



# Cadmium isotope constraints on heavy metal sources in a riverine system impacted by multiple anthropogenic activities

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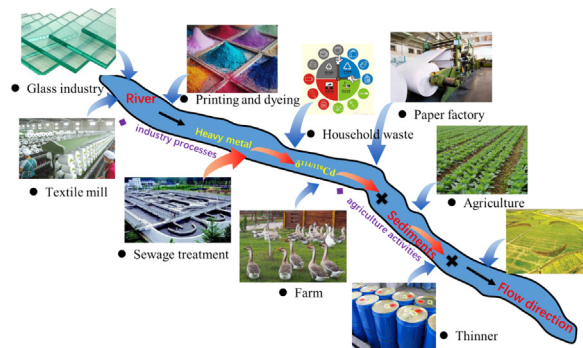
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## HIGHLIGHTS

- The dominant Cd pollution was distinguished from multiple sources with similar Cd concentrations based on Cd isotopes.
- Cd pollution in river sediments was primarily derived from sewage treatment and outlets.
- The Cd isotope technique is effective to trace Cd sources in riverine systems.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Heavy metals pollutants are global concern due to their toxicities and persistence in the environment. Cd isotope signatures in soils and sediments change during weathering, and it remains unclear if Cd isotopes can effectively trace Cd sources in a riverine system. In this study, we investigate Cd concentration and its isotope compositions, as well as other heavy metals of sediments and related potential Cd sources in a riverine system. The results showed that the two river sediments evaluated were moderately polluted by Zn, Cr, and Cd, while the source samples (soil, sludge, waste, and raw materials) were seriously polluted by heavy metals derived from anthropogenic activities. According to comprehensive ecological risks, the two sediments have a moderate to low potential risk and more than half of all anthropogenic activities in the study area were at considerable or moderate potential risk. We determined that Cd pollution in river sediments was primarily derived from sewage treatment and outlets based on river flow direction and the isotope geochemical behaviors of the Cd isotope in nature conditions. This study further confirmed that analyzing Cd isotopes could be a powerful tool for tracing the source and destination of environmental Cd for multiple sources with similar Cd concentrations.

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## 1. Introduction

Heavy metals pollutants are a global concern due to their toxicities and persistence in the environment and pose major health risks to

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animals and humans (Li et al., 2014). Cd can accumulate to extremely toxic amounts in food chains because it has a low biocidal dose for mammals (WHO, 2010). Previous studies have shown that Cd enters human tissues primarily through air inhalation (smoking) and digestion, concentrated Cd can interfere with liver, kidney, lung, and bone functions (Godt et al., 2006; Rahmi et al., 2017). Itai-Itai Disease in Japan is a typical event caused by consumption of Cd-contaminated rice (Staessen et al., 1999; Kjellström, 1985). Unfortunately, recent studies have shown that elevated Cd concentrations in rice pose a world-wide problem, especially in Asian countries such as China, Bangladesh, Sri Lanka, and Japan (Hu et al., 2016; Meharg et al., 2013; Proshad et al., 2020). Investigations from Hunan Province (China) showed that Cd concentrations of 60% of the test rice grains exceeded the standard (Du et al., 2013; Wang et al., 2016; Wu et al., 2018). Therefore, Cd pollution is a serious global threat to the environment and human health, and Cd pollution sources and pathways in the environment must be identified to better control Cd exposure.

Cd in the environment currently originates primarily from natural sources (e.g. volcanic activities) (Godt et al., 2006) and anthropogenic emissions (e.g., Zn—Pb mining and refining) (Shotyk et al., 2002; Imseng et al., 2018). Anthropogenic emission sources include Cd consumption in industry processes (e.g., Ni—Cd batteries and Zn—Pb mining) (Shiel et al., 2010), and agricultural activities (e.g., mineral fertilizers) (U.S. Geological Survey, 2013, 2016; Martinkova et al., 2016). Cd emitted into the atmosphere and hydrosphere is subsequently deposited in sediments and soils. Environmental crises are created when the Cd is absorbed by biota and enters the food chain. Therefore, tracing Cd sources is critical and helps provide effective measurements to reduce Cd emissions and health risks in local environments. Previous studies have shown that Cd concentrations in various environmental matrices are potential geochemical tracers for tracking Cd sources in heavy metal-polluted areas (Wen et al., 2020). However, Cd sources commonly have similar Cd concentrations. Therefore, it is thus a big challenge to distinguish Cd contributions among sources only basing on their Cd concentrations.

Instrumental development and methodological refinement in the last two decades have improved the precision of metal isotope analyses for monitoring minor changes in stable metal isotope compositions (Wiederhold, 2015). The Cd isotope has become a powerful geochemical tracer for Cd transportation in plants (Wei et al., 2016, 2018, 2019), soil-fertilizer-plant systems (Wiggenhauser et al., 2016, 2019; Imseng et al., 2018), and industrial processes (e.g., coal burning, smelting, refining, metal coating and glass industry) (Shiel et al., 2010; Martinkova et al., 2016; Fouskas et al., 2018; Wang et al., 2019). Analyzing the amount of Cd isotopes is a promising tool to track Cd sources in the environment, because Cd sources have different isotope signatures and concentrations (Cloquet et al., 2006; Gao et al., 2013; Salmanzadeh et al., 2017). Most studies focus on contaminated areas with Cd concentrations higher than 1 mg/kg, including ore, soil and sediment samples from Zn—Pb deposits (Cloquet et al., 2006; Wen et al., 2015; Chrastný et al., 2015; Martinkova et al., 2016; Zhang et al., 2016; Yang et al., 2019). However, Cd concentrations in soils and sediments contaminated by industrial and agricultural processes are commonly very low (0.1–1 mg/kg; Smolders and Mertens, 2013). Additionally, some studies have demonstrated that rock and mineral weathering processes could result in significant Cd isotope fractionation during Cd transportation (Zhang et al., 2016; Zhu et al., 2018), suggesting that Cd isotope signals were likely changed in samples and may provide false information. Thus, it remains unclear if Cd isotopes are a useful geochemical tracer to track Cd pathways in such areas, and the application of Cd isotopes needs to be further examined.

