

LINHUA SUN^{1,2}

STATISTICAL APPROACHES FOR IDENTIFICATION AND QUANTIFICATION OF SOIL TRACE ELEMENTAL POLLUTION NEAR THE TRAFFIC WAY

The concentrations of eight trace elements (As, Co, Cr, Cu, Fe, Mn, Pb and Zn) in the soil near a traffic way of Suzhou, Anhui province, China have been determined for the pollution assessment and source identification (along with quantification). The results indicate that Fe is the most abundant element followed by Mn, Zn, Cr, Pb, Cu, Co and As. These elements have low-medium coefficients of variation (0.059–0.293), indicating that some of them might have multisources. The combination of single pollution, geoaccumulation and the Nemerow composite indices suggest that the soils in this study are slightly polluted. Based on multivariate statistical analyses (including correlation, cluster and factor analyses), three sources responsible for the trace elemental concentrations in the soils have been identified, including geogenic, agricultural and traffic-related sources. Their mean contributions calculated based on the Unmix model are 35.9, 31.8 and 32.4%, respectively.

1. INTRODUCTION

With the vigorous development of China's national economy, the pace of road construction is growing. According to the *Statistical Bulletin on Transportation Industry Development in 2016, China*, China's total traffic way mileage has reached 4.70 million kilometres at the end of 2016. Along with this situation, the environmental problems (e.g., noise, vibration, emission of gases, water, residue and waste) related to the traffic have attracted a lot of attention. And therefore, a large number of studies have been carried out for the solution of these environmental problems and most of them focused on the noise and air pollution [1–4].

¹School of Resources and Civil Engineering, Suzhou University, Anhui 234000, China, e-mail address: sunlinh@126.com

²Key Laboratory of Mine Water Resource Utilization of Anhui Higher Education Institute, Suzhou University, Anhui 234000, China.

Because of their harmful effects for human beings, some of the trace elements, especially the toxic ones (e.g., Hg, Cd, Pb, Zn), have long been concerned by scientists, and a large number of studies related to their toxicological characteristics [5, 6], concentrations, distribution and forms in the environments [7, 8], sources [9], migration, enrichment and transformation [10] have been carried out. With the development of the traffic way of China, the vehicle exhaust emissions have become an important factor for the increasing concentration of trace elements such as Pb, Cu, Zn and Cd in the atmosphere [11], and which can increase the trace elemental concentrations in soil on both sides of traffic way (mostly, Pb, Cu, Zn, Cd and Mn) [12–16].

In this study, soil samples have been collected from the side of a traffic way with high density of traffic in the Suzhou city, Anhui province, China, and the concentrations of As, Co, Cr, Cu, Fe, Mn, Pb and Zn have been measured for the pollution assessment and source approximation (especially the identification and quantification of the traffic-related pollution of trace elements). The study can provide information for the environmental management of the study area.

2. MATERIALS AND METHODS

2.1. THE STUDY AREA

Suzhou is the north gate of the Anhui province, China. It is located at the south of the Huang-Huai plain, adjacent to Xuzhou of Jiangsu and Heze of Shandong in the north, Yongcheng of Henan in the west, Suqian of Jiangsu in the east. There are many rivers in the area, including the Kui, Sui, Tuo and Hui Rivers, all of them flow from northwest to southeast, and end in the Huai River or the Hongze lake. The annual precipitation is 857 mm, with an average temperature of 14.4 degrees (centigrade). Agriculture and coal related industries are the most important industries in the area. The main crops in the area include wheat, corn, soybean, cotton, potato, rapeseed, peanuts and fruit etc. And therefore, the quality of soil is important for the development of the area.

During the past ten years, the economy of Suzhou has undergone rapid development, especially the development of transportation, including the railways and traffic ways. And now, people in Suzhou can arrive in Beijing and Shanghai in three hours, and Xi'an and Wuhan in four hours. In relation to this high speed of development, many kinds of environmental problems such as air, water and soil pollution occurred and a series of studies have been carried out [17–19].

