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Environmental Magnetic Characteristics and Heavy Metal Pollution Assessment of Sediments in the Le'an River, China

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Abstract: Environmental magnetism parameters have become a useful tool in addressing environmental issues. Due to the rapid, sensitive, economical and non-destructive characteristics of environmental magnetism, the present contribution focuses on magnetism parameters as proxy for heavy metal pollution, especially from their relationship with contents of heavy metal. We evaluated heavy metals pollution and examined environmental magnetism in the Dexing section of the Le'an River. The pollution load index (PLI) of Cr, Pb, As, Cu and Zn, as well as the concentration of other heavy metals, were analyzed, and the magnetic indexes of various sediments were analyzed. The results showed that the concentrations of all heavy metals far exceeded the local background values, and that the average contamination factor of Cu was as high as 22.88, making it the element of most serious contamination. The problem of heavy metal pollution near the mine is very serious. The content of magnetic minerals in sediments of Le'an River is relatively high and the composition of magnetic minerals is relatively stable. The stable-single domin (SSD) content is high at S1 and S10, indicating that ferromagnetic mineral content is relatively rich here, which dominates the magnetic characteristics of the sample. In general, it was found that environmental magnetism indicators did not exist in the Dexing section of the Le'an River that could clearly indicate the concentration of heavy metal pollution. Only a few heavy metals can be effectively indicated by magnetic parameters. IRM_{-20mT} and S_{-ratio} can be used as indicators of Cr, Pb, As, Cu and Zn, but they are not accurate. The correlation between Sr and magnetic indexes IRM_{200mT}, IRM_{300mT}, SIRM, IRM_{-300mT} and HIRM is significant, which can be used as an indicator of Sr concentration. IRM_{20mT} can also be used as an indicator of Hg concentration.

Keywords: heavy metal pollution; Le'an River; magnetic properties; surface sediments

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Citation: Rong, S.; Wu, J.; Liu, J.; Li, Q.; Ren, C.; Cao, X. Environmental Magnetic Characteristics and Heavy Metal Pollution Assessment of Sediments in the Le'an River, China. *Minerals* **2023**, *13*, 145. https://doi.org/10.3390/min13020145

Academic Editor: Alexandra Courtin-Nomade

Received: 3 December 2022
Revised: 26 December 2022
Accepted: 9 January 2023
Published: 18 January 2023

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1. Introduction

Heavy metal pollution has always been an unavoidable topic accompanying economic development. With the acceleration of industrialization and urbanization, heavy metal pollution of the aquatic ecosystem has become a global problem of increasing concern Z [1]. Heavy industry is not only polluting through wastewater discharge, but also aggravating environmental pollution through the burning of fossil fuels and atmospheric deposition [2,3]. Rivers are one of the most sensitive continental environments. They respond to natural and anthropogenic disturbances through physical, chemical and biological changes that are basically recorded in sediments (sedimentary facies, geochemistry, microorganisms) [4]. As the sediments of many rivers around the world are contaminated with heavy metals to varying degrees, people are facing increasing threats to water security [5]. It is therefore an urgent task to develop a set of low-cost and sensitive procedures for the

detection and monitoring of water quality and thereby avoid heavy metal poisoning. The magnetic properties of sediments are influenced by the type, content and grain size of magnetic minerals, and can reflect a combination of information on the physical origin, transport patterns, level of diagenesis and human activity relating to the sediments [6]. Environmental magnetism is a relatively new discipline that originated in many interdisciplinary studies involving UK lake sediments, but one that has quickly developed into an archive that can identify past global changes [7], with the basic principle of relating the magnetic properties of mineral assemblages to the environmental processes that control them for the purpose of understanding sediment or soil formation processes [8].

The study of mineral magnetism is widely used in geo-scientific research, such as in reconstructing paleoclimates to adapt to the latest climate changes and environmental risks [9]. In addition, environmental magnetism can also characterize the composition of litho-units, and explore and describe sediment transport and sedimentary pathways, diagenesis and the natural variation of rocks, etc. [9–14]. However, until now, no studies have been conducted on the Le'an River using environmental magnetism methods for sediment source-to-sink analysis.

Environmental magnetism can be used as an indicator of heavy metals, because the presence of heavy metals in water may become fixed in stream sediments, participating in absorption, co-precipitation, formation of complexes, and co-adsorption with iron oxides and hydroxides or other particulate forms [15,16]. Thus, river sediments are not only major concentrations of heavy metals, but also potential secondary sources of pollutants in the water environment. Previous conventional geochemical methods for studying heavy metal contamination in sediments, while highly accurate and revealing the intensity and extent of contamination in the study area, are cumbersome, time-consuming and expensive, and are not suitable for large-scale contamination [1]. The use of environmental magnetism in environmental research was initiated by Oldfield [17]. After Oldfield pioneered this method, many scholars around the world began to use environmental magnetism measurements to replace and supplement the expensive and complex traditional chemical analysis [18–20].

Thompson and Oldfield studied the relationship between sediment magnetism and environmental processes, and the results showed that the surface soil in northern industrial areas would have higher susceptibility, which would be caused by the atmospheric deposition of magnetic particles generated by the combustion of fossil fuels [18]. Friedrich Heller et al. (1998) studied the environmental magnetism characteristics and sources of magnetic particles of forest surface soil in Upper Silesia, Poland. The study found that unusually strong soil susceptibility was not caused by natural causes, but by deposition of industrial dust and fly ash containing man-made magnetic particles [20]. High magnetic susceptibility values in forest topsoil are often accompanied by the presence of potentially dangerous heavy metals, such as Zn, Pb and Cd, as Strzyszcz suggested in 1993 [19]. Most studies have shown that magnetic measurements are promising and useful for identifying pollution types in contaminated areas.