The South-to-North Water Diversion is a strategic project for the diversion of water resources in China, and the Nansi Lake is one of the most important water storage lakes in the east route of the South-to-North Water Diversion Project. The water pollution of River-A—a tributary that flows into Nansi Lake from the southeast—greatly affects Nansi

Lake and the South-to-North Water Diversion Project (Cao et al., 2015). Sediments and soils have elevated Cd concentrations that are likely related to anthropogenic activities, but the dominant Cd sources in the area remain unidentified (Cao et al., 2017). In this study, sediments, soils, sludge, and raw materials from possible anthropogenic sources around the sediments, were systematically collected near River-A. The heavy metals concentrations, associated with the Cd isotope ratios of sediments and potential pollution sources were investigated. The aims of this study are 1) to estimate the contamination extent of heavy metals in sediments and potential pollution sources; 2) to investigate the variation of Cd isotopic compositions in samples around various polluted plants; and 3) to identify Cd sources in sediment based on Cd concentrations and isotope signatures. This study further constrains Cd-contaminated soils impacted by multiple anthropogenic activities and extends Cd isotope applications in riverine environments.

## 2. Materials and methods

### 2.1. Sampling and sample preparation

River-A—the dominant river mentioned in the national “South-to-North Water Diversion East Line Pollution Control Plan”—has a length of 84 km and total drainage area of 928 km<sup>2</sup> (Zhang et al., 2008). The many factories near River-A heavily pollute the river with industrial wastewater and domestic sewage. River-A is a seasonal river with floods concentrated during the wet season and insufficient water flow during the dry season (Zhang et al., 2008; Cao et al., 2015) (Fig. 1).

The studied samples are river sediments, soils, wastes, sludge, and raw materials from a riverine system. The sediments and sludge were collected using a stainless-steel grab sampler at a depth of 0–5 cm from the middle of River-A or from a pool. Soils, wastes, and raw materials were collected by shovel at three locations at each site; the samples were mixed together and stored in sealed bags for transportation. Table 1 lists the detailed sample information: TW1 and TW2 are river sediments; TW3 and TW4 are soils sampled from vegetables and wheat farmlands; TW5 and TW6 are soils sampled from geese and duck farms; TW7 is a soil sample collected near household waste; TW8 and TW9 are the soil and waste from paint thinner plants. TW10 and TW11 are sediments from sewage outlets; TW12, TW13, and TW14 are soils from a paper factory, a glass industry and a textile mill, respectively; TW15 is raw material from a paper factory; TW16 and TW17 are soils and sludge from a printing and dyeing mill, respectively. TW18 is sewage treatment sludge.

### 2.2. Sample treatment and elemental analysis

Samples were first air-dried at room temperature (~20 °C) and then crushed to a size less than 200 mesh (0.074 mm) using a ball mill. For trace element analysis: ~50 mg samples were weighed into Teflon digestion vials, and reacted with 3 mL of aqua regia and heated at 180 °C for 24 h. Samples were then digested using 1 mL of concentrated HF and heated to dryness. Finally, the samples were dissolved using 10 mL of 1% HNO<sub>3</sub> (v/v). After centrifuging, the supernatants were diluted and transferred for elemental analysis by inductively coupled plasma quadrupole mass spectrometry (ICP-QMS) (Elan DRC-e, Perkin Elmer, USA) at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. The related standard deviations were typically lower than 10%.

### 2.3. Cd isotope analysis

For Cd isotope purification: previous studies suggest that ashing below 550 °C is unlikely to result in significant Cd isotope fractionation in organic rich samples (Pallavicini et al., 2014). In this study, 150 ng Cd of each sample were weighed into a ceramic and burned at 400 °C for 4 h in a muffle furnace to remove organic matter. After cooling, the

