

Materials and methods Study area description To test the integrated approach, a typical agricultural watershed in Eastern China was selected as the case study area. For a specific sampling site, the MLR–APCS model can be expressed as follows: $C_i = X_{0i} + \sum_{j=1}^n X_{ji} \text{APCS}_j$ where C_i is the excessive concentration of trace metal i in sediment; APCS_j is the absolute principal component score of anthropogenic source j ; X_{ji} is the regression coefficient; X_{0i} is the contribution of undefined anthropogenic sources by PCA; and the combined term $\sum_{j=1}^n X_{ji} \text{APCS}_j$ represents the contribution of anthropogenic source j .

Lead isotopic mixing model Lead isotopic composition was characterized to discriminate the different Pb sources, and their respective contributions were calculated by using mixing model. The calculation equations in this software are as follows: $f_s = p_1 f_1 + p_2 f_2 + \dots + p_n f_n$ where f_s is the Pb isotopic composition of sediment sample; f_1, f_2, \dots, f_n are the Pb isotopic compositions of different sources; p_1, p_2, \dots, p_n are the contributions of different sources (%). In this study, there are 2 Pb isotopic compositions ($^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$) and 4 sources (background soil, chemical fertilizer, livestock manure, and atmospheric deposition). If there are n isotopic compositions and $n + 1$ sources, we can find certain contribution values, but if there are $n + 1$ sources, feasible solutions can be obtained according to isotopic mass balance (Phillips and Gregg 2003). The total concentrations of Cd, Cu, Ni, Pb, Cr, Zn, Fe, and Al in the digestion solutions were then analyzed by an inductively coupled plasma–atomic emission spectroscopy (ICPAES; IRIS Intrepid II XSP, Thermo Electron, USA). With the EF value for each trace metal, its excessive concentration in sediment can be determined as follows (Huang et al. 2018): $X_{\text{excessive}} = X_{\text{sediment}} - Y_{\text{sediment}}$ where X_{sediment} is the total concentration of trace metal in sediment and Y_{sediment} is the concentration of trace metal in sediment calculated from the EF value.

Multiple linear regression of absolute principal component scores The MLR–APCS model was used to estimate respective contributions of major anthropogenic trace metal sources in the river sediments. Because the source discrimination power of Pb stable isotopes is mainly due to ^{206}Pb , ^{207}Pb , and ^{208}Pb (Sangster et al. 2000), they were measured for sediment, soil, and anthropogenic source samples by an inductively coupled plasma–mass spectrometry (ICP–MS; Agilent 7500, Agilent Technologies, USA).

1 Location of the study area showing land uses and sampling sites For sediment and soil samples, they were digested in a closed polytetrafluoroethylene system with an acid mixture of HNO_3 (5 mL)– HF (1 mL)– HClO_4 (1 mL) at 180°C for 10 h (Huang et al. 2015). The method detection limits, defined as 3 times the standard deviation of blank measurements, were 0.1, 0.4, 0.4, 1.4, 0.5, 1.2, 8.9, and 8.9 mg/L for Cd, Cu, Ni, Pb, Cr, Zn, Fe, and Al, respectively.

Quantitative source identification methods Enrichment factor (EF) The EFs were calculated to determine the excessive concentrations of trace metals in the river sediments. In addition, 5 atmospheric deposition samples were collected from long–term monitoring sites, which evenly distributed in the watershed for collecting total suspended particulates (Fig. 1). Currently, the dry farmland has occupied the largest watershed area, where wheat is the main crop being cultivated and rainfall, surface, and groundwater supply all irrigation water. APCS were obtained from the principal component analysis (PCA), which is a data dimensionality reduction analysis and can identify the major trace metal sources (Mico et al. 2006; Cai et al. 2019b). A multi–element standard solution (GSB04–1767–2004, Guobiao Testing & Certification Co., Ltd., China) was used to establish calibration curves. For quality control, each digestion batch included 2 reagent blanks, 1 standard reference material, and 1 duplicate sample to

assess the accuracy and precision of the measurements. Replicate analysis of the standard reference material GBW-07304 (National Research Center for Geo analysis, China) showed good accuracy, with overall recovery rates ranging from 97 to 106%. Metal concentration and Pb isotope analyses Fig. 1).
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