

RESEARCH ARTICLE

Tree-ring recorded variations of 10 heavy metal elements over the past 168 years in southeastern China

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Heavy metal pollution is a serious concern in the urban area of China. Understanding metal pollution history is crucial for setting up appropriate measures for pollution control. Herein, we report a record of concentrations of 10 heavy metals (Fe, Mn, Cu, Zn, Ni, Cr, Cd, Pb, Co, and Sr) in *Pinus massoniana* tree rings from Fuzhou City over the past 168 years, which represents the longest tree-ring chronology of heavy metals in China. The studied metals displayed contrasting distribution patterns. Among them, Mn and Sr showed the strongest migration trend with peak concentrations at the pith. Co, Cd, and Pb also showed distinctively high concentrations near the boundary between heartwood and sapwood. Ni, Cu, Cr, and Fe showed an increasing trend possibly due to migration toward bark caused by physiological activities and increasing tourism activities and traffic pollution. The other elements (Cr, Fe, and Zn) with low migration revealed the historical pollution possibly discharged by the Fuzhou Shipping Bureau and other anthropogenic activities. Strong correlations between Cu content and temperature were found, which provides an alternative tree-ring proxy for climate reconstruction. This study provides a long-term perspective of the joint impacts of physiological, environmental, and climatological factors on the concentrations of heavy metals in southeastern China.

Keywords: Tree ring, Heavy metal element, Pollution, Fuzhou

1. Introduction

With the acceleration of industrialization and urbanization, pollution caused by increasing concentration of heavy metal elements has become a serious concern in Anthropocene epoch, particularly for urban areas, due to heavy traffic, coal combustion, various industrial activities, and waste disposal (Craul, 1999; Buszewski et al., 2000; Rucandio et al., 2011; Parzych and Jonczak, 2013, 2014; Wang et al., 2020a). Heavy metals with molecular weights over 40 are difficult to be decomposed or removed, and even a low concentration of heavy metals in soil and vegetation can cause harmful effects to survival and health of plants, animals, and human beings (Tan, 2004; Liu et al., 2017, 2020a,

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2020b, 2021). To effectively control contamination, it is prerequisite to comprehend the temporal evolution of heavy metal elements and their interactions with biospheres, atmosphere, hydrosphere, and soil (Yang et al., 2012; Liu et al., 2019a, 2019b, 2019c, 2020c; Wang et al., 2020b, 2020c; Wei et al., 2020). Unfortunately, routine monitoring for the heavy metal elements often has a short time span with strong industrial activities. Therefore, long-term proxy data are crucial to evaluate the anthropogenic pollution history of heavy metals. Among these proxy data, tree-ring proxy is widely used, since it is not only accurately dated and highly resolved but also widely distributed, which can provide the evolution of chemical components across both space and time (Wen et al., 2004; Xu, 2004).

A basic hypothesis of dendrochemistry is that the chemical composition of tree rings reflects the environmental chemical composition of the year when tree rings were formed (Watmough, 1999). It was widely accepted that the heavy metal elements tend to translocate after entering from phloem to xylem (Bondietti et al., 1989). Migrations of heavy metal elements in tree rings are influenced by both environmental conditions and tree physiological processes (Hagemeyer and Lohrie, 1995; Watmough and Hutchinson, 2002, 2003; Bindler et al., 2004; Monticelli et al., 2009). Knowledge on the element concentration in tree rings can not only provide information of forest health (e.g., Innes, 1993), soil chemistry (e.g., Augustin

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et al., 2005; Wang et al., 2005; Kuang et al., 2007, 2008), pollution (e.g., Nabais et al., 1999; Smith et al., 2008), climate (e.g., St. Clair et al., 2008; Witt et al., 2017; Hevia et al., 2018), and environmental events (e.g., volcanic eruptions; Pearson et al., 2005, 2006, 2009a, 2009b; Sheppard et al., 2008, 2009), but, more importantly, it can provide important information on element exchanges between environment and biospheres.