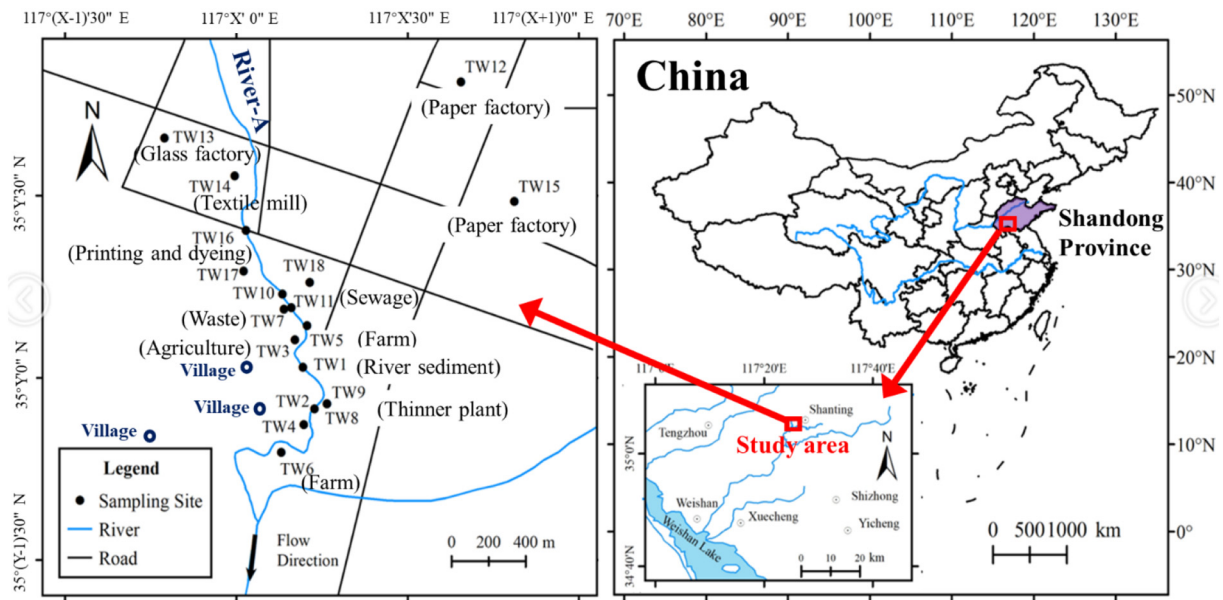


Fig. 1. Sampling sites around River-A, Shandong province, China.

samples were transferred to 50 mL Teflon beakers and mixed with  $^{110}\text{Cd}$ – $^{111}\text{Cd}$  double spike solution (made from  $\text{CdO}$ , ~96.0% purity) to achieve a Cd sample-spike ratio of ~2. Samples were digested using 10–15 mL of aqua regia at 180 °C for 24 h, reacted with 5 mL concentrated HF and heated to dryness. Samples were dissolved in 8 mL of 2 mol/L HCl. An anion exchange resin (AG-MP-1 M) was employed for Cd isotope purification using a method described by Zhu et al. (2013). In order to avoid isobaric elements interferences (e.g., Sn) during Cd isotope analysis, samples were purified twice as suggested by Zhang et al. (2018). This method recovers more than 85% Cd for all the samples. Acids used in this study were purified by sub-boiling distillation and the water was 18.2 M $\Omega$  grade from a Millipore system.

For Cd isotope measurements: Cd isotope compositions of the samples were measured by a Thermo Scientific Neptune plus multi collector ICP-MS instrument at the State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences. The true Cd isotope ratio of the double spike solution was measured over 6 months using an Ag isotope external standard (NIST SRM 978a) to correct instrumental mass fractionation (Zhang et al., 2018). During the analysis, a NIST SRM 3108 was used as a zero internal reference standard. Two Cd secondary reference standards (Nancy Spex Cd and JMC Cd) and a geological reference material (Sgr-a-1, USGS) were used to monitor the chemical separation and mass spectrometry measurements. The secondary reference standards were measured after every

Table 1

Concentrations of heavy metals and Cd isotope compositions in river sediments and sources from the study area.

Samples	Co mg/kg	Cd	Zn	Pb	Cu	Cr	Ni	As	$\delta^{114/110}\text{Cd}_{\text{NIST 3108}}$ (‰)	Description	Anthropogenic activities
TW1	18.91	0.29	414.75	28.15	39.61	212.31	32.84	8.58	$0.12 \pm 0.01$	Sediment	River
TW2	16.20	0.14	304.59	19.99	43.89	202.34	26.27	5.80	$-0.03 \pm 0.02$	Sediment	
TW3	12.06	0.11	51.61	22.17	17.51	139.08	25.95	12.15	$-0.16 \pm 0.11$	Soil	Agriculture
TW4	14.17	0.12	57.89	25.40	20.42	163.44	31.03	13.98	$-0.20 \pm 0.03$	Soil	
TW5	15.07	0.20	84.07	27.35	24.45	173.60	31.79	14.34	$-0.27 \pm 0.02$	Soil	Farm
TW6	14.89	0.21	84.08	26.87	23.38	191.31	31.76	14.55	$-0.39 \pm 0.13$	Soil	
TW7	18.79	0.24	502.21	28.67	47.92	114.59	30.34	10.38	$0.29 \pm 0.09$	Soil	Household waste
TW8	18.19	0.28	440.19	30.06	45.23	160.95	33.35	10.41	$0.95 \pm 0.00$	Soil	Paint thinner plants
TW9	15.27	0.80	250.00	41.45	109.15	265.98	29.58	8.64	$0.05 \pm 0.01$	Waste	
TW10	43.04	0.60	426.05	107.69	73.15	562.62	78.50	46.86	$-0.13 \pm 0.01$	Sediment	Sewage outlet
TW11	16.66	0.20	221.71	28.36	20.40	217.72	30.22	11.35	$-0.16 \pm 0.12$	Sediment	
TW12	3.80	0.14	40.60	17.28	11.35	283.76	10.39	5.07	$0.26 \pm 0.02$	Soil	Paper factory
TW13	7.31	1.08	114.78	33.54	18.30	264.32	48.17	24.78	$0.01 \pm 0.04$	Soil	Glass industry
TW14	6.32	0.09	52.71	9.96	12.55	49.66	17.24	6.03	$0.24 \pm 0.08$	Soil	Textile mill
TW15	8.27	1.06	191.90	27.80	49.30	46.45	14.98	3.51	$0.35 \pm 0.11$	Raw material	Paper factory
TW16	43.30	0.44	286.37	4.76	44.02	41.36	41.89	7.52	$0.08 \pm 0.06$	Soil	Printing and dyeing plant
TW17	11.26	0.26	160.96	31.00	45.81	84.59	24.13	10.05	$0.28 \pm 0.10$	Sludge	
TW18	14.46	0.53	2550.75	9.22	40.91	127.78	49.27	13.24	$-0.05 \pm 0.07$	Sludge	Sewage treatment plant
Shandong <sup>a</sup>	12.6	0.07	60.9	24.5	22.3	64.3	24.4	8.9			
China <sup>a</sup>	–	0.1	82	26	23	61	26.9	11.2			
World <sup>a</sup>	–	0.4	90	35	30	70	50	6			
Level I <sup>b</sup>	–	0.2	100	35	35	90	40	15			
Level II <sup>b</sup>	–	0.3	200	250	50	250	40	40			
Level III <sup>b</sup>	–	–	500	500	400	300	200	40			