2.2. SAMPLING AND ANALYSIS

The Suzhou Avenue is a urban express connecting the urban area and the high railway east station of Suzhou, and it is a traffic way with high density of traffic (Fig. 1). It

is an eight-lane road with two non-motorized lanes, the width is 40 m, with an average traffic volume of near 10 000 vehicles per day and a peak period of nearly 1500 vehicles per hour. A total of 30 surface soil samples (less than 10 cm deep) near the traffic way have been collected in March 2019. The detailed sampling distributions are shown in Fig. 1. All of the samples were collected at the southern edge of the traffic way (within 1 m from the roadside). The distance between each sampling point was near 150 m.

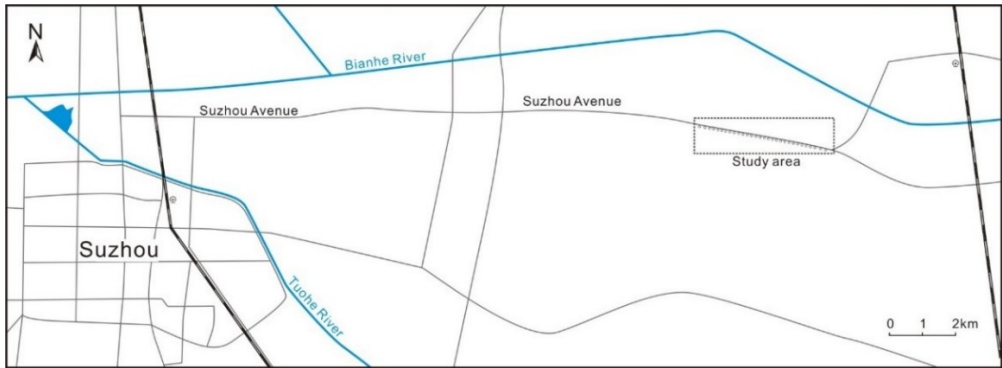


Fig. 1. Location of the study area and sample distributions

After collection, all samples were air-dried in natural conditions, and the debris of animals and plants were removed by hands. Then the samples were powdered to 200 meshes (<0.075 mm) after parching for 24 h at 80 °C in a dryer. Samples were tableted using a 30 t condenser, and then analyzed by XRF (Innov-X Explorer 9000 SDD, USA) for measuring the concentrations of trace elements such as As, Co, Cr, Cu, Fe, Mn, Pb and Zn in the Key Laboratory of Mine Water Resource Utilization of Anhui Higher Education Institute, Suzhou University, Anhui Province, China. National standard sediment sample of China (GSS-16) was analyzed simultaneously for calibration (once per 10 samples). And the final concentrations of the trace elements were calculated from:

$$C_m = \frac{C_t S_s}{S_m} \quad (1)$$

where C_m is the concentration of a sample, C_t is its concentration recorded with the instrument, S_s and S_m are the standard and measured concentrations of the standard samples (GSS-16), respectively.

2.3. DATA TREATMENT PROCEDURES

All of the data were firstly processed for statistical analysis by the Mynstat 12 software, and the minimum, maximum, mean, and standard deviation, the coefficient of

variation and the p -value of the normal distribution test have been obtained. And then, a series of parameters, including the single pollution index P_i [20], the geoaccumulation index I_{geo} [21] and the Nemerow composite index P_s [22] have been determined for the pollution assessment of the soil samples. Finally, the statistical analyses (including the correlation, cluster and factor analyses) [23] have been performed for information on the sources of the pollution, and then the Unmix model provided by the US Environmental Protection Agency (EPA) [24] has been used to obtain the quantitative information about the source of them.

