ENRICHMENT, RISK ASSESSMENT AND SOURCE IDENTIFICATION OF METAL LEAD IN CHANGHU RESERVOIR SEDIMENTS OF SOUTH CHINA

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Abstract. Evaluating the ecological risks of metals and identifying their sources is useful for preventing and controlling heavy metal pollution in water bodies. Four sediment cores (S1~S4) were collected from the Changhu Reservoir of South China to determine lead (Pb) concentrations and geochemical fractions, as well as the isotopic compositions of core S1. The results show that Pb concentrations increased from the upstream site (S1:173.2 mg kg^{-1}) to the downstream site (S4:313.5 mg kg^{-1}), resulting in a moderate to significant enrichment in the sediments. Sediment Pb in the geochemical fractions followed a decreasing order of residual (F4:54.7%) > reducible (F2: 23.1%) > oxidizable (F3: 16.6%) > acid-soluble fraction (F1: 5.8%). The geoaccumulation index (I_{geo}) and risk assessment code (RAC) showed that sediments were moderately polluted by Pb in S1 and S2 core, while sediments were moderately to heavily polluted in S3 and S4 core. The ecological risk of Pb in all sediment samples is generally at a low risk level, except for the sediments at a depth of 30-40 cm in the S4 core. Significant correlation between Pb concentration and $^{206}Pb/^{207}Pb$ ratios suggested possible binary mixing of Pb. In the present study, mining activities, which was the major anthropogenic Pb source base on its isotopic composition, contributed significantly (means: 45.3-77.5%) to sediment Pb. The anthropogenic Pb in sediments is most likely to come from Sphalerite and Galena.
Keywords: *human activities, stable Pb isotopes, sediment core, heavy metal speciation*

Introduction

Reservoirs are important water resources and play an important role worldwide in preventing floods, regulating climate, generating hydroelectric power, agricultural irrigation, drinking and other activities (Zhu et al., 2017). However, with the rapid development of industry and agriculture in recent years, the water quality of many reservoirs has significantly deteriorated (Frémion et al., 2016; Wang et al., 2012). Research on ecological impacts of reservoir caused by these human behaviors becomes more important, as aquatic systems suffer from the increasing pressure of reservoir constructions (Bai et al., 2009). Heavy metals resulting from natural and anthropogenic inputs can seriously impact aquatic organisms in reservoirs and threaten human health via the food chain due to the toxicity, persistence and bioaccumulation problems associated with these metals (MacDonald et al., 2000; Roman et al., 2007). Lead (Pb) is the fifth highest metal used throughout the world and is considered to have a potential carcinogenic risk to aquatic organisms and human beings (Karrari et al., 2012; Silbergeld, 2003). Therefore, Pb contamination in reservoirs has become an increasing concern in recent years (Li et al., 2019; Nartey et al., 2019).

In reservoir ecosystems, most of the lead (Pb) are accumulated and sequestered in the particulate phase in sediments when the water environment conditions are relatively stable (Zhang et al., 2016). Sediments often act as integrators and amplifiers of the concentrations of Pb in the waters which pass over and transport them because of the

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small variation in time and space of sediments (DelValls et al., 1998). Therefore, sediments provide an excellent proof of anthropogenic impact, allowing more consistent assessment of spatial and temporal contamination (Alves et al., 2014; Beiras et al., 2003; Gao et al., 2017, 2018; Guevara et al., 2005). However, previous studies have mainly focused on the spatio-temporal distribution and ecological risk assessment of Pb content in sediments in natural water bodies, such as rivers (Gao et al., 2018; Huang and Lin, 2003), lakes (Liu et al., 2021; Xiao et al., 2014) and coastal zones (Pekey, 2006). There are still not enough well-documented studies on reservoir systems in which the Pb in sediments might be affected by the formative reservoirs and prolonged water renewal time (Kummu and Varis, 2007; Wang et al., 2012).

The total Pb concentration in sediment provides useful information on the degree of sediment pollution (Sun et al., 2011). The enrichment factor (EF) is a useful tool for evaluating the impact of anthropogenic Pb on sediment (Xu et al., 2017). However, the total Pb concentration cannot effectively evaluate the environmental behaviors (bioavailability, mobility, and toxicity) and ecological risks of lead, because only a specific fraction of Pb may have bioavailability and have adverse effects on the environment (Li et al., 2019; Sundaray et al., 2011). Generally, a high concentration of Pb in the acid-soluble fraction will lead to more bioavailability in the sediment, thereby resulting in more severe toxic effects on aquatic organisms, whereas Pb in the residual fraction is not bioavailable and presents a low ecological risk (Rosado et al., 2016). Environmental behaviors of Pb in sediment can be significantly affected by anthropogenic activities. For example, anthropogenic activities noticeably affected the non-residual fractions of Pb in the Shima River (Gao et al., 2018). Thus, the European Community Bureau of Reference (BCR) sequential extraction procedure has been widely used to determine the chemical speciation of Pb, owing to evaluate ecological risks posed by Pb within sediments (Cuong and Obbard, 2006; Nemati et al., 2011; Wang et al., 2015).

In terms of reservoir sediments, there are many potential sources of Pb, including the natural weathering of parent rocks, and anthropogenic inputs, such as mining activities, vehicle exhaust, industrial emissions and coal combustion (Chiaradia et al., 1997; Farmer et al., 1999; Gao et al., 2012; Walraven et al., 2014). Therefore, how to identify the main sources of Pb in sediment is crucial for preventing and controlling Pb contamination in the reservoir. Many methods (such as traditional statistical approaches, enrichment factor and lead stable isotope tracing, etc.) have been developed in recent years to address this challenge (Audry et al., 2004; Gao et al., 2012; Hass and Fine, 2010). However, traditional statistical approaches and enrichment factor have drawbacks (e.g., large-sample, ambiguous results) that cannot be ignored, making them difficult to accurately identify the source of Pb in sediments (Zhang et al., 2016). On the contrary, stable Pb isotopic compositions are considered an effective tool for identifying the sources of Pb in sediments, because the Pb isotopes are not significantly affected by the physical and chemical fractionation processes associated with human activities, and is only related to the different sources (Veysseyre et al., 2001).

The Changhu Reservoir is located downstream of the Wengjiang River, a primary tributary of the Beijiang River in Guangdong Province. It is also an important source of drinking and irrigation water for local residents in Yingde City. However, with the rapid development of industry and agriculture in the upper reaches of the Wenjiang River in recent years, a large amount of wastewater was discharged into the river, leading to continuous degradation of the water quality in the reservoir (Zhu et al., 2015).

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Consequently, the water quality of reservoir is arousing growing concerns among the public. Up to now, most of the studies focused on the levels and sources of nutrients (Chen et al., 2009; Zeng et al., 2017). However, reports on the pollution, environmental behaviors and sources of heavy metals in the reservoir sediment are still inadequate, especially for Pb. The goals of this paper, were to (1) analyze the contents, geochemical fractions and enrichment level of Pb; (2) assess the pollution and ecological risk levels of Pb in sediment cores from the Changhu Reservoir; and; (3) identify the contamination sources and quantitatively determine their contribution to sediment Pb using the stable Pb isotope compositions. The results obtained in this study will provide a scientific basis for controlling Pb contamination in the reservoir.

