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Assessment of Heavy Metals Enrichment and Sources in Different Functional Areas of Sixian City

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Abstract: To investigate soil heavy metal pollution in different functional areas of Sixian City, 48 soil samples were collected in residential, industrial, green, and commercial areas. The concentrations of V, Cr, Zn, Cu, Pb, and as were determined by the geoaccumulation index method and the enrichment factor method, and their pollution levels were evaluated. At the same time, the possible sources of heavy metals were identified by the factor analysis method. The results showed that except for V, the concentrations of the other five heavy metals were higher than the soil background values of Anhui Province. The geoaccumulation indexes revealed that V, Cr, and as were free of pollution, while some sampling sites of Zn, Pb, and Cu were slightly polluted in different functional areas. Heavy metal pollution in different functional areas ranked as commercial area>industrial area>residential area>green area. Given the enrichment factor, V was pollution-free, and as was mildly enriched in all functional areas. Cr was slightly enriched except for the green areas; Zn and Cu were mild to moderately enrichment; Pb was mild to moderately enriched except for the green areas and the pollution in commercial areas was serious. The factor analysis showed that the large contribution rate of Pb and Zn in the first factor may be related to traffic; the second factor (Cr, Cu, and as) possibly come from electronics, metallurgy burning, and machinery manufacturing, and the third factor was a natural process. It can be seen that Zn, Cu, and Pb are the main soil pollution elements in the functional areas of Sixian City.

Keywords: Heavy Metal, Geoaccumulation Index, Enrichment Factor, Source Analysis, Sixian City

Introduction

With the rapid development of urbanization and industrialization, the problem of the urban ecological environment has become increasingly prominent. As an important part of the urban ecosystem, urban soil is the source and sink of different pollutants in urban transportation, industrial production, building construction, and residents' daily activities. It contains specific environmental information and has a good indicator effect on environmental quality (Wang *et al*., 2018). Soil heavy metals are important pollutants with refractory degradation, easy accumulation, highly toxic, and long-term latent (Sun *et al*., 2010; Zhang *et al*., 2022). Once in the soil, they migrate and transform with the change of urban environmental media and enter and endanger human health through floating contact, respiration, or food chains of surface dust and particulate matter (Wei and Liu, 2017; Wang *et al*., 2021). Therefore, heavy metal pollution in urban soil or street dust is attracting extensive academic attention. However, different urban functional areas have different social and economic activities, land use patterns, and different impacts on the urban soil environment. Since the 1970s, scholars have carried out a large number of studies on heavy metal pollution in urban soil and street dust, such as heavy metal content characteristics, enrichment status, spatial distribution, pollution sources, risk assessment, and occurrence forms (Pekey and Doğan, 2013; Haijing *et al*., 2016; Zhou *et al*., 2018; Li *et al*., 2015a). Foreign studies on heavy metals in urban soil are earlier. Linde *et al*. (2001) analyzed the content and enrichment of heavy metals in the urban soil of Stockholm by collecting soil samples; Peter and Adeniyi (2011) studied the spatial

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relationship between urban land use patterns and soil heavy metals in Lagos. Although domestic-related research started late, it has developed rapidly and obtained fruitful research results. Taking Xiamen Island as the research area, Li *et al*. (2017) conducted a comparative study on the characteristics of heavy metal pollution of soil and street dust in different urban functional areas. Xiong *et al*. (2017) studied heavy metals in surface soil with different particle sizes in Beijing and the results showed that heavy metal pollution increased with the decrease of particle size. Zhang *et al*. (2018a) carried out a comprehensive evaluation of heavy metals in Nanjing green soil by using the matter-element extension model. Liu *et al*. (2016) carried out the ecological risk assessment of heavy metals in different functional areas of Luoyang and analyzed the sources of heavy metals. These studies were mainly based on large cities or prefecture-level cities and there were few reports on county-level units. Due to the rapid development of urbanization and industrialization in Sixian County, population expansion and traffic volume growth have brought great pressure to the ecological environment in the strategy of accelerating the rise of northern Anhui. Based on this, surface soil samples were collected from residential areas, industrial areas, green areas, and commercial areas in Sixian, Anhui Province, and the concentrations of V, Cr, Zn, Cu, Pb, and as were tested. The soil heavy metal pollution of different functional areas in Sixian was studied by the geoaccumulation index method and enrichment factor method. The results can provide a reference for the construction of an ecological environment and sustainable economic development of Sixian.

