Hazard Ranking of Wastewater Sources in a Highly Polluted River in Northern Taiwan by Using Positive Matrix Factorization With Metal Elements

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1 Hazard ranking of wastewater sources in a highly polluted river in northern
2 Taiwan by using positive matrix factorization with metal elements

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10 **Abstract**

11 Improving water quality is a critical issue worldwide. However, the general parameters (i.e.,
12 temperature, pH, turbidity, total solids, fecal coliform, dissolved oxygen, biochemical oxygen demand,
13 phosphates, and nitrates) used in water quality index estimations are unable to identify pollution from
14 industrial wastewater. This study investigated pollution sources at a river pollution hotspot by using
15 the positive matrix factorization (PMF) model. A two-phase sampling collection along a highly
16 polluted river in northern Taiwan was designed. The sampling spots were distributed along the river in
17 Phase I to monitor the spatial variation of river pollutants. A pollution hotspot was determined based
18 on two indices, namely the summed concentrations of elements and a metal index (MI). In Phase II,
19 the river water samples were collected from the hotspot twice daily over 30 consecutive days to
20 monitor the temporal variation of river pollutants. Source profiles of metal elements were obtained
21 during the monitoring period. The Phase II samples were then factorized using the PMF model. Factor
22 profiles retrieved from the PMF model were further assigned to industrial categories through Pearson
23 correlation coefficients and hierarchical classification. The results indicated that the main pollution
24 source was bare printed circuit boards (BPCB), which contributed up to 92% of the copper in the
25 pollution hotspot. In terms of MI apportionment of 11 metals related to health effects, BPCB
26 contributed 91% of the MI in high pollution events. Overall, the MI apportionment provides linkages
27 between pollution level and human health. This is an evidence for policymakers that the regulation of
28 the effluents of BPCB is an effective means to controlling copper concentrations and thus improving

29 water quality in the study area.

30 **Keywords:** River water pollution; Industrial wastewater; Source profile; Source apportionment

31 **1. Introduction**

32 On September 25, 2015, the 193 member states of the United Nations adopted the 2030 Agenda for
33 its 17 Sustainable Development Goals (SDGs) [1]. The agenda was expected to guide the actions of
34 international communities over the next 15 years (2016–2030). One of the 17 SDGs involves
35 improving water quality by reducing river water pollution. The causes of river water pollution include
36 industrial activity, domestic sewage, livestock wastewater, and agricultural wastewater.

37 The water quality index (WQI) is commonly used to evaluate general water quality [2-4]. Multiple
38 parameters are involved in the estimation of WQI scores, and weighted coefficients are assigned to
39 each parameter based on statistical surveys. The general parameters are temperature, pH, turbidity,
40 total solids, fecal coliform, dissolved oxygen, biochemical oxygen demand, phosphates, and nitrates
41 [5, 6]. However, an index using these parameters generally cannot be used to measure pollution from
42 industrial wastewater.

43 River water influenced by discharge from an industrial district usually has a complex composition
44 including metal elements, water-soluble ions, and volatile organic compounds. Stable and non-
45 degradable metal elements could act as suitable tracers for monitoring pollution discharged by
46 industries [7, 8]. A metal index (MI) based on maximum allowable concentration (MAC) has been
47 introduced to evaluate the quality of water resources [9, 10]. Usually, the MAC of an element is set by

48 regulatory agencies to protect human health and ecological environment, which makes the MI a
49 valuable indicator.

50 To decrease the health hazards of polluted water and improve water quality, identifying pollution
51 sources is critical. Various statistical techniques have been applied for source apportionment. Principle
52 component analysis (PCA) has been widely used in the source apportionment of water pollution [11-
53 15]. PCA yields linear combinations of original features and can transform large datasets into a set of
54 factors with reduced dimensions. However, PCA can only provide qualitative information, and it is
55 susceptible to outliers. Furthermore, the results of PCA does not have physical meaning because the
56 values of factors decomposed using PCA can be negative. Positive matrix factorization (PMF) is
57 recognized as an effective scientific tool and as an improved factor analysis tool for source
58 apportionment [16]. Many studies have successfully applied PMF to the source apportionment of
59 ambient particulate matter [17, 18]. In recent years, PMF has also been used to investigate pollution
60 sources in aqueous environments [e.g., 19, 20-23]. PMF has the following advantages: (1) it includes
61 the integration of non-negative constraints; (2) uncertainties in the data are introduced into the model;
62 (3) it does not need to be orthogonal, which makes the formed factors close to real profile of pollution
63 sources; (4) it quantifies source contributions; and (5) the factors are not excessively influenced by
64 outliers [24-26]. However, in most of these studies, source apportionment was estimated using spatial
65 samplings, which neglected temporal variation in the source contributions. Furthermore, the number
66 of metal species was limited and may be insufficient to distinguish complex industrial sources.