Materials and methods

Study area and sampling

The Changhu Reservoir (113°28′26″E, 24°8′23″N) is located in Yingde City, Guangdong Province, which is one of the most developed areas of China (*Fig. 1*). It is a runoff type daily regulation reservoir with comprehensive functions such as power generation, flood control, and irrigation. Changhu Reservoir was built in 1972, with a total storage capacity and normal water storage level are 1.55×10^8 m^3 and 62.0 m, respectively. The catchment area of this reservoir is about 4800 km^2, accounting for about 97% of the total area of the Wengjiang River Basin (Zeng et al., 2017). The Dabaoshan polymetallic mine (mainly producing lead, zinc, and copper, etc) is located upstream of the reservoir and discharge a large amount of Pb containing wastewater into the reservoir year-round (Li et al., 2019). In addition, a large number of small industrial factories (e.g., such as metallurgical plant, power plant and chemical plant) and arable land are distributed within the watershed, posing a serious threat to the water environment of the reservoir. Specially, a serious heavy metals pollution incident occurred in October 2012, resulting in the death of 1.81×10^5 kilograms of cage cultured fish.

In order to obtain representative sediment cores, sampling sites were evenly distributed from upstream to downstream of the reservoir, and were located near the central axis of the reservoir, away from the influence of human activities. Due to the fact that the reservoir is a typical river-type reservoir with a narrow water surface, four representative sedimentary cores (S1~S4) were collected using a gravity sampler in July 2022 (*Fig. 1*). Moreover, the particle compositions of the collected sediment cores were all mainly composed of clay and silt, suggesting the stable sedimentary environment of the reservoir. The lengths of cores S1, S2, S3 and S4 were 42, 44, 30 and 40 cm, respectively, because the sedimentation rate of particulate matter varies at different sampling sites. Two background soil samples (T1, T2) were also collected near the reservoir (*Fig. 1*). In areas located far from human activities, which were believed to have negligible anthropogenic metal inputs, representative forest soil samples at the top 0~10 cm surface layer were collected with a stainless steel auger. After sampling, sediments were sectioned at 2 cm intervals. All soil and sediment subsamples were packed in a clean plastic bag, stored in a cool box, returned to the laboratory and freeze-dried at -80°C for 72 h. The dried soil and sediment samples were then ground in an agate grinder and sieved through a 0.149 mm mesh for further analysis. The GPS coordinates of sediment and soil sampling points were listed in *Table A1*.

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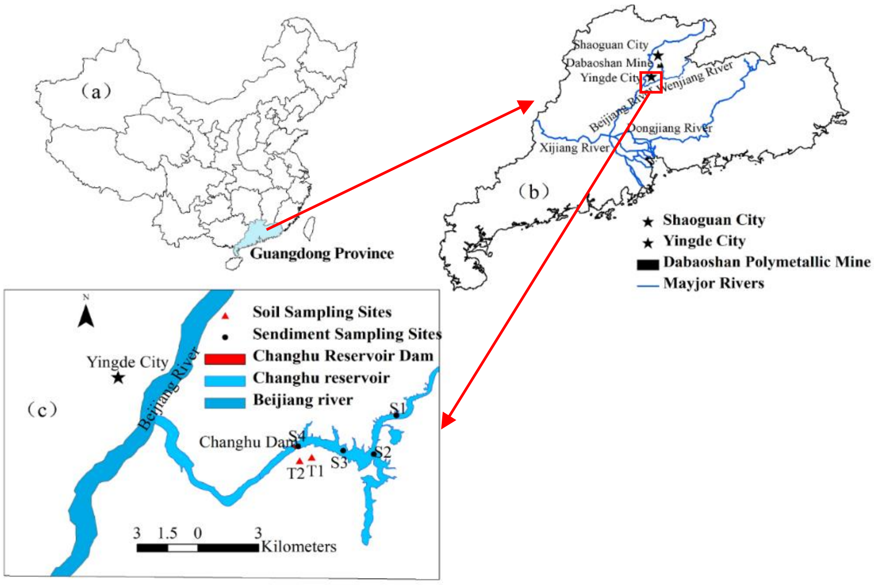

Figure 1. *The study area and the sampling sites. (a) Guangdong Province, (b) study area and the major pollution source, (c) location of the sampling sites in the Changhu Reservoir*

Analytical methods

Physicochemical properties

The pH of the sediment was measured by a pH meter in a solution with a sediment/water (CO_2-free) ratio of 1:2.5. Organic matter (OM) was determined by wet oxidation at 180℃ via a mixture of potassium dichromate and sulfuric acid (Li et al., 2019). The cation exchange capacity (CEC) was determined by Hexamminecobalt trichloride solution-Spectrophotometric method (Gray et al., 2016), and the grain size distribution was analyzed using a Mastersizer 2000 (Malvern Instruments Ltd., UK). Reagent blanks and duplicate samples were used to ensure the reliability of experimental analysis processes for physicochemical properties such as OM and CEC. The relative deviations for the duplicate samples of all testing items are less than 6.8%.

Trace metal concentration

The total Pb, Fe and Al content was analyzed by digestion with nitric acid, hydrofluoric acid and Perchloric acid. Briefly, approximately 0.2 g of sample (sediment) was placed into a Teflon tube and digested in a mixture of HNO_3 (GR, 10 mL) and HF (40%, 2 mL) under high pressure and temperature. After the sample was completely dissolved, the HF was removed by evaporation at 120℃, and the residual was then dissolved with HNO_3 again and adjusted to a suitable volume with 2% HNO_3. The total metals (Pb, Fe and Al) concentrations were determined by flame atomic absorption spectrophotometer (FAAS) (AA-7000, Shimadzu, Japan). The accuracy and precision of the analyzed data were assessed using a quality assurance and quality control (QA/QC) program that included a reagent blank, duplicate samples, and certified geochemical reference materials (GSD-12, GSF-5). The recoveries of Pb and Fe for the standard samples was 92.1% and 90.4% and the standard deviation of the duplicates was < 5% (*Table A2).*

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Fraction concentration of trace metals

To investigate the geochemical fractions of Pb and assess their bioavailability and ecological risk in the studied sediments, metal speciation was performed in the sediment samples according to the modified BCR method (Ure et al., 1993). Four fractions of sediment Pb were extracted from a 0.5 g sediment sample, as follows: (F1) acid-soluble fraction (20 mL 0.11 mol L^{-1} CH_3COOH, shaken for 16 h), (F2) reducible fraction (20 mL 0.5 mol L^{-1} $NH_2OH{\cdot}HCl$ at pH 1.5, shaken for 16 h), (F3) oxidizable fraction (10 mL 0.88 mol L^{-1} H_2O_2 + 25 mL 1.0 mol L^{-1} CH_3COONH_4 at pH 2, shaken for 2 h + 16 h). The residual fraction was digested in a Teflon tube with the mixture of HNO_3 (65~68%, GR) and HF (40%). The geochemical fractions of trace metals were measured by FAAS. A reagent blank, duplicate samples and the overall recovery rate for Pb (sum of the four fractions/independent total content) were used to assess the accuracy and precision of the determined metal contents. The overall recovery rate for Pb was 88.6%.

Stable Pb isotopic compositions

Stable Pb isotopic compositions were measured at the Beijing Createch Testing Co., Ltd, Beijing, China. The samples were pretreated according to Hao et al. (2008) and Zhang et al. (2016). The Pb isotopic compositions were determined using a multi receiver inductively coupled plasma mass spectrometer (MC-ICP-MS) (Neptune Plus, Thermo Fisher, USA). The measured values for the standard reference material (NBS 981) were $^{206}Pb/^{204}Pb = 16.9418 \pm 0.0012$ (certified value: 16.9205), $^{207}Pb/^{204}Pb = 15.4993 \pm 0.0010$ (certified value: 15.5017), and $^{208}Pb/^{204}Pb = 36.7232 \pm 0.0020$ (certified value:36.7525). The Pb blank from the procedure is lower than 1 ng and the analytical uncertainties in 2σ (2σ, 2 standard deviation, n = 10) for Pb isotopic ratios are better than 0.2%.