Lepp (1975) first proposed the concept of dendrochemistry and successfully reconstructed the history of trace elements using tree rings. Many studies have documented coherent variations of element concentration in tree rings and polluted environment and suggested the efficiency of the tree rings as environmental biomonitors for the history of heavy metal elements in urban and industrial areas as well as in the rural areas (Base and Mclaughlin, 1984; Watmough, 1999; Patrick and Farmer, 2006; Lageard et al., 2008; Zhang et al., 2008; Liu et al., 2009; Mihaljevič et al., 2011). In China, Liu et al. (2009a, 2009b) revealed the history of chemical element pollution in northwestern China. Wang et al. (2005) found different adsorption levels of elements in different tree species. Pinus massoniana is widely distributed in southern China and is sensitive to air pollution (acid deposition), and heavy metals in the tree rings of P. massoniana are closely related to the local environmental changes (Hou et al., 2002a; Kuang et al., 2007). Although numerous tree-ring-based pollution reconstructions have been conducted, researches on urban pollution in China were limited to a few decades and a few cities. A short-term tree-ring data may limit the ability to fully comprehend the migrations of heavy elements across tree rings. In this study, we developed 10 heavy metal element sequences for the past 168 years from P. massoniana in Fuzhou city, provincial capital of Fujian province, which are to our knowledge the longest tree-ring-based heavy metal series in southeast China. Based on these series, we aim to reveal their responses to physiological, environmental, and climatic factors and to provide a long context of the heavy metal element history of the environment over the past 168 years.

2. Data and methods

2.1. The study area and sampling

The study area of Fuzhou city is located western to the Taiwan Strait, about 41 km to the East China Sea (**Figure 1**). It is characterized as a typical subtropical marine monsoon climate with an annual mean temperature of 19.9 °C and an annual total precipitation of 1391 mm according to the measurements during 1953–2016 at the Fuzhou meteorological station.

Our tree-ring sampling site (26.06° N, 119.40° E, 870.3 m a.s.l.) of Gu Mountain is located to the southeast Fuzhou city, which is the highest mountain in Fuzhou city. The sampling site is near roads and hiking trails and was influenced by human activities such as tourism and industrial activities. Soil of the study site is classified as Humic Acrisols (pH = 4.32; Chen, 2001). Soil in the low-lying area of Fuzhou City generally has high soil organic matter content and is subjected to different types of heavy metal pollution associated with the different types of industrial activities (Chen et al., 2011). The study site is dominated

by *P. massoniana* and intermixed with other species such as *Cunninghamia lanceolata* and *Castanopsis carlesii*.

The tree-ring cores were collected from trees near a major road from the foot (elevation 119.43 m) to the top (elevation 525.79 m) of the mountain. Two to three cores were collected from each tree using 5-mm-diameter increment borer at the breast height of different orientations. The samples were mounted, air-dried, and polished with sandpaper until the cellular structure can be clearly identified. The cross-dated series were measured to a precision of 0.001 mm. Finally, we retained a total of 54 cross-dated tree-ring samples from 27 trees with a length of 168 years. Surface soil samples were collected from 10 plots under sampling trees using a stainless steel trowel and then were air-dried and stored in plastic bags prior to analysis.

2.2. Measurement of the heavy metal elements in tree rings and topsoil

The dated tree-ring cores were ultrasonically cleaned by Double deionized water (Milli-Q Millipore 18.2 resistivity) for 1 h in order to eliminate any surface contaminants introduced by coring or handing, which were dried afterwards. The annual rings of the cores were stripped with a thin stainless steel blade under a binocular microscope. The rings formed in the same calendar year were mixed together and stored in a sealed bag. A 0.05 g sample was immersed in 2 ml of HNO₃ and 2 ml of H₂O₂ in a PTFE vessel digesting at 150 °C for 18 h. The solutions were then diluted with 5% nitric acid to a final volume of 40 ml and were subsequently filtered using 0.45 µm syringe filters. For calibration, the standard material and a blank sample were digested simultaneously. Soil samples for chemical analysis were sieved and pestled in an agate mortar. Soil samples (0.04 g) were digested in 0.5 ml HNO_3 and 1.5 ml HF for 14 h at 150 $^\circ\text{C}.$ Add 0.25 ml HClO₄ after cooling, the mixture was dried on an electric hot plate until it turned into white ash. And 2 ml dd-H₂O and 1 ml HNO₃ were added to the white ash. After digested at 150 °C for 14 h, samples were diluted to 40 ml using dd-H₂O at final volume.