67 The objective of this study was to use metal species with a receptor model to estimate potential
68 source profiles and their contributions in a river pollution hotspot. The Ta-Liao-Keng River was
69 selected as an example to demonstrate the feasibility of the approach. To the best of our knowledge,
70 this is the first study adopting sequential time series data of river water samples for PMF modeling
71 with factor profiles identified by comparison with profiles obtained from industrial effluents. Potential
72 sources of MI and their contributions were apportioned to clarify the relationship between pollution
73 levels and human health.

74 **2. Material and Methods**

75 *2.1. Study Area and River Water Sample Collection*

76 The Ta-Liao-Keng River is a tributary of the Dahan River, which is a major river in Taiwan (Fig. 1).
77 The length of the Ta-Liao-Keng River is 12.3 km, and its catchment area is approximately 29.4 km².
78 The river has four branches and flows eastward from Taoyuan City to New Taipei City (A fishbone
79 diagram is provided as Fig. S1). The main industrial area is located at a downstream section of the
80 river and is especially concentrated on Tandigou, a tributary (S4 in Fig. 1). According to a report
81 published by the local government in 2017, the Ta-Liao-Keng River was the main contributor of copper
82 (Cu) to the Dahan River. Thus, further investigation of the source pollution, especially for Cu, in the
83 Ta-Liao-Keng River is imperative.

84 For this study, a sampling scheme with two phases was designed. In the first phase (Phase I, end of
85 April 2019), four sampling sites along the Ta-Liao-Keng River were selected to locate a hotspot for

86 further investigation. The river water quality was monitored from downstream to upstream. Four
87 additional sampling sites at four branches served as background sites. A total of eight river water
88 samples were collected during this phase.

89 Two pollution indices, the sum of elemental concentrations and MI, were applied to investigate the
90 pollution hotspot. The MI was defined as

$$MI = \sum_i \frac{C_i}{(MAC_i)} \quad (1)$$

91 where C_i is the concentration of one of 11 controlled elements, i.e., silver (Ag), arsenic (As), cadmium
92 (Cd), Cu, hexavalent chromium (Cr^{6+}), mercury (Hg), manganese (Mn), nickel (Ni), lead (Pb),
93 selenium (Se), and zinc (Zn). Table 1 presents the MAC values of these 11 elements, which are
94 enforced by Taiwan Environmental Protection Administration (TEPA), for surface water. Because
95 trivalent chromium and Cr^{6+} can convert back and forth, a measurement of total chromium can avoid
96 missing one of these. Instead of using Cr^{6+} , total chromium was measured and used to estimate the MI.
97 Pollution is a cause for concern when the MI is greater than one.

98 In the second phase (Phase II, July 2019), samples were collected twice daily over 30 consecutive
99 days ($N = 60$) at the hotspot identified in Phase I. The collected samples were used to evaluate temporal
100 variation in river water pollution and for PMF modeling.

101 2.2. Sampling of Industrial Wastewater

102 To investigate potential pollution sources and assign them to industrial categories, representative
103 source profiles were needed. A total of 20 wastewater samples from 9 effluent discharges were

collected as source profiles. Furthermore, because the river could be contaminated by untreated wastewaters which were discharged by factories unintentionally, three manufacturing units were selected for sampling based on previous violations. Most industrial wastewater samples were collected twice during the sampling time to reduce uncertainty in the source profiles (Table S1). Overall, samples were collected for six industrial categories: chemical materials and products (CMP), bare printed circuit boards (BPCB), electroplating products (EP), food manufacturing (FM), finishing of textiles (FT), and metal surface treatment (MST). To further investigate the association between human activities and the river pollution, domestic sewage (DS) was collected as a potential source. The wastewater samples were collected and preserved in accordance with the standard method [27].