Study Area

Sixian is subordinate to Suzhou, located in the northeast of Anhui Province, between 33°16'-33°46'N and 117°40 '-118°10' E. The terrain is flat and dominated by plain, which accounts for about 90% of the total area. It is a warm temperate semi-humid monsoon climate, with an average annual temperature of 14℃, a frost-free period of about 210 days, and average annual precipitation of about 860 mm. The four seasons are distinct and the rain and heat are the same periods. The soil is dominated by Shajiang black soil. By the end of 2021, Sixian governs 15 townships and 1 provincial economic development zone, covering an area of 1,787 km^2, with a resident population of 763310 and a regional GDP of 28 billion yuan.

Materials and Methods

Sample Collection and Analysis

To investigate the soil heavy metals concentration in different functional areas in Sixian City, 48 soil samples were collected in residential areas, industrial areas, green areas, and commercial areas, respectively. Among them, 10 samples were randomly and evenly arranged in residential areas, green areas, and industrial functional areas, and 18 samples were arranged in commercial areas due to the strong influence of human activities. At each sampling site, 0-20 of topsoil was collected by the multi-point sampling method. After mixing evenly, 1kg soil samples were obtained by the quartz method and brought back to the laboratory. In the laboratory, the soil samples were dried naturally to remove gravel, impurities, and plant residues and then tested by grinding the soil samples through a 200-mesh sieve. The samples were analyzed by X-ray fluorescence spectroscopy (X-RF, Instrument Model Explorer 9000SDD) to determine the concentration of heavy metals. This method is widely used in the determination of heavy metal elements because of its high speed and multiple types of elements (Li *et al*., 2015b; Morgenstern *et al*., 2001). The specific operation method is to accurately weigh 4 g soil sample powder, press it into a 6 mm thick flake with a fly-15 manual tablet press, and then put it into an X-ray fluorescence spectrum analyzer (x-rf) for detection. At the same time, to improve the accuracy of sample detection, the national standard sample (GBW07307) is calibrated in the test, so that the measurement error is controlled by 10%.

Geoaccumulation Index Methods

The geoaccumulation index method was proposed by German Professor (Muller, 1979) to evaluate the enrichment of heavy metals in sediments (Muller, 1979). This method not only takes into account the environmental geochemical background value and the impact of human activities on the environment, but also the changes in environmental background value caused by natural geological processes. As such, it has been widely used in the pollution evaluation of different heavy metals (Zhang *et al*., 2018b). Its calculation formula is as follows:

$$I_{geo} = \log_2\left[\left(C_n / kB_n\right)\right] \tag{1}$$

where, I am the geoaccumulation index; C_n is the measured concentration of heavy metal n in soil; B_n is the chemical background value of the heavy metal n in the sample or the background value of the local soil. In this study, the soil background values in Anhui Province were selected as the reference standard. k is to reduce the impact of background value changes on evaluation results, usually k = 1.5. I_{geo} is usually divided into seven levels, as shown in Table 1.

Table 1: Criteria for an index of geoaccumulation (I_{geo})

Rank	I_{geo}	Pollution level
0	$I_{geo} \leq 0$	No pollution
1	$0<I_{geo} \leq 1$	No pollution to light pollution
2	$1<I_{geo} \leq 2$	Light pollution
3	$2<I_{geo} \leq 3$	Light to moderate pollution
4	$3<I_{geo} \leq 4$	Moderate pollution
5	$4<I_{geo} \leq 5$	Moderate to strong pollution
6	$I_{geo}>5$	Strong pollution

Table 2: Classification standard of enrichment factor

Rank	Enrichment Factor (*EF*)	Degree of enrichment (pollution)
1	$EF \leq 1$	Non-enrichment (Pollution-free)
2	$1 < EF \leq 2$	Mild enrichment (mild contamination)
3	$2 < EF \leq 5$	Moderate enrichment (moderate contamination)
4	$5 < EF \leq 20$	Intensity enrichment (intensity pollution)
5	$20 < EF \leq 40$	Extremely enriched (extremely polluted)