Quality control/assurance of the measurements includes: (1) the calendar years of heavy metal elements were determined by the cross-dating, which was checked by the COFECHA program (Homes, 1983) to ensure the accuracy of cross-dating; (2) in order to remove the insoluble residue on the experimental vessel, all the experimental PTFE was heated at 150 °C for 12 h, washed three times with ultrapure water, and soaked overnight; (3) all instruments were rinsed with pure alcohol after the treatment of each sample to avoid potential contamination of samples; (4) the reagents used in the digestion process are analytically pure reagents; (5) recoveries of standard plant and soil samples ranged from 93% to 102%; and (6) when performing elemental analysis, the correlation coefficient of the standard curve is controlled above 0.999, and a correction is performed when a certain sample amount is tested.

Concentrations of heavy metal elements of Fe, Mn, Cu, Zn, Ni, Cr, Cd, Pb, Co, and Sr were measured by the inductively coupled plasma mass spectrometry. In order





Figure 1. Location and study region. (a) Location of the study region in China, locations of the (b) Fuzhou city and (c) the Gu Mountain in the study region, and the (c) photos of the sampling site at the Gu Mountain. DOI: https://doi.org/10.1525/elementa.2020.20.00075.f1

to reduce the matrix effect of the sample solution, internal standard elements of Rhodium and Rhenium, which are not contained in the solution and are close to the mass number of measured elements, were used as internal standard elements. The parallel test of relative standard deviation was lower than 5%, indicating that the machine runs smoothly. The calibration curve furnished good linear correlation coefficients (0.99982–0.99999) in our study.

2.3. Statistical analysis

Pearson correlations were calculated between different elements to detect their linkages and between elements and climatic variables (temperature and precipitation) during their common period from 1953 to 2016 to study the potential influence of climate. In addition, we calculated the autocorrelation as the correlation between consecutive years to represent the dependence of element contents in current year to the previous years. To alleviate the influence of trends on correlations, we additionally calculated the Pearson correlations for the first-order difference data. The first-order difference data were calculated as the residuals between consecutive years, which were normalized by their mean.

Apart from the Pearson correlation (**Figure 2a and b**), we employed an agreement measure of the year-toyear variation called Gleichläufigkeit coefficient (Eckstein and Bauch, 1969; **Figure 2c**) to evaluate the degrees of



Figure 2. Correlation between elements from 1848 to 2016. (a) Direct correlation and (b) first-order difference correlations between elements during their common period (1849–2016); (c) gleichläufigkeit score of 10 metal element concentrations of *Pinus massoniana* during 1848–2016 in Gu Mountain. *Means significant correlation at 0.05 level. **Means significant correlation at 0.01 level. DOI: https://doi.org/10.1525/elementa.2020.20.00075.f2

agreement between elements on the high frequency domain. This statistic only examines whether the variations of two sequential values are matched or not but does not take into account the differences between the values. It is expressed as the percentage of cases of agreement (Allan Buras and Martin Wilmking, 2015), representing the degree of similarity within a number of time series on the high frequency domain (Schweingruber et al., 1993).

Principal component analysis (PCA; Richman, 2010) was used to identify the covariation patterns of elements. This method was widely applied to group different elements, which can be used to help assess the sources and absorption mechanisms of heavy metal elements in tree rings (Rodríguez-Catón et al., 2015; Marija et al., 2017). Hierarchical Cluster analysis was used to analyze the similarity of the concentrations of different elements in *P. massoniana* from 1848 to 2016 (**Figure 3**).

3. Results

3.1. Heavy metal elements in soil and tree rings

As shown in Table 1, six elements (Cr, Co, Ni, Cu, Zn, and As) in topsoil are lower than the allowable threshold concentrations of the national standards (GB15618-1995), except for Sr and Pb. A low concentration of most of the heavy metal elements standard suggests that pollution in Gushan area is not severe due to relatively low industrial activities compared with other low-lying areas. The content of Pb surpassed the first-level national soil standard (35 mg/kg) but still is much lower than the second-level national soil standards (250 mg/kg) set by the National Environmental Protection Agency. The ratios were calculated between element concentration in tree rings and soil as the absorption coefficient ($K_f = T/S$) (**Table 1**). Cr has the highest absorption coefficient ($K_f = 0.710$), followed by essential nutrients for plants such as Zn and Cu. The elements of the Ni, Co ($K_f = 0.023$) and Pb ($K_f = 0.018$) have the lowest absorption coefficient. There is no significant correlation between heavy metal elements and tree-ring width.