Pollution and potential ecological risk assessment method

(1) Enrichment factor (EF)

The EF, which normalizes the content of a trace metal to that of a conservative element, has been widely used to quantitatively describe the anthropogenic enrichment of trace metals (Audry et al., 2004; Chen et al., 2016; Gómez-Álvarez et al., 2011). Here, Al was adopted as a reference element because of its wide distribution in crustal rocks and scarcity in various pollution sources (Audry et al., 2004). The EF is calculated using *Equation 1:*

$$EF = \frac{(C_i/Al)_{\text{sample}}}{(C_i/Al)_{\text{background}}} \quad \text{(Eq.1)}$$

where $(C_i/Al)_{sample}$ is the ratio of the concentration of metal to that of Al in a sediment sample, and $(C_i/Al)_{background}$ ratio was calculated based on Guangdong soil background values (Li et al., 2019). The corresponding relationships between the EF value and the enrichment level are presented in *Table A3.*

(2) Geoaccumulation index (I_{geo})

To assess Pb pollution in sediments, the geoaccumulation index (I_{geo}) introduced by Müller (1969) is expressed as the follows (*Eq. 2*):

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$$I_{\mathrm{geo}} = Log_2\left(\frac{C_{\mathrm{i}}}{1.5 \times B_{\mathrm{i}}}\right) \quad \text{(Eq.2)}$$

where C_i is the content of metal Pb, and B_i is its geochemical background value. In this paper, we used soil background value of Guangdong Province (Li et al., 2019), and the factor 1.5 is the coefficient associated with the earth movement and rock formation. The relationships between the I_{geo} value and the pollution level are also given in *Table A3*.

(3) Risk assessment code (RAC)

The risk assessment code (RAC) was established by Perin et al. (1985) and is based on the release ability of metals. Because Pb in acid-extractable fractions are weakly adsorbed onto solid surfaces by electrostatic interactions, we used this fraction to evaluate its potential ecological risk in the Changhu Reservoir (Wang et al., 2015). The criteria for the risk assessment code are given in *Table A3*.

Quantification of anthropogenic Pb contribution

The measured Pb isotope ratios of sediment samples represent a mixture of natural and anthropogenic Pb. The individual $^{207}Pb/^{206}Pb$ ratios of a mixture of two Pb sources can be determined with a hyperbolic mixing equation under the condition that the $^{207}Pb/^{206}Pb$ ratios of the two Pb sources differ substantially (Walraven et al., 2014). The equation for two component mixture is given as follows (*Eqs. 3* and *4*):

$$Pb_{\mathrm{m}} \times \left(\frac{Pb^{207}}{Pb^{206}}\right)_{\mathrm{m}} = Pb_{\mathrm{geo}} \times \left(\frac{Pb^{207}}{Pb^{206}}\right)_{\mathrm{geo}} + Pb_{\mathrm{anth}} \times \left(\frac{Pb^{207}}{Pb^{206}}\right)_{\mathrm{anth}} \quad \text{(Eq.3)}$$

$$Pb_{\mathrm{anth}}\% = \frac{Pb_{\mathrm{anth}}}{Pb_{\mathrm{m}}} \quad \text{(Eq.4)}$$

where Pb_m, and Pb_{geo} represent the content of metal Pb in sediment and background soil, respectively. Pb_{anth} represents anthropogenic Pb content which can be calculated from *Equation 3*. $(^{207}Pb/^{206}Pb)_m$ and $(^{207}Pb/^{206}Pb)_{geo}$ are the measured isotope ratio in the sediment and background soil, respectively. $(^{207}Pb/^{206}Pb)_{anth}$ is the isotope ratio of anthropogenic Pb which was introduced by Xu et al. (2008). The relative contribution of anthropogenic Pb ($Pb_{anth\%}$) can be obtained by the ratio of anthropogenic Pb content to the total Pb content in the sediment.

Statistical analysis

All the figures were drawn by the software of Origin 2017 (OriginLab Inc., USA), except for *Figure 1* (ArcMap 10.0, ESRI inc., USA). Pearson's correlation analysis was carried out to identify the relationships of sediment properties, metal concentrations, Pb isotopic ratios, geochemical fractions and the EF value of Pb. Differences in linear regressions between the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios were tested using analysis of covariance. Differences and correlations were considered significant at $p < 0.05$. All statistical analyses were carried out using the SPSS 25.0 software (SPSS Inc., USA).

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Results

Physicochemical parameters in the sediments of the Changhu Reservoir

The average pH in the sediment at each sampling site were slightly acidic and presented values of 6.3 for S1, 6.4 for S2, 6.1 for S3 and 6.9 for S4 (*Table A4).* The average Fe and CEC contents in the sediment were similar, and both showing the maximum value at site S3 in the Changhu Reservoir. The OM content in the S1 core was the highest, with the mean value of 33.1 g/kg, while the average organic matter contents in other cores are roughly the same. The texture of the sediment at each sampling site were all belong to silty loam. However, the sand contents in the sediments of Changhu Reservoir decreased from 40.3% upstream (S1) to 23.6% downstream (S4), suggesting relatively strong hydrodynamic conditions at the upstream sites. The variation of clay, powder, and fine particles content along the Changhu Reservoir is opposite to that of sand. The analysis results of Pearson's correlation show that, CEC was significant positive correlated with fine-grained components and OM, with correlation coefficients of 0.227 and 0.223, respectively. The content of Fe and Al showed extremely significant positive correlation with the fine particle components, with correlation coefficients of 0.686 and 0.670, respectively.

With respect to the vertical distribution, the content of Fe, Al, FPC, and OM in S1 core showed increasing trend with depth from 0-20 cm, and gradually decreasing from 24 cm. The peak values of CEC, Fe, Al, FPC, and OM were found at depths of 28-32 cm for the core S2 and S3. The sediment pH decreased gradually with depth in core S3 and increased with depth in core S2. Relatively stable FPC was observed in core S4 (except 4~8 cm), indicating a relatively regular sedimentation process at that time, while the elevated sand contents were observed at depths of 3-4 cm and 7-8 cm, which consistent with the valley value of OM, Fe and Al, indicating heavy flood events in the catchment (Détriché et al., 2010). Similar records were also found in cores S2 and S3 at depths of 0–6 cm and 21–24 cm, respectively (*Fig. A1*).

Pb concentration and EF value

The mean contents of Pb in the sediments increased from S1 upstream to S4 downstream, with the mean value of 173.2, 187.8, 233.4, 313.5 mg kg^{-1}, respectively (*Fig. 2*). The vertical distributions of Pb were similar and generally increased with depth in cores S1, S2 and S4, whereas, it presented a noticeably increasing trend from the surface sediment to depths of 22 cm in core S3, then decreased with depth from 24 cm. As shown in *Table A3, Pb co*ncentration was significant positively related to the FPC ($p < 0.01$). A significantly positive correlation ($p < 0.01$) was observed between Fe content and Pb concentration in the sediment with a correlation coefficient of 0.462, while non-significant correlation ($r = 0.09$) was observed between OM content and Pb concentration. In addition, a drastic reduction in the contents of Pb as well as a decrease in FPC were found in the sediment at depths of 9-10 cm in S1, 17-18 cm in S2 and S3. (*Figs. 2* and *A1*).

The EF value was calculated by *Equation 1*. Generally, the mean EF values of Pb were 4.5 for S1, 4.0 for S2, 4.8 for S3, and 6.8 for S4 (*Fig. 2*), respectively, reflecting moderate enrichment in sediments S1~S3 and significant enrichment in S4. The gradually decrease in EF values were found from the depth of 12 cm to the surface sediments of cores S1, S3 and S4, and their enrichment levels reduced from significant to moderate enrichment, suggesting that the impact of human activities on the Pb content of sediment in Changhu Reservoir has gradually decreased. However, the EF

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values based on the total Pb concentration do not reflect reliable information for Pb mobility in sediments, necessitating further investigation regarding labile Pb fractions in sediments (Wang et al., 2017).

