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# Source apportionment of heavy metals in soil of Guangzhou: Comparison of three receptor models

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**Abstract**: Receptor models are useful tools to identify the types of pollution source and estimate the contributions of each source of the observed samples. To analyze the concentrations, distributions and sources of eight heavy metals including lead (Pb), cadmium (Cd), zinc (Zn), mercury (Hg), arsenic (As), copper (Cu), chromium (Cr), and nickel (Ni) in soils, 208 topsoil samples were collected in the main urban area of Guangzhou, China. Three receptor models (Multi-Linear Regression of the Absolute Principal Component Scores (APCS-MLR) method, Positive Matrix Factorization (PMF) method and UNMIX method) were employed to identify the potential pollution sources of heavy metals and to apportion the pollution sources. Results show that the mean concentrations of eight heavy metal elements are higher than the corresponding background values, with the mean concentration of Cd being almost five times its background value. The three receptor models all identify three potential pollution sources, which are nature source, traffic source and industry source. Moreover, PMF and UNMIX can identify an agricultural source besides the three pollution sources, which better distinguishes the different types of pollution sources. Comparison among the results of APCS-MLR, PMF and UNMIX shows that there are some significant differences in the estimated contributions for each potential pollution source. It is also found that PMF appears to be more plausible for this investigation. It is advisable to use multiple receptor models to perform source identification and source apportionment, and the results could be very useful to local administrations for the control and management of pollution and better protection of important soil quality.

**Keywords**: heavy metal; APCS-MLR method; PMF method; UNMIX method; source apportionment
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## 1 Introduction

With the fast growth of industrialization, urbanization and population, heavy metal pollution of soil becomes more and more serious. A large number of heavy metals enter the soil through human industrial activities, atmospheric deposition, sewage irrigation, etc.[1]. Heavy metals have properties of persistence, non-degradability and bioaccumulation. Accumulation of heavy metals in soil may degrade the quality of farmland crops and environment, and then affect human health via food chain or dermal contact[2]. Source identification and source apportionment of polluted soil systems can provide basis for better soil management practices to improve the quality of the soil, and thus, they deserve more attention.

Receptor models are useful tools to identify pollution sources and to quantify the contributions of all sources to each measured pollutant based on environmental dataset[3-4]. Currently, main receptor models include chemical mass balance (CMB), positive matrix factorization (PMF), multi-linear regression of the absolute principal component scores (APCS-MLR), and UNMIX[5-7]. The different methods have different advantages and disadvantages and there are listed in Table 1.

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**Table 1.** Advantages and disadvantages of the three models.

| Method | Advantages | Disadvantages |
|---|---|---|
| APCS-MLR | principal component analysis (PCA); simple and fast | negative source contribution value |
| PMF | data pretreatment (datasets with missing data, uncertainty estimated and data rationality analysis[8-9]) | negative source contribution value[10] |
| UNMIX | singular value decomposition (SVD); without data conversion; does not require prior knowledge of pollution sources or source profiles | lots of data samples |

Many investigations use one receptor model for identification of pollution sources and apportionment of heavy metals in the soil. However, due to different pre-treatments of raw data, the methods may have multiple solutions in the process, and the results obtained by different methods are greatly different and sometimes even self-contradictory[11]. In order to compensate for the deficiency of using a single method, researchers usually compare and evaluate the results of different methods to improve the reliability of the conclusions. In recent years, applications of multi-receptor models to apportion the pollution sources in PAHs has increased[12-14]. However, only a few studies have used multivariate statistical techniques to identify pollution sources and to apportion their contributions for each pollutant of heavy metals in soil[15-16]. In this study, 208 soil sample were collected in Guangzhou, and concentrations of eight heavy metal elements, i.e. Pb, Cd, Zn, Hg, As, Cu, Cr, and Ni were analyzed. APCS-MLR, PMF and UNMIX were used for the identification of pollution sources and the apportionment of heavy metals in soil. The results from three receptor models were compared and evaluated, which provided scientific and comprehensive information on policy-making decision for local government. Besides, the results of the three methods are not consensus, which implies that these methods are not universal ones, but rather case-dependent. Therefore, for complicated data such as soil metals, it is advised to use more than one method.