Figure 3. Cluster analysis for variations of 10 element concentrations in the tree rings from 1848 to 2016. DOI: https://doi.org/10.1525/elementa.2020.20.00075.f3

ID	Cr	Co ^c	Ni	Cu	Zn	As	Sr ^c	Pb
GS01	30.912	4.142	11.345	7.734	54.190	4.647	28.478	35.333
GS02	13.617	3.848	5.297	7.816	86.212	3.992	43.354	63.120
GS03	16.468	4.631	6.591	6.268	58.690	3.765	35.745	42.791
GS04	22.105	4.938	7.827	9.708	67.618	5.281	38.013	49.454
GS05	18.330	4.028	7.150	9.194	63.442	4.948	38.595	46.325
GS06	25.456	8.019	10.454	13.369	74.574	6.421	30.238	64.697
GS07	26.757	6.242	10.904	14.437	78.942	7.012	41.950	54.990
GS08	19.074	2.953	5.087	8.324	53.932	4.263	54.295	42.338
GS09	23.167	3.388	7.883	10.136	70.903	5.291	36.236	41.697
GS10	14.184	1.834	4.645	5.249	40.877	3.764	29.064	30.219
Average	21.007	4.402	7.718	9.224	64.938	4.938	37.597	47.096
STD1 ^a	90		40	35	100	15		35
STD2 ^b	41.3	7.41	13.5	21.6	82.7	5.78	34	34.9
K _f	0.710	0.023	0.125	0.190	0.333		0.047	0.018

Table 1. Element concentrations (mg/kg) in topsoil. DOI: https://doi.org/10.1525/element

^aSTD1 means the background values of the suburban soil in Fujian province.

^bSTD2 means the background values of the suburban soil in China. The environmental quality standard for soils is GB15618-1995.

^cCo and Sr have no soil standard value in China at present.



Figure 4. Time series of four groups for the element concentration revealed in tree rings. (a) Mn and Sr; (b) Ni and Cu; (c) Co, Cd, and Pb; (d) Cr, Zn, and Fe. The thin line represents the original data of the element, and the thick line is the curve after Savitzky–Golay smoothing. DOI: https://doi.org/10.1525/elementa.2020.20.00075.f4

3.2. Temporal variations of heavy metal elements and their correlations with climate

Heavy metal element concentration in our tree rings spans from 1848 to 2016. Trends of heavy metal elements of the Gu Mountain can be divided into four categories according to cluster analysis and PCA results (**Figure 3**). There is higher within-group correlations (**Figure 2a, b**) and Gleichläufigkeit score (**Figure 2c**) than between groups. We classify Mn and Sr as Type 1, which shows a steady declining trend (**Figure 4a**) ranging from 40.0 to 324.6 μ g/g and 1.8 to 9.6 μ g/g, respectively. Relative to Sr, Mn shows a slight upward trend from 1860 to 1876. Ni and Cu were classified as Type 2, which showed an increasing trend (**Figure 4b**) with a correlation of 0.55.

Different from a continuous upward trend for Cu, Ni shows stronger interdecadal variations such as a downward trend from 1880 to 1917. Concentrations of Co, Cd, and Pb, classified as Type 3, showed an increasing trend before 1940 but a lapsing trend afterwards, particularly for Pb (**Figure 4c**). Concentrations of Co and Cd then increase since 1864 and reach the peak during the 1920s–1940s. The correlations between Co and Cd, between Cd and Pb, and between Co and Pb are 0.73, 0.69, and 0.56, respectively. The remaining elements of Cr and Fe were classified as Type 4 with a correlation of 0.83, which display

interdecadal fluctuations but no clear trend (**Figure 4d**). Mn, Sr, Co, Cd, and Pb with strong trends showed a stronger autocorrelation of a 3-year lag effect, whereas the rest elements (Ni, Cu, Cr, Fe, and Zn) have a weak autocorrelation (**Table 2**).

