Geochemical baseline determination and contamination of heavy metals in the urban topsoil of Fuxin City, China postprint

Authors: ZHANG Hua, YU Miao, XU Hongjia, WEN Huan, FAN Haiyan, WANG Tianyi, LIU Jiangang, LIU Jiangang

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Abstract

Urban topsoil is the most frequent interface between human society and natural environment. The accumulation of heavy metals in the urban topsoil has a direct effect on residents' life and health. The geochemical baseline of heavy metals is an objective description of the general level of heavy metals in the urban topsoil. Meanwhile, the determination of geochemical baseline is necessary for regional environmental management, especially in coal cities prone to heavy metal pollution. Heavy metal pollution has become an environmental problem in Fuxin City, China for a long time. To establish the geochemical baseline of heavy metals in the topsoil of Fuxin City and to evaluate the ecological risk of the topsoil, we collected 75 topsoil samples (0–20 cm) and analyzed the concentrations of Cu, Ni, Zn, Pb, Cr, Cd, Hg and As through X-ray fluorescence spectrometry, atomic absorption spectrometry and inductively coupled plasma optical emission spectrometry. We determined the geochemical baseline of heavy metals in the topsoil of Fuxin City by using iteration removal, box-whisker plot, cumulative frequency curve and reference metal normalization; evaluated the contamination risk and ecological risk of the topsoil by using the baseline factor index, Nemerow index and Hakanson potential ecological risk index; and identified the source category of heavy metals in the topsoil by using a pedigree clustering heatmap. Results showed that the geochemical baseline values were 42.86, 89.34, 92.23, 60.55, 145.21, 0.09, 0.08 and 4.17 mg/kg for Cu, Ni, Zn, Pb, Cr, Cd, Hg and As, respectively. The results of Nemerow index and Hakanson potential ecological risk index indicated that the urban topsoil in the study area was slightly contaminated and suffering low potential ecological risk. The main contaminated areas dominated in the middle part and northeast part of the study area, especially in the western Haizhou Strip Mine. The result of baseline factor index indicated that Hg and Cd were the major pollution elements. Using a pedigree clustering heatmap, we divided the sources of these heavy metals into three types: type I for Ni and Cr, largely represented the enrichment of heavy metals from natural sources; type II for Cu, Pb, Zn, Cd and As, mainly represented the enrichment of heavy metals from anthropogenic sources; and type III for Hg, represented the form of both natural and anthropogenic inputs.

Full Text

Abstract

Urban topsoil represents the most frequent interface between human society and the natural environment. The accumulation of heavy metals in urban topsoil directly affects residents' lives and health. The geochemical baseline of heavy metals provides an objective description of the general concentration level of heavy metals in urban topsoil, and its determination is essential for regional environmental management, particularly in coal cities prone to heavy metal pollution. Heavy metal pollution has long been an environmental concern in Fuxin City, China. To establish the geochemical baseline of heavy metals in Fuxin' s topsoil and evaluate associated ecological risks, we collected 75 topsoil samples (0-20 cm depth) and analyzed concentrations of Cu, Ni, Zn, Pb, Cr, Cd, Hg, and As using X-ray fluorescence spectrometry, atomic absorption spectrometry, and inductively coupled plasma optical emission spectrometry. We determined the geochemical baseline using iteration removal, box-whisker plots, cumulative frequency curves, and reference metal normalization; assessed contamination and ecological risks using the baseline factor index, Nemerow index, and Hakanson potential ecological risk index; and identified heavy metal source categories via pedigree clustering heatmap analysis. Results showed baseline values of 42.86, 89.34, 92.23, 60.55, 145.21, 0.09, 0.08, and 4.17 mg/kg for Cu, Ni, Zn, Pb, Cr, Cd, Hg, and As, respectively. Nemerow and Hakanson indices indicated that urban topsoil in the study area was slightly contaminated with low potential ecological risk. Contaminated areas were concentrated in the middle and northeastern parts of the study area, particularly in the western Haizhou Strip Mine. Baseline factor index results identified Hg and Cd as the major polluting elements. Pedigree clustering heatmap analysis divided heavy metal sources into three types: Type I (Ni and Cr) primarily representing natural enrichment; Type II (Cu, Pb, Zn, Cd, and As) mainly representing anthropogenic enrichment; and Type III (Hg) representing mixed natural and anthropogenic inputs.