The use of magnetic parameters as a proxy for quantifying heavy metal concentrations in river sediments has been demonstrated in recent years, with one study on suspended sediments showing a significant correlation between magnetic susceptibility and the heavy metal content of iron and zinc [8,21]. Magnetic susceptibility and saturation isothermal remanence can be used as indicators of heavy metal pollution in estuaries and deltas [6,22–25]. Zhang et al. found a substantial correlation between heavy metal concentrations and magnetic parameters in river sediments near an iron refinery in China [1]. These studies all suggest that magnetic indicators of sediment can be used as indicators of heavy metal contamination in some ranges. However, environmental magnetism methods are not suitable for the study of heavy metal contamination under all conditions. Knab et al., after studying the Vltava River (Czech Republic), demonstrated that the applicability of magnetic methods may be limited when the geologically genetic background shows major magnetic anomalies [26]. Stanislav et al. studied the magnetic, geochemical, and mineralogical characteristics of the sediments of karstic and flysch rivers (in Croatia and

Slovenia). They found that these rivers serve as local databases of natural magnetic susceptibility background values. However, the Celje area of Slovenia is heavily polluted due to mining, metallurgy and other activities, so the magnetic parameters are not of reference significance [27]. This indicates that the relationship between magnetic parameters and potentially toxic elements may not be generalized to all environments [4], so the correlation between local magnetic parameters and pollution indicators must be studied before using different environmental magnetism parameters as proxies for pollution indicators.

Located in the north of Jiangxi Province in China, the Le'an River is a major tributary of Poyang Lake, China's largest freshwater lake, and has important ecological, social, economic and recreational value [28]. The Le'an River is not only the main source of drinking water for local residents, but also the main source of water for industrial and agricultural activities in the area. Since the 1950s, many mines have been built in the area along the Le'an River, such as the Dexing copper mine (the largest copper mine in Asia), the Huaqiao gold mine and the Chung Shan coal mine. In addition, there are many sources of heavy metal discharges along the Le'an River, such as paper mills, chemical plants and non-ferrous metal smelters. The discharge of domestic sewage along the river makes many pollution indicators of the Le'an River exceed the standard. The pollution of heavy metal elements such as Zn, Cu and Pb turn the farmland downstream of Dexing Copper Mine into wasteland [29,30]. Even the bottom mud of Poyang Lake has a great negative impact [31]. Zhang J. et al. investigated the heavy metal pollution from non-ferrous metal mining and smelting activities along the Le'an River, and studied the distribution of heavy metals in the waterways of the area and the potential threat to the aquatic ecosystem. The study found that the waterways in the area had become heavily contaminated with heavy metals due to mining activities. The concentrations of Cu, Cd and As are all at high levels in the whole waterway and their sources are relatively complex [32].

In the current research on the Le'an River, most scholars only analyze the pollution status of the river by traditional chemical methods [5,28,33,34], and there are few studies on the indicator effect of heavy metal concentration by means of environmental magnetism. In this study, we carried out heavy metal contamination analysis and environmental magnetism analysis on the surface sediments of the Dexing section of the Le'an River to obtain the contamination status and environmental magnetism characteristics of the surface sediments and to explore the connection between them in order to obtain the connection between the local environmental magnetism parameters and geochemistry. The results of this study will provide an idea for seeking a low cost and high sensitivity heavy metal pollution monitoring technology in Le'an River. At the same time, the research results may provide solutions for alleviating the severe heavy metal pollution in Poyang Lake, and provide help to ensure the stable water supply for life, agriculture and industry in Dexing area.

2. Materials and Methods

2.1. Study Area

The Le'an River (116.5°~117.9° E, 28.7°~29.3° N) originates from the western foot of Huaiyu Mountain at the border of Jiangxi Province and Zhejiang Province; it is the upper main stream of Rao River, a tributary of Poyang Lake in Yangtze River Basin, with a total length of 279 km, a watershed area of 8989 km^2, an average annual runoff of 12.6 billion m^3, and the main tributaries include the Lianxi River, Fuchun River, Jishui River, Changle River, Jianjie River and Zhuxi River. The environmental condition of its water body affects the water body environment of Poyang Lake, the largest freshwater lake in China, and is of great significance for understanding the whole Poyang Lake basin. The Le'an River flows through the counties and cities of Wuyuan, Dexing, Leping and Boyang, and enters Poyang Lake at Longkou city. Geologically, the strata are well developed and distributed throughout the study area, except for the Silurian, Devonian and Tertiary [35], and the geological composition is mostly limestone. The climate of the study area is subtropical warm and humid monsoonal with an average annual temperature of about 17 °C and an

average annual rainfall of 1900 mm [5]. In this study, a portion of the middle section of the Le'an River within the city of Dexing was intercepted for analysis (Figure 1; Table S1).

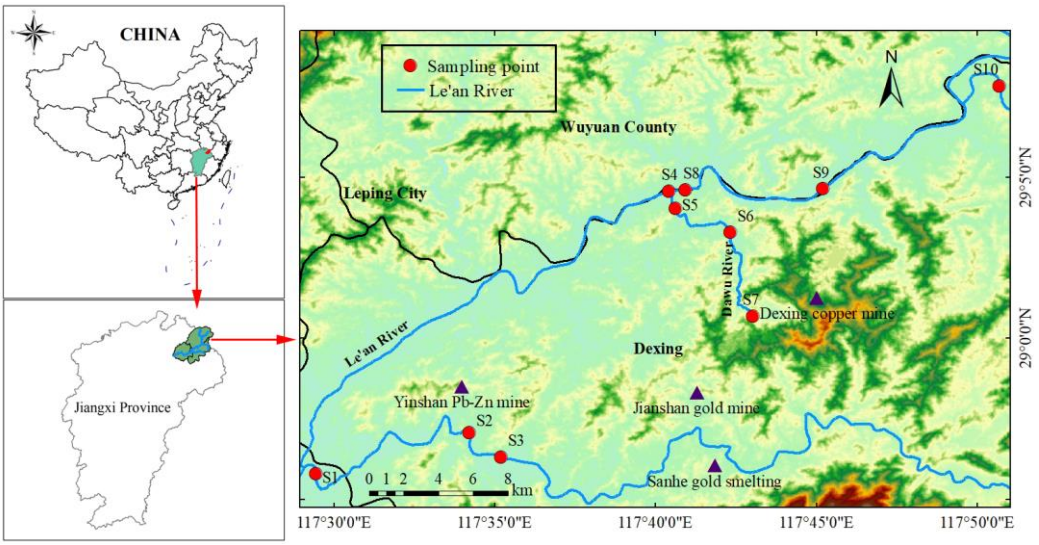


Figure 1. Study area and sampling sites of the Le'an River.