## 2 Materials and methods

### 2.1 Sample collection

To assess the soil heavy metal pollution, 208 topsoil samples were collected in Guangzhou from October 2011 to October 2014. The sampling points were randomly distributed in the study area based on a regular grid of 4 km×4 km, and the spatial site of each sampling point was recorded using a global positioning system (GPS). Surface soil samples of depth 0−20 cm were collected and mixed into a composite sample. The original weight of per sample was greater than 1 kg.

### 2.2 Data analysis

Data pre-processing and transformation were conducted with Microsoft Excel version 2010. PCA and MLR were conducted with MATLAB version R2019a. The analysis of PMF was conducted with PMF version 5.0 (US EPA 2014). The analysis of UNMIX was conducted with USEPA UNMIX version 6.0.

### 2.3 Source apportionment methods

#### 2.3.1 APCS-MLR

APCS-MLR is an effective multivariate factor analysis method for the apportionment of pollution sources. In 1985, Thurston and Spengler proposed APCS-MLR method, which was first applied to estimate sources of particulate matter in Boston[17]. It is based on the assumption that the total concentration of each contaminant is made up of the sum of elemental contributions from each of the pollution source components. Hence,

$$Z_{ij} = \sum_{k=1}^{p} W_{ik} P_{kj} \quad (1)$$

Where $i$ is the total number of observations; $j$ is the number of measured species; $k=1, \cdots, p$, the number of pollution sources influencing the data; $Z_{ij}$ is the normalized concentration of variable; $W_{ik}$ is the coefficient matrix of the components; $P_{kj}$ is $k$th component's value for observation $j$.

$Z_{ij}$ in Eq. (1) is a normalized value of variable, it can not be used directly for computation of quantitative source contributions, so the normalized factor scores determined in Eq. (1) were converted to un-normalized APCS. The contribution from each factor was then estimated by multivariate linear regression, using the APCS values as the independent variables and the measured concentration of the particular contaminant as the dependent variable, and the equation is:

$$A_i = b_0 + \sum_{k=1}^{p} b_k \times APCS_{ki} \quad (2)$$

Where $A_i$ is the measured mass concentration in sample $i$, $b_0$ is the mass contribution from sources that are unaccounted for in the principal component analysis; $APCS_{ki}$ is the rotated absolute component score for the $k$th component with the $i$th sample; $b_k \times APCS_{ki}$ is the

contribution of the $k$th source to $A_i$.

2.3.2 PMF

PMF is one of the receptor models that the U. S. Environmental Protection Agency has recommended for source apportionment. It was produced by Paatero and Tapper (1994)[18]. PMF aims to calculate the source profiles and source contributions of pollutants in the environment, as shown in Eq. (3):

$$X_{ij} = \sum_{k=1}^{p} G_{ik}F_{kj} + E_{ij} \quad (3)$$

where $X_{ij}$ is composed of the $j$th compound concentration measured in the $i$th sample; $G_{ik}$ is the contribution of the $k$th source to the $i$th sample; $F_{kj}$ is made of the $j$th compound from the $k$th source, and $E_{ij}$ is the residual error matrix.

Factor profiles and factor contributions are derived by minimizing the objective function $Q$:

$$Q = \sum_{i=1}^{n}\sum_{j=1}^{m}\left(\frac{E_{ij}}{U_{ij}}\right)^2 \quad (4)$$

Where $U_{ij}$ is estimated uncertainty ($Unc$).

PMF 5.0 requires proper species concentrations and uncertainty files. The uncertainty of the concentration is calculated with the following equation:

$$Unc = \begin{cases} 5/6 \times MDL (c \leqslant MDL) \\ \sqrt{(E \times c)^2 + (MDL)^2} (c > MDL) \end{cases} \quad (5)$$

Where, $c$ is the concentrations of heavy metals; $MDL$ is the species-specific method detection limit, and $E$ is the error fraction, which represents a percentage of the measurement uncertainty[19].

2.3.3 UNMIX

UNMIX method is based on factor analysis. Compared with the traditional factor analysis method, the main feature of the UNMIX is that it can obtain a non-negative source contribution rate, so the result is more reasonable[20], and the calculation process is simpler. Each dimension in the multidimensional space represents a measured species, and then the principal component analysis method is used to reduce the dimension of the data space to estimate the number of sources, the composition of source, and the source contribution. Details of UNMIX method can be found in Refs. [21] and [22].

