from these methods are interpreted with reference to empirical evidence and by
53 conducting a comparison of databases. However, the retrieved profiles may represent
54 mixed profiles from more than one source. By contrast, effective-variance chemical
55 mass balance (EV-CMB) model uses actual source compositions to evaluate unknown
56 source contributions in aerial and aqueous environment (Antony Chen et al., 2010;
57 Chow et al., 2007; Soonthornnonda and Christensen, 2008; Watson et al., 1984). The
58 EV-CMB model is expected to provide superior results than other models for the
59 clarification of sources when major source profiles in the study areas are available.
60 However, there is no application of this receptor model to investigate the river pollution
61 because of the difficulty in obtaining authentic wastewater samples.

62 In this technical report, we demonstrate the utility of using the EV-CMB model for
63 quantitative source apportionment of river pollution by measuring actual source
64 compositions of various industrial effluents, identifying and quantifying the pollutants
65 in surface river water, and estimating the spatial variation of pollution influences from
66 industrial activities.

67

2. Materials and methods

2.1 Study area and surface water sampling

Nankan River is a major river that flows through the administrative center of Taoyuan City in northern Taiwan. The overall length and drainage area of Nankan River are approximately 30.7 km and 214.6 km², respectively. Two industrial parks (**Fig. 1**), one downstream and one upstream, are located in the research area. Numerous industrial effluents are discharged into Nankan River. The middle of the river is in a metropolitan area with a high population density and various industries. To investigate the pollution area where people focus on, the midstream to upstream section of the Nankan River is selected.

Five sampling sites (S1, S2, S3, S4 and S5, sequentially arranged from downstream to upstream) were selected at the main stream along the river (**Fig. 1**). To monitor the effects of the pollution from the tributaries, three additional sites (S1^T, S5^{T1} and S5^{T2}) were selected at the mouth of different tributaries. S6 was regarded as background water in this targeted river section. These sites (N = 9) were monitored to assess the spatial variations of water pollution. Each sample was collected using the standard sampling method (TEPA, 2004), supplemented with nitric acid, and stored in a refrigerator at 4°C.

87 *2.2 Sampling of industrial effluents*

88 To estimate the influences of industrial activities on river pollution, multiple
89 industrial effluents discharged into the river were collected as source profiles for the
90 measurement of wastewater compositions. Nine potential sources representing different
91 industrial classification were identified according to the daily flow of sewage treatment
92 (i.e., 3,600–28,100 m³ per day), as displayed in **Fig. 2**. The selected industries included
93 wastewater treatment plants (WTP); optoelectronic materials and components
94 manufacturing (OMCM); semi-conductors manufacturing (SCM); finishing of textiles
95 (FT); bare printed circuit boards (BPCB); textiles mills (TM) and metal surface
96 treatment (MST). Since the river could be polluted by untreated wastewater, four
97 manufacturing units (SCM-p, FT-Ap, BPCB-p, and TM-p, where “p” means process
98 water) were collected based on previous violation. The effluents and process water from
99 these industries were collected in accordance with the standard method (TEPA, 2019)
100 and preserved with nitric acid at 4°C.

101

102 *2.3 Chemical analysis*

103 Surface-water samples and industrial effluents were analyzed to determine their
104 elemental compositions. Inductively coupled plasma-mass spectrometry was conducted
105 to quantitatively determine elemental compositions according to the standard method

(NIEA W313). A total of 52 metal elements were analyzed in this study (**Table S1**). The method detection limits (MDL) of these elements ranged from 0.03 µg L⁻¹ to 1.67 µg L⁻¹.

2.4 Source apportionment

In EV-CMB model, the mass balance equation can be written as

$$X_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij} \quad (1)$$

where X_{ij} is the j th species concentration measured in the i th sample, g_{ik} is the contribution of the k th source pollution in the i th sample, p is the number of source pollution, f_{kj} is the source profile defined by the j th species concentration in the contribution of the k th source pollution and e_{ij} is the residual. The model uses known source profiles to evaluate the unknown source contributions estimated from the optimal resolution of mass-balance equations between the measured and calculated pollutant concentrations. The model operation strategies and parameters are described as follows:

(1) Selection of pollution compositions:

Al and Fe are the common elements in the crust. A large amount of these crustal elements are dissolved in the river. Thus they are not suitable tracers and were

excluded from the following analysis. Pollution compositions with concentrations less than MDL in all of the surface-water and source samples (i.e., Ir, Ru, and Tm) were excluded in the modeling process as well. For the remaining 47 compositions with concentrations less than the method detection limit (MDL), half of the MDL value was set as the concentration.