3. RESULTS AND DISCUSSION

3.1. TRACE ELEMENTAL CONCENTRATIONS

The concentrations of the trace elements in 30 soil sampled are given in Table 1. As can be seen from the table, iron is the element with the highest mean concentration (22,987–30,889 mg/kg, mean 26,689 mg/kg), and then followed by the Mn, Zn, Cr, Pb, Cu, Co and As, their mean concentrations are 389, 119, 49.6, 35.9, 24.2, 12.1 and 9.96 mg/kg, respectively.

Table 1

Descriptive statistics of trace elemental concentrations in the soil samples

Species	As	Co	Cr	Cu	Fe	Mn	Pb	Zn
Minimum, mg/kg	7.82	9.00	31.3	15.3	22,987	328	27.9	66.3
Maximum, mg/kg	14.0	12.9	68.7	43.4	30,889	497	50.3	191
Mean, mg/kg	9.96	12.1	49.6	24.2	26,689	389	35.9	119
Standard deviation, mg/kg	1.82	0.721	7.17	6.13	2,028	33.5	6.01	34.9
Coefficient of variation	0.183	0.059	0.145	0.254	0.076	0.086	0.167	0.293
p -value	<0.01	<0.01	>0.15	0.144	>0.15	0.113	0.034	>0.15
Mean P_i	0.889	0.957	0.813	1.07	0.908	0.667	1.38	1.61
Highest P_i	1.25	1.01	1.13	1.92	1.05	0.853	1.93	2.58
I_{geo}	0.162	0.150	0.091	0.118	0.035	0.058	0.108	0.080
Highest I_{geo}	0.170	0.160	0.097	0.127	0.035	0.059	0.112	0.086
Background	11.2	12.7	61.0	22.6	29 400	583	26.0	74.2

The background data are from the CEPA [26].

The coefficient of variation (CV – standard deviation/mean) is an index showing the degree of variability with respect to the mean of the population. A high CV (>0.90) means a high degree of spatial variation and a high degree of anthropogenic contribution (point pollution), whereas a low CV (<0.10) means low degree of spatial variation and low degree of anthropogenic contribution or surface pollution [25]. In this study, Co, Fe and Mn have low CV s, which means that the concentrations of these elements vary

slightly from sample to sample, indicating that they have undergone low degree or no anthropogenic influence. As to other elements, they have a medium CV s values between 0.145 and 0.293, which indicates a moderate spatial inhomogeneity with moderate anthropogenic contribution. Such results can also be achieved from the p -values of the normal distribution test. As can be seen from the table, most of the elements except for As, Co and Pb have p -values higher than 0.05, implying that they can pass the normal distribution test, which may also suggest that the elements except for As, Co and Pb might have single source.

3.2. POLLUTION ASSESSMENT

Previous studies revealed that the single pollution index P_i is a good indicator for monitoring the degree of pollution

$$P_i = \frac{C_m}{C_s} \quad (2)$$

C_m and C_s are the concentrations of the sample and background, respectively. $P_i < 1$ means light pollution, P_i between 1 and 3 means moderate pollution, and $P_i > 3$ means considerable pollution [20].

The soil environmental background values of China [26] were chosen to be the C_s values, and the calculated mean P_i values are listed in Table 1. The results indicate that the soils in this study are moderately polluted with Cu, Pb and Zn, (P_i equal to 1.07, 1.38 and 1.61, respectively), whereas for other elements $P_i < 1$. Despite the fact that most of the average concentrations of the trace elements with light pollution (As, Co, Cr and Fe) in this study are lower than the soil environmental background values, there are differences between the samples from different locations: it can be seen from the table that the maximum concentrations of As, Co, Cr and Fe (14.0, 12.9, 68.7 and 30 889 mg/kg, respectively) are higher than those of the background (11.2, 12.7, 61.0 and 29 400 mg/kg, respectively), and the highest P_i values are 1.25, 1.01, 1.13 and 1.05, respectively, implying that the distribution of trace elements in the study area is heterogeneous.