# 3 Results and discussion

## 3.1 Descriptive statistics of soil heavy metals

The statistical parameters of heavy metals are listed in Table 2. The variation coefficients of Cd, Zn and Hg are all more than 100%, indicating serious variability of these heavy metals, which is probably influenced by exogenous factors such as human activities. The coefficient variances of Hg reached 148%, indicating that Hg may be the most seriously disturbed heavy metal by human activities.

## 3.2 Results of APCS-MLR

The results of PCA are listed in Table 3. Based on the results, three principal components (PCs) with eigenvalues higher than 1 are extracted. PCA leads to a reduction of the initial dimension of the dataset to three components which account for 76.06% of the total variance of the original data. The first PC (PC1) accounts for 42.50% of the total variance, with high loadings for Cd, Zn, As, Cu, Cr and Ni. Parent material, rock weathering, and pedogenic process are the major contributions of these heavy metals concentration distributions[24]. It can be seen from Table 1 that the variation coefficients of As, Cu, Cr and Ni in soil samples are relatively low, suggesting a natural factor controlling their distribution. Therefore, PC1 represents a natural source.

**Table 2.** Descriptive statistics of heavy metals in the soils of the investigated area (mg/kg).

| Element | Min | Max | Arithmetical Mean | Geometric Mean | SD | CV(%) | Skewness | Kurtosis | BGV (mg/kg) |
|---|---|---|---|---|---|---|---|---|---|
| Pb | 1.00 | 299.50 | 57.19 | 45.36 | 40.85 | 71.43 | 2.67 | 14.64 | 29.8 |
| Cd | 0.005 | 3.49 | 0.30 | 0.21 | 0.34 | 112.29 | 5.37 | 43.13 | 0.0408 |
| Zn | 5.40 | 1215.10 | 140.21 | 104.55 | 143.07 | 102.04 | 3.82 | 22.89 | 36.3 |
| Hg | 0.001 | 2.71 | 0.25 | 0.12 | 0.37 | 148.43 | 3.36 | 17.01 | 0.0552 |
| As | 3.10 | 137.30 | 16.07 | 13.62 | 14.26 | 88.74 | 5.67 | 42.93 | 6.8 |
| Cu | 0.80 | 132.20 | 25.42 | 18.02 | 21.10 | 83.02 | 1.85 | 8.18 | 10.0 |
| Cr | 2.30 | 364.10 | 62.21 | 48.81 | 45.92 | 73.81 | 2.60 | 15.27 | 35.6 |
| Ni | 0.90 | 125.00 | 19.92 | 14.53 | 16.01 | 80.37 | 1.95 | 10.90 | 9.6 |

[Note] SD: Standard deviation; CV: Coefficient of variation; BGV: Background values at the provincial level from the report "The Background Concentrations of Soil Elements of China"[23].

**Table 3.** Principal component analysis (PCA) results for the heavy metal concentrations (mg/kg).

| Element | Principal components | | |
|---|---|---|---|
| | PC1 | PC2 | PC3 |
| Pb | 0.360 | −0.550 | 0.158 |
| Cd | 0.649 | −0.557 | −0.181 |
| Zn | 0.856 | −0.130 | −0.102 |
| Hg | 0.288 | 0.527 | 0.662 |
| As | 0.639 | −0.265 | −0.622 |
| Cu | 0.767 | 0.239 | 0.330 |
| Cr | 0.690 | 0.588 | −0.054 |
| Ni | 0.749 | 0.539 | 0.087 |
| Eigenvalue | 3.400 | 1.671 | 1.013 |
| Variance contributes(%) | 42.50 | 20.89 | 12.67 |
| Contribution of accumulated variance(%) | 42.50 | 63.39 | 76.06 |

The second PC (PC2) accounts for 20.89% of the total variance. It is heavily weighted by Pb, Cd and Hg, which indicates the same source for the three elements. One study shows that, both Pb and Cd are heavy metals from traffic sources, mainly from vehicle exhaust[25]. Another study shows that traffic pollution can cause the accumulation of Hg in the soil[26]. Besides, Cr and Ni also have high loads in PC2, earlier studies showed that traffic was responsible for enrichment of Cr and Ni in soil[27-28]. Traffic emissions include vehicle exhaust, tire wear particles, street surface weathering particles and vehicle braking friction wear particles. Compared with PC2, Cr and Ni have higher loads in PC1 which means them are more likely to be caused by natural source. Therefore, PC2 represents the traffic source.