2.3. Chemical Analysis

To quantify metal elements and trace elements in river water and wastewater samples, inductively coupled plasma–mass spectrometry was used according to the standard method [28]. A total of 52 elements were analyzed and the method detection limit (MDL) of these elements ranged from 0.03 $\mu\text{g L}^{-1}$ to 1.67 $\mu\text{g L}^{-1}$ (Table S2).

2.4. Source Apportionment

The PMF 5.0 software released by U.S. Environmental Protection Agency was used for source apportionment in the second phase [29]. In PMF modeling, the mass balance equation is expressed as

$$X_{ij} = \sum_{k=1}^p g_{ik} f_{kj} + e_{ij} \quad (2)$$

where X_{ij} is the j th species concentration measured in the i th sample, g_{ik} is the contribution of the

122 k th source pollution in the i th sample, f_{kj} is the source profile defined by the j th species concentration
 123 in the contribution of the k th source pollution, and e_{ij} is the residual.

124 The uncertainty of measurements in PMF is calculated using

$$u_{ij} = \sqrt{(0.5 \times MDL_{ij})^2 + (0.1 \times X_{ij})^2} \quad (3)$$

125 when the measured concentration is higher than the MDL [29]. When the measured concentration is
 126 less than the MDL, the concentration is replaced with half the MDL, and the uncertainty is estimated
 127 as follows:

$$u_{ij} = \frac{5}{6} \times MDL_{ij}. \quad (4)$$

128 In PMF, the objective function is defined using

$$Q(E) = \sum_{i=1}^n \sum_{j=1}^m \left(\frac{e_{ij}}{u_{ij}} \right)^2 \quad (5)$$

129 where n is the number of samples and m is the number of species. The optimal values of contributions
 130 (g_{ik}) and sources profiles (f_{kj}) can then be retrieved by minimizing $Q(E)$.

131 To determine the number of factors, PMF was run sequentially using a varied number of factors
 132 from 3 to 8. The scaled residual (r_{ij}) of each run is used to calculate the maximum individual column
 133 mean (IM),

$$IM = \max_{j=1 \dots m} \left(\frac{1}{n} \sum_{i=1}^n r_{ij} \right) \quad (6)$$

134 and the maximum individual column standard deviation (IS),

$$IS = \max_{j=1\dots m} \left(\sqrt{\frac{1}{n-1} \sum_{i=1}^n (r_{ij} - \bar{r}_i)^2} \right). \quad (7)$$

135 The appropriate number of factors is that for which the derivatives of IM and IS seem to level off [30].

136 In PMF modeling, bootstrapping is performed to estimate the stability of the solution. The
137 reproducibility of bootstrapping on each run (three to eight factors) is used to determine the number
138 of factors, as well. In this study, 100 was chosen for the number of bootstrap runs.

139 **3. Results and Discussion**

140 *3.1. Spatial and Temporal Variations in River Water Measurements*

141 The sum of elemental concentrations was low upstream and gradually increased along the river in
142 Phase I (Table S3, Sites S8, S5, S3, and S1). The two species with the highest concentrations were
143 aluminum (Al) and iron (Fe); the sum of Al and Fe at S6 was 86% of the elemental concentrations. Al
144 and Fe are the most abundant metals in the Earth's crust. To focus on industrial pollutants, Al and Fe
145 were eliminated from the following estimations. The highest elemental concentration was observed at
146 Tandigou (S4), a tributary of the Ta-Liao-Keng River. The concentration at S4 was almost six times
147 greater than that of the background water (S8). The second highest value was observed in the other
148 tributary, S2. The high concentrations in tributaries instead of in the main stream was probably due to
149 inputs from domestic wastewater and industrial effluents in the downstream area. The MI at S4 was
150 up to 42.8, 17 times higher than that at S8, which indicated high levels of pollution at S4. Based on the
151 spatial analysis of the metal elements in Phase I, S4 was chosen as the pollution hotspot.