The geoaccumulation index I_{geo}

$$I_{\text{geo}} = \log_2 \frac{C_m}{1.5C_s} \quad (3)$$

enables the assessment of contamination degrees by comparing the current and preindustrial concentrations [21]. There are no local preindustrial concentrations of trace elements, and therefore, the soil environmental background values [26] were chosen as the C_s values. The values of $I_{\text{geo}} < 0$ correspond to unpolluted samples, those between

0 and 1 light pollution, 1–3 moderate pollution, 3–5 heavy pollution, and > 5 serious pollution [21]. The calculated I_{geo} values listed in Table 1 point to light pollution with all the elements ($0 < I_{\text{geo}} < 1$).

The Nemerow composite index P_s method takes into account all the individual evaluation factors:

$$P_s = \left(\frac{(P_{im})^2 + (P_{ix})^2}{2} \right)^{1/2} \quad (4)$$

where P_{im} is the average of single pollution index of all elements, and P_{ix} is the maximum value of the single pollution index of all elements. $P_s < 0.7$ means safety domain, $0.7 \leq P_s < 1.0$ precaution domain, $1.0 \leq P_s < 2.0$ slightly polluted domain, $2.0 \leq P_s < 3.0$ moderately polluted domain, and $P_s > 3.0$ seriously polluted domain [22]. In this study, the calculated P_s values for all of the samples range from 0.98 to 2.01 (mean 1.40), only one sample has $0.7 \leq P_s < 1.0$ and another $P_s > 2.0$, which means that most of the soil samples in this study can be classified to be slightly polluted.

3.3. STATISTICAL ANALYSES FOR SOURCE IDENTIFICATION AND QUANTIFICATION

Correlation analysis. The correlation analysis between species is useful as it can point out associations between variables that can show the overall coherence of the dataset, and thus indicate the participation of the individual chemical parameters in several influence factors [27]. The results of the correlation analysis are shown in Table 2. As can be seen from the table, close positive relationships have been identified between the following elements: Co–Mn, Cr–Cu–Fe–Mn, Cu–Fe, Fe–Mn and Pb–Zn. Such results suggest that these elemental pairs might have similar sources or, have been affected by similar factors. However, Pb and Zn show negative correlations with almost all of the other elements except for Co, implying that they have different sources.

Table 2

Results of the correlation analysis

	As	Co	Cr	Cu	Fe	Mn	Pb
Co	-0.214						
Cr	0.260	0.291					
Cu	0.242	0.213	0.476 ^a				
Fe	0.176	0.277	0.537 ^a	0.423 ^a			
Mn	0.005	0.421 ^a	0.529 ^a	0.068	0.521 ^a		
Pb	0.080	0.214	-0.319	-0.178	-0.643 ^a	-0.194	
Zn	-0.186	0.295	-0.330	-0.121	-0.598 ^a	-0.052	0.791

^aMeans significant at $\alpha = 0.05$, $r_\alpha = 0.361$.

Cluster analysis. Cluster analysis comprises of a series of multivariate methods which are used to find true groups of data. In clustering, the objects are grouped such that similar objects fall into the same class. The method has long been used for environmental studies [13]. In this study, the hierarchical *R*-mode cluster analysis has been applied to the data, and the “Ward” linkage and the “Pearson” distance have been chosen for calculation, and the results are shown in Fig. 2 as a dendrogram. As can be seen from the figure, two main groups can be identified: Pb–Zn (group 1) and As–Co–Cr–Cu–Fe–Mn (group 2), which indicate that the elements in the similar group might have similar sources.

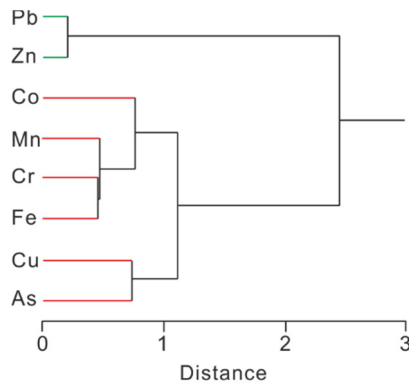


Fig. 2. Dendrogram of R-mode cluster analysis

Factor analysis. Factor analysis is a commonly used statistical method for classification, simplification of the data and finding the most important variables in the dataset. In geochemical studies, factor analysis has long been used for tracing elemental sources [28]. In this study, based on the criterion of initial eigenvalue higher than one, three factors have been obtained based on the factor analysis (Mystat version 12.0) (Table 3).