Enrichment Factor Methods

The enrichment factor (Fan *et al*., 2016) is an important indicator to judge the impact of environmental heavy metal pollution and human activities on heavy metal enrichment. Elemental concentrations of the samples were compared to relatively stable elements in selected soils to identify and characterize anthropogenic contamination of heavy metal elements in environmental media. The enrichment factor is calculated as:

$$EF = \left(C_i \ / C_n\right)_s / \left(C_i \ / C_n\right)_b \qquad (2)$$

where, *EF* is a heavy metal enrichment factor that is usually divided into five grades, as shown in Table 2; C_i and C_n represent the concentration of heavy metal elements to be measured and the concentration of inert reference elements, respectively. He was selected as a reference element considering the local parent material and natural conditions in Suzhou City (Gao *et al*., 2018); *s* and *b* are the soil samples and crustal background, respectively. When $EF \leq 1$, the soil is pollution-free and all heavy metals come from natural processes; when $1<EF\leq 2$, the heavy metals are mild enrichment and the source of heavy metals is influenced by natural processes and human activities; when $2<EF\leq 5$, the soil is moderate enrichment and the heavy metals mainly come from human activities (Su *et al*., 2021).

Results and Discussion

Statistical Analysis of Heavy Metals in Different Functional Areas

The contents of soil heavy metals in indifferent functional areas of Sixian City can be obtained from Fig. 1 and Table 3. As shown in Table 3, the average values of V, Cr, Zn, Cu, Pb, and as were 82.41, 68.20, 88.33, 35.10, 34.60, and 12.03 mg/kg, respectively. Except for V, the average values of the other 5 heavy metals in Sixian City were higher than the soil background values in Anhui Province. Therefore, heavy metal elements were relatively enriched in Sixian City due to human influence. The mean values of Cu, Zn, As and Pb are 1.50, 1.42, 1.34, and 1.27 times the background value, respectively. The coefficient of variation can reflect the difference in the spatial distribution of sample data and the discrimination of heavy metal content by human activities (Zhang *et al*., 2016; GB156182-1995, 2006). From the variation coefficient of soil heavy metals in Sixian City, the variation coefficient of As, Pb and Zn were all above 45%, belonging to strong variation. The variation coefficient of Cu was 31.22%, belonging to moderate variation, indicating that these heavy metal elements were strongly disturbed by human activities.

It can be seen from Fig. 1 and Table 3 that the contents of V and Cr in each functional area are significantly different. The content of Cu in the industrial area was slightly larger and the mean value of it in each functional area was higher than the background value of Anhui Province. Zn (111.06 mg/kg) in a commercial area, Pb (43.11 mg/kg) in commercial and industrial areas (34.60 mg/kg) was much higher than the other areas and background values. The residential areas were higher than the other functional areas due to the outliers. The contents of Pb and Zn in the industrial and commercial areas were higher, which may be related to the pollution of the electronics and machinery manufacturing industry. The dense population and heavy traffic in commercial areas will also lead to the emission of heavy metals.

Analysis of Geoaccumulation Index

The geoaccumulation indexes of heavy metals in the Sixian urban area and different functional areas were calculated by the formula (1), as shown in Fig. 2 and Table 4. Figure 2 shows that the geoaccumulation pollution of heavy metals in the Sixian urban area ranked as Cu>As>Zn>Pb>Cr>V. Among them, V and Cr were pollution-free; Cr shows pollution-free to mild pollution at some sampling points; 4.17% of Zn, 3.82% of Pb, and 2.10% of Cu samples are light pollution; and as shows mild to moderate pollution. Table 4 shows that the spatial distribution of soil heavy metals in different functional areas was different and the pollution in each functional area ranked as commercial area>industrial area>residential area>green area. V and Cr were pollution-free in all functional areas. Zn and Pb were light pollutions in commercial areas and the sampling points of $I_{geo}>0$ Are over 55%. For Cu in industrial and residential areas, the sampling points of $I_{geo}>0$ were 70 and 60%, respectively. The I_{geo} values of as were relatively uniform in all areas. $I_{geo}>0$ was due to the outlier value (2.10) in residential areas. According to the boxplot, Zn, Cu, Pb, and as have skew distribution, indicating that the enrichment of heavy metals at different sampling points is greatly different.