152 In Phase II, the pollution hotspot was monitored twice daily over 30 consecutive days beginning on
153 July 1, 2019. Summary statistics for the measured elemental concentrations are provided in Table S2.
154 The three elements with the highest mean concentrations (exclude Al and Fe) were Cu ($1245 \mu\text{g L}^{-1}$),
155 Zn ($558 \mu\text{g L}^{-1}$), and Ni ($313 \mu\text{g L}^{-1}$). When applying the PMF model, data pretreatment is crucial.
156 Species must be removed if more than 70% of the data points are below the detection limit. In this
157 study, the following 13 species were excluded: dysprosium, erbium, europium, hafnium, holmium,
158 iridium, platinum, ruthenium, samarium, tellurium, thulium, ytterbium, and zirconium. Most of the
159 excluded species are rare earth elements and precious metals. Furthermore, data quality is evaluated
160 by signal-to-noise ratios in PMF modeling and inadequate species can be weighted down or eliminated
161 during the optimization. We eliminated six elements with poor fit, namely gold, boron, cobalt,
162 molybdenum, antimony, and tantalum. Finally, 31 of the 50 elements were included in the PMF model.

163 The highest total elemental concentration at S4 was observed on July 1 when the concentration was
164 up to $13465 \mu\text{g L}^{-1}$ (Fig. 2). The second highest total elemental concentration, $9100 \mu\text{g L}^{-1}$, was
165 observed on July 15. In terms of the MI, the largest value, 258, was also observed on July 1 (Fig. 3).
166 The second largest MI value, 170, was observed on July 4. A discrepancy was discovered when
167 defining the high pollution events using two indices. This is discussed in the following sections.

168 *3.2. Characteristics of the Metal Elements in Industrial Wastewater*

169 Most industrial wastewater was collected twice, and the samples for each factory were averaged to
170 create a composite profile. The composite profiles of eight industrial and three manufacturing unit

(with “m” in front of the category) discharges are illustrated in Fig. 4. CMP was represented by a battery factory, which emitted a high concentration of Pb. The profiles for BPCB were dominated by Cu, which comprised up to 82% of total elemental concentrations. The profiles of the EP were dominated by Ni, with proportions of up to 88%. FM was represented by a factory making frozen food, where discharge had high concentrations of strontium (Sr) and rubidium. The profile of FT was dominated by Sr and Mn. The MST was represented by a manufacturer of aluminum-related products, and Mn and Ni were dominant in its profile. The profile of DS was collected at an apartment complex and was dominated by Mn and Sr. All compositions followed the effluent standards established by the TEPA.

3.3. Source Apportionment

IM and IS analyses indicated that possible solutions were around six factors (Fig. S2). To identify the optimal solution, bootstrap analysis was introduced (Table S4). This revealed that five factors provided the most stable solution with the mapping rate > 80% for each factor. The averaged source contributions of total elemental concentrations (the sum of 31 elements) and of Cu are depicted in Fig. 5. Factor 4 was the greatest contributor (36%) to total elemental concentrations, followed by Factor 1 (19%) and Factor 5 (16%). For Cu, Factors 4 and 1 offered even larger contributions (64% and 28%, respectively).

The measured total elemental concentrations and the contributions of Factors 1, 4, and 5 over time are presented in Fig. 2. The contribution of Factor 4 closely matched certain high pollution events. On

July 4, Factor 4 contributed 86% of total elemental concentrations and decreased in the afternoon. Factor 1 was the main contributor (76%) of the highest pollution event on July 1 even though it was not a persistent pollution source. By contrast, Factor 5 was a stable, persistent source of pollution, but its contribution was relatively small. Concentrations of Cu were greater than $3000 \mu\text{g L}^{-1}$ in many high pollution events (Fig. S3), and the ratio of Cu to total elemental concentration was $> 50\%$. Factor 1 was the significant contributor of Cu on July 1. Factor 4 was the main source of Cu in high pollution events, except for the highest one.