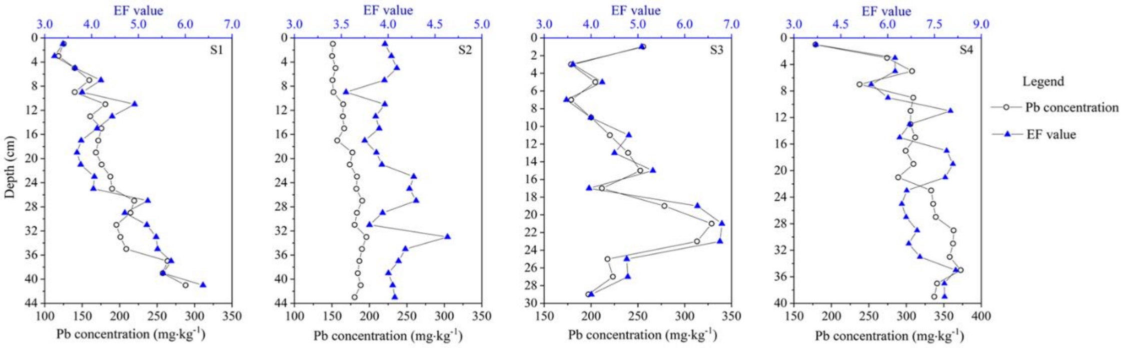

Figure 2. *Depth profiles of the EF values and Pb concentration in sediment cores (S1~S4)*

Fractions of trace metals

The sequential extraction steps revealed that the geochemical fractions of lead varied significantly (*Fig. 3*). On the whole, the mean value of geochemical fractions of sediment Pb followed a decreasing order: residual (F4:54.7%) > reducible (F2: 23.1%) > oxidizable (F3: 16.6%) > acid-soluble fraction (F1: 5.8%). Sediment Pb in acid-soluble fraction is considered to be the most mobile fraction, especially under acidic conditions. The residual Pb is immobile because it is bound to the stable crystalline structures of the parent materials (Nemati et al., 2011; Rodríguez et al., 2009). Reducible Pb is considered to be labile and is likely released upon dissolution of Fe/Mn oxides under reducing conditions (Rodríguez et al., 2009). Oxidizable Pb, which is bound mainly to OM by complexation and chelation (Nemati et al., 2011), is mobilized due to the decomposition of OM by mineralization in an oxidizing environment (Zhuang et al., 2016). In the present study, the residual Pb accounted for 53.0~65.5%, 48.0~54.5%, 51.2~56.7%, and 46.8~59.4% of the total concentrations in cores S1~S4, respectively, and was higher at site S4 than the other sites. The residual fraction of Pb in the sediment was the highest, because the sediment Pb of the Changhu Reservoir mainly comes from sulfide minerals such as Sphalerite, Pyrite, Galena, as well as some Silicate mineral, which are difficult to extract by acetic acid, ammonium acetate, Hydroxylammonium chloride (Dold, 2003). Excluding the residual fraction, Pb in the sediments mainly exist in the reducible fraction, with an average proportion of 25.6%, 23.5%, 21.6%, and 21.7% for core S1~S4, respectively. A relatively high reducible fraction of lead in sediments is mainly due to a large amount of Pb was bound in iron manganese oxides (Vega et al., 2010). The relatively low concentration of acid extractable and organic bound states in sediment indicates a relatively weak migration ability of Pb in an oxidizing environment.

With respect to the vertical distribution, the highest amount of Pb in the reducible fractions appeared at depths of 16 cm for S2, and 42 cm for S3, 42 cm for S1, which corresponded to the highest total content of Pb and EF value, further verified the anthropogenic contributions in the Changhu Reservoir (*Figs. 2* and *3*). In addition, similar to the vertical distribution of the total Pb content, the acid-soluble fraction of Pb in sediment increases with increasing depth indicating that the increase in sediment Pb content enhances the migration ability of Pb.

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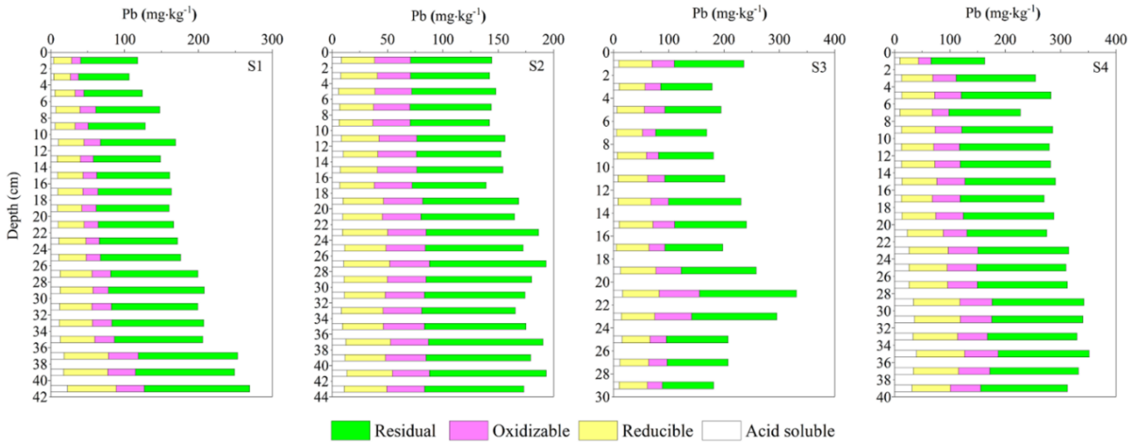

***Figure 3.** Vertical distributions of the geochemical fractions of Pb in sediment cores*

Assessment of heavy metal pollution and ecological risk

Geoaccumulation index (I_{geo})

The I_{geo} value was calculated by *Equation 2* and the contamination levels of trace metals accumulated in sediment cores were assessed (*Fig. 4*). In general, the accumulation index of Pb in the sediment of the Changhu Reservoir shows a gradual upward trend from upstream (S1) to downstream (S4), with mean value of 1.76 for S1, 1.68 for S2, 2.09 for S3, and 2.52 for S4, respectively, suggesting moderately contaminated status for S1 and S2 and moderately to heavily contaminated for S3 and S4. More specifically, all sediment samples at S1 and S2 sites in the Changhu Reservoir have Pb content that reaches moderate pollution levels, while 60% and 95% sediment samples at S3 and S4 sites, respectively, have Pb content belonging to moderately to heavily pollution levels. The vertical variation characteristics of the I_{geo} value are similar to that of Pb content in the cores. The maximum values of I_{geo} were at depths of 42 cm for S1, 34 cm for S2, 22 cm for S3, and 36 cm for S4, respectively (*Fig. A2*).