Analysis of Enrichment Factor

Based on the mean values of heavy metals in all urban soil samples and functional areas, Fe was selected as the reference standard to calculate enrichment factors in different functional areas in Sixian City. The evaluation results are shown in Fig. 3 and Table 5. Figure 3 shows that the heavy metal pollution in Sixian City ranked as Cu>As>Zn>Pb>Cr>V. The calculated results are consistent with the geoaccumulation indexes, indicating that the two methods are feasible to evaluate the heavy metal pollution enrichment in Sixian City. Except for the industrial area, the *EF* value of Cr was $1<EF\leq 2$, indicating the soil was mild enrichment, and the heavy metals were affected by both natural processes and human activities. As such, human activities have an impact on the enrichment of Cr. The *EF* values of Zn and Cu were greater than 1 in all functional areas. The pollution of Zn ranked as commercial area>industrial area>green area>residential areas and that of Cu ranked as industrial area>commercial area>residential areas>green areas. In particular, the *EF* values of Zn in a commercial area and Cu in an industrial area were larger than 2 at moderate concentration. $EF>2$ indicates that heavy metals were mainly derived from human activities. The pollution of Pb ranked as commercial area>industrial area>residential area>green area. The *EF* values in a commercial area and industrial area were greater than 2, belonging to moderate enrichment and as in all functional areas were mild enrichment. There by, Zn, Cu, and Pb were the main soil pollution elements in different functional areas of Sixian City.

Source Analysis of Soil Heavy Metals

The above analysis shows that the heavy metal contents of urban soil in Sixian City were higher than the background value of soil. Except for V, the heavy metal content of the soil was disturbed by human activities. From the analysis of the enrichment factor, it can be seen that the *EF* values of Pb, Zn, and Cu were basically between 1 and 2 in each functional area, especially in commercial and industrial areas greater than 2. This indicates that heavy metals in industrial and commercial areas are largely derived from human activities, while the other functional areas have both natural sources and human sources. To further analyze the sources of heavy metals in the soil of Sixian City, Minitab was used for factor analysis. The correlation coefficient between elements and principal components with three characteristic roots greater than 1 were extracted and the principal components were rotated with the maximum variance. The results were shown in Fig. 4 and Table 6. It can be seen that Pb and Zn have a better correlation and the contribution rate was higher in the first principal component. Their means were higher than environmental soil background values. Due to dense population and heavy traffic, the high values of these samples mainly appear in commercial and industrial areas. Some studies have found (Dai *et al*., 2015; Liu *et al*., 2012) that traffic emissions, brake devices and automobile tire wear all release Pb and Zn, and the high contents of Pb and Zn may be related to traffic factors. Cr, Cu, and as contribute more to the second factor, and Cr and Cu were correlated well. This shows that these elements may have the same sources and the sources of Cr and Cu may be related to electronics, metallurgy, combustion, and mechanical manufacturing. The source of as should be related to the combustion of chemical fuels and agriculture and the sampling sites were mainly in urban areas (Shan *et al*., 2016). Therefore, the source of as should be coal combustion and northern Anhui Province is an important coal-producing area. The third factor is mainly V. Considering that V was a pollution-free state in the study area, V was considered to be mainly from natural sources.

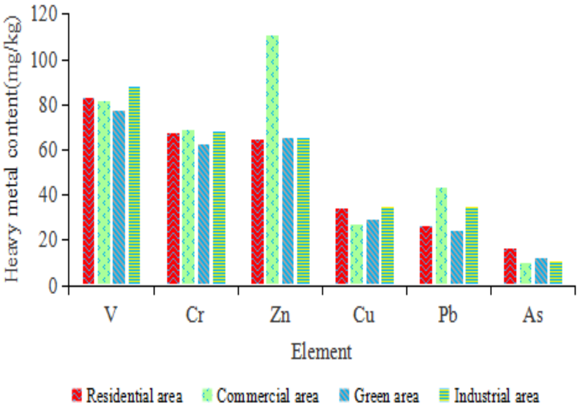

Fig. 1: Distribution of heavy metals in different functional areas in Sixian City