Keywords: heavy metals; urban topsoil; geochemical baseline; contamination index; pedigree clustering heatmap

Introduction

The geochemical baseline provides crucial information about both original geological background and anthropogenic disturbance effects, with important applications in regional topsoil pollution studies and environmental change trend prediction [?, ?, ?, ?, ?, ?, ?]. The concept of a generalized geochemical baseline was first introduced in the 1970s [?, ?]. After more than two decades of development, geochemical baseline research has gained widespread attention, with consensus emerging on unifying the baseline concept, deepening theoretical understanding, and identifying influencing factors [?, ?, ?]. Systematic surveys and mapping of regional geochemical baselines have been developed concurrently [?, ?, ?, ?, ?, ?]. Following geochemical mapping projects in European countries, China launched a multi-objective regional geochemistry survey in the early 1990s, initiating large-scale nationwide research that established geochemical foundations across various regions [?, ?]. These results remain in use and continue to have far-reaching impacts.

In recent years, increasing attention has focused on promoting the practical application of geochemical baseline principles, extending research to basin environments, river water quality, atmospheric dust, farmland soil, urban topsoil, and other landscape areas, making it a crucial component of global change research [?, ?, ?, ?, ?]. As geochemical baseline research deepens and expands, new questions continuously emerge: Are laws obtained from previous large-scale studies applicable to small-scale areas? Are common methods suitable for all objects? These issues remain in the exploratory stage and require further investigation.

As a typical mining city with abundant mineral resources, Fuxin City has experienced nearly 50 years of continuous mining. Due to backward technology and extensive mining methods, resource depletion and environmental damage have occurred, with environmental risks from frequent mining activities not fully assessed. Establishing the geochemical baseline can currently provide guidance for environmental management and serve as a benchmark for evaluating industrial development sustainability. Urban topsoil represents the most important interface for material and energy exchange, and its geochemical baseline level carries significant environmental implications.

Most existing studies on the topsoil environment in this area have focused on heavy metal pollution in mining areas [?, ?, ?, ?, ?, ?], while research on urban topsoil geochemical baselines remains limited. Therefore, this study employed four common methods—iterative removal, box-whisker plots, cumulative frequency curves, and reference metal normalization—to determine the geochemical baseline of Fuxin City' s urban topsoil. We subsequently used the baseline factor index, Nemerow index, and Hakanson potential ecological risk index to evaluate ecological risks, and briefly analyzed heavy metal source classification using a pedigree clustering heatmap. These findings will enhance understanding of topsoil quality in Fuxin City and provide fundamental data support for future environmental protection policies.

Study Area

Fuxin City is located in northwestern Liaoning Province, China (41°41 -42°56 N; 121°01 -122°56 E), adjacent to the Horqin Sandy Land in the north, the Liaohe River in the southeast, and the Nulu' erHu Mountain in the west. The terrain is higher in the northwest and lower in the southeast [?, ?]. Fuxin belongs to a semi-humid and semi-arid continental monsoon climate zone, with an annual average temperature of 8.6°C and average annual precipitation of 565.6 mm. The dominant wind direction is southwest in summer and northwest in winter, with an average wind speed of 2.8 m/s. Sampling plots in Fuxin' s main urban area covered the Xihe, Haizhou, and Taiping districts, totaling 176.0 km^2 [Figure 1: see original paper].

Sampling and Analysis

Following the Technical Specification for Soil Environment Monitoring [?, ?], we collected topsoil samples from Fuxin' s main urban area in August 2018. Sampling points were distributed according to land type, population density, and intensity of human activity [Figure 1: see original paper]. At each site, we collected one topsoil sample from 0–20 cm depth and four replicated samples within a 5 m × 5 m grid. After removing animal and plant debris, the five soil samples were mixed evenly, and approximately 1 kg of the composite sample was stored in a polyethylene sealing bag. A total of 75 samples were collected, with 15 samples from each functional zone including traffic, industrial mining, commercial, residential, and green space areas.

In the laboratory, topsoil samples were naturally air-dried, crushed, sieved through a 2-mm mesh, and prepared for pressing slices or acid digestion (using a mixture of HNO_3, HF, and $HClO_4$). Concentrations of Al, Fe, Ti, Rb, Cu, Ni, Zn, Pb, and Cr were measured by X-ray fluorescence spectrometry (ZSX Primus II, Tokyo, Japan). Arsenic concentration was measured by atomic absorption spectrometry (Hitachi Z2000, Beijing, China), while Hg and Cd concentrations were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, PE, USA).