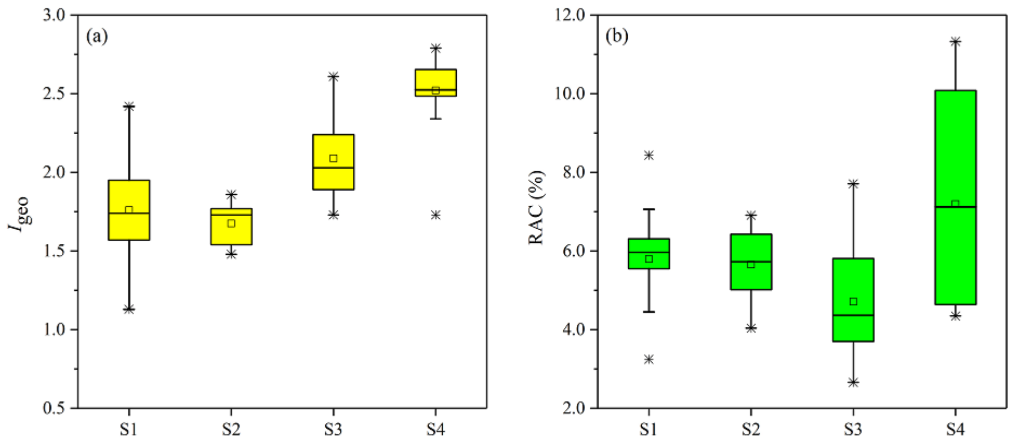

***Figure 4.** Box plot of geoaccumulation index (a) and risk assessment code (b) at different sampling sites. Square frame represents the average value of statistical data. Asterisk represent outlier. The bottom line of the box diagram represents the 25th percentile of the statistical data. The middle line in the box diagram represents the 50th percentile of the statistical data. The top line of the box diagram represents the 75th percentile of the statistical data*

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Risk assessment code (RAC)

Because of the I_{geo} value based on the total amount of heavy metals cannot effectively reflect the ecological risks, the risk assessment code (RAC) based on acid-soluble fraction of heavy metals was introduced to reveal the ecological risk level of Pb in Changhu Reservoir. As shown in *Figure 4*, the average values of RAC index in S1~S4 cores were 5.80, 5.66, 4.71, 7.20, respectively, indicating that the sediment in the Changhu Reservoir is generally at a low risk level (*Fig. 4*). Similar to the variation of the I_{geo} values from the upstream to the downstream, the mean RAC index value in the S4 core was higher than the other sediment cores, especially at the depth of 30-40 cm, which the RAC index exceeds 10, and the ecological risk reached a medium risk level (*Fig. A2*).

Pb isotopic composition in sediments

Changhu Reservoir receives a variety of inputs of Pb from nature and anthropogenic sources according to the high Pb concentrations in sediments. Therefore, the Pb isotopic compositions of some natural and anthropogenic sources in this region can be used to differentiate between the anthropogenic inputs and the natural geological Pb of the background soil in Wenjiang River Basin.

Pb isotope results are shown in *Figure 5a*. As a whole, the observed Pb isotopic ratio ($^{206}Pb/^{207}Pb$) varied from 1.194 to 1.210 in core S1, which was close to the Pb isotopic ratio of Beijiang River sediments (Gao et al., 2012). A downward decreasing trend in the $^{206}Pb/^{207}Pb$ ratio was found in cores S1, with the ratios of $^{206}Pb/^{207}Pb$ about 1.210 in the top sediments (0-4cm), and then decreased to about 1.194 at depths of 40-42 cm. The mean $^{206}Pb/^{207}Pb$ ratio of the background soils was 1.213, while application of Pb-containing ore could lead to $^{206}Pb/^{207}Pb$ ratio < 1.20 in the sediments (Eades et al., 2002; Sun et al., 2011). From the present results, it can be seen that about two-thirds of sediment samples in the core S1 have Pb isotope ratios less than 1.20, suggesting the influence of anthropogenic inputs in the Changhu Reservoir. In order to assess Pb contamination and identify potential Pb sources of sediments, the Pb isotopic compositions and 1/Pb concentrations in sediments were analyzed (*Fig. 5b*). The distribution of 1/Pb concentrations and $^{206}Pb/^{207}Pb$ ratio showed that Pb concentration of the sediments increased with decreasing $^{206}Pb/^{207}Pb$ ratio. The linear relationship between 1/Pb and $^{206}Pb/^{207}Pb$ ratio was significantly correlated (r = 0.917), indicating the content of Pb in sediment is jointly influenced by anthropogenic inputs and the natural geological Pb (Gao et al., 2012). Interestingly, the Pb content was low and the $^{206}Pb/^{207}Pb$ ratio was high in surface sediment, while the Pb content in bottom sediments is high and the Pb isotope ratio is low. That is to say, with the increase of sedimentary depth, there is an opposite trend between the content of Pb and the ratio of Pb isotopes. Due to the fact that surface sediments are younger than the bottom, the opposite trend indicates that the contribution of anthropogenic inputs to Pb in sediment has gradually increased over time.

Source identification of Pb

The $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios in sediment samples were taken into consideration to accurately identify the anthropogenic Pb sources. The sediment Pb isotopic ratios from the Changhu Reservoir were shifted slightly upwards from the Pb growth curve (*Fig. 6*), which was mainly attributed to enrichment with thorium (Th) in the Chinese continental crust (Mukai et al., 2001), which elevated the $^{208}Pb/^{206}Pb$ ratio. The distribution of Pb isotope ratios in sediments near the China Pb line indicates that

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sediment Pb mainly originated from Chinese domestic Pb (Zhu et al., 2010). Furthermore, the isotopic ratios of metallurgic dust and vehicle exhaust derived from leaded gasoline showed distinctly low $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios, which were below the Pb growth curve (*Fig. 6*). Consequently, these two sources contributed little to enrichment of sediment Pb in the study area. The isotopic ratios of air deposition may be derived from many different sources. thus, they might serve as the main pathway for anthropogenic Pb input into the sediments and cannot be considered as a contamination end-member (Gao et al., 2018; Yu et al., 2016). In addition, the linear regression between the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios showed a significantly decreasing trend in slope from high Pb content sediments to low Pb content sediments, suggesting that Pb in the sediments might have originated from two geological sources, one with high $^{206}Pb/^{207}Pb$ and low $^{208}Pb/^{206}Pb$ ratios and the other with low $^{206}Pb/^{207}Pb$ and high $^{208}Pb/^{206}Pb$. In fact, the Pb isotope ratios ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$) of all sediment samples are distributed near the Pb isotope connection line between the natural background soil and sediments which collected from Dabaoshan AMD. Therefore, natural geological sources and mining activities are considered the most likely sources of Pb in the sediments of the Changhu Reservoir. Because of the impact of mining activities on Pb isotope composition in sediments is mainly depends on the Pb isotopic composition of lead-bearing ore, and we found that the Pb isotope compositions ($^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$) of Galana ore and Sphalerite ore are quite similar to the sediments collected from the upstream of Wenjiang River. Therefore, the Pb in Sphalerite and Galena ore may be the main contributor to the high content of Pb in the sediments of Changhu Reservoir.

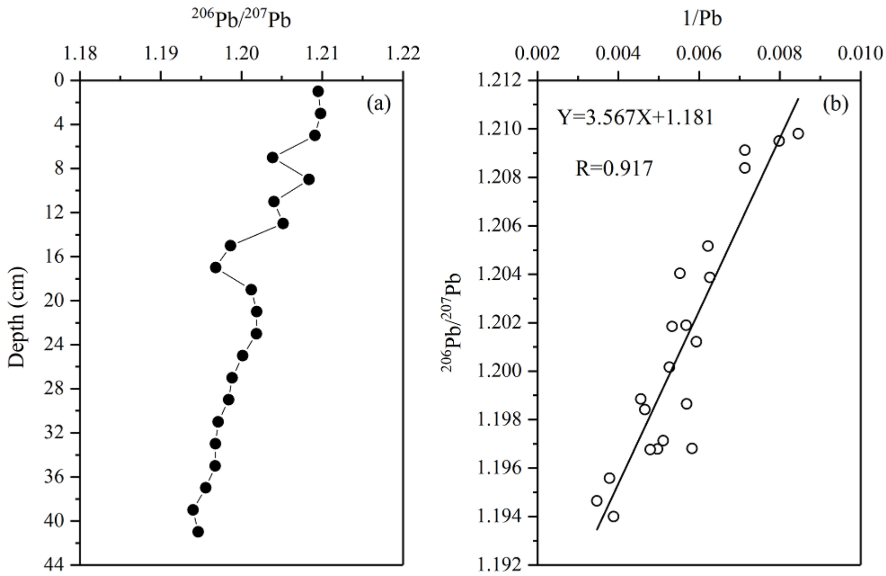

Figure 5. *The distribution of $^{206}Pb/^{207}Pb$ ratios (a) and the relationship between $^{206}Pb/^{207}Pb$ ratios and 1/Pb (b) in sediment core S1*