<sup>a</sup> Background values from Wei et al. (1990).

<sup>b</sup> Soil environmental quality standard of China (GB15618-1995)

five samples to monitor instrumental stability and reproducibility. Samples and standards were diluted to ~70 ng/mL using 1% HNO<sub>3</sub> (v/v), analyzed at an uptake rate of ~100 μL/min, and generally yielded a total Cd voltage of ~1.1 V for <sup>114</sup>Cd. Samples and standards were measured in two blocks with 30 cycles per block. Each sample was analyzed at least twice.

The δ<sup>114/110</sup>Cd<sub>NIST 3108</sub> values of Nancy Spex Cd and JMC Cd are -0.13 ± 0.06‰ and -1.73 ± 0.21‰, respectively, and are consistent with previously reported values (Zhang et al., 2018). Although there are no reported Cd isotope compositions of Sgr-a-1, duplicates of Sgr-a-1 agree with the δ<sup>114/110</sup>Cd<sub>NIST 3108</sub> values of 0.41 ± 0.07‰.

2.4. Pollution risk assessment

2.4.1. Geo-accumulation index (I<sub>geo</sub>)

The degree of pollution of each heavy metal in the sediments was evaluated based on the I<sub>geo</sub>, which considers anthropogenic influences based on the environmental geochemical background (Muller, 1969). The I<sub>geo</sub> is calculated using the following Eq. (1):

$$I_{geo} = \text{Log}_2 (C_i/1.5 S_i) \tag{1}$$

where C<sub>i</sub> and S<sub>i</sub> are the monitored and background concentrations of heavy metal i, respectively. Based on the I<sub>geo</sub> values, pollution is classified into seven levels: uncontaminated, uncontaminated to moderately, moderately, moderately to strongly, strongly, strongly to extremely, and extremely contaminated when the I<sub>geo</sub> is <0, 0-1, 1-2, 2-3, 3-4, 4-5, and >5, respectively (Muller, 1969).

2.4.2. Potential ecological risk index (RI)

The comprehensive ecological risks of heavy metals in sediments were evaluated based the RI established by Hakanson (1980). The RI method assesses pollution status and toxicological effects to determine a representative index level.

The ecological risks of heavy metals in the sediments (E<sub>r</sub>) were calculated with the following equation:

$$E_r = T_i \times (C_i/S_i) \tag{2}$$

The comprehensive ecological risks of heavy metals in the sediments (RI) were calculated with the following equation:

$$RI = \sum_{i=1}^m E_r \tag{3}$$

where C<sub>i</sub> is the monitoring concentration of heavy metal i, S<sub>i</sub> is the background concentration of heavy metal i, and T<sub>i</sub> is the biological toxicity factor of heavy metal i (Cu = Pb = Ni = 5, Zn = 1 and Cr = 2). Based on E<sub>r</sub> values, the ecological risks of heavy metals in the sediments were divided into five levels: Low, Moderate, Considerable, High and Very high for E<sub>r</sub> values of <40, 40-80, 80-160, 160-320 and >320, respectively. Based on RI values, the comprehensive ecological risks of heavy metals in the sediments were divided into four levels: Low, Moderate, Considerable, and High for RI values of <150, 150-300, 300-600 and >600, respectively.

2.5. Statistical analysis

The data were calculated using SPSS18 and tested for homogeneity of variance and normal distribution. A one-way ANOVA complemented by the least significant difference (LSD) was used in all case with a significance level of 0.05.