Jiangxi Province has superior metallogenic geological conditions and is extremely rich in mineral resources. There are 164 kinds of mineral resources found in China, 153 of which can be found in Jiangxi Province, with more than 5000 mineral producing areas. Among them are gold, silver, copper, tungsten, uranium, rare earth, and tantalum niobium; these seven metal ores occupy an important position in China and even the world. Le'an River is located in the northeast of Jiangxi Province. Adjacent to Le'an River, Dexing City has the largest open-pit copper mine in Asia, as well as dozens of large and small metal mines such as Jinshan Gold mine, Damaoshan Copper mine, Zhulin Gold mine, Toad gold mine, Huaqiao gold mine, Yinshan lead-zinc mine, Xijiang gold mine, Bashiyuan gold mine, Fujiawu Copper mine, Shibei Gold mine and Yuankeng Gold mine. Its mineral resources are rich and varied.

2.2. Sampling

A total of 10 surface sediment samples (S1 to S10) were collected from 1 to 7 December 2020 in the inner section of the Dexing boundary of the Le'an River, and the sampling points were located using the Global Positioning System (GPS) during the sampling process. The location of each sampling site is marked in Figure 1. As much as possible, samples were collected from the center of the river to avoid interference from organic matter. A Van Veen grab was used to collect sediment samples from the top 2 cm of the river bottom. Two samples were collected to measure the magnetic parameters and chemical elemental characteristics of the sediment respectively. After collection, the samples were packed in clean polythene bags and transported to the laboratory in a cooler at 4 °C.

2.3. Analyses

2.3.1. Magnetic Measurement

All samples were dried naturally in the laboratory, and the roots were removed, crushed with a wooden pestle and mortar passed through a 2 mm nylon sieve, and then weighed and wrapped tightly in plastic cling film and compacted in 10 cm^3 sample boxes dedicated to magnetism for testing. Magnetic field intensity was applied with an ASC IM-10 pulsed magnetizer (Sensor Co., State College, PA, USA) and isothermal remanent magnetization (IRM) values were obtained at room temperature with a Molspin Spinner Magnetometer (Molspin Co., Oxfordshire, UK). Positive magnetic fields of 20, 200 and 300 mT and negative magnetic fields of −20 and −300 mT were applied to the samples

successively to test the corresponding IRM. IRM_{20mT} (20 mT positive magnetic field for the corresponding isothermal remanent magnetization) was used to indicate the content of ferrimagnetic minerals, particularly multi-domain and pseudo-single-domain magnetic particles. $SOFT_{-IRM}$, HIRM and S_{-ratio} are obtained from the above measured parameters, respectively [18,36].

$$SOFT_{-IRM} = (SIRM - IRM_{-20mT})/2 \quad (1)$$

$$HIRM = (SIRM + IRM_{-300mT})/2 \quad (2)$$

$$S_{-ratio} = \frac{-IRM_{-300mT}}{SIRM} \quad (3)$$

In the formula, $SOFT\text{-}_{IRM}$ is soft isothermal remanent magnetization, which can indicate the ferromagnetic minerals content, Am^2/kg; SIRM is the saturation isothermal remanence, which has strong correlation with stable-single domain (SSD) magnetite concentration, Am^2/kg; IRM_{-20mT} is the isothermal remanent magnetization for the 20 mT negative magnetic field test, which can reflect the content of soft magnetic minerals, Am^2/kg; HIRM is hard isothermal remanent magnetization, which can estimate the content of antiferromagnetic minerals in the sample, Am^2/kg; IRM_{-300mT} is the isothermal remanent magnetization for the 300 mT negative magnetic field test, Am^2/kg; S_{-ratio} indicates the relative ratio of antiferromagnetic minerals to ferromagnetic minerals, with high values representing more ferromagnetic minerals.

2.3.2. Chemical Analysis

Samples used to measure heavy metal concentrations were removed from stones and other debris and then dried naturally at room temperature and used to measure heavy elemental content. Heavy metal content, such as Soil and sediment—Determination of mercury, arsenic, selenium, bismuth, antimony (HJ680-2013) and Soil and sediment—Determination of aqua regia extracts of 12 metals (HJ803-2016), were measured using the methods mentioned in the standards set by the People's Republic of China. Concentrations of As, Hg, Sb, Bi and Se were measured using atomic fluorescence spectrometry (AFS) following the method described by Dai and Wang et al. [6,37]. Concentrations of V, Sr, Ti, Cr, Mo, Ni, Zn, Pb and Cu were determined by inductively coupled plasma mass spectrometry (ICP-MS) following the method of Dai et al. [37,38].

Accuracy and precision were verified using certified reference materials from the National Oceanic Administration (GB 17378.5-2007) (Table S2). Data processing and quality control of the analysis was carried out according to the National Oceanic Administration's certified reference materials (GB 17378.2-2007). The analysis yielded recoveries of heavy metals that varied between 87.9% and 102%.

There are a number of methods used to determine the concentration of heavy metals in sediments, and, based on Bhuiyan et al. [39], we chose the pollution load index (PLI) to assess the pollution status of heavy metals in the study area, which is mathematically defined as [40]:

$$PLI = \sqrt[n]{\left(C_{f1} \times C_{f2} \times C_{f3} \times \ldots \times C_{fn}\right)} \quad (4)$$

$$C_f = Metal_{sample}/Metal_{background} \quad (5)$$

In this study, the concentration data of Cr, Pb, As, Cu and Zn were selected to calculate PLI, and the background values were chosen from the geochemical background values in sedimentary rocks (Table 1) [41]. When $PLI \leq 1$, there is no contamination; when $1 < PLI \leq 2$, moderate contamination; when $2 < PLI \leq 3$, strong contamination; when $PLI > 3$, extremely serious contamination.

Table 1. Geochemical background values in sedimentary rocks (mg/kg).

Elements	Cu	Zn	Pb	Cd	Cr	As
$Metal_{background}$	45	118	34	0.4	62	13

2.4. Analyses

SPSS software was used for statistical analysis of the data. Correlation analysis of heavy metal concentrations with magnetic parameters was performed using Pearson correlation analysis, with the significance level set at $p < 0.01$ (two-tailed).