(2) Setting uncertainties for surface-water samples and source profiles:

In this study, the uncertainty of the total pollutant mass for the surface-water samples was assumed as 20% of the total mass according to empirical practice. For measured compositions, the uncertainties were estimated by

$$u_{ij} = \sqrt{(0.5 \times MDL_{ij})^2 + (0.1 \times X_{ij})^2} \quad (2)$$

when the concentration was higher than the DL. Otherwise, the uncertainties were set as 5/6 of the DL in accordance with previous studies (Polissar et al., 1998).

(3) Selection of significant sources and fitting species:

The sample collected from the background site is one type of pollution source (background river water, S6). In the beginning, all the source profiles were assumed to be potential sources of water pollution in the model. The sources with high T-values (i.e., T-value ≥ 2) were retained in the model as the major pollutant sources, and the remaining sources were removed from the model sequentially until all the sources had T-values larger than 2. Then, if the model performance

did not meet all the criteria [i.e., R-square value (R^2) ≥ 0.8 , chi-square value (χ^2) ≤ 4.0 , the percent of measured and calculated mass concentration (%MASS) ranged from 80% to 120%, and the degree of freedom (DF) ≥ 5], the pollution compositions were reselected to improve the model performance. Compositions with large values for the scaled residual (absolute R/U value > 2 , where R is the residual and U is the uncertainty) were removed individually, and the model was rerun after each removal until the results met all the criteria. Notably, when removing one fitting species which is not performing well from the model, the sources that had previously been removed were reinput into the model to examine the confounding effects of that species on source identification. Finally, the model result with significant T-values and a good fit was regarded as the optimal result of source apportionment.

3. Results and discussion

3.1 Characteristics of the metal elements in surface water samples

The results of the analysis of the surface water samples are presented in **Table S1**. The concentrations of common crustal elements, Al, Fe, and Sr, were over 100 $\mu\text{g L}^{-1}$ in all nine sampling sites. The concentration of W was the highest at S5^{T2} (an upriver tributary) and gradually decreased from upstream to downstream. As indicated

in **Table S1**, the concentrations of Cu and Mn were the highest at S1^T (another tributary), which might be why S1, where the S1^T tributary merged into the mainstream, had high concentrations of these two elements as well.

3.2 Characteristics of the metal elements in wastewater

The profiles of the nine samples of industrial wastewater and four process waters are displayed in **Fig. 2**. The compositions of all the samples met the effluent standards established by the Taiwan Environmental Protection Administration (TEPA, 2019). In addition, the high population density in the area surrounding the targeted river section necessitates a profile of domestic wastewater. The penetration rate of sewer construction in the study area was approximately 15% in 2019, which makes domestic wastewater a potential source of pollution. To determine an accurate profile of the domestic wastewater discharged into Nankan River, a sample of untreated domestic wastewater was collected from a domestic sewage treatment plant.

3.3 River pollution level: metal index

To monitor the levels of industrial pollutants in the water samples on the basis of the concentrations of regulated elements, the metal index (MI) is used. The MI is defined as

$$MI = \sum_i \frac{C_i}{(MAC_i)}, \quad (3)$$

where C_i is the concentration of a regulated element. **Tabel 1** presents the TEPA-enforced maximum acceptable concentrations (in surface water) of 11 elements (Ag, As, Cd, Cu, Cr^{6+} , Hg, Mn, Ni, Pb, Se, and Zn). Because of their chemical properties, Cr^{3+} and Cr^{6+} can convert back and forth. To avoid underestimating the concentration of Cr^{6+} , total chromium was measured and used to estimate the MI.