Methods

Geochemical Baseline Value

Four methods were used to determine geochemical baseline values, with the arithmetic average of results considered as the final value.

Box-whisker plot method: This effective approach calculates baseline values using minimum, first quartile, median, third quartile, and maximum values. The process involves successively eliminating outliers beyond 1.5 times the interquartile range, with the median of remaining data considered as the geochemical baseline value.

Iteration removal method: This method employs double-standard deviation to quantitatively determine baseline values [?, ?]. For normally distributed data, outliers beyond $±2*standarddeviations*(±$2s) are successively removed until no outliers remain, with the arithmetic mean of remaining data used as the baseline value. For log-normally distributed data, a natural logarithm transformation is applied before identical processing.

Cumulative frequency curve method: This approach plots heavy metal concentration on the abscissa and cumulative distribution frequency on the ordinate [?, ?, ?, ?]. Typically, one or two inflection points indicate outlier limits. To locate inflection points, consecutive linear fitting is applied. As high-concentration samples are included in fitting, inflection points are identified under a linear model with $R^2 > 0.95$ and $P < 0.05$. When only one inflection point exists, baseline value is calculated using all data points below it. With two inflection points, the curve shape between them determines which data participate in computation: if the middle segment resembles the forepart, data before the lower inflection point are used; if it resembles the following part, data before the upper inflection point are used. The average of selected data is considered the geochemical baseline value.

Reference metal normalization method: This method establishes a correlation equation between active and inert elements [?, ?, ?]:

$$C_m = a \cdot C_i + b$$

where C_m is the active element concentration (mg/kg), C_i is the inert element concentration (mg/kg), a is the regression coefficient, and b is the constant. A suitable reference element is fundamental to this method. Many studies have used Al, Fe, Ti, Rb, Li, and V as normalizers [?, ?, ?]. In this study, Al, Fe, Ti, and Rb were evaluated as candidates, with the optimal normalizer selected based on the most significant correlation coefficient. Samples outside 95% confidence intervals were iteratively eliminated until no outliers remained, finalizing regression parameters a and b. The geochemical baseline value was then calculated by substituting the average inert element concentration into the equation.

Contamination Index

Baseline factor index: This index reflects element contamination degree [?, ?]:

$$P_i = \frac{C_i}{B_i}$$

where P_i is the contamination index for heavy metal i, C_i is the polluted element concentration (mg/kg), and B_i is the theoretical baseline value (mg/kg). Contamination grades are: $P_i \leq 1.20$ (no contamination), $1.20 < P_i \leq 1.50$ (slight contamination), $1.50 < P_i \leq 2.00$ (moderate contamination), and $P_i > 2.00$ (heavy contamination).

Nemerow index: This index evaluates comprehensive contamination of multiple heavy metals, emphasizing the most contaminated element [?, ?]:

$$P_N = \sqrt{\frac{P_{ave}^2 + P_{max}^2}{2}}$$

where P_N is the Nemerow index for the nth sample, P_{ave} is the average P_i index, and P_{max} is the maximum P_i index. Classification criteria are: $P_N < 0.70$ (safety), $0.70 \leq P_N < 1.00$ (precaution), $1.00 \leq P_N < 2.00$ (slight contamination), $2.00 \leq P_N < 3.00$ (moderate contamination), and $P_N \geq 3.00$ (serious contamination).

Hakanson potential ecological risk index: This classic method assesses heavy metal threats by simultaneously considering concentration, ecological effects, environmental effects, and toxicological influences [**?**, **?**]:

$$RI = \sum_{i=1}^{n} E_i = \sum_{i=1}^{n} (T_i \cdot P_i)$$

where RI is the Hakanson potential ecological risk index, E_i is the potential toxicity index for heavy metal i, and T_i is the toxic response factor. Toxicity coefficients are 5 for Cu, 5 for Ni, 1 for Zn, 5 for Pb, 2 for Cr, 30 for Cd, 40 for Hg, and 10 for As [**?**, **?**]. Risk grades are: $RI < 150$ (low ecological risk), $150 \leq RI < 300$ (moderate ecological risk), $300 \leq RI < 600$ (considerable ecological risk), and $RI \geq 600$ (serious ecological risk).