3. Results and Discussion

3.1. Sediment Chemistry

The C_f and PLI values for the selected heavy metals (Cr, Pb, As, Zn and Cu) are shown in Figure 2. The maximum and minimum values for the different heavy metal concentrations at each point are shown in Table 2, and the C_f and PLI values can be seen in Table S3. As can be seen from Table 2, there is a great spatial variability in the spatial distribution of the concentrations of each heavy metal element, with the average value of each element far exceeding the average value of the sediment of the national water system and the background value of the sediment of the Le'an River, and this is most obvious in the case of Zn, which varies from 31.6 to 4260 mg/kg, with a difference of 135 times between the lowest and highest values. Based on the mean values of the pollution coefficients of various heavy metals, it can be concluded that the pollution levels are Cu > As > Zn > Pb > Cr, with all elements far exceeding the background values, especially Cu, with an average pollution coefficient of 22.88 and a maximum value of 74.67. The highest pollution coefficients of Pb, As and Zn are also above 30. As can be seen from Figure 2, the C_f values of Pb, As and Zn have more or less the same distribution trend at different points, reaching the maximum value at point S3. Although the distribution curve of C_f values of Cu and other heavy metals are not the same, they are also at the highest value at the S3 sampling point, because the sampling point S3 is located near the De Xing copper mine and Yin Shan Pb-Zn mine, so its heavy metal content is higher. From the PLI results, it can be seen that the pollution status of points S1 to S3 and S6 is extremely serious, which is mainly due to the fact that these points are located near various mines. Only two sites, S7 and S9, are free of pollution. These two sites are located in the upper reaches of the Le'an River, where the principal sources of heavy metal discharge and sewage discharge from domestic areas are located, so the river bottom sediment pollution is better. Overall, the pollution situation in the Le An River is getting worse along the river flow, and after reaching the peak, the pollution situation gradually recovers as the river self-purifies.

Combined with the special geographical location of Dexing section of Le'an River, the pollution sources of heavy metals can be identified. Cu and As are mainly from the mining activities of Dexing copper mine. The main sources of Pb and Zn are the mining and smelting activities in Yinshan lead-zinc mine, followed by the deposition of Pb and Zn elements by the activities of the Dexing Copper Mine and the urban pollution in the middle reaches. The Cr comes from the mining associated with Cr element in the mining area, as well as the compound effects of urban industrial activities, domestic sewage and traffic factors.

Table 2. Concentrations of heavy metals in sediment of different sampling section (mg/kg).

	Cr	Pb	As	Cu	Zn
Min	<3.0	11.7	11.1	38.8	31.6
Max	176	1200	802	3360	4260
Average	104.91	193.94	117.81	1029.68	846.47

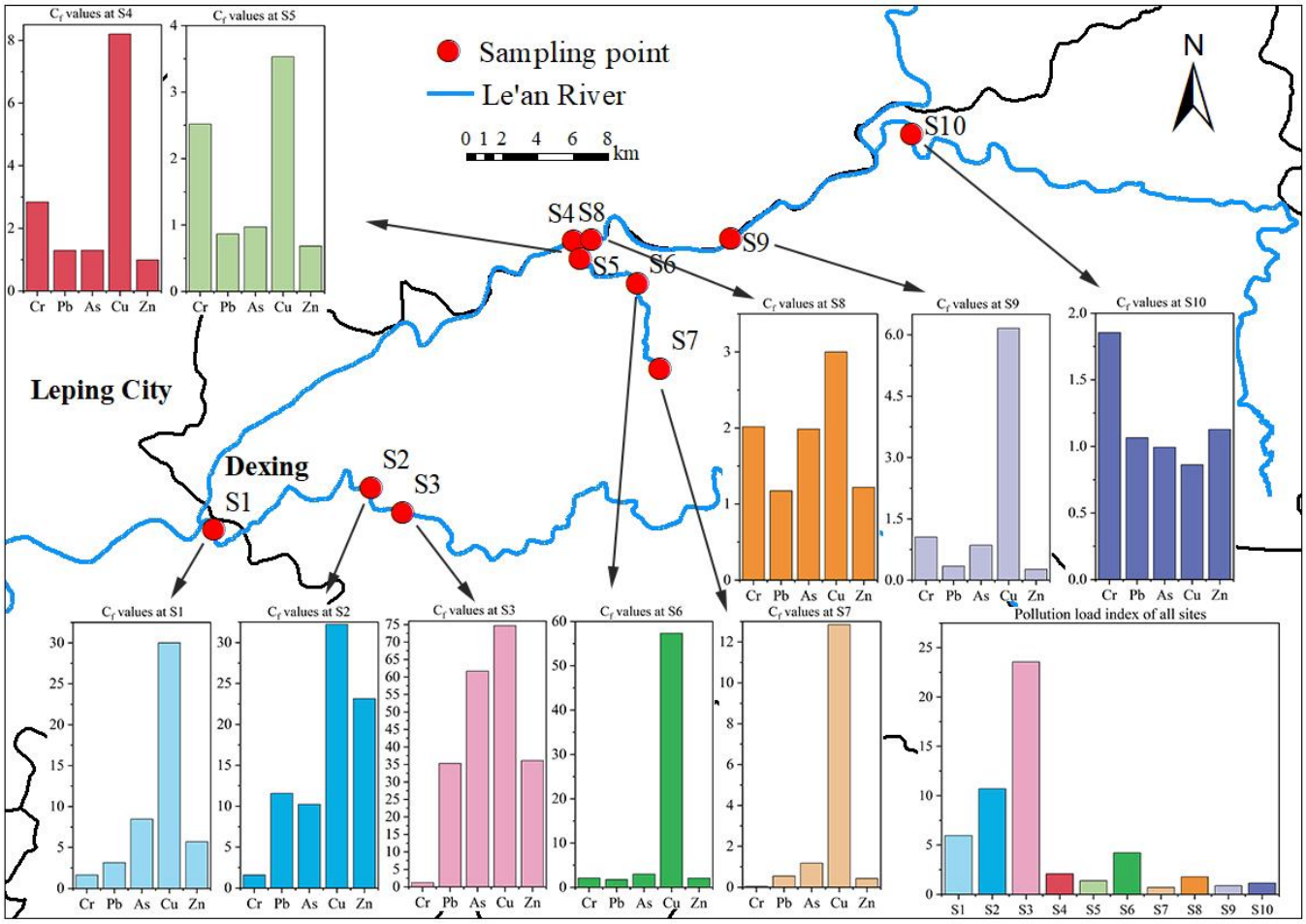


Figure 2. Comparison of C_f values and pollution load index (PLI) changes in sediments at various sampling sites in the Le'an River.