The third PC (PC3) is strongly correlated with Hg, and accounts for 12.67% of the total variance. Some studies have shown that coal combustion and non-ferrous metal smelting are the main pollution sources of Hg[29-30]. Coal is still the main energy source in China, and the atmospheric Hg released from coal combustion enters the soil through subsidence, resulting in the increase of concentration of Hg in soil. The higher concentrations of Hg appeared in the southern and southwestern parts of Guangzhou, where a coal-fired power plant was located[31]. Besides, As also has high loads in PC3, while agricultural source contribute to As. APCS-MLR can not identify agricultural source, it combined the industrial source and agricultural source into one source, that is, industrial source. Therefore, PC3 represents the industrial source.

### 3.3 Results of PMF

The method of PMF is used to analyze 208 soil samples, and the results of source profiles and source contributions of heavy metals are shown in Figure 1. Figure 1 shows that the main loading elements of factor 1 are Ni, Cr, and Cu. The average concentrations of these heavy metals are not high, close to the background values, as shown in Table 1. Parent material is the main source of Cu, Cr, and Ni. Therefore, factor 1 represents a natural source.

The main loading element of factor 2 are Pb, Zn and As. The hotspots of high concentrations are concentrated near main roads and in urban area with highly dense population and vehicle[31]. Generally, element Pb mainly comes from automobile exhaust emissions[32]. Element As is a mainly marker of oil leakage, rubber tire wear, motor vehicle parts wear, asphalt or cement pavement wear, etc.[33-34]. Therefore, factor 2 represents the traffic source.

The main loading element of factor 3 is Hg. The average concentration of Hg in investigated area is highest. Hg is typically emitted from a mixture of industry sources, including coal-fired power production, mineral ore, petroleum refining, and electroplating. The high concentrations of Hg are mainly distributed in the circumjacent area of a coal-fired power plant. Therefore, factor 3 represents the industrial source.

The main loading elements of factor 4 are Cd and As. The two heavy metals have high enrichment levels, suggesting that they may come from anthropogenic inputs. Cd and As are commonly found in fertilizers and pesticides and Cd is usually considered as marker element of agricultural activities[35]. Agrochemicals, fertilizers and pesticides containing inorganic compounds and minerals are usually the main sources of Cd and As in agricultural soils. Long-term use of excessive amounts of fertilizers and pesticides result in Cd and As enrichment in topsoil. Based on the above discussion, factor 4 represents the agricultural source.

### 3.4 Results of UNMIX

For our data, the UNMIX method identifies four sources. The minimum of the decision coefficient $R^2$ is 0.85, higher than threshold value 0.8 required by the system. The minimum signal-to-noise ratio is 2.14, greater than the threshold of 2 required by the system. Therefore, the results show that the method is effective.

As shown in Figure 2, the contribution rate of source 1 to Hg is relatively high, indicating that source 1 mainly causes the accumulation of Hg. Wet sedimentation is the main form of mercury from atmosphere into soil. The main sources of sedimentation include coal burning from thermoelectricity generation, coal-fired heaters in enterprises, and mercury vapor in