Discussion

The influence of physico-chemical properties on Pb content and fractions

Many studies have shown that the physico-chemical properties significantly affect the content and geochemical fractions of heavy metals in sediments. Jain and Ram (1997) reported that the extent of absorption of Pb by bed sediment, increases with the

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increasing of pH value. Gao et al. (2018) found a significant positive correlation ($p < 0.05$) between OM content and Pb concentration with higher correlation coefficient compared with those between FPC and Pb concentration, indicating a more important role of sediment OM in trapping Pb. However, a higher correlation coefficient between Fe content and Pb concentration (0.462) compared with those between OM content and Pb concentration (0.009) was observed in our study. This indicates that iron oxides caused by mining activities plays a more important role in trapping Pb than sediment OM (*Table A5*). In addition, there is a significant negative correlation between the content of sand and the content of Pb, Fe, and Al, reflecting the influence of hydrodynamic conditions (Nartey et al., 2019).

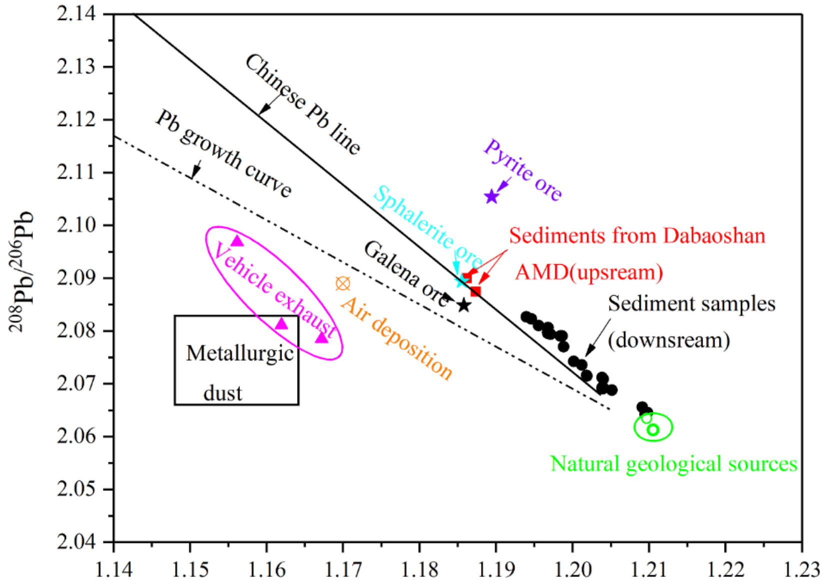

Figure 6. *The Pb isotopic composition ($^{206}Pb/^{207}Pb$ vs $^{208}Pb/^{206}Pb$) of sediment samples and the potential sources of Pb. Black circle dots represent sediment samples at different depths of S1 core and other symbols of different types and colors represent eigenvalue of Pb isotopes from different sources. Pb isotope data come from: Natural background soil (this study), sediments from Dabaoshan AMD (this study), vehicle exhaust (leaded gasoline) in the Pearl River Delta (Zhu et al., 2001), atmospheric deposition in the PRD (Wong et al., 2003), metallurgic dust (Gao et al., 2018; Li et al., 2012), and Galana, Sphalerite, Pyrite ore (Gao et al., 2018). The Pb growth curve (Gao et al., 2018) and Chinese Pb line (Mukai et al., 2001) are also presented*

There is a significant positive correlation between Fe content in sediment and the reducible fraction of Pb ($r = 0.422$), indicates that Fe oxides are the major sink for sediment Pb in the Changhu Reservoir (*Table A6*). Because iron oxides are the main products of Dabaoshan mining activities, therefore, the high correlation between Fe content and the reducible fraction of Pb indicates a significant impact of mining activities (Liu et al., 2018). It is worth mentioning that the metals extracted by $NH_2OH \cdot HCl$ (reducible fraction) are mainly combined with easily reducible Fe oxides (such as amorphous iron oxide), suggesting that Pb has great potential to be released from the sediment into the water column under a reductive environment, as amorphous iron oxides are more sensitive to changes in redox at the sediment-overlying water interface (Zhao et al., 2021). The residual fraction (%) of Pb is significantly positively

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correlated with the sand content, while significantly negatively correlated with the content of OM and FPC (*Table A6).* This indicates that the coarsening of sediment particle size caused by hydrodynamic conditions is likely to lead to an increase in metal residual fractions (*Fig. 3*). This result is also consistent with the result reported in Liu et al. (2011), which showed that the residual fraction of trace metals in the sediment core of the Pearl River estuary was significantly and positively correlated with the sand content. In addition, pH significantly affects the oxidizable fraction of Pb in sediments, while CEC significantly affects the acid-soluble fraction.

The impact of human activities on sediment Pb

Human activities not only affect the content and distribution of Pb in sediments, but also significantly affect the fractions of Pb in sediments. Chen et al. (2016) reported that approximately 53.2% of the sediment samples in the Le'an River has Pb content exceeding the moderate enrichment level, with the mean EF value of 2.3. Whereas, in our study, almost all sediment samples have reached moderate enrichment level, and even 39.7% of sediment samples have reached significant enrichment level, indicating that more severe impact of human activities on sediment Pb. Similar to the result of some previous studies, a significant positive correlation (0.415) was observed between the non-residual (F1 + F2 + F3) fraction of Pb in the sediments and the EF values (Gao et al., 2018; Li et al., 2019). It is indicated that human activities mainly affect the non-residual fractions of Pb in sediments. Moreover, the acid-soluble fraction of Pb is also significantly positively correlated with EF values (0.492), indicating that human activities increase the acid-soluble fraction of Pb and enhance its migration ability.

Anthropogenic Pb emissions from historical leaded-gasoline exhaust, coal combustion and metallurgy or effluents from mining and industrial activities wastewater, can be sedimented into reservoir water (Li et al., 2012). *Table A7* showed the impact of human activities on sediment Pb in some reservoirs. Obviously, sediment Pb in the Three Gorges Reservoir was mainly affected by coal combustion and the percentage contribution of coal combustion to total sediment Pb ranged from 20.2% to 91.7% (Han et al., 2015). Similar to the Three Gorges Reservoir, the contribution of coal consumption to the Shilianghe Reservoir has reached 30.6%. Leaded gasoline is another important source of sediment Pb for the Shilianghe Reservoir, which contributes less than 25% of sediment Pb in the Reservoir (Zhang et al., 2016). However, for the Shuanglong Reservoir, automobile manufacturing was considered the main source of sediment Pb (Zhou et al., 2020). In this study, the sediment Pb in the Changhu Reservoir was significantly affected by mining activities. This result is consistent with that of the Juam Reservoir and Lot River Reservoirs (Audry et al., 2004; Lee et al., 2013). In order to quantitatively evaluate the impact of human activities on sediment Pb of the Changhu Reservoir, the average values of the Pb isotope ratio ($^{206}Pb/^{207}Pb$) of the background soil and lead-bearing ore (Sphalerite and Galena) were used as the end-member to calculate the contribution (*Eqs. 3* and *4*). As shown in *Figure A3*, the contributions of mining activities ranged from 45.3% to 77.5%, with mean values of 63.1%. Sediments in the core (S1) with a depth greater than 4 cm are mainly affected by mining activities, which contribution percentage exceeding 53.7%, while sediments in the top layer (0-4 cm) have a greater impact on natural geological sources (>50%). It is found that the contribution of mining activities to sediment Pb gradually increases with depth, which is consistent with the increase in Pb content. This indicates that the government's environmental management measures have become increasingly strict in recent years.