3.2. Sediment Magnetic Parameter

The IRM results obtained for the Le'an River sediments under the effect of positive magnetic fields of 20, 200 and 300 mT and negative magnetic fields of −20 and −300 mT are shown in Figure 3. From the figure it can be seen that the trend of IRM of the Le'an River sediments at different magnetic field strengths is the same, with higher values of IRM at each point as well as SIRM at points S1 and S10 at both ends of the river, with the IRM mainly indicating the soft magnetic fraction of the sample, suggesting that the sediment samples at points S1 and S2 are characterized by soft magnetic minerals controlling the magnetic properties. Paramagnetic and anti-magnetic minerals do not influence the SIRM, which is mainly indicative of ferromagnetic minerals and stable-single domain (SSD) materials [18]. The SIRM of the Le'an River sediments varies from 1.45×10^{-3} to 9.71×10^{-3} Am^2/kg, with a small variation and a mean value of 4.11×10^{-3} Am^2/kg, indicating a relatively high content of magnetic minerals in the Le'an River sediments, and the IRM curves at various magnetic field strengths are in general agreement with the SIRM curves, indicating a relatively stable magnetic mineral composition in the samples. The lower values at sites S2 to S4 and S6 to S9 are probably due to the proximity of these sites to the mines along the Le'an River, especially the Dexing copper mine, where heavy metal contamination from the mines has led to an increase in the concentration of antiferromagnetic minerals in the sediments.

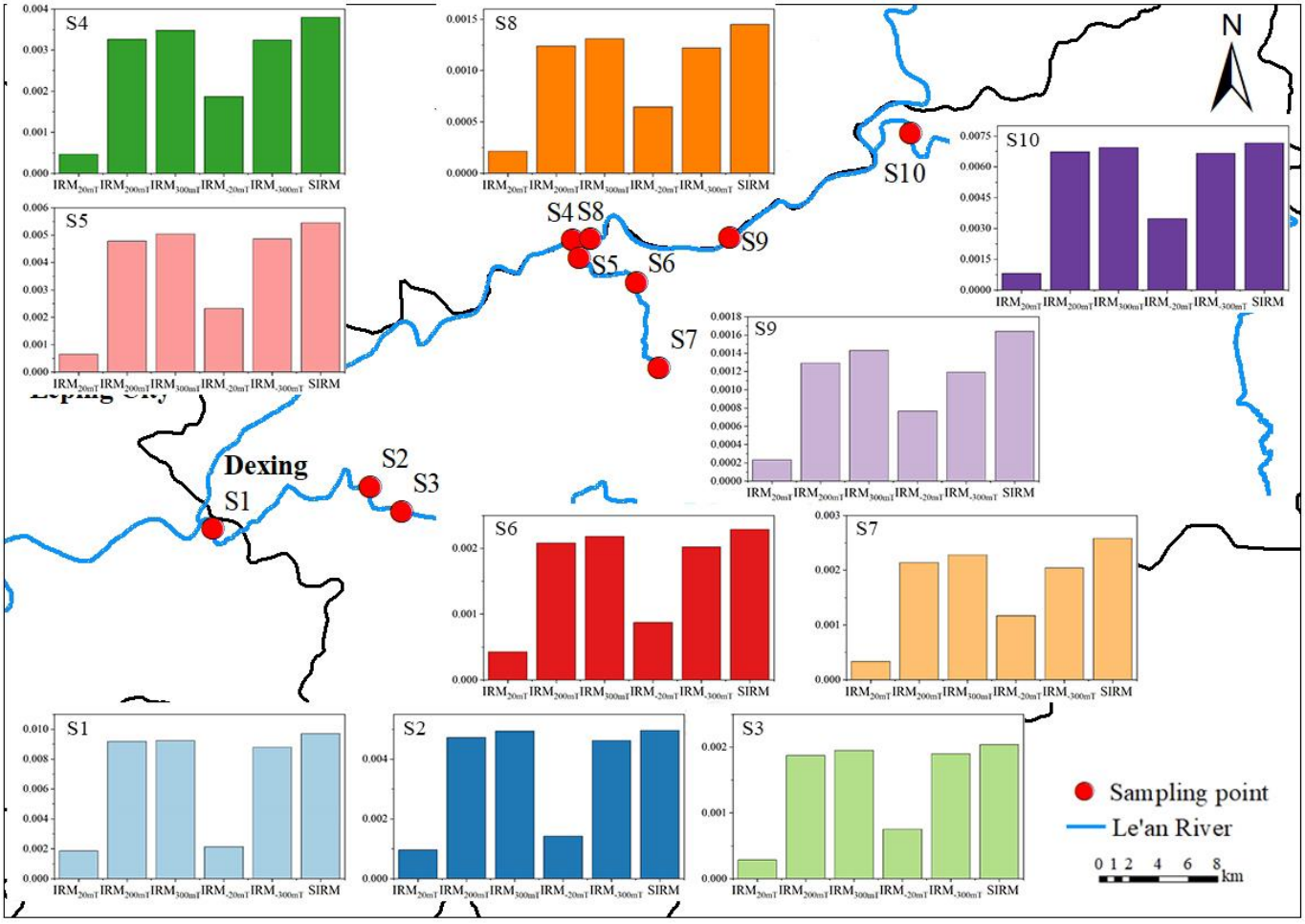


Figure 3. IRM characteristics at each sampling site in the Le'an River.

ARM is generally used to reflect the ferrimagnetic mineral content and particle size of the sample, and is especially sensitive to small single domain and quasi single domain magnetic minerals. There is a nonlinear correlation between ARM and magnetic mineral content, which is mainly the result of the interaction of magnetic particles during ARM acquisition [42]. From Figure 4, high values of ARM in the Le'an River sediment occur at points S1, S6 and S10, with a maximum value of 8.76 $\times$ 10^{-6} m^3/kg, which may be due to the effluent from the steel mill and fly ash from the coal plant near the points. At these three points, the sediment has a high content of single domain particles in the magnetic minerals. Also, the SIRM values for S1 and S10 are relatively high, suggesting a high content of SSD in the sediments at these two points.