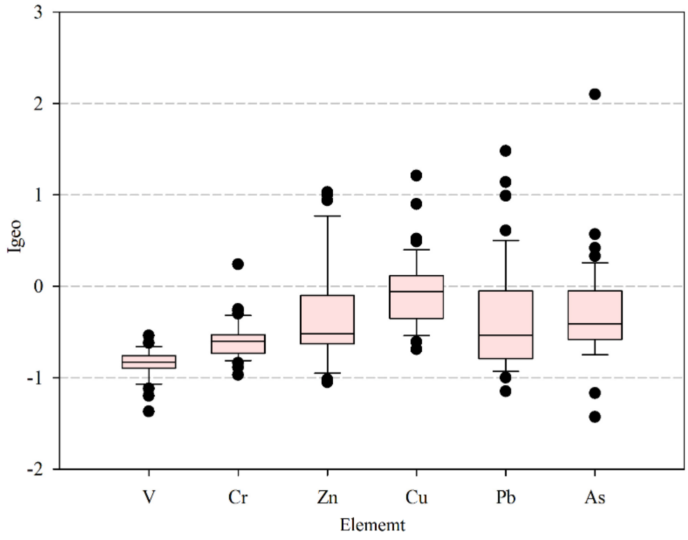

Fig. 2: Boxplot of heavy metals geoaccumulation index in Sixian City

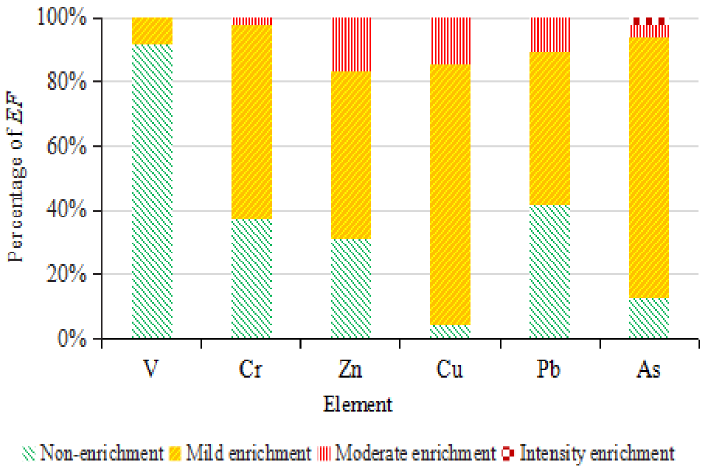

Fig. 3: Distribution of enrichment factor value in Sixian City

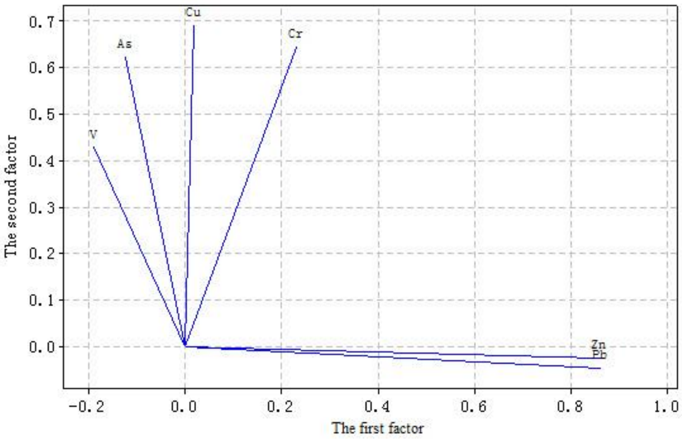

Fig. 4: Loading plot of principal component factors of soil heavy metals in Sixian City

Table 3: Statistical results of heavy metals in different functional areas of Sixian City (unit: mg/kg)

Functional area	Data	V	Cr	Zn	Cu	Pb	As
Residential area	Scope	79-890	51-810	56-830	23-57	21-310	8-58
	Mean	83.300	67.500	64.600	34.10	26.100	16.50
Industrial area	Scope	68-960	56-830	45-152	25-71	18-111	8-16
	Mean	87.970	68.190	65.100	35.11	34.600	10.80
Green area	Scope	64-840	54-690	56-820	20-39	20-320	9-18
	Mean	77.300	62.600	65.550	28.98	24.100	11.90
Commercial area	Scope	57-101	54-118	48-190	19-44	22-880	5-20
	Mean	81.720	68.610	111.060	26.94	43.110	10.28
All city	Scope	57-101	51-118	45-190	19-71	18-111	5-58
	Mean	82.410	68.240	82.330	30.56	33.830	12.03
CV (%)		10.010	15.980	48.680	31.22	54.150	62.48
Background value of Anhui Province		98.200	66.600	62.000	20.40	26.600	9.00