For Factor 1, Cu comprised 65% of the normalized profile (Fig. S4). Cu was also dominant in Factor 4 and represented up to 78% of total elemental concentrations. Instead of Cu, Mn and Sr were significant in Factor 5. To identify the industrial categories of the factors we focused on, Pearson correlations and hierarchical classifications were used. Table 2 lists the correlations of Factors 1, 4, 5, with all source profiles collected in this study. Factors 1 and 4 had strong correlations ($r \geq 0.96$) with BPCB1, BPCB2, and their manufacturing unit discharges. The correlation between Factor 1 and Factor 4 was as high as 0.99. This indicated that Factors 1 and 4 were in the same industrial category. Factor 5 was highly correlated with DS ($r = 0.95$). Fig. 6 depicts a cluster dendrogram of the hierarchical classification of the factors and source profiles. Factor 1 was similar to BPCB1 and its manufacturing unit discharge, and Factor 4 was similar to BPCB2 and its manufacturing unit discharge. Among all source profiles and factors, BPCB1 and BPCB2 were prominent in the hierarchical clustering. Moreover, Factor 5 was closely related to DS. BPCB1 and BPCB2 are Cu-dominated, and the profile

of DS is dominated by Mn and Sr. Overall, the profile matching based on the two methods was consistent, and the markers for the estimated factors corresponded to those in the measured profiles. Factors 1 and 4 were classified as BPCB1 and BPCB2, respectively, and Factor 5 was classified as DS.

3.4. MI Apportionment

These analyses in the previous section have focused on source apportionments for mass concentrations. From the perspective of protecting human and ecological health, further quantifying the contributions of sources to MI, which considered both the concentrations and MAC of the main toxic elements, is needed. The source-specific MI of the p th source (MI_p) was calculated using

$$MI_p = \sum x_{jp}^* MI_j \quad (8)$$

where x_{jp}^* is the mean concentration of species j in source p , based on the model results, and MI_j is the unit MI for species j .

The averaged MI was 53.9, with Cu contributing up to 77%. The other highly polluting species was Mn (10%), followed by Ni (6%). Fig. 5(c) presents the MI apportionment results. Factor 4, which was classified as BPCB2, was the main MI contributor (53%) at S4. The second highest contributor (24%) was Factor 1, which was classified as BPCB1. The sum of MI contributions from BPCB1 and BPCB2 was up to 77%, indicating that BPCB was the industrial category with the greatest health risk at S4.

Fig. 3 presents the time series of the measured MI scores and those of the two largest contributors. To compare the source contribution during pollution events and nonevents, high pollution events (HPEs) were defined as those with $MI > 99.3$ (mean MI plus one standard deviation), and other events

classified as general conditions (GCs). Nine HPEs were identified. The averaged MI of the HPEs was 143, whereas the averaged MI of the GCs was 38. The health risk of the HPEs was approximately 3.8 times greater than that of the GCs. For Events 2, 4, 6, 7, 8, and 9, BPCB2 was the main MI contributor; for Event 1, BPCB1 was the main contributor. By contrast, the pollutants of Event 5 were almost equally contributed by both BPCB1 and BPCB2. For Event 3, no obvious contributor was identified, which was also evidenced by the PMF model not fitting this event well. Overall, BPCB1 and BPCB2 were the main MI contributors to HPEs; the sum of their MI contributions was up to 91% (Fig. 7). During GCs, BPCB1 and BPCB2 were also the largest health risk contributors, and the sum of their contributions was 79%. DS contributed the second greatest health risk, with a 15% contribution. Although DS was not a dominant source pollution in HPEs, it was a stable source pollution that contributed 9% of the averaged MI.

3.5. Limitations

In this study, the MI was considerably higher than the reference value because of stringent MAC of Cu in Taiwan. The guideline for drinking water quality published by the World Health Organization [31] is $2000 \mu\text{g L}^{-1}$ for Cu, but the MAC of Cu is $30 \mu\text{g L}^{-1}$ in Taiwan. This makes estimates of the MI higher if Cu is the main pollutant. Another limitation is that the result estimated by the PMF model provided only information on source contributions by industrial categories and not the exact source locations. Nevertheless, this modeling approach is valuable in narrowing down pollution sources to specific industrial categories.