The results of HIRM, S_{-ratio} and $SOFT_{-IRM}$ are shown in Figure 5. The $SOFT_{-IRM}$ ranges from 4.025 $\times$ 10^{-4} Am^2/kg to 3.785 $\times$ 10^{-3} Am^2/kg, a wide range of variation, indicating that the concentration of ferrous minerals fluctuates significantly. The HIRM can be used as a proxy for the concentration of the antiferromagnetic mineral hematite [43,44]. The mean value of HIRM in the Le'an River sediments was 3.88 $\times$ 10^{-3} Am^2/kg, with a high overall value and a sawtooth-shaped high-amplitude distribution of the HIRM curve, indicating that the sediment formation process in the Le'an River was very unstable and that various pollution sources had a great influence on the sediment deposition process.

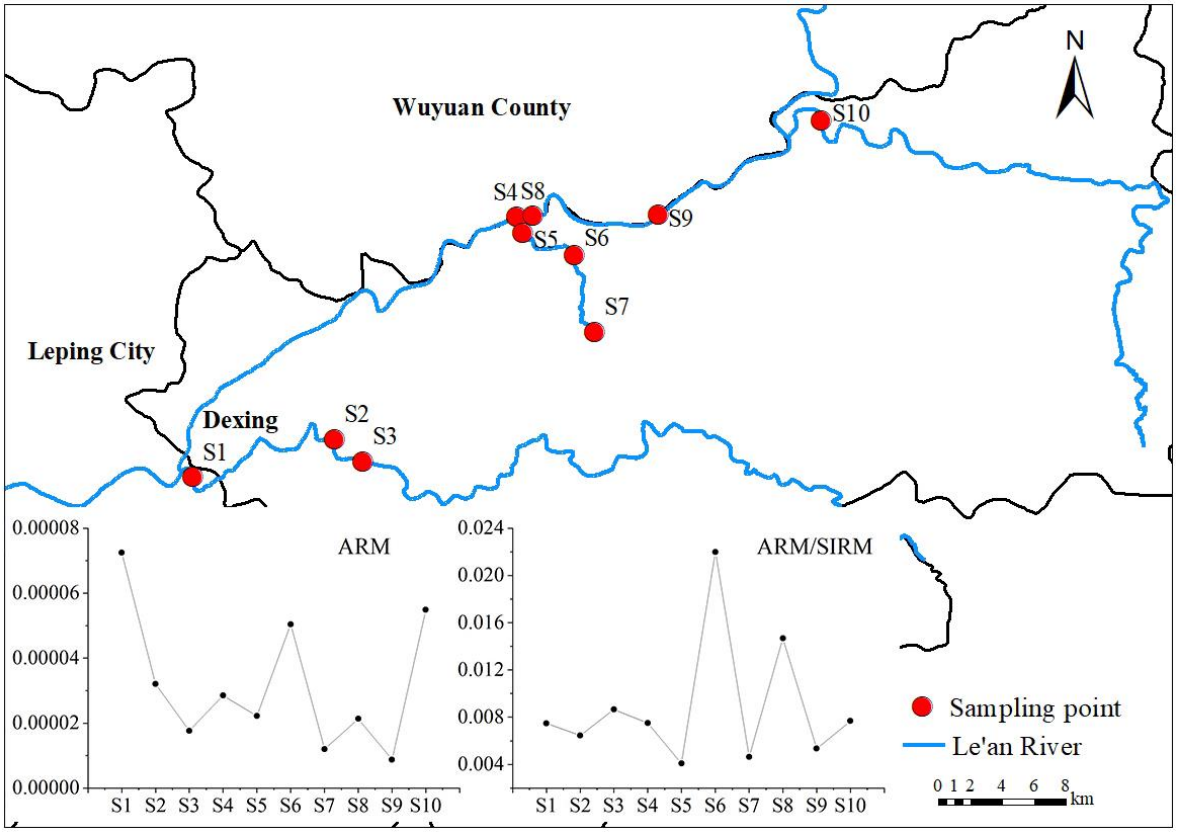


Figure 4. ARM characteristics at each sampling site in the Le'an River.