3. Results

Trace element concentrations associated with Cd isotope compositions of the studied samples are listed in Table 1. The highest Zn and Ni, Cd, Cr, Co, Pb and As, Cu concentrations were from the sewage

treatment plant sludge (2550.75 and 49.27 mg/kg; TW18), glass factory sediments (1.08 mg/kg; TW13), paper factory sediments (283.76 mg/kg; TW12), printing and dyeing plant soils (43.3 mg/kg; TW16), sewage outlet sediments (107.69 and 46.86 mg/kg; TW 10), and thinner waste soils (109.15 mg/kg; TW9), respectively. In contrast, the lowest Zn, Cu and Co concentrations were from paper factory sediments (40.6, 11.35, and 3.8 mg/kg, respectively; TW12). The lowest Ni and As, Pb and Cr, and Cd concentrations were from paper factory raw materials (14.98 and 3.51 mg/kg; TW15), printing and dyeing plant soils (4.76 and 41.36 mg/kg; TW16), and agricultural (vegetable) soils (0.11 mg/kg; TW3), respectively. Therefore, most of samples have higher heavy metal concentrations than those from the background of the Shandong province (Table 1), suggesting that soils and river sediments in the study area were polluted by Cd, Zn, Cr, and Cu. Interestingly, no strong correlations were observed between Cd and other elements, indicating that Cd has independent pollution sources. In contrast, Cr has significant correlation with Pb, As, and Ni, suggesting that Cr has the same sources as Pb, As and Ni (Table 2).

The δ<sup>114/110</sup>Cd<sub>NIST 3108</sub> values of Cd sources by anthropogenic activities varied from -0.39 ± 0.13‰ to +0.95 ± 0.00‰ (Table 1). The soil sample from thinner plant material (+0.95 ± 0.00‰ for TW8) had the highest δ<sup>114/110</sup>Cd<sub>NIST 3108</sub> value, whereas the lowest value occurred in the duck sample (-0.39 ± 0.13‰ for TW6). The δ<sup>114/110</sup>Cd<sub>NIST 3108</sub> values of two river sediments (TW1 and TW2) (-0.03 ± 0.02‰ to 0.12 ± 0.01‰) are the highest and the lowest values of all anthropogenic sources.

4. Discussion

4.1. Heavy metal pollution levels in the study area

The Cd, Zn, Cu, Cr, and Ni concentrations of the two river sediments (TW1 and TW2) are higher than those of the background values from Shandong province. Unfortunately, Cd concentrations of all studied samples are exceeded its background value of Shandong province. The environment quality standards for soils are divided into three levels based on the hazard potential of heavy metals for soil function and human health (Liang et al., 2017). Heavy metal concentrations in soils that exceed the level II value are harmful to human health (Liang et al., 2017). In the study area, Zn is the only element that exceeded the corresponding level II value in the two river sediments. The concentrations of all heavy metals from anthropogenic sources—except Pb—are higher than the corresponding level II values, indicating that the anthropogenic sources are potentially harmful to the local environment and humans.

4.2. Heavy metals risk assessment

4.2.1. Geo-accumulation index

For the two river sediments, the degree of heavy metal pollution in TW1 and TW2 decreased in the following order: Zn > Cr > Cd > Cu.

Table 2 Correlations of heavy metals in the studied samples (N = 18).

	Cd	Zn	Pb	Cr	Cu	As	Ni	Co
Cd	1							
Zn	0.150	1						
Pb	0.295	-0.117	1					
Cr	0.166	-0.051	0.838**	1				
Cu	0.462	0.178	0.492*	0.303	1			
As	0.264	0.068	0.853**	0.789**	0.191	1		
Ni	0.322	0.375	0.670**	0.626**	0.335	0.881**	1	
Co	0.051	0.105	0.462	0.339	0.426	0.504*	0.712**	1

\*\* P < 0.01.  
\* P < 0.05.



The two sediments were moderately polluted by Zn, Cr, and Cd. According to Muller (1969), the  $I_{geo}$  of Pb, Ni, As, and Co in TW1 and TW2 are less than zero ( $I_{geo} < 0$ ), suggesting that the sediments were not polluted by the four heavy metals.

For the sixteen potential source samples, the values of  $I_{geo}$  range from  $-0.29$ – $3.36$  for Cd,  $-1.17$ – $4.8$  for Zn,  $-2.95$ – $1.55$  for Pb,  $-1.56$ – $1.71$  for Cu,  $-1.22$ – $2.54$  for Cr,  $-1.29$ – $1.10$  for Ni,  $-1.93$ – $1.81$  for As, and  $-2.32$ – $1.2$  for Co (Fig. 2), respectively. The degree of pollution of each metal in terms of  $I_{geo}$  decreased in the following order: Zn > Cd > Cr > Cu > Co > As > Ni > Pb. The pollution of the sources can be summarized as follows (Fig. 2): 1) the agriculture and farm soils (TW3–6) were unpolluted to moderately polluted by Cd, Cr, As and unpolluted by Zn, Pb, Cu, Ni and Co; 2) household waste (TW7) was moderately to strongly polluted by Zn, moderately by Cd, and unpolluted to moderately by Cu and Cr, with level decreasing in the following order: Zn > Cd > Cu > Cr; 3) soil and material from the thinner plant (TW8–9) were moderately to strongly polluted by Cd and Zn, and moderately polluted by Cu and Cr; 4) the sewage outlet sediment (TW10) was moderately to strongly polluted by Cd, Zn, and Cr, and moderately polluted by other heavy metals, and the pollution at TW11 (moderate for Zn and Cr) was less than that of TW10; 5) the paper factory soil (TW12) was moderately polluted by Cr, and paper factory material (TW15) was strongly polluted by Cd, moderately polluted by Zn; 6) the glass factory soil (TW13) was strongly polluted by Cd, and moderately polluted by Cr; 7) textile mill soil (TW14) was unpolluted by heavy metals; 8) printing and dyeing plant soil (TW16–17) was moderately to strongly polluted by Cd, moderately polluted by Zn and Co; 9) sewage treatment plant sediment (TW18) was strongly to extremely polluted by Zn, and moderately to strongly polluted by Cd. Industrial pollution is usually more serious than agricultural pollution.