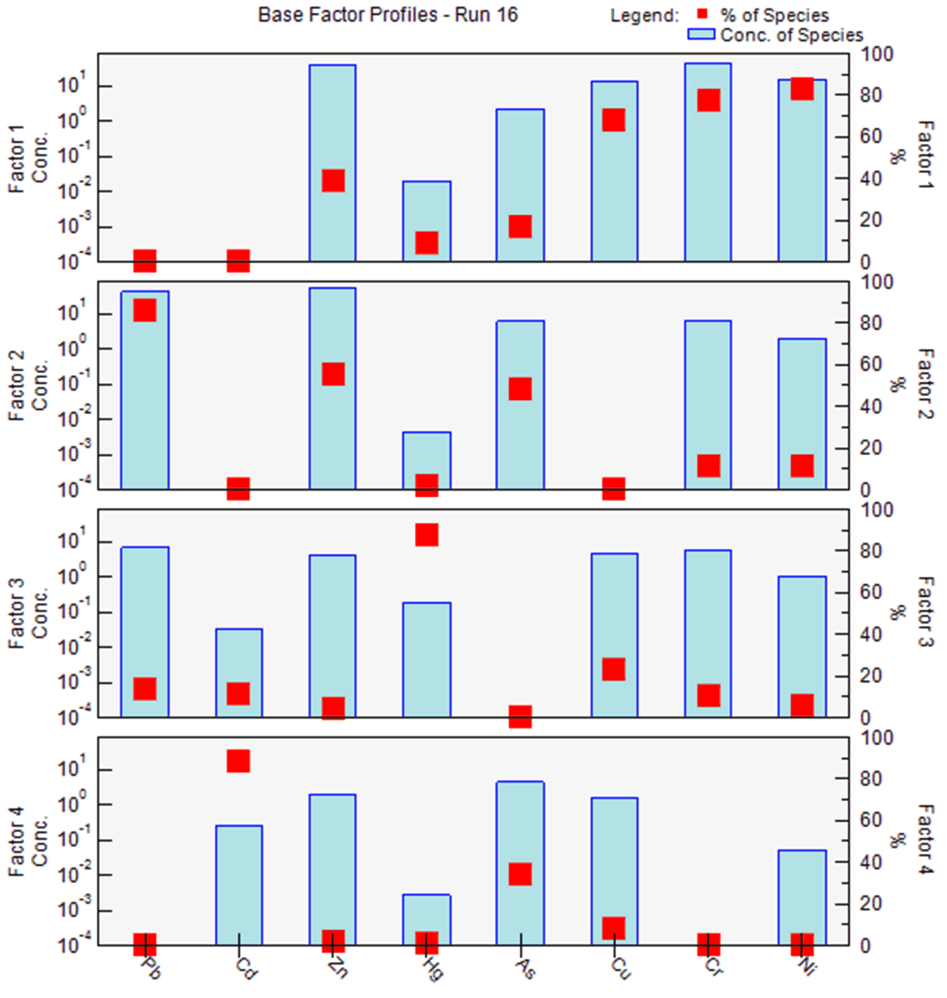


**Figure 1.** Source profiles and source concentrations of soil heavy metals from PMF.

the process of PVC production by calcium carbide method, etc. As shown in Figure 3, source 1 made greater contributions to sampling points numbered 139–153, and these sampling points are located in coal-burning agglomeration areas, so source 1 represents the industrial source.

The contribution rates of source 2 to Cd and As are high, indicating that source 2 mainly causes the accumulation of Cd and As. Nicholson et al. found that an important percentage of Cd contained in agricultural soils of England was due to manure application[36]. Pesticides or herbicide used in agriculture contain inorganic As compounds such as calcium arsenate, lead arsenate, sodium arsenate, thus, they may be an important source of As to soil. As shown in Figure 3, the source has relatively high contribution rates to sampling points numbered 146, 147, and 176, and these points are located in agricultural intensive areas, which further verifies that source 2 represents the agricultural source.

Source 3 is the dominant source in Pb. Vehicle exhaust is one of the main sources of Pb in urban soil, and there is a positive correlation between traffic volume and Pb concentrations in surface soil[37]. As shown in Figure 3, source 3 made great contributions to sampling points numbered 141 – 171 and these points are concentrated in urban area with highly dense population and vehicle. Therefore, source 3 represents the traffic source.

Source 4 has a large contribution to Cu, Cr and Ni, which is mainly related to the formation process of the parent material of soil. As shown in Figure 3, the investigated area has a similar contribution rate to each sampling point, so source 4 represents the natural source.

### 3.5 Comparison of APCS-MLR, PMF and UNMIX results

Three methods, i. e. APCS-MLR, PMF, and UNMIX, are employed for source apportionment, and the numbers of identified pollution sources are different. Figure 4 shows a comparison of the contributions of different sources by three methods. According to results