The spatial variations in total mass concentration (i.e., the sum of the metal elements) and MI are presented in **Fig. 3**. The total mass concentration was high in the upriver area where the industrial park was located and gradually decreased with distance. However, the MI did not follow the same pattern. The highest MI was observed at S1 (8.9), which might have been influenced by the S1^T tributary, which had an $MI \leq 14.3$. In terms of the individual elements, **Fig. 4** presents the unit MIs of the 11 regulated metal elements. All the MIs of the regulated elements were less than one at the background site (S6). The MIs of Cu and Mn increased from upstream to downstream and both were larger than one at S1. However, the MI of Hg exhibited a different pattern. The unit MI of Hg was the highest at S5^{T2}. After the tributary merged into the mainstream, the unit MI of Hg decreased gradually with distance.

3.4 Source apportionment of the metal elements

197 The EV-CMB model performed well for the data collected at all the receptor sites
198 (S1 to S5). The estimated percent mass concentrations (%MASS) of the samples ranged
199 from 80.2% to 93.2%. The model results fit the evaluation criteria ($\chi^2 \leq 4$, $R^2 \geq 0.8$,
200 $80\% \leq \%MASS \leq 120\%$, and $DF \geq 5$).

201 The contributions of major industrial effluents along the mainstream are presented in
202 **Fig. 5**. SCM was the main contributor, and its contribution decreased gradually from
203 upstream to downstream. At S5, the contribution from SCM was $1658 \mu\text{g L}^{-1}$,
204 accounting for 78% of the total contribution (**Fig. 6**). Among the elemental
205 contributions of SCM, W had the highest proportion and was observed at all the
206 receptor sites (**Fig. S1**). This result corresponded to the profile of SCM, of which W
207 also comprised the greatest proportion (94.6%, **Fig. 2**). Although W is not a regulated
208 element, studies have reported that W alloys may be carcinogenic (Van der Voet et al.,
209 2007; Wasel and Freeman, 2018; Witten et al., 2012).

210 OMCM and WTP-A were other major pollution sources, and their contributions
211 decreased with distance (**Fig. 5**). A small amount of background water was observed,
212 but its contribution diminished before reaching S1. By contrast, the contribution from
213 domestic wastewater increased from upstream to downstream because of the high
214 population density in the metropolitan area (around S1 and S2, **Fig. 1**).

215 All the pollution sources integrated at S1, which complicated the compositions of the

samples. Domestic wastewater was the main source of pollution at S1 (21%; **Fig. 6**), followed by BPCB (19%), SCM (18%), and WTP-B (16%). BPCB at S1 mainly came from the nearby tributary (S1^T), and its contribution was up to 49% the CMB modeling results (**Fig. S2**). WTP-B was another pollution source from S1^T (20%).

A comparison of the industrial effluent contributions at different receptor sites (**Fig. 1**) revealed that the pollutants at the sampling sites were affected by upstream industrial effluents. For example, the WTP-B effluent entered the river through the upstream of S1^T (**Fig. 1a**), and its contribution was only observed at S1^T and the downstream of S1 (**Fig. 6** and **Fig. S2**). This result made physical sense and indicated that the EV-CMB model could effectively evaluate the influence of specific sources of pollution in the river.

3.5 MI apportionment

To effectively manage and control the quality of river water, investigating the source pollution of metal elements that are harmful to humans and the environment is crucial. In this study, we analyzed MI apportionment among 11 elements.

Fig. 7 illustrates the contributions of industrial effluents to MI at the receptor sites. SCM was the main contributor to MI upstream and accounted for 64% of the total MI at S5. The contribution of SCM decreased with distance and was only 4% at

S1. WTP-A was the second largest contributor to MI upstream (19% at S5), but its contribution diminished at S1. The contribution of MST emerged in the middle of the river and was 12% at S3. Domestic wastewater flowed into the river through widely distributed ditches. The largest contribution of domestic wastewater was observed at S2 (35%), which was close to the metropolitan area with a high population density. BPCB was the main contributor to MI downstream (59% at S1), followed by domestic wastewater (15%).