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Conclusion

The spatial distribution patterns, enrichment, ecological risk and sources of Pb in reservoir sediments were clearly illustrated in this study via the total Pb concentration, Pb isotopic ratios, and by reference to the geochemical fractions and EF of Pb. The mean contents of Pb in the sediments increased from upstream (S1) to downstream (S4), with the mean value of 173.2, 187.8, 233.4, 313.5 mg kg^{-1}, respectively. The vertical distributions of Pb in all sediment cores were similar and presented a generally increasing trend with depth. The distribution characteristics of sediment Pb were significantly affected by FPC and iron oxides. The mean EF values of Pb in the sediment cores were 4.5, 4.0, 4.8, and 6.8 for S1~S4, respectively, suggesting a significant Pb enrichment in the reservoir sediments. Geochemical fractions of Pb in the sediment of the Changhu Reservoir mainly exists in the residual (54.7%) and reducible fractions (23.1%), indicating that the sediment Pb may primarily originate from mining activities. Anthropogenic inputs led to obvious Pb enrichment in the sediment, and increasing its non-residual fraction. The I_{geo} and RAC results showed that sediment Pb of the Changhu Reservoir is at a moderately to heavily pollution degrees, whereas its ecological risk is relatively low because of the low acid soluble fraction.

On the whole, the Pb isotope ratio ($^{206}Pb/^{207}Pb$) of S1 core varied from 1.194 to 1.210, consistent with that ratio of Beijiang river sediments. The linear relationship was found between 1/Pb and $^{206}Pb/^{207}Pb$ ratio, with correlation coefficient of 0.917, indicating the concentration of Pb in the sediment is jointly influenced by anthropogenic inputs and the natural geological Pb. Mining activities, was identified as the major anthropogenic Pb source, contributing significantly (45.3-77.5%) to sediment Pb based on its isotopic compositions. Less of a contribution was derived from natural weathering of parent rocks. Furthermore, Sphalerite and Galena ore may be the main contributor to the high content of Pb in the sediments of the Changhu Reservoir. Integrating distribution characteristics, geochemical fractions, and isotopic compositions of sediment Pb provided a clearer understanding of the contamination, origins and environmental behavior of Pb in the reservoir.

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APPENDIX

Table A1. *The GPS coordinates of sediment and soil sampling points*

Sampling sites	Longitude	Latitude
S1	113°30′41″	24°9′16″
S2	113°30′5″	24°8′8″
S3	113°29′57″	24°8′1″
S4	113°28′39″	24°8′13″
T1	113°28′38″	24°7′59″
T2	113°28′30″	24°7′55″

Table A2. *The recovery rate and relative deviation of total Pb and total Fe standard substance samples*

Item	Batch	Sample number	Certified value (mg/kg)	Measured value (mg/kg)	Recoveries (%)	Relative deviation
Pb (GSD-12)	1	Sample 1	285 ± 16	267.1	93.7	0.70%
		Sample 1#		263.5	92.4	
	2	Sample 2		260.2	91.3	0.56%
		Sample 2#		259.7	91.1	
		Average value		262.6	92.1	0.63%
Fe (GSF-5)	1	Sample 1	675 ± 36	614.2	91.0	1.30%
		Sample 1#		598.1	88.6	
	2	Sample 2		619.7	91.8	0.82%
		Sample 2#		609.5	90.3	
		Average value		610.4	90.4	1.06%

Table A3. *Contamination and ecological risk categories based on EF, I_{geo} and RAC values*

EF	Categorisation	I_{geo}	Pollution intensity	RAC	Ecological risk
< 1.5.	No enrichment	< 0	Unpolluted	< 1	No risk
1.5-5	Moderate enrichment	0-1	Unpolluted to moderately polluted	1-10	Low risk
5-20	Significant enrichment	1-2	Moderately polluted	10-30	Medium risk
20-40	Very high enrichment	2-3	Moderately to heavily polluted	30-50	High risk
> 40	Extremely severe enrichment	3-4	Heavily polluted	> 50	Very high risk
		4-5	Heavily to extremely polluted		
		> 5	Extremely polluted		

Table A4. *Mean ± standard deviation of physico-chemical parameters in the sediment cores (n = 78)*

Sampling sites	pH	OM ($g\ kg^{-1}$)	Fe ($g\ kg^{-1}$)	Al ($g\ kg^{-1}$)	CEC ($cmol\ kg^{-1}$)	Clay (<2μm) (%)	Silt (2-20μm) (%)	Sand (>20μm) (%)	FPC (<63μm) (%)
S1(n = 21)	6.9 ± 0.3	33.1 ± 7.1	47.4 ± 4.6	83.3 ± 8.6	5.9 ± 1.9	10.9 ± 2.4	48.7 ± 10.8	40.3 ± 12.8	85.9 ± 9.5
S2(n = 22)	6.1 ± 0.6	26.0 ± 2.9	51.0 ± 3.9	86.2 ± 6.0	9.1 ± 1.3	11.0 ± 3.2	55.2 ± 8.8	33.8 ± 11.5	91.5 ± 5.0
S3(n = 15)	6.4 ± 0.2	26.5 ± 3.5	48.4 ± 2.7	97.5 ± 5.5	3.6 ± 1.6	12.5 ± 1.5	59.9 ± 7.0	27.6 ± 8.3	92.8 ± 4.4
S4(n = 20)	6.3 ± 0.2	26.1 ± 2.3	51.2 ± 4.7	92.7 ± 10.9	5.6 ± 1.3	13.0 ± 1.0	63.5 ± 4.8	23.6 ± 5.7	95.6 ± 2.3

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Table A5. *Correlation coefficients between total Pb content and physicochemical properties in sediments*

Item	Clay	Silt	Sand	FPC	CEC	Fe	Al	pH	OM	Pb
Clay	1									
Silt	0.787**	1								
Sand	-0.857**	-0.992**	1							
FPC	0.808**	0.867**	-0.885**	1						
CEC	0.077	0.083	-0.085	0.227*	1					
Fe	0.531**	0.543**	-0.559**	0.686**	0.551**	1				
Al	0.690**	0.676**	-0.703**	0.670**	-0.043	0.576**	1			
pH	0.247*	-0.127	0.056	-0.096	-0.235*	-0.070	0.020	1		
OM	0.362**	0.200	-0.239*	0.310**	0.223*	0.334**	0.127	0.397**	1	
Pb	0.434**	0.474**	-0.482**	0.454**	-0.072	0.462**	0.450**	-0.136	0.009	1

**P < 0.01 represents an extremely significant correlation
*P < 0.05 represents a significant correlation

Table A6. *Correlation coefficients between fractions of Pb and physicochemical properties in sediments*

Item	Acid-soluble	Reducible	Oxidizable	Residual	pH	OM	Fe	FPC	Sand
Acid-soluble	1								
Reducible	-0.035	1							
Oxidizable	0.015	-0.204	1						
Residual	-0.415**	-0.181	-0.774**	1					
pH	0.077	0.083	0.308**	-0.349**	1				
OM	0.010	-0.195	0.492**	-0.333**	0.231*	1			
Fe	-0.222	0.422**	0.266	-0.396**	0.155	0.395**	1		
FPC	0.081	0.500**	0.027	-0.293**	-0.187	-0.217	0.034	1	
Sand	-0.124	-0.530**	-0.021	0.314**	0.177	0.214	-0.064	-0.981**	1
CEC	0.264*	-0.510**	-0.380**	0.466**	-0.115	0.050	0.176	-0.643**	0.613**