Pedigree Clustering Heatmap

The pedigree clustering heatmap is a visual multivariate statistical method that performs hierarchical clustering on data matrices along reordered columns and rows, displaying results as a heatmap with dendrogram. This clustering makes groups with similar or different expression values easily visible [**?**, **?**]. In this study, the "heatmap with dendrogram" plugin in OriginLab 2018 software was used to analyze heavy metal sources. Based on a selected color key, inputted heavy metal concentrations were automatically standardized and color-coded. Smaller cluster distances indicate higher similarity between objects. Average Euclidean distance and Ward Euclidean distance were employed to measure distances among eight heavy metals and among 75 samples, respectively.

Results

Concentrations of Heavy Metals

Results showed that Ni concentration was normally distributed, while the other seven heavy metals followed log-normal distributions . Except for As, mean concentrations of all elements exceeded Liaoning Province background values. Notably, the maximum Cr concentration reached 1095.4 mg/kg, nearly 20 times the background value, while the maximum Hg concentration was 0.64 mg/kg, approximately 17 times the background value. The mean concentrations of eight heavy metals divided by corresponding Liaoning Province background values increased in the order: As < Cd < Zn < Cu < Hg < Cr < Pb < Ni. Additionally, heavy metal concentrations showed strong variations, with coefficients of variation (CVs) for As, Zn, Cr, Hg, and Cd exceeding 50.0%. Particularly, CVs for Hg and Cd were 93.8% and 132.1%, respectively. High spatial variation in these elements suggested point source pollution influenced by human activities, especially for Cd and Pb in traffic areas. Concentrations and CVs of Cu, Zn, and Hg in industrial mining areas were higher than in other functional areas. Similarly, CVs of Hg and Zn were higher in commercial and residential areas. Differences in heavy metal concentrations among functional areas primarily reflected the intensity or frequency of industrial activities and power generation. Although Zn concentration was slightly lower in green space areas, Cr concentration was higher, possibly attributable to human activities such as industrial wastewater discharge.

Geochemical Baseline Values

The box-whisker plot for eight heavy metals in Fuxin City topsoil is shown in Figure 2 [Figure 2: see original paper]. After repeated outlier removal, baseline values calculated by this method were 42.34, 92.33, 86.77, 60.80, 141.63, 0.08, 0.07, and 4.95 mg/kg for Cu, Ni, Zn, Pb, Cr, Cd, Hg, and As, respectively. Using the iterative removal method, baseline values were 42.08, 87.35, 88.82, 63.56, 137.69, 0.08, 0.07, and 3.58 mg/kg for the same elements.

Cumulative frequency curves for the eight heavy metals showed single inflection points for Cu, Hg, and As [Figure 3: see original paper]. Sample points participating in baseline calculation accounted for 87.5% and 85.0% of data for Cu and As, respectively, but only 44.4% for Hg, suggesting consistent accumulation trends for Cu and As but abnormal contamination for Hg. Baseline values for Cu, Hg, and As calculated using samples below the inflection point were 42.08, 0.06, and 3.87 mg/kg, respectively. Ni, Zn, Pb, Cr, and Cd showed two inflection points, with curve shapes between inflections similar to those after the upper outlier. Therefore, baseline values for these five elements were calculated as 84.62, 87.87, 58.73, 140.01, and 0.09 mg/kg using data before the upper outlier. Final baseline values from this method were 42.08, 84.62, 87.87, 58.73, 140.01, 0.09, 0.06, and 3.87 mg/kg for Cu, Ni, Zn, Pb, Cr, Cd, Hg, and As, respectively.

For reference metal normalization, correlation analysis between active and inert elements yielded correlation coefficients . Using significance criteria ($P < 0.01$), optimal normalizers were identified as Ti-Cu, Fe-Ni, Al-Zn, Ti-Pb, Fe-Cr, Al-Cd, Al-Hg, and Ti-As. Linear regressions for eight active elements on reference elements were performed after iteratively eliminating samples outside 95% confidence intervals. New linear equations for predicting baseline values were established . Substituting average reference element concentrations into these equations yielded baseline values of 44.93, 93.06, 105.47, 59.09, 161.51, 0.11, 0.10, and 4.25 mg/kg for Cu, Ni, Zn, Pb, Cr, Cd, Hg, and As, respectively.