246 **4. Conclusions**

247 This study investigated the source contributions at a river pollution hotspot by using PMF. This was
248 the first study to apply sequential time series data of metal species in PMF to apportion sources and
249 their contributions by industrial category. The results revealed that the main source was BPCB, and
250 the sum of BPCB1 and BPCB2 contributions was up to 55% of the total elemental concentrations and
251 92% of copper in the study area. Because Cu element was the main pollutant in BPCB which was the
252 main contributor, this leads to severe copper pollution in Tandigou. BPCB contributed 75% of total
253 elemental concentrations in MI. For both elemental concentrations and the MI, which is related to
254 human and ecological health, BPCB was the main contributor. In further investigation of the source
255 pollution in HPEs, the MI contribution from BPCB was up to 91%. The results indicated that BPCB
256 contributed toxic pollutants and that led to a high percentage of MI contribution.

257 In this study, we demonstrated the feasibility of using metal species with a receptor model to identify
258 source pollution. The model results might provide useful information to policymakers for the effective
259 management of river environments. For further investigation of river pollution, establishing a
260 comprehensive source profile database is highly recommended for source identification.

261 **Declarations**

262 **Availability of data and materials**

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

265 Laboratory, Environmental Protection Administration, Taiwan.

266 **Competing interests**

267 The authors declare that they have no competing interests.

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273 **Author's contributions**

274 **Peo-Yuan Hsieh:** Conceptualization, Methodology, Software, Formal Analysis, Investigation, Writing
275 – original draft, Visualization. **Huan-Chun Lin:** Investigation, Writing - review & editing. **Gen-Shuh**
276 **Wang:** Conceptualization, Supervision, Project administration. **Yuan-Jeng Hsu:** Investigation, Data
277 curation, Resources, Supervision, Project administration. **Yi-Ju Chen:** Resources, Data curation. **Tzu-**
278 **Hui Wang:** Resources, Data curation. **Ren-De Wang:** Resources, Data curation. **Chun-Yu Kuo:**
279 Resources, Data curation. **Di-Wen Wang:** Resources, Data curation. **Ho-Tang Liao:** Validation,
280 Writing - review & editing. **Chang-Fu Wu:** Conceptualization, Supervision, Project administration,
281 Writing - review & editing.

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366 **Table 1** Water quality standards of TEPA for heavy metal content in surface water.

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

367 *MAC = maximum allowable concentration.

368 **Table 2** Correlations of Factors 1, 4, 5, with all source profiles.

Source Pollution	Factor 1	Factor 4	Factor 5
CMP ^a	-0.04	-0.02	0.68
BPCP1	0.98	0.98	0.24
EP1	0.04	0.06	0.51
BPCP2	0.96	0.98	0.21
FM	0.01	0.03	0.63
FT	0.03	0.05	0.72
MST	0.03	0.06	0.63
EP2	0.49	0.49	0.14
DS	0.03	0.05	0.95
BPCP1m ^b	0.98	0.98	0.16
EP1m	0.01	0.02	0.16
BPCP2m	0.98	0.98	0.13

369 ^aCMP = chemical materials and products; BPCB = bare printed circuit boards; EP = electroplating
370 products; FM = food manufacturing; FT = finishing of textiles; MST = metal surface treatment; DS =
371 domestic sewage. Three manufacturing unit collected from BPCP1, EP1 and BPCP2 are with “m” in
372 front of the category.

373 ^bThe category with m means the manufacturing unit.

374
 375 **Fig. 1.** Locations of the sampling sites in the Ta-Liao-Keng River.

376

377 **Fig. 2.** Measured total elemental concentrations and the contributions of Factors 1, 4, and 5 over time.

378

379 **Fig. 3.** Measured MI and contributions of Factors 1 and 4 estimated using PMF.

380

381 **Fig. 4.** Composite profiles of industrial effluents and manufacturing unit discharges.

382

383 **Fig. 5.** Source contributions of five factors to (a) total elemental concentrations, (b) Cu, and (c) MI.

384

385 **Fig. 6.** Cluster dendrogram of hierarchical classification.

386

387 **Fig. 7.** MI apportionment in high pollution events (HPEs) and in general conditions (GCs).

Supplementary Files

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