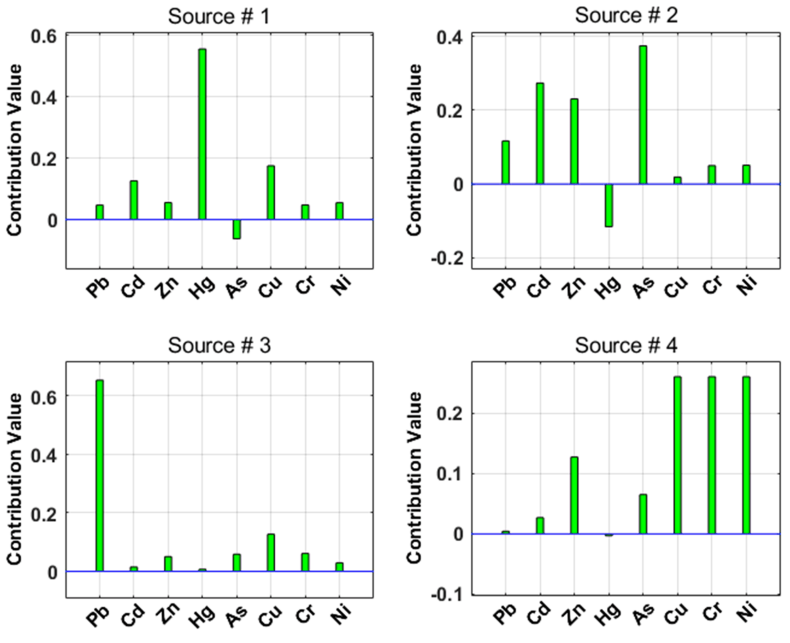


**Figure 2.** Source profiles of soil heavy metals from UNMIX.

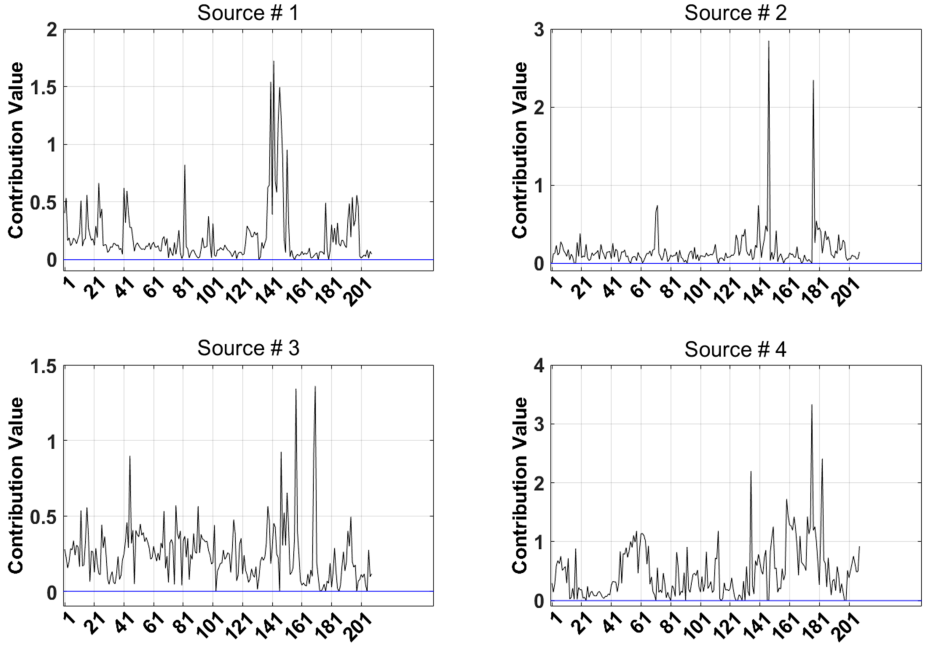


**Figure 3.** Contributions of different sources to each sampling point.

of APCS-MLR, natural background, traffic, and industry are the three sources of heavy metals pollution in soil in Guangzhou. The three sources contribute 41.8%, 33.4%, and 24.8% of the pollution, respectively. Compared with APCS-MLR, PMF and UNMIX obtain four pollution sources, which include a natural source, a traffic source, an industrial source, and an agricultural source. For PMF, the contribution rates of natural sources, traffic activities, industrial activities, and the agricultural activities are 42.3%, 23.7%, 15.3%, and 18.7%, respectively. Meanwhile, for UNMIX, the four sources contribute 44.3%, 18.5%, 14.9%, and 22.3% of the pollution, respectively. The natural source accounts for the largest proportion for the three methods. Therefore, the main pollution source of heavy metals in Guangzhou soil is from nature.