The arithmetic average of results from the four methods was considered the final value. Consequently, final geochemical baseline values for Fuxin City urban topsoil were 42.86, 89.34, 92.23, 60.55, 145.21, 0.09, 0.08, and 4.17 mg/kg for Cu, Ni, Zn, Pb, Cr, Cd, Hg, and As, respectively . Among the eight heavy metals, baseline values for Cd and As were lower than Liaoning Province background values, while baseline values for the remaining metals were significantly higher. Baseline values for Ni, Pb, and Cr were nearly triple the background values, while those for Cu, Hg, and Zn were approximately double, indicating serious heavy metal accumulation. Comparison with other resource-oriented cities showed that Ni, Pb, and Cr concentrations were higher in Fuxin City, while Cd and As were lower than in most other cities. Cu, Zn, and Hg concentrations were similar to those reported elsewhere , suggesting that differences among resource-oriented cities are relatively obvious and likely related to economic activity.

Contamination Assessment

In this study, P_i, P_N, and RI were used to assess contamination levels and potential risks in Fuxin City' s urban topsoil. P_i values for Cu, Ni, Zn, Pb, Cr, Cd, Hg, and As ranged from 0.47–3.65, 0.43–2.32, 0.44–5.53, 0.46–2.79, 0.52–7.54, 0.23–13.23, 0.39–8.31, and 0.18–2.02, respectively. Mean P_i values decreased in the order: Hg (1.46) > Cd (1.45) > Zn (1.17) > Cr (1.12) > Cu (1.05) > As (1.04) > Pb (1.03) > Ni (1.02) [Figure 4: see original paper]. According to grading criteria, P_i values of 1.20–1.50 indicate slight contamination, while values <1.20 suggest minimal enrichment. Among the eight heavy metals, Hg and Cd were identified as major pollutants causing slight contamination, while other metals showed minimal contamination. However, some P_i values for Cd, Hg, Cr, and Zn exceeded 2.00, with maximum values of 13.23 for Cd and 8.31 for Hg, indicating severe contamination likely from anthropogenic point sources.

Comparison of mean P_i values across functional areas revealed that P_i values for Cd, Hg, Cu, Zn, Pb, and As—especially Cd and Hg—were highest in traffic and industrial mining areas, likely resulting from high-intensity human productive activities. In contrast, commercial and residential areas showed relatively low P_i values. In green spaces, Ni and Cr enrichment was higher than in other functional areas, suggesting different pollution sources than for Cd and Hg.

P_N values for 75 samples ranged from 0.80 to 9.56, with a mean of 1.96 . Although classified as slight contamination, the mean P_N was close to 2.00. Some samples were evaluated as seriously contaminated, indicating relatively obvious heavy metal enrichment, particularly in traffic areas ($P_N = 2.93$) and industrial mining areas ($P_N = 2.04$).

RI values varied between 56.63 and 483.98, with a mean of 131.54 , indicating low potential ecological risk overall. However, 76.0% of samples showed low potential risk, 17.3% moderate risk, and 6.7% considerable risk. Most contaminated samples were located in traffic areas ($RI = 186.78$) and industrial mining areas ($RI = 148.22$), followed by commercial areas. Residential and green space areas showed the lowest ecological risk.

Spatial distributions of P_N and RI were similar, with high values in the middle and northeastern parts of the study area [FIGURE:5, FIGURE:6]. Specifically, the middle section of Meicheng Road (sample 12), located west of the Haizhou Strip Mine, was the most polluted ($P_N = 9.56$, $RI = 483.98$). Lower contamination was observed in the eastern section of Yulong Road (sample 60), the middle part of Xihe District (sample 54), and the region between Meicheng Road and Bayi Road, where over 70% of residents live and most economic activities (traffic emissions, coal combustion, industrial production, thermal power generation) occur, leading to mixed accumulation of multiple heavy metals. Additionally, a sample south of Yulong Lake was seriously contaminated ($P_N = 5.50$) but showed lower potential ecological risk due to anomalous Cr enrichment from anthropogenic activities, though Cr enrichment has low toxicity.