Table 4: Geoaccumulation index of heavy metals of different functional areas in Sixian City

	V	Cr	Zn	Cu	Pb	As
Residential area	-0.82	-0.58	-0.53	0.11	-0.63	0.10
Industrial area	-0.75	-0.56	-0.42	0.14	-0.43	-0.35
Green area	-0.94	-0.68	-0.51	-0.11	-0.74	-0.21
Commercial area	-0.86	-0.57	0.13	-0.23	0.08	-0.49

Table 5: Enrichment factor of heavy metals in different functional areas in Sixian City

	V	Cr	Zn	Cu	Pb	As
Residential area	0.88	1.05	1.09	1.46	1.03	1.89
Industrial area	0.86	0.98	1.60	2.02	2.11	1.06
Green area	0.82	1.04	1.14	1.05	0.94	1.35
Commercial area	0.93	1.16	2.21	1.83	2.63	1.14

Table 6: Pearson correlation matrix of soil heavy metals in Sixian City

	V	Cr	Zn	Cu	Pb	As
V	1					
Cr	0.301	1				
Zn	-0.379	0.352	1			
Cu	0.228	0.606	0.104	1		
Pb	-0.474	0.294	0.742	-0.263	1	
As	0.283	0.231	-0.114	0.455	-0.271	1

Conclusion

Through soil sampling, the pollution assessment of soil heavy metals in different functional areas of Sixian City was carried out by using the geoaccumulation index method and the enrichment factor method and the sources of heavy metals were analyzed. The following conclusions were drawn.

The mean values of V, Cr, Zn, Cu, Pb, and as in different functional areas of Sixian City were 82.41, 68.20, 88.33, 35.10, 34.60, and 12.03 mg/kg, respectively. Except for V, the mean values of the other five heavy metals in Sixian City were higher than the soil background values in Anhui Province. The mean values of Cu, Zn, As and Pb were 1.50, 1.42, 1.34, and 1.27 times the background values, respectively. The variation coefficient of As, Pb, and Zn was above 45%, belonging to strong variation. The variation coefficient of Cu was 31.22%, belonging to moderate variation. This indicates that these heavy metal elements are strongly disturbed by human activities.

The geoaccumulation index of heavy metal pollution in Sixian City ranked as Cu>As>Zn>Pb>Cr>V. Among them, some sampling points of Zn, Pb, and Cu were mildly polluted, and as was light-moderate pollution. The pollution of each functional area ranked as commercial area>industrial area>residential area>green area. V, Cr, and as were pollution-free in each functional area. Zn and Pb were light pollutions in commercial areas. Cu was light pollution in industrial areas and residential areas, accounting for 70 and 60%, respectively. The pollution order of enrichment factors in Sixian City was consistent with the geoaccumulation index. Among them, V and as were pollution-free and mind polluted in each functional area, respectively. Except for the industrial areas, Cr was mild enrichment in other functional areas. Zn and Cu were mild to moderately enriched in all functional areas, while Zn in a commercial areas and Cu in industrial areas were strongly affected by human activities. Except for the green areas, Pb was mild to moderate enrichment and the commercial areas were moderately enriched. Therefore, it can be seen that Zn, Cu, and Pb are the main pollution elements in different functional areas of soil in Sixian City.

The correlation analysis showed that Pb and Zn contributed significantly to the first factor. Combined with the sampling data, Pb and Zn may be related to traffic factors. Cu and Cr had a larger load in the second factor, which may come from electronics, metallurgy, combustion, and mechanical manufacturing. As mainly comes from coal combustion and the third factor comes from natural sources.

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Author's Contributions

Haimin Su: Designed and performed the experiments, and work.

Dongsheng Xu: Participated to collect the materials related to the experiment.

Gao Yang and Peng Sun: Designed the experiments and revised the manuscript.

Ethics

There is no conflict of interest in the submission of this manuscript.

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