Results of PMF and UNMIX are similar. The two methods yield the same main load elements on each corresponding source, but there is a subtle difference in the identification of the source type. For instance, the

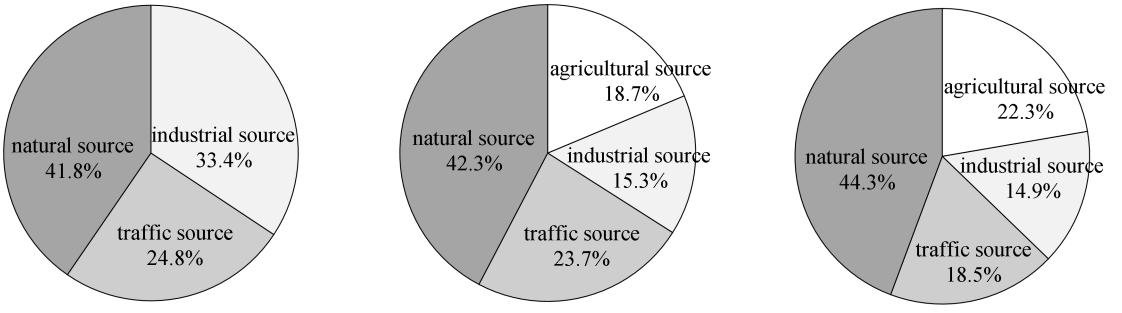


**Figure 4.** Estimated average source contribution (%) for three receptor models.

load elements of factor 2 by PMF are Pb, Zn and As, while the load element of source 3 by UNMIX is only Pb. Wang found that Zn is the main component of tire rubber, and tire wear and rubber debris are the main sources of Zn in soil[38]. It is believed that Zn in soil mainly comes from tire wear of road vehicles. Therefore, PMF is more reasonable than UNMIX in this investigation.

APCS-MLR, PMF and UNMIX yield different results for source identification and apportionment of heavy metals in the soil, which is directly related to the factorization calculation process of the three methods. Although the three methods share the basic principle of least squares, there are obvious differences in the calculation processes. APCS-MLR uses singular value decompositions (SVD) to obtain loading and scoring. Usually, factors with eigenvalue greater than 1 and cumulative variance contribution greater than 75% are selected as main component factors[39]. PMF and UNMIX methods use the non-negative restriction, meaning that negative results would not be obtained. PMF is based on point-by-point estimation of the uncertainty error of the data set, while UNMIX can automatically remove outliers.

## 4 Conclusions

In this work, we applied APCS-MLR, PMF and UNMIX for identification of pollution source and the apportionment of heavy metals in the soil of Guangzhou. The three methods yield consistent results. In the investigated area, APCS-MLR, PMF and UNMIX all identify three major pollution sources, among which natural sources contribute the most with relative contribution rates of 41.8%, 42.3% and 44.3%, respectively. The relative contribution rates of industrial source by APCS-MLR, PMF and UNMIX methods are 33.4%, 15.3% and 14.9%, respectively. The relative contribution rate of traffic source is the least, and the results calculated by APCS-MLR, PMF and UNMIX method are 24.8%, 23.7% and 18.5% respectively. Besides, APCS-MLR fails to identify the agricultural source, while PMF and UNMIX succeed and the contributions rates are 18.7% and 22.3%, respectively. The overall performance of PMF is better in this investigated area.

Through the comparison and verification analysis of these three receptor models, the reliability of the source analysis results is improved, and our understanding of the receptor models is deepened. In addition, these results will provide more information on the major emission sources in Guangzhou, and are a necessary prerequisite for controlling pollution sources and improving regional environmental quality.

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## Conflict of interest

The authors declare no conflict of interest.

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# 广州市土壤重金属元素源解析:三种受体模型的比较

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**摘要**: 受体模型是识别特定污染物来源和定量估计每种污染源贡献的有效工具. 为了分析广州市主要城区土壤中铅(Pb)、镉(Cd)、锌(Zn)、汞(Hg)、砷(As)、铜(Cu)、铬(Cr)、镍(Ni)8 种重金属的含量、分布及来源,采集了广州市主要城区 208 个表层土壤样本. 通过 APCS-MLR、PMF 和 UNMIX 3 种受体模型对土壤中重金属的潜在源进行了研究. 结果表明:8 种重金属元素的平均浓度均高于相应的背景值浓度,其中 Cd 的浓度几乎是其背景值的 5 倍. 三种受体模型均识别出三种污染源,即自然源、交通源和工业源. 但 PMF 和 UNMIX 模型还能识别出一个农业源,可以更好地区分不同类型的污染源. 此外,将三种受体模型的结果进行比较,发现各潜在污染源的源识别类型和源贡献均存在差异. 最终可得知: PMF 方法更适合本研究. 由此一般也建议采用多种受体模型来确定来源分配. 研究结果可为地方政府控制和管理污染,更好地保护重要土壤质量提供参考.

**关键词**: 重金属;APCS-MLR 模型;PMF 模型;UNMIX 模型;源解析