Pedigree Clustering Heatmap

Pedigree clustering heatmap analysis divided 75 samples into three groups at a Euclidean distance of 23.10: groups S-a, S-b, and S-c [Figure 7: see original paper]. Group S-a samples were characterized by high color key values for single or multiple elements, containing maximum values for Cu, Pb, Zn, Cd, Hg, and Cr, indicating abnormal heavy metal enrichment from human activities. Group S-b samples showed no significant differences in color key values, though As values were generally higher than other elements, suggesting nonpoint source As pollution. Group S-c samples, except for a few enriched in Ni and Hg, had low color key values, indicating minimal contamination.

The eight heavy metals were divided into three types at a Euclidean distance of 12.27 [Figure 7: see original paper]. Type I (Ni and Cr) showed low color key values except for a few isolated high values. Type II (Cu, Pb, Zn, Cd, and As) showed correlation among Cu, Pb, and Zn (average distance 9.68), which grouped with Cd and As (average distance 11.31), suggesting Cu, Pb, and Zn share homology with Cd and As. Color key values in this group reflected simultaneous enrichment of multiple heavy metals in some samples, likely from common anthropogenic sources. Type III (Hg) showed relationships with Type II at an average distance of 12.29 but formed an independent group at 12.27, indicating different clustering characteristics and tendency to pair with Type II at certain levels.

Discussion

Comparison of Geochemical Baseline Values Obtained from Different Methods

Heavy metal accumulation in urban topsoil has attracted considerable attention, particularly regarding the type and intensity of anthropogenic enrichment. However, ideal heavy metal standard reference values are often unavailable for specific areas due to limitations such as outdated timescales or mismatched spatial scales. Establishing an environmental geochemical baseline applicable to the study area is necessary for assessing urban topsoil quality and human impacts. Different methods may yield different baseline results. For example, iteration removal and box-whisker methods both eliminate outliers before calculating baseline values, but the former uses double-standard deviation and arithmetic mean, while the latter uses 1.5 times interquartile range and median. Therefore, if heavy metal concentration distributions are relatively concentrated, results should be similar; however, if distributions are discrete, baseline results will likely differ.

The cumulative frequency curve and reference metal normalization methods are more complex. The cumulative frequency curve method focuses on identifying abnormal enrichment, with the key step being inflection point determination, often considered the limit between different heavy metal sources. All sample data with concentrations below the inflection point participate in baseline calculation, including abnormally low values. Consequently, baseline values obtained by this method may be slightly lower than others. The reference metal normalization method, while reducing granularity effects, introduces reference elements into baseline calculations, and the concentration distribution of reference elements themselves influences results to some extent. Based on literature reports and this study' s results, baseline values obtained by this method are slightly higher than those from the aforementioned methods. Of course, differences among these four methods are also influenced by data dispersion; greater dispersion produces larger differences between results. Each method has its advantages, but the core processing concept involves eliminating outliers and locating the lower outlier limit. Therefore, actual research should employ multiple baseline determination methods simultaneously to greatly improve accuracy and usability of geochemical baseline values.

Indicative Significance of the Lower Limit of Abnormal Values

In geochemistry research, distinguishing the lower limit of abnormal values and calculating geochemical baseline or background accordingly is conventional for identifying heavy metal sources. However, using topsoil geochemical baseline as background and considering the lower abnormal value limit as the boundary between natural and anthropogenic sources is common practice. Although mathematical methods for determining baseline and background values are similar, the meaning of the lower abnormal value limit differs substantially. Topsoil geochemical baseline represents the ordinary concentration level of heavy metals, with its primary function being to establish a reference standard for heavy metal concentrations at sampling time. The "ordinary concentration level" premise involves eliminating abnormal enrichment—a key step in various baseline determination methods—where excluded abnormal values are considered anthropogenic disturbances [?, ?]. Remaining data involved in baseline calculation represent "natural concentration" almost without human effect, though some human influence may remain [?, ?].

In stable deposition layers or soil horizons, bottom samples have lower probability of human disturbance compared to top samples, making the lower abnormal value limit more reliable as a boundary between natural and anthropogenic sources [?, ?]. If significant concentration differences in topsoil are uncertain, the lower abnormal value limit only indicates the boundary between global and regional enrichment. Therefore, determining concentrations maintained without human disturbance is difficult. Precisely, if nonpoint source contamination from human activities exists, this portion of concentration—indistinguishable from the natural environment and not revealed as outliers—is extremely likely to be considered natural environmental concentration. Many topsoil geochemical baseline studies for different objects, particularly resource-based cities, have generally observed that baseline values for various heavy metals are significantly higher than earlier values [?, ?, ?, ?]. This study observed similar widespread multi-element accumulation, with concentration increases likely including this indistinguishable portion. Accordingly, not all lower abnormal value limits represent boundaries between natural and anthropogenic sources, particularly when topsoil is the experimental material.