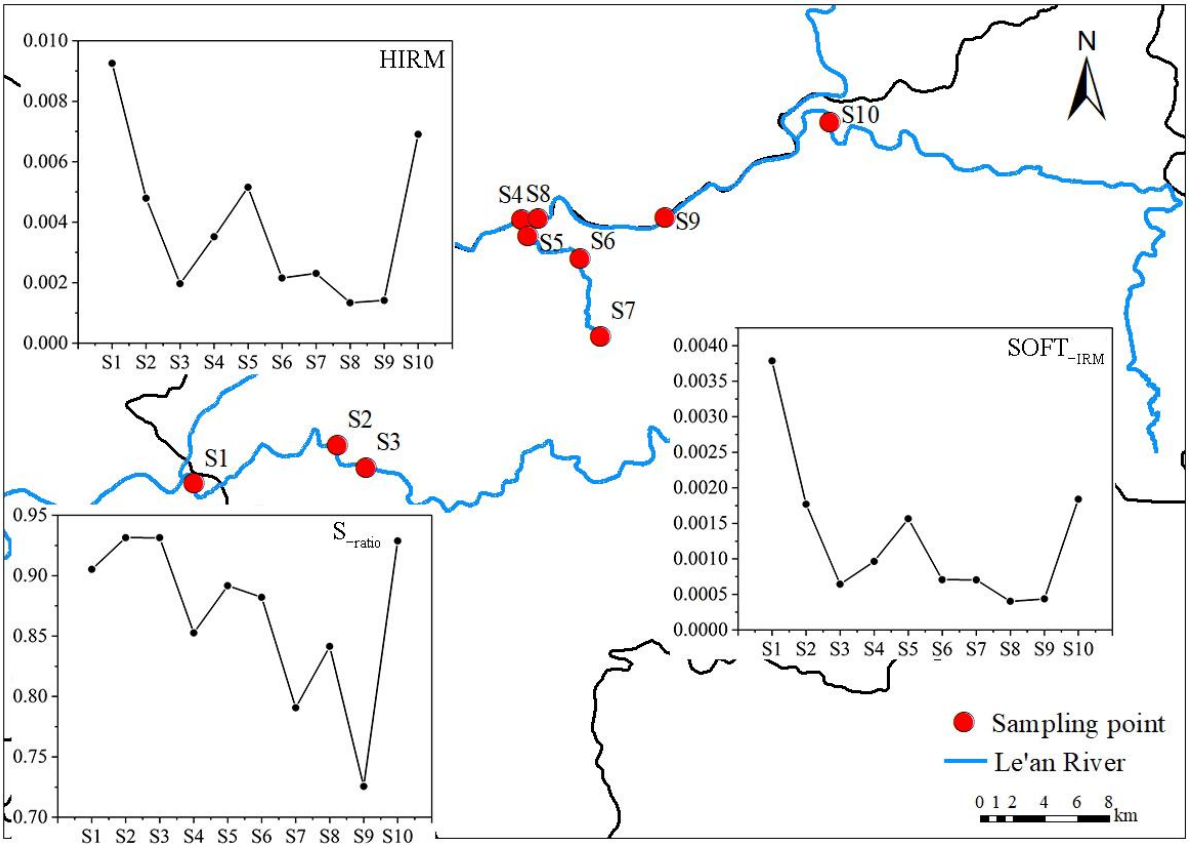


Figure 5. Other magnetic indexes' characteristics at sampling sites in the Le'an River.

The S_{-ratio} mainly reflects the relative importance of the ferromagnetic and antiferromagnetic minerals [36]. In the Le'an River sediments, the S_{-ratio} varies from 0.73 to 0.93, with a mean value of 0.87, essentially reaching saturation, indicating that the isothermal remanence IRM is close to saturation under the applied magnetic field of 300 mT, and with the increase of sediment deposition process and soft ferromagnetic mineral composition, the ferrous magnetic mineral composition becomes the main contributor of magnetic susceptibility. The same low values on the HIRM curve are found at sampling points S7 to S9 where S_{-ratio} is low, suggesting that the concentration of magnetic minerals is stable at the headwaters of the Le'an River and its tributary, the Dawu River, meaning that the presence of contaminants downstream of the Dawu River is increasing the concentration of antiferromagnetic minerals in the sediment. Magnetite is the main ferric magnetic carrier in the sediments of river basins and reservoirs. The characteristics of magnetite lead to the easy adsorption of toxic elements in the sediments of the Le'an River [4].

3.3. Correlation between Magnetic Parameter and Heavy Metal Content

The Pearson correlation coefficients of each environmental magnetism index and each element are shown in Table S4. As can be seen from Table S4 and Figure 6, the S_{-ratio} is positively correlated with the concentrations of Cr, Pb, As, Cu and Zn, but not significantly. These two indicators reflect the relative importance of ferromagnetic and antiferromagnetic minerals. It shows that the concentration of these heavy metals is related to the content of ferritic magnetic minerals. From the point of view of each heavy metal, the correlation between various environmental magnetism indices and Cr, Pb, As, Cu and Zn is not strong, which is different from the results of many previous studies [21,45,46]. It also indicates that in areas with more mines, heavy metal pollution and the outflow of various minerals may lead to the weakening of the indicator effect of environmental magnetism indices on heavy metals. The highest correlation coefficient for each of the environmental magnetism indices with the main heavy metals (Cr, Pb, As, Cu and Zn) was 0.528 for S_{-ratio} and Zn, but the correlation was not significant. Two elements, Pb and As, had negative correlation coefficients, except for two positive correlations with S_{-ratio}. The correlation coefficients between most heavy metals and environmental magnetism are negative. According to the results in the table, IRM_{-20mT} and S_{-ratio} have certain indicative effects on Cr, Pb, As, Cu and Zn. This is not consistent with the findings of Zhang et al., that is, that SIRM has no indicative effect on metallic elements. In that study, the authors also give reasons that the differences in the correlation between magnetic parameters and heavy metals may depend on their source [1].

ARM exhibited significantly positive correlations with HIRM, $SOFT_{-IRM}$, IRM_{-300mT}, SIRM, IRM_{20mT}, IRM_{200mT} and IRM_{300mT} ($p < 0.01$). The IRM obtained under different magnetic field intensities have little correlation ($p < 0.01$). ARM/SIRM is negatively correlated with all environmental magnetic indicators except ARM and S-ratio, and the correlation is not significant. On the whole, the correlation between the environmental magnetic indicators is not high.

Sr is significantly correlated with multiple environmental magnetic indices ($p < 0.01$), but its correlation coefficient was negative, and Sr correlated negatively with all environmental magnetism indices, indicating that the higher the concentration of Sr in the sediment, the smaller the environmental magnetic index of the sediment. Of all the correlation coefficients, the largest correlation coefficient was between Hg and ARM at 0.798 ($p < 0.05$). As can be seen from the table, there is a positive correlation between ARM and the V, Hg, Ni and Sr, and the correlation coefficients are large. However, in terms of magnetic indices, there is no one indicator that is indicative of all heavy metal indicators, which is different from the conclusions obtained from many previous studies [1,22,23], which also indicates that in different locations, due to different deposition processes and different sources of pollution, the environmental magnetism indices for heavy metals also vary from place to place due to different deposition processes and pollution sources. According to the results in Table S4 and Figure 6, it can be seen that IRM_{200mT}, IRM_{300mT}, SIRM, IRM_{-300mT}

and HIRM have significant correlation with Sr ($p < 0.05$), has a certain indicative role. ARM is a strong indicator of V and Hg, and Zhang C.X. et al., in 2011, also pointed out a strong correlation between ARM and V [1]. IRM_{20mT} was significantly correlated with Hg ($p < 0.01$). ARM/SIRM has strong indicative effect on Mo and Ni, which is consistent with Chaparro's finding that ARM/SIRM can be used as a proxy for Ni after studying the sediment of reservoir in Mexico. He did not study the relationship between Mo element and magnetic parameters [4]. This parameter indicates Mo and Ni concentrations because ARM/SIRM cancels out the effect of magnetic mineral concentrations and enhances the signal caused by grain size changes [47].