#### 4.2.2. Potential ecological risk index

The geo-accumulation index was used to evaluate the degree of pollution of each heavy metal in the sediments of rivers or lakes while the potential ecological risk index (RI) was used to evaluate the ecological risk of sediments by considering various harmful elements (Yi et al., 2011). According to the RI, the river sediments (TW1 and TW2) have a moderate and low potential risk (Table 3). This result agrees with a study by Cao et al. (2017) and suggests that sediment samples from River-A are at medium potential risk. Five sites, TW9, TW10, TW13,

TW15, and TW18 (thinner waste, sewage outlet sediment, glass factory soil, paper factory material, and sewage treatment plant sediment) have a considerable potential risk. Meanwhile, four sites, TW7–8, and TW16–17 (waste factory soil and thin plant material, and printing and dyeing plant soil and material), have a moderate potential risk. Therefore, these sediments, soil and material from factories have a potential pollution risk when improperly discharged or disposed.

#### 4.3. Cd sources in river sediments

##### 4.3.1. Locations of different Cd sources

Cd concentrations in sediments decreased from upstream to downstream at a Cd source area (Gao et al., 2013), suggesting that Cd in river sediments decreases in the flow direction. TW2 has lower Cd, Zn, Pb, Cr, Ni, and As concentrations than those of TW1, suggesting that there are no Cd, Zn, Pb, Cr, Ni, and As sources located between TW1 and TW2. If at least one Cd source is located between the two river sediment sites, TW2 must have a similar or higher Cd concentration than TW1. According to the river flow direction, TW8 and TW9 have higher Cd concentrations than TW2 and are located between the two river sediments. Thus, if TW8 and TW9 contributed Cd to TW2, the concentration will increase and surpass that of TW1. So we rule out Cd contributions from TW8 and TW9 and from TW4 and TW 6, which are located downstream of TW1 and TW2. Therefore, Cd in sediments was derived from the paper factory, printing and dyeing factory, textile factory, glass factory and sewage-treatment plant.

##### 4.3.2. Cd isotope constraints on Cd sources

Many researches have proven that natural (rock and mineral) weathering could result in widespread Cd isotope fractionation, and weathered products are rich in lighter Cd isotopes (e.g., Zhang et al., 2016; Salmanzadeh et al., 2017; Zhu et al., 2018). Zhang et al. (2016) measured the Cd isotope composition of soils and river sediments from a Cd-polluted riverine system and found that all soils were more enriched in lighter Cd isotopes than the corresponding sediments; additionally, simulated natural weathering processes confirmed that natural weathering could result in significant Cd isotope fractionation with  $\Delta^{114/110}\text{Cd}_{\text{parent material (PM)}-\text{weathering product (WP)}}$  of  $0.36$ – $0.53\%$ . Salmanzadeh et al. (2017) reported that the  $\delta^{114/110}\text{Cd}_{\text{NIST 3108}}$  values of fertilizer are  $-0.17$  ~  $+0.25\%$ , and become gradually lighter from

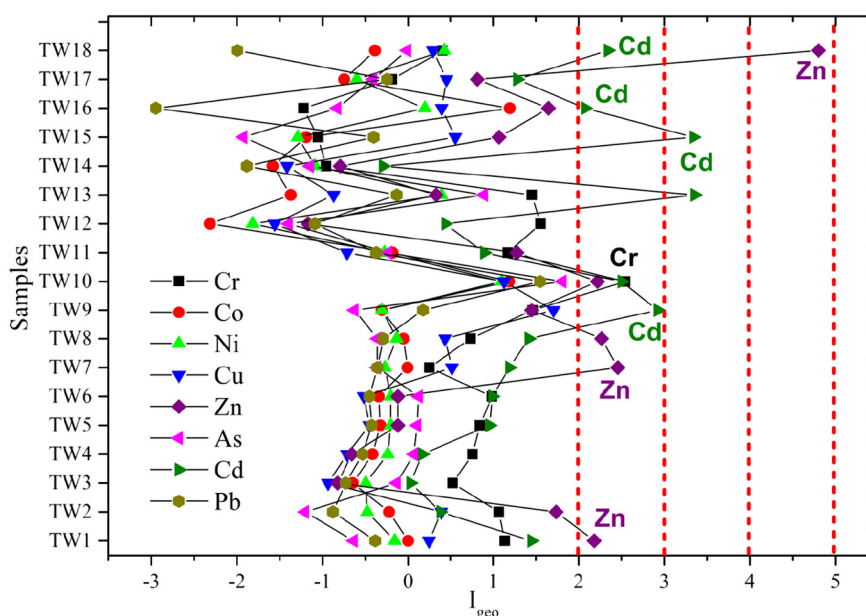


Fig. 2. The  $I_{geo}$  and degree of pollution of heavy metals in samples.