The heavy metal elements showed significant correlations with climate variables, except for Zn (Figure 5). In general, these elements have positive correlations with the temperature from August to November and the precipitation in October, and negative correlations with the relative humidity. Cr shows a significant correlation with precipitation in October (0.44) and is negatively correlated with relative humidity in August and September. The correlations between Fe, Ni, and Cu concentrations and relative humidity are more significant than the monthly temperature and precipitation. Ni shows significant negative correlations with relative humidity, particularly in August (-0.43). The correlations with climate are similar between Cu and Fe, which shows close correlations with the temperature in August-November and the relative humidity in July-September. The relationship between climate factors of the previous year and elements in tree rings show that the elements have no significant correlation with the precipitation of the previous year, but it still keeps the correlation with the temperature from May to August (Figure 6).

Table 2. The autocorrelation coefficients of the 10 ele-ments. DOI: https://doi.org/10.1525/elementa.2020.20.00075.t2

No.	Mn	Sr	Ni	Cu	Со
1	0.94**	0.96**	0.67**	0.47**	0.61**
2	0.92**	0.94**	0.65**	0.39**	0.53**
3	0.90**	0.94**	0.58**	0.41**	0.42**
	Cd	Pb	Cr	Fe	Zn
1	0.89**	0.94**	0.39**	0.35**	0.16*
2	0.84**	0.92**	0.22**	0.17*	0.23**
3	0.81**	0.90**	/	/	/

*Means significant correlation at 0.05 level. **Means significant correlation at 0.01 level.



Figure 5. Correlations between elements and (a) temperature, (b) precipitation, and (c) of the previous year. DOI: https://doi.org/10.1525/elementa. 2020.20.00075.f5



Figure 6. Correlations between elements and (a) temperature of the previous year. The line means significant correlation at 0.05 level. DOI: https://doi.org/10.1525/elementa.2020.20.00075.f6

4. Discussion

4.1. Transportation of heavy metal elements from soils to tree rings

There are three ways for heavy metal elements to enter trees: (1) absorbed by root from soil moisture, (2) by leaves from air, and (3) direct deposition onto stem segments (Lepp, 1975). Previous studies have shown that most heavy metal elements were absorbed by roots (Watmough and Hutchinson, 2003). Absorption of different heavy metal elements varies for different tree species, soil types, and pH (Injuk et al., 1987; Vimmerstedt and McClenahen, 1995; Kirchner et al., 2008). The lowest absorption ratio for Co and Pb may be because that they are toxic to trees. Although the absorption ratio for Pb is low, its concentration is higher than national quality standard. This may be caused by the use of lead petrol from vehicles as the study sites are close to road (Lombardo et al., 2001).

4.2. Radial migration of heavy metal elements

The mobility of elements across tree rings varies in different tree species at different biological traits such as different tree age, heartwood–sapwood patterns, under different regions of changing environmental conditions such as pollution sources, climate patterns, acid depositions, requiring such investigations for different trees in different regions (Smith and Shortle, 2003; Cui et al., 2013). Influences of physiological processes on element concentration vary depending on tree species and element (Brackhage et al., 1996). These physiological processes can cause biased element concentration in tree rings from the environment, such as a steady decline from pith to bark and a peak element concentration between the heartwood and sapwood (Liang and Huang, 1992).

The strong decline trends from pith to bark for Sr and Mn observed in this study were also found in Jeffrey pine (*Pinus jeffreyi*) from the Tahoe Basin, California, (Kirchner et al., 2008). The strong decline trend for Mn may be because that it is an essential element for metabolic processes of photosynthesis and respiration (Marija et al., 2017). Continuous consumption of Mn in soil can contribute to the lapsing trend in bioavailability in soil, causing a decline trend in Mn from pith to bark (Hevia et al., 2018).

Accumulation of heavy metal elements at the heartwood–sapwood boundary from the 1920s to 1940s was also reported in previous studies (Donnelly et al., 1990; Xu, 2004)–for example, a peak concentration of Pb and Cd near the heartwood–sapwood boundary in *P. massoniana* (Xu, 2004) and *Ponderosa pines* (Cui et al., 2013) in Shenyang city. Watmough and Hutchinson (2002) found that the concentrations of Pb in *Scots pine* and *oak* peaked near the heartwood–sapwood boundary. These elements are often toxic elements, and trees can trigger a "detoxification mechanism" by transporting them from the active part, sapwood, to the inactive part, heartwood (Donnelly et al., 1990; Xu, 2004; Cui et al., 2013).