**P < 0.01 represents a extremely significant correlation
*P < 0.05 represents a significant correlation

Table A7. *The impact of anthropogenic Pb sources on sediment Pb in some reservoirs*

Study area	Anthropogenic source	Contribution (%)	Literature source
Lot River Reservoirs (France)	Mining and smelting activities		Audry et al. (2004)
Three Gorges Reservoir (China)	Coal consumption	20.2% - 91.7%	Han et al. (2018)
Shilianghe Reservoir (China)	Coal combustion dust	31% - 62%	Zhang et al. (2016)
	Leaded gasoline	< 25%	
Shuanglong Reservoir (China)	Automobile industry		Zhou et al. (2020)
Juam Reservoir (Korean)	Mining activities		Lee et al. (2013)
Changhu Reservoir	Mining activities	45.3% - 77.5%	This study

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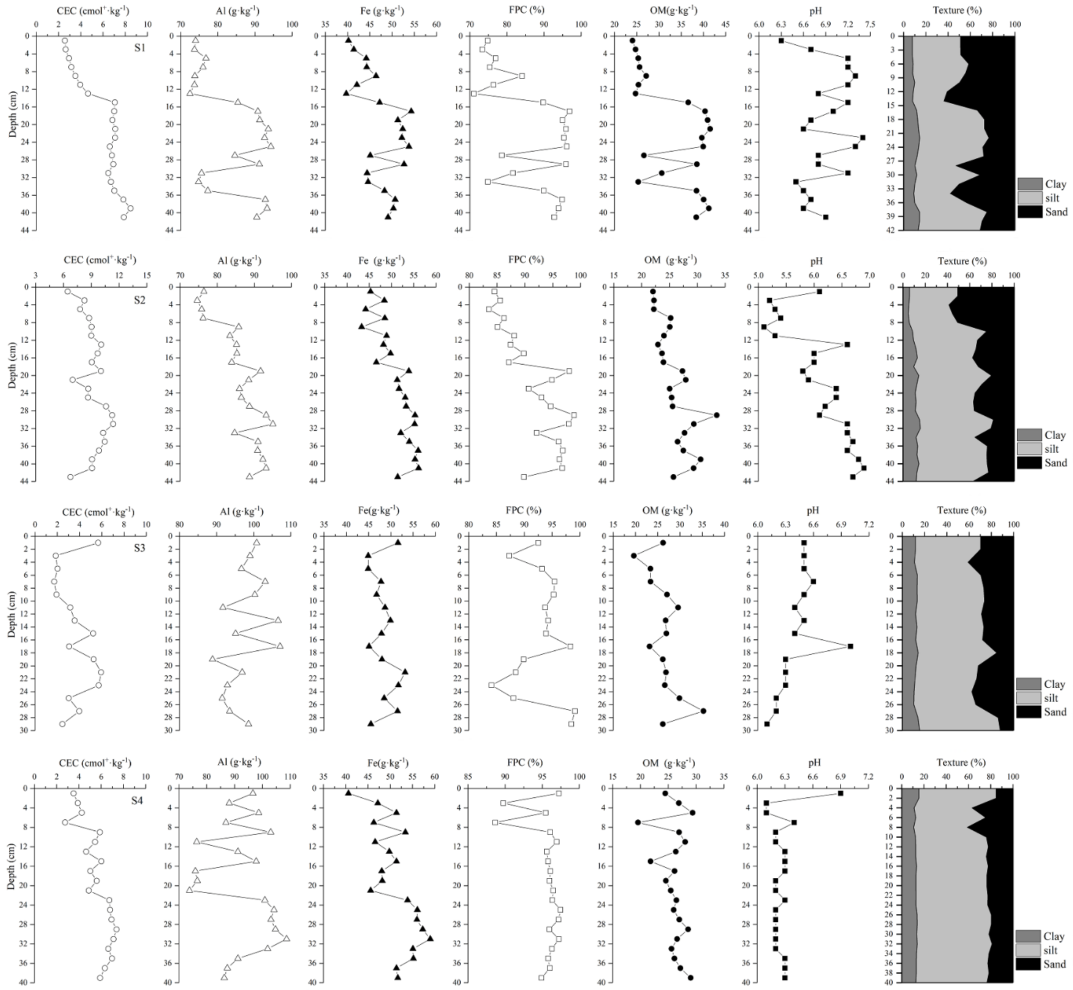

Figure A1. *Depth profiles of the physico-chemical properties in sediment cores (S1~S4)*

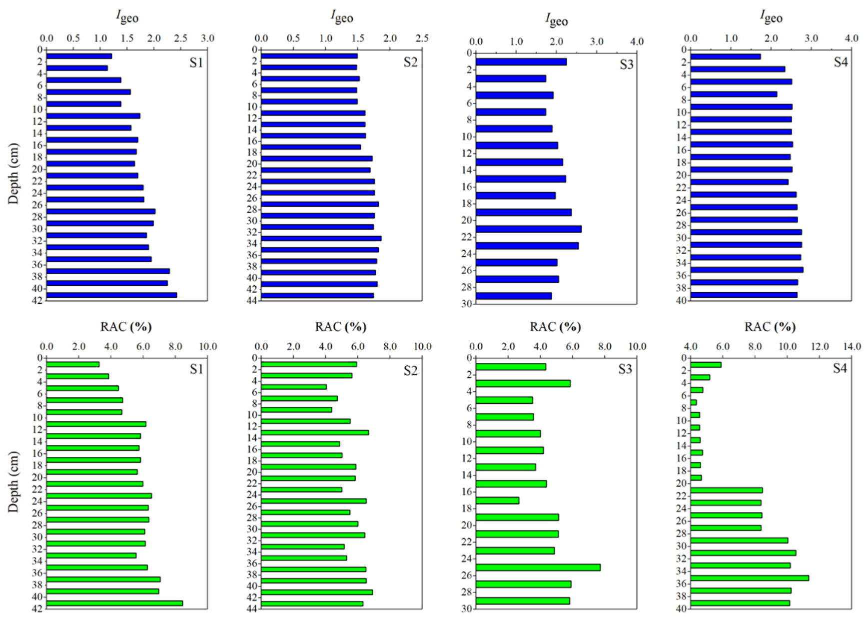

Figure A2. *Depth profiles of the I_{geo} and RAC values in sediment cores (S1~S4)*

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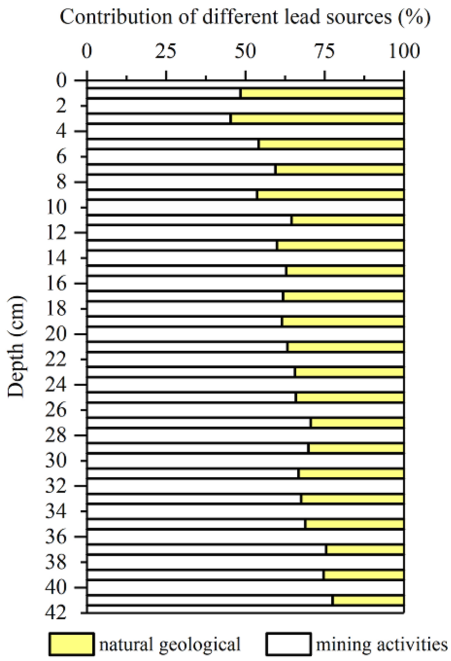

Figure A3. *Contributions of different sources to sediment Pb of core S1*

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