The main difference between the source contribution estimates based on total mass concentration and the MI estimates is the influence of BPCB at S1 (19% in **Fig. 6** and 59% in **Fig. 7**). This is because Cu and Mn were the main elements contributing to the MI at S1 (**Fig. 4**) and the elements comprising the two highest proportions of the BPCB profile (**Fig. 2**). From the perspective of risk management, enhanced regulations of BPCB discharge should be considered.

3.6 Study limitations

In this study, only a limited number of samples were collected to represent the major sources of industrial effluents in the study area. Because effluents from different factories in the same industry may exhibit similar pollution profiles, the EV-CMB modeling results alone cannot be used to identify the exact sources of pollution.

Nevertheless, this modeling approach can be used to narrow down the potential sources to inform further investigation.

4. Conclusions

The total mass concentrations of the surface water samples collected along Nankan River decreased from upstream to downstream, but the MI values followed the opposite pattern. To evaluate the differences in source contributions determined using the total mass concentration and MI, the EV-CMB was employed. The modeling results revealed that SCM and BPCB were the main pollution sources upstream and downstream, respectively. In addition to SCM and BPCB, domestic wastewater was one of the main sources of water pollution in the metropolitan area.

In this technical report, we demonstrated the feasibility of applying the EV-CMB model in the strategic investigation of river pollution. Establishing a comprehensive source profile database is recommended for effective source identification and apportionment.

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275

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281 **Competing Interests**

282 The authors declare that they have no competing interests.

283 **Author Contributions**

284 Conceptualization: Pei-Yuan Hsieh, Chi-Chang Ho, Gen-Shuh Wang, Yu-Man Shang,
285 and Chang-Fu Wu; Methodology: Pei-Yuan Hsieh and Chi-Chang Ho; Software: Pei-
286 Yuan Hsieh; Visualization: Pei-Yuan Hsieh; Formal Analysis: Pei-Yuan Hsieh;
287 Investigation: Pei-Yuan Hsieh, Chi-Chang Ho, Yuan-Jeng Hsu, and Yu-Man Shang;
288 Data curation: Yuan-Jeng Hsu and Di-Wen Wang; Resources: Yuan-Jeng Hsu and Di-
289 Wen Wang; Writing – original draft: Pei-Yuan and Chi-Chang Ho; Writing – review &
290 editing: Chang-Fu Wu; Supervision: Gen-Shuh Wang, Yuan-Jeng Hsu, and Chang-Fu
291 Wu; Project administration: Gen-Shuh Wang, Yuan-Jeng Hsu, and Chang-Fu Wu.

Data Availability

Restrictions apply to the availability of these data, which were used under license for this study. The data are available from the corresponding author with the permission of Environmental Analysis Laboratory, Environmental Protection Administration, Taiwan.

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382

383 **Tabel 1**

384 Water quality standards of TEPA for heavy metal content in the surface water

Element	Ag	As	Cd	Cr ⁶⁺	Cu	Hg	Mn	Ni	Pb	Se	Zn
MAC (µg L ⁻¹)	50	50	5	50	30	1	50	100	10	10	500

385

Fig. 1. Locations of the sampling sites and industrial effluents in Nankan River. (a) A fishbone diagram of the locations of the sampling sites and industrial effluents in Nankan River; (b) research area map.

Note. WTP = wastewater treatment plants; OMC = optoelectronic materials and

390 components manufacturing; SCM = semi-conductors manufacturing; FT = finishing
391 of textiles; BPCB = bare printed circuit boards; TM = textiles mills; MST = metal
392 surface treatment.

Fig. 2. Source profiles of industrial effluents, untreated unit discharges and untreated domestic wastewater. Only 47 species used in EV-CMB are displayed (Section 2.4).

Fig. 3. Spatial variation in total mass concentration and metal index (MI) at sampling sites along Nankan River. S6 is the background river water.

Fig. 4. Heatmap of 11 unit MIs along Nankan River. Black triangles indicate sites near mouths of tributaries.

Fig. 5 Concentration contributions of each pollution source at five receptor sites.

Fig. 6. Proportions of concentration contributions from industrial effluents at five receptor sites.

Fig. 7. Proportions of MI contributions from industrial effluents at five receptor sites.

Supplementary Files

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