4.3. Pollution history recorded in heavy elements

Previous studies have proved ability of the tree rings of P. massoniana to record pollution history (Hou et al., 2002a, 200b; Kuang et al., 2007). The increases in Cu and Ni generally agree with the enhancement of tourism and industrial activities and the known pollution history, specifically recorded undulations (Wang, 2005). Although Cr, Fe, and Zn (Type 4) have weakest migration across rings in our species, different species can have varying migration ability for Zn. For example, Zn can migrate across rings in Pinus tabulaeformis and Toona sinensis for 3 years, but there is no migration for Zn in Firmiana simplex (Liu et al., 2009a, 2009b). Since Cr, Fe, and Zn have the lowest migration ability, they can well reflect the environmental history (KabataPendias, 2011). The peak concentration of Cr, Fe, and Zn that occurred from 1880 and 1900 may be associated with the heyday of iron ship construction from 1880 to 1907 of the Fuzhou Shipping Bureau including shipyards, iron foundries, and other enterprises, which is less than 4 km from our tree-ring site.

4.4. Climate —element relationships

Heavy metal concentration in tree rings can also be modulated by climate by affecting the pollution pathways (e.g., via leaf stomata) and physical processes (metabolism activities) of trees (Jónsdóttir et al., 2005; Sardans and Peñuelas, 2007; Sardans et al., 2008). This may explain the strong correlations (0.44, 0.39, and 0.44) between Cr, Fe, and Cu and the precipitation in October. There is no significant correlation between elements and precipitation in the previous year, which may indicate that the effect of precipitation on element absorption is more immediate. Actually, their correlations with climate are even higher than the correlations with tree-ring width and stable carbon isotopes in this area (Li et al., 2016). During wet conditions, these elements may be more soluble and easier to be absorbed by trees. In addition, some elements can easily enter leaves due to high stomatal conductance under wet conditions (Hagemeyer and Prasad, 1999; Fernández, 2013). On the other hand, a wet condition can cause stomata closure and plant cuticles to contract, inhibiting heavy metal elements from entering the leaves (Shahid et al., 2016). Tree-ring data have been widely used for climate

reconstructions in arid and cold China, but they are less sensitive to hot and humid regions (Fang et al., 2017a, 2017b). The high correlations between heavy metal elements and climate suggest that they could be considered as alternative tree-ring proxy for reconstructing past climate in hot and humid regions.

5. Conclusions

This study provides the longest series of 10 heavy metal elements in tree rings of the past 168 years collected from Gu Mountain of Fuzhou areas in southeastern China. Heavy metal elements in tree rings are jointly modulated by environmental pollution, migrations across rings, and climate change. The 10 elements were classified into four types with Type 1 (Mn and Sr) showing strongest migration effect from the bark to peak, leading to a lapsing trend from pith to bark. Type 2 (Co, Cd, and Pb) has moderately strong migration ability to shift these elements to the boundary between heartwood and sapwood. The other two types show limited migration, and Type 3 (Ni and Cu) seems to indicate an intensified pollution caused by tourism development and increased transportation. The high concentration of Cr and Fe in Type 4 between 1880 and 1900 coincides with the pollution associated with the heyday of iron ship construction in Fujian Shipping Bureau. We also found Cu and Fe showed strong correlations with the relative humidity in July-September. This suggests the modulation of climate on heavy metal in tree rings and the potential for using the heavy metal elements for climate reconstruction in regions where other tree-ring proxies have little climate sensitivity.

Data accessibility statement

The following data sets were generated for this study:

Time series of four groups for the element concentration from 1848 to 2016 revealed in tree rings.

These data are uploaded as online supporting information as part of this article.

Supplemental files

The supplemental files for this article can be found as follows:

Data S1. Raw data. Xlsx.

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Competing interests

The authors have no conflict of interest to declare.

Author contributions

- · Contributed to conception and design: CSY, FKY, CXL.
- Contributed to the experiment performance: CSY, FKY, CXL, ZZP, DZP.
- Contributed to analysis and interpretation of data: CSY, FKY, DZP, CXL.
- $\cdot\,$ Drafted and/or revised the article: all authors.
- Approved the submitted version for publication: all authors.

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