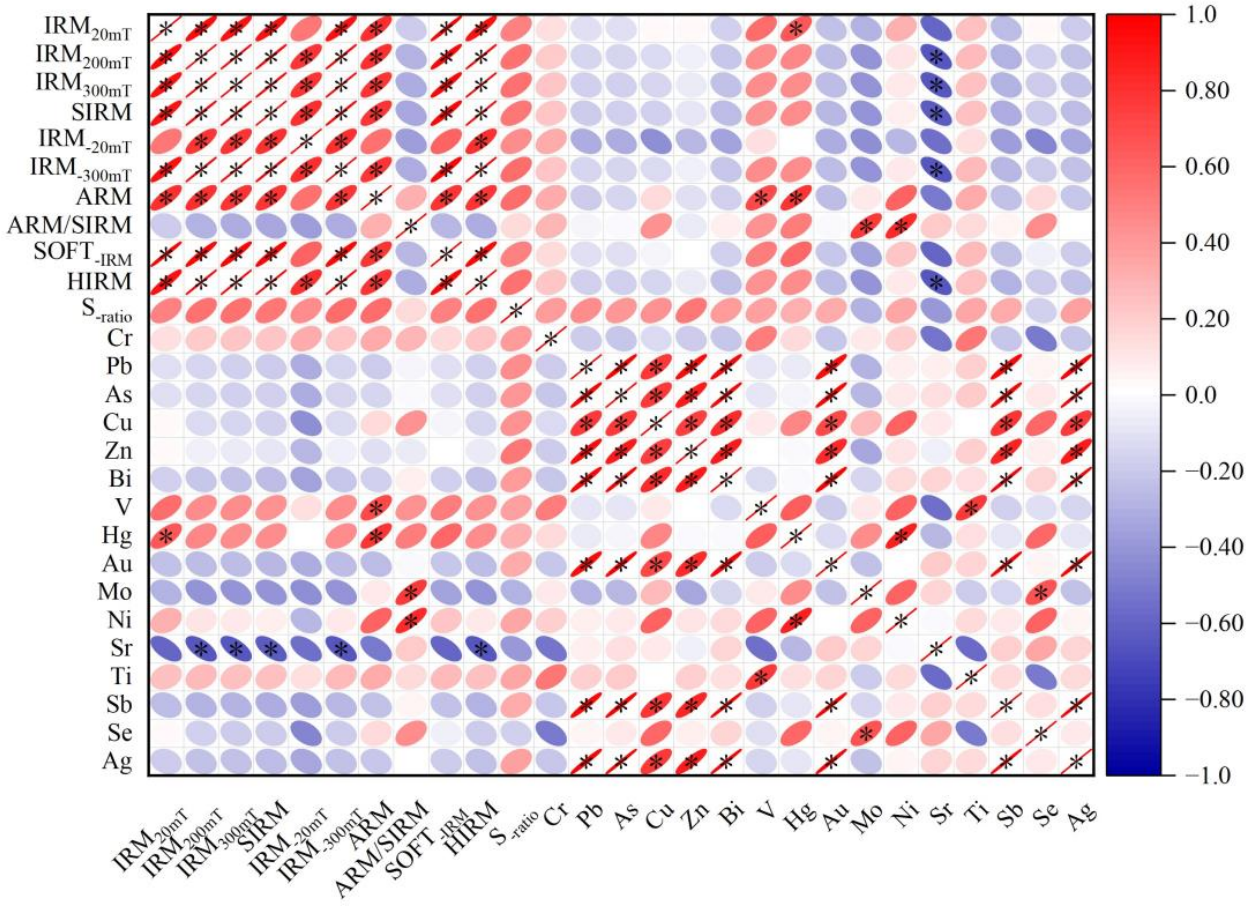


Figure 6. Plot of correlation coefficients between magnetic parameters and heavy metal concentrations (* $p \leq 0.05$).

4. Conclusions

The concentration of each heavy metal element in the sediment of the Dexing section of the Le'an River has great spatial variability in spatial distribution, and heavy metal pollution is more serious; the average value of each heavy metal concentration far exceeds the background value of heavy metal in the sediment of the Le'an River, especially Cu. The highest value of pollution coefficient is 74.67; from the pollution coefficient C_f can be seen that the pollution degree of various heavy metal pollution is Cu > As > Zn > Pb > Cr. Combined with the PLI, the results show that the degree of pollution is extremely serious at the points located near each mine, while the two points located in the upper reaches of the river are free of pollution, and the sediment pollution is better. The isothermal remanent magnetization IRM of the Le'an River sediments is consistent across magnetic field strengths, and the SIRM curve is consistent with the IRM, indicating that the magnetic mineral composition of the samples is relatively stable. From the other environmental magnetism indicators, it can be seen that the ferromagnetic mineral fraction becomes the main contributor to the magnetization rate and its concentration fluctuates more obviously,

while each pollution source has a greater influence on the deposition process of the Le'an River sediments.

The correlation analysis between environmental magnetism indicators and heavy metals did not show a significant pattern, with the S_{-ratio} having a non-significant positive correlation with the concentration of each major heavy metal, suggesting that heavy metals are more readily enriched in ferromagnetic minerals. Overall, the magnetic parameters IRM_{-20mT} and S_{-ratio} were indicative of Cr, Pb, As, Cu and Zn, but not strongly so. In combination with other heavy metals, Sr had a more significant correlation ($p < 0.05$) with the magnetic indicators IRM_{200mT}, IRM_{300mT}, SIRM, IRM_{-300mT} and HIRM, which can be used as indicators of pollution in response to Sr concentrations; ARM was indicative for V ($p < 0.05$) and strongly indicative for Hg ($p < 0.01$). IRM_{20mT} was significantly correlated with Hg ($p < 0.01$); ARM/SIRM was highly indicative of Mo and Ni ($p < 0.01$). The combination of environmental magnetism and geochemistry is an important method for environmental assessment. In some areas environmental magnetism can be a good indicator of heavy metal concentrations, but in this study, no single environmental indicator was found to accurately and effectively reflect the concentrations of various heavy metals, which also indicates that in different areas, due to the sediment formation process and the pollution sources in the study area, the indication of environmental magnetism indicators can have a large impact.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min13020145/s1, Table S1. sampling sites; Table S2. Precision and accuracy of each method; Table S3. Statistical analysis of pollution load index; Table S4. Pearson correlation (PC) coefficient matrix of all elements and magnetic parameters in the study area.

Author Contributions: S.R. contributed significantly to the study design, literature review, statistical analysis, and writing and revising the manuscript. J.W. was responsible for improving the study design, literature screening, data validation, and review and revision of the manuscript. J.L. improved the study ideas and revised the manuscript. Q.L. and C.R. were responsible for collecting data and revising the manuscript, and liaising with the editorial team. X.C. improved the study's ideas and revised the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This study was supported by "the Fundamental Research Funds for the Central Universities", No. 2022.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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