According to previous studies [29], factor loadings can be classified as strong, medium and weak with the values of >0.75 , $0.75-0.50$ and $0.50-0.30$, respectively. As can be seen from the table, the first factor, which accounts for 38.7% of the total variance explanation, has moderate negative loadings of Fe and strong positive loadings of Pb and Zn. As to factor 2, it accounts for 22.6% of the total variance explanation and has strong positive loadings of Co and Mn and moderate positive loadings of Cr and Fe. The third factor has 15.5% of the total variance explanation and has strong positive loadings of As, and moderate positive loadings of Cr and Cu. In combination with previous studies, the first factor with high Pb and Zn loadings can be explained to be the Pb–Zn related sources (e.g., the traffic-related, because Pb and Zn are the most abundant elements released by vehicle exhaust emissions and wearing of tyres) [25]. The second factor can be explained to be the geogenic source because the elements with high loadings in this factor are mostly geogenic (e.g., Co, Cr, Fe and Mn). The third factor with

high loadings of As and Cu, to a lesser extent, Cr, might be an indication of agricultural activities, especially the pesticides and fertilizers (because As and Cu are the most popular elements applied for pesticides production).

Table 3

Results of factor analysis

Element	Factor 1	Factor 2	Factor 3
As	-0.01	-0.23	0.85
Co	0.30	0.84	-0.04
Cr	-0.33	0.58	0.53
Cu	-0.11	0.30	0.68
Fe	-0.69	0.53	0.29
Mn	-0.20	0.78	0.03
Pb	0.95	-0.07	0.04
Zn	0.92	0.12	-0.16
Eigen value	3.10	1.81	1.24
Variance explained, %	38.7	22.6	15.5

Unmix model analysis. The Unmix model is a mathematical receptor model used for quantifying the sources of contaminants contributing to sediment, water and air samples [24]. It is based on the reducing of a large number of variables in complex analytical data sets to combinations of species called source types and source contributions. The source types are identified by comparing them to measured profiles, whereas the source contributions are used to determine how much each source contributed to a sample [30]. Based on the calculation, three sources have been identified and the results are listed in Table 4 and shown in Fig. 3.

Table 4

Source profiles [mg/kg] and proportions [%]

Element	Source 1	Source 2	Source 3	Proportion 1	Proportion 2	Proportion 3
As	2.29	1.99	5.72	22.9	19.9	57.2
Co	2.68	3.40	6.05	22.1	28.0	49.9
Cr	14.3	9.33	26.0	28.8	18.8	52.4
Cu	11.8	5.07	7.29	48.8	21.0	30.2
Fe	6810	5570	14200	25.6	21.0	53.4
Mn	83.4	95.7	209	21.5	24.7	53.9
Pb	4.77	14.6	16.5	13.3	40.7	46.0
Zn	12.7	67.5	39.1	10.6	56.6	32.8

These three sources have Min Rsq = 0.98 and Min Sig/Noise = 2.17, higher than the minimum requirement of the model (Min Rsq > 0.8 and Min Sig/Noise > 2), suggesting

that the modeling is efficient [24]. As can be seen from the table, the first source is characterized by highest Cu content (48.8%) relative to other sources, and then followed by Cr (28.8%), Fe (25.6%), As (22.9%), Co (22.1%), Mn (21.5%), Pb (13.3%) and Zn (10.6%), whereas the second source is characterized by the highest contents of Zn (56.6%) relative to other sources, and then followed by the Pb (40.7%), Co (28.0%), Mn (24.7%), Cu and Fe (21.0%), As (19.9%) and Cr (18.8%). The third source is characterized by the highest proportions of most of the elements (As (57.2%), Mn (53.9%), Fe (53.4%), Cr (52.4%), Co (49.9%) and Pb (46.0%)), and then followed by the Zn (32.8%) and Cu (30.2%).