Identification of Heavy Metal Contamination Sources

Since topsoil was selected as the study object, directly distinguishing heavy metal sources based on geochemical baseline values is inappropriate. Therefore, pedigree clustering heatmap analysis was used to classify and identify main source types. Among eight heavy metals, Ni and Cr formed one group. Few high-concentration samples were mostly distributed in green spaces and factory courtyards on the city' s fringe. The sample with maximum Cr concentration occurred in green space near the Municipal Infectious Disease Hospital south of Yulong Lake, possibly contaminated by chromium-containing medical materials. Soil composition at other sites consisted of coal ash backfill and excavation slag mixtures. Except for obviously human-impacted samples, most other samples showed little concentration variation, with slightly higher concentrations evenly distributed in fringe areas of the main urban zone, particularly underdeveloped northern and southern urban areas with low population density and minimal human disturbance. This indicates Ni and Cr enrichment is controlled not by social production activities but by regional geological conditions and soil parent materials. Moreover, Ni and Cr belong to the iron group elements and often show high correlation in soil, especially under strong adsorption by naturally formed soil colloids that facilitate enrichment [?, ?, ?]. Therefore, enrichment sources for this group are primarily natural (mixed with very few point source enrichments from human activities).

Cu, Pb, Zn, Cd, and As classified in the same group, indicating similar accumulation sources. Considering sample clustering, pollution evaluation, and ecological risk assessment results, some samples showed simultaneous enrichment in several of these five elements, primarily concentrated in central and northeastern parts of the main urban area where heavy metal pollution and potential ecological risks were most serious [FIGURE:5-7], suggesting these elements likely share common sources. These regions not only contain most of Fuxin City' s population but also concentrate various socioeconomic activities including industry, mining, commerce, manufacturing, and transportation, indicating enrichment mainly originates from anthropogenic activities. Specifically, economic activities such as coal washing, coal preparation, thermal power generation, chemical manufacturing, leather processing, and mining transportation related to Haizhou Strip Mine, plus mechanical processing and building materials processing in the city' s northeastern part, provide sources for Cu, Pb, Zn, and Cd enrichment. The old mining area in southern Xi River has caused large-scale As enrichment. Additionally, planting, animal husbandry, garbage incineration, and waste discharge have been confirmed to cause heavy metal accumulation [?, ?, ?, ?, ?, ?, ?].

Hg enrichment differed from other elements, with most contaminated samples distributed along the prevailing southwest-to-northeast wind direction. Hg accumulation is often closely related to coal and metal ore resources [?, ?, ?]. As a volatile liquid element, Hg enrichment direction aligns with prevailing wind direction when volatile [?, ?]. This suggests Hg enrichment is controlled by natural conditions to some extent. However, high concentration variability and serious contamination in some samples reflect significant human impact. Haizhou Strip Mine, once Asia' s largest strip mine, has a long history of coal-fired power generation and heating, providing an important Hg enrichment source. Human activities may contribute relatively more to Hg enrichment. Therefore, Hg enrichment sources represent mixed anthropogenic and natural inputs.

Additionally, contamination degrees in different functional areas of Fuxin City' s topsoil are relatively similar, differing from some non-resource-based cities. This phenomenon precisely reflects Fuxin City' s development characteristics as a coal-based city. Economic activities and urban expansion developed almost entirely around mining areas, resulting in nested functional areas with minimal differences in heavy metal contamination.

Conclusions

The geochemical baseline of urban topsoil is an important index representing topsoil environmental quality. As a typical coal city in a critical economic transformation period, Fuxin City' s topsoil environmental quality serves as a reference standard for evaluating whether transformation practices meet environmental friendliness criteria. Our results not only analyze current geochemical baselines of heavy metals in Fuxin City' s urban topsoil but also summarize accumulation trends, which can be divided into anthropogenic sources, natural sources, and mixed sources. Contamination and ecological risks from heavy metal accumulation were evaluated, identifying relatively low overall contamination risk in the study area, with spatial contamination characteristics dominated by the middle and northeastern parts, particularly west of the Haizhou Strip Mine.

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