**Table 3**  
The ecological risk ( $E_r$ ) and Potential ecological risk index (RI) of heavy metals in samples.

Samples	$E_r$									RI	Levels
	Cr	Co	Ni	Cu	Zn	As	Cd	Pb			
TW1	6.60	7.50	6.73	8.88	6.81	9.64	123.04	5.75	174.95	Moderate	
TW2	6.29	6.43	5.38	9.84	5.00	6.51	58.67	4.08	102.21	Low	
TW3	4.33	4.79	5.32	3.93	0.85	13.65	45.89	4.52	83.27	Low	
TW4	5.08	5.62	6.36	4.58	0.95	15.71	50.45	5.18	93.95	Low	
TW5	5.40	5.98	6.51	5.48	1.38	16.12	87.56	5.58	134.02	Low	
TW6	5.95	5.91	6.51	5.24	1.38	16.35	89.64	5.48	136.46	Low	
TW7	3.56	7.46	6.22	10.75	8.25	11.66	102.76	5.85	156.51	Moderate	
TW8	5.01	7.22	6.83	10.14	7.23	11.70	120.30	6.13	174.57	Moderate	
TW9	8.27	6.06	6.06	24.47	4.11	9.71	341.76	8.46	408.90	Considerable	
TW10	17.50	17.08	16.09	16.40	7.00	52.65	255.32	21.98	404.01	Considerable	
TW11	6.77	6.61	6.19	4.57	3.64	12.75	83.95	5.79	130.28	Low	
TW12	8.83	1.51	2.13	2.55	0.67	5.70	61.03	3.53	85.93	Low	
TW13	8.22	2.90	9.87	4.10	1.88	27.84	461.29	6.85	522.96	Considerable	
TW14	1.54	2.51	3.53	2.81	0.87	6.77	36.72	2.03	56.79	Low	
TW15	1.44	3.28	3.07	11.05	3.15	3.95	456.10	5.67	487.72	Considerable	
TW16	1.29	17.18	8.58	9.87	4.70	8.45	189.74	0.97	240.78	Moderate	
TW17	2.63	4.47	4.94	10.27	2.64	11.29	109.65	6.33	152.22	Moderate	
TW18	3.97	5.74	10.10	9.17	41.88	14.88	228.49	1.88	316.11	Considerable	

the 1980s (0.25‰) to 2015 (−0.17‰) with  $\Delta^{114/110}\text{Cd}_{\text{PM-WP}}$  of 0.42‰. Zhu et al. (2018) investigated Cd isotope fractionation between parent material and weathering products; the fractionation is estimated at  $\Delta^{114/110}\text{Cd}_{\text{PM-WP}} = 0.33\text{‰}$ .

Although it is still unclear the scale of Cd isotope fractionation during the formation of river sediments, Wasylenki et al. (2014) pointed out that only minor Cd isotope fractionation effect was observed during Cd deposition at low ionic strength fluid. Thus, we assume the fractionation is small during the formation of river sediments in the studied area. Therefore, natural weathering and deposition must be evaluated when using Cd isotopes to trace anthropogenic activities, and sediments likely have higher  $\delta^{114/110}\text{Cd}_{\text{NIST 3108}}$  values than their parent Cd sources (e.g., soil).

In this study, large Cd isotope fractionations occurred between the soils, waste, sludge and raw materials related to local industrial processes. The  $\delta^{114/110}\text{Cd}_{\text{NIST 3108}}$  value of soil in thinner plants (TW8) is  $+0.95 \pm 0.00\text{‰}$ , which is much higher than that of the corresponding material (TW9); however, TW8 has a much lower Cd concentration than TW9, suggesting that 1) most Cd was lost in TW8 or 2) Cd in TW8 did not originate from TW9. Because TW8 was surface soil collected from the thinner plant, TW9 (0.8 mg/kg) has much a higher Cd concentration than TW8 (0.2 mg/kg); we conclude that Cd in TW8 was likely derived from TW9. Natural weathering is not likely to explain Cd isotope fractionation between TW8 and TW9, because TW8 is richer than TW9 in heavier Cd isotopes. Previous studies showed that the evaporation process could result in extremely widespread Cd isotope fractionation as molten Cd evaporates into a vacuum, and heavier Cd isotopes are rich in residual (Wombacher et al., 2008). Although this process did not occur during the formation of our samples, organic solvents used in thinner plant are easily evaporated, and this process is likely the key factor lowering Cd concentration and heavier Cd isotope enrichment in TW8, because lighter Cd isotopes easily evaporate. Thus, thinner plants are not likely a dominant Cd contributor to river sediments, because of the much higher  $\delta^{114/110}\text{Cd}_{\text{NIST 3108}}$  value in soil (TW8) than in river sediments. This conclusion is consistent well with the result based on Cd concentrations and locations of TW8, TW9 and the river sediments.

Soil (TW12) and material (TW15) samples from the paper factory have similar Cd isotope compositions, and the soil sample is relatively richer in lighter Cd isotopes (Fig. 3). However, the material (TW15) has much higher Cd concentration than that of soil (TW12), suggesting that the paper factory has a good pollution control for Cd discharge. Thus, we conclude that Cd in river sediments is not dominantly derived from the paper factory.