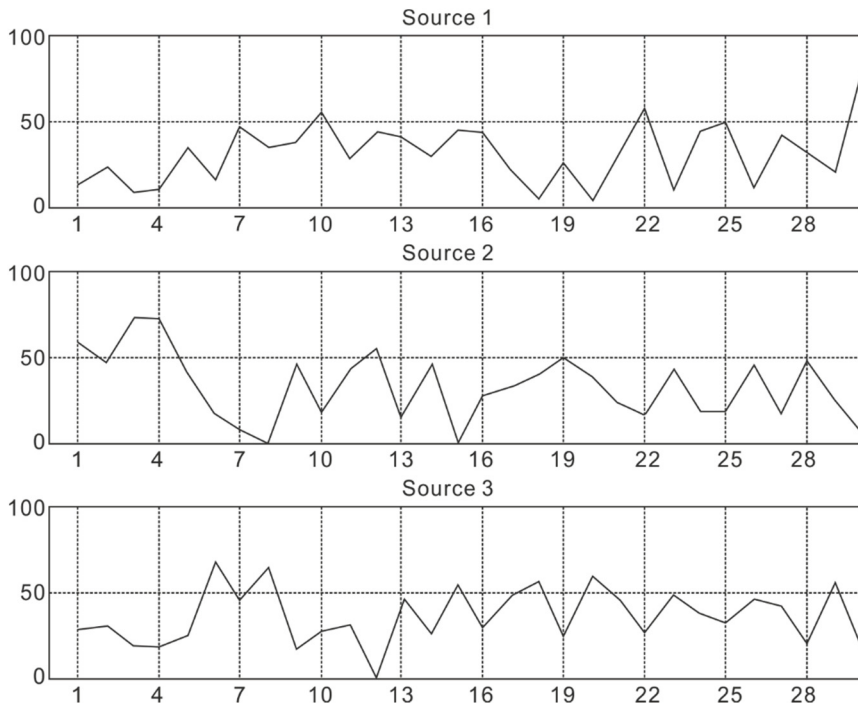


Fig. 3. Variations of source contributions

In consideration with the natural condition of the study area, there are three sources responsible for the soil trace elements in this study: the geogenic source related to the formation of the soil, the agricultural activities (application of fertilizers and pesticides) and traffic-related activities (vehicle exhaust emissions and wearing of tyres). In combination with the above analyses, the Source 3 can be explained to be the geogenic source, because most of the elements including Fe and Mn (mostly, geogenic) are contributed by this source. The contribution of this source for the elemental concentrations of all of the samples range from 0 to 68.0% (mean 35.9%). Comparatively, the source 1 can be explained to be the source related to the agricultural activities because this source is

characterized by highest content of Cu, and then followed by As and others, which are always related to the productions of pesticides. The contribution of this source for the elemental concentrations of all of the samples range from 2.40 to 81.2% (mean 31.8%). The source 2 should be explained to be the traffic related source as it is characterized by high contents of Zn and Pb, and its contributions are 0 to 73.4% (mean 32.4%).

4. CONCLUSIONS

- The elemental concentrations are $Fe > Mn > Zn > Cr > Pb > Cu > Co > As$. They have low-medium coefficients of variation (0.059–0.293).
- The single pollution, geoaccumulation and the Nemerow composite indices suggest that the soils in this study are slightly polluted.
- Statistical analyses indicate that three sources are responsible for the soil elemental concentrations, the geogenic, agricultural and traffic-related sources, and their mean contributions calculated by the Unmix model are 35.9%, 31.8% and 32.4%, respectively.

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