The printing and dyeing factory is also not likely to be a Cd contributor. The sludge (TW17) has a higher  $\delta^{114/110}\text{Cd}_{\text{NIST3108}}$  value and lower Cd concentration than dose the workshop soil (TW16) because of natural weathering. The  $\delta^{114/110}\text{Cd}_{\text{NIST3108}}$  values of river sediments would be much higher than those of TW16 and TW17 if the Cd in the river sediment originated from these locations. As shown in Fig. 3, sludge and the local soil have higher and similar  $\delta^{114/110}\text{Cd}_{\text{NIST3108}}$  values compared with river sediments, respectively. Thus, we rule out Cd contribution from the printing and dyeing factory. Similarly, we exclude Cd contribution from the textile mill (TW14) and from household waste (TW7) because of their lower Cd concentrations and higher  $\delta^{114/110}\text{Cd}_{\text{NIST3108}}$  values compared to the river sediment (TW1). The glass factory has been closed for several years and was also eliminated because of the distance from river sediment sample sites; additionally, the  $\delta^{114/110}\text{Cd}_{\text{NIST3108}}$  value of soil (TW13) is lower than that of the river sediment (TW1; Fig. 3).

In this study, we suggest that Cd in river sediments was likely derived from the sewage treatment plant (TW18), sewage outlets (TW10 and TW11), farm (TW5) and agricultural site (TW3), which have lower  $\delta^{114/110}\text{Cd}_{\text{NIST3108}}$  values than those of river sediments. As soils from farms (TW5) and agricultural activities (TW3) have lower Cd concentrations than river sediments (TW1), we suggest that limited Cd in TW1 was derived from TW5 and TW3, and Cd in river sediments is predominantly derived from sewage treatment and the related sewage outlet. This conclusion is consistent well with a previous study, which reported that abundant sewage and wastewater were emptied into the river (Zhang et al., 2008).

## 5. Conclusion

(1) The two river sediments were moderately polluted by Zn, Cr, and Cd. The anthropogenic sources are seriously polluted with heavy metals, with the degree of pollution shows in the following order:  $\text{Zn} > \text{Cd} > \text{Cr} > \text{Cu} > \text{Co} > \text{As} > \text{Ni} > \text{Pb}$ . Moreover, compared with soils from agriculture and farms, the industrial pollution is more serious. (2) According to risk ranked by RI, the two river sediments were at moderate and low potential risk. More than half of the sources (9/16) were at considerable or moderate potential risk. Therefore, the improper discharge or disposal of these sediments, soil and material from factories creates a potential risk of pollution. (3) Based upon Cd concentration and the geochemical behaviors of Cd isotopes in natural conditions and river flow direction, we suggest that Cd in river sediments was dominantly derived from sewage treatment and the sewage outlets. This study suggests that Cd isotopes could be an effective

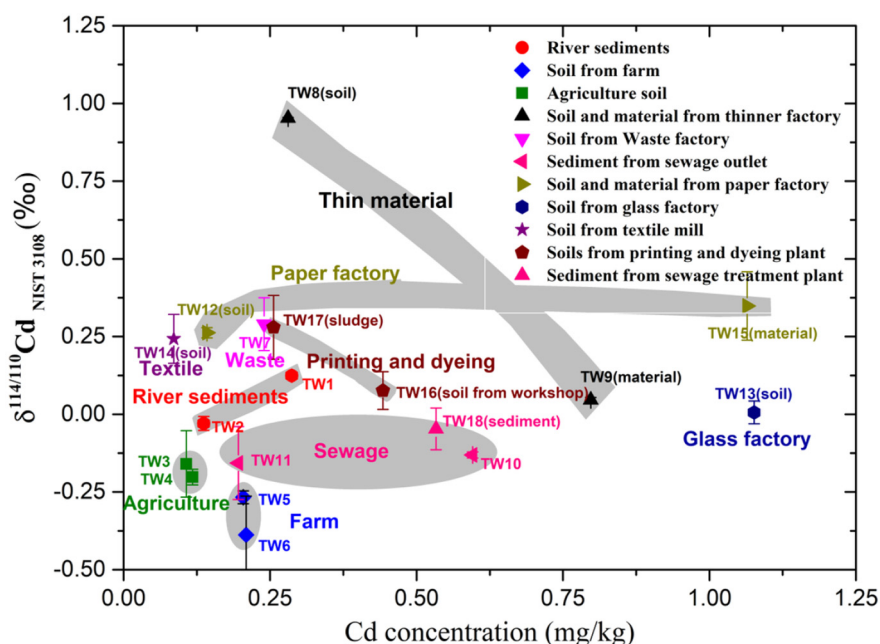


Fig. 3.  $\delta^{114/110}\text{Cd}_{\text{NIST 3108}}$  VS Cd concentration of river sediments and sources from anthropogenic activities around River-A, Shandong province, China.

geochemical tracer to identify Cd sources impacted by various anthropogenic activities, and the conclusions of this study are also valuable for the application of Cd isotopes in multiple Cd-polluted areas.

#### CRedit authorship contribution statement

**Xiuzhen Yin:** Writing - original draft, Writing - review & editing. **Rongfei Wei:** Conceptualization, Methodology, Data curation, Supervision, Writing - review & editing. **Huadong Chen:** Visualization, Investigation. **Chuanwei Zhu:** Methodology, Supervision, Writing - review & editing. **Yizhang Liu:** Software, Validation. **Hanjie Wen:** Conceptualization, Methodology, Supervision. **Qingjun Guo:** Conceptualization, Methodology, Supervision. **Jie Ma:** Writing - review & editing.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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