Cadmium isotopes as tracers in environmental studies: A review

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HIGHLIGHTS

- The analytical methods for isotopic composition of cadmium (Cd) are reviewed.
- Cd isotopic compositions in major Cd pollutants are summarized.
- Cd isotopes are powerful to trace pollution in different environmental systems.

GRAPHICAL ABSTRACT
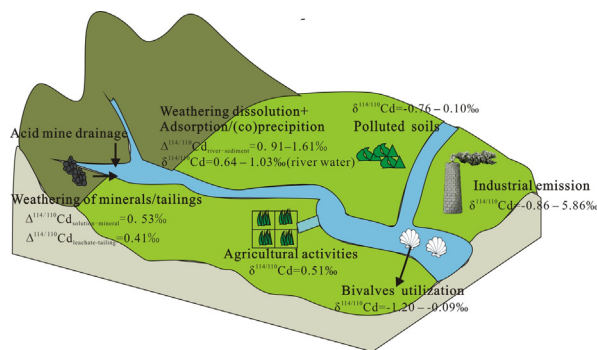
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ABSTRACT

Cadmium isotopic compositions in non-contaminated systems and anthropogenic sources of Cd generally have different isotopic signatures. Cadmium isotopes, as a novel tracer, can be useful for fingerprinting the anthropogenic Cd sources, providing a promising source tracing technique in environmental studies. This review presents: (i) analytical techniques for Cd isotopic composition; (ii) isotopic signatures of Cd derived from anthropogenic activities; (iii) isotopic compositions of Cd in the industrial-impacted environmental samples; (iv) cadmium isotopic fractionation induced by geochemical process. Finally, the perspectives of using Cd isotopic compositions in environmental studies are also briefly discussed.

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1. Introduction

Considerable attention has been given to toxic metal pollution occurrences in recent decades in developing nations typical of China due to increased industrial activities (Duan et al., 2018; Huang et al., 2019; Liu et al., 2019; Lan et al., 2019; Huang et al., 2020; Wang et al., 2020a). The content of cadmium (Cd) is about 0.1–0.5 μg/g in the earth's crust, and the atmospheric Cd concentrations in industrial areas and rural areas are approximately 15–150 ng/m^3 and 0.1–5 ng/m^3, respectively (Sigel et al., 2013). In environmental systems, Cd mainly exists as Cd (I) and Cd (II), but the latter occurs in higher concentrations (Cullen and Maldonado, 2013). Cadmium can be emitted into the environment through industrial activities such as mining, metal smelting, and electroplating, and also through batteries, aerospace coatings, preservatives, pigments, mineral phosphorus fertilizer and neutron absorbers from nuclear power plants (Sigel et al., 2013; Madala et al., 2013; Salmanzadeh et al., 2017; Rahmi et al., 2017; Fouskas et al., 2018; Yang et al., 2019; Wang et al., 2020b).

Cadmium has little biological function in animals and plants, except for its recognized role as a zinc replacement at the catalytic site of a particular class of carbonic anhydrases in some marine diatoms (Lane et al., 2005; Sigel et al., 2013; Scott et al., 2019). Cadmium is an acutely toxic metal element and has a very low biocidal dose for mammals, which could damage liver, kidneys, lungs, renal disorder, bone fracture and destruction of red blood cells in a human body (Godt et al., 2006; Sigel et al., 2013; Rahmi et al., 2017). The uptake of Cd into the body is mainly by inhalation of atmosphere particulate matter, smoking or by ingestion from the diet and water (Sigel et al., 2013). It is readily for Cd to enter into the food chain and eventually be accumulated in human bodies (Rizwan et al., 2018; Imseng et al., 2018; Wiggenhauser et al., 2019). Owing to the extreme toxicity of Cd, the pollution arising from Cd has been widely recognized as a serious threat to environment and human health (Wang et al., 2019; He et al., 2019).

It is well-known that source identification is crucial for metal pollution control (Liu et al., 2017; Yin et al., 2019; Liu et al., 2020a; Liu et al., 2020b; Wang et al., 2020c). Traditional methods including principal component analysis, hierarchical cluster analysis and pearson correlation coefficients can indicate the pollutants from different sources, but cannot quantify specific contributions from each source (Sakan et al., 2015; Gao et al., 2016; Sun et al., 2018; Mirza et al., 2019). Cadmium isotopes, as new geochemical tracers, can be potentially used for quantitative source apportionment of Cd contamination from different sources (Wiederhold, 2015; Salmanzadeh et al., 2017; Wiggenhauser et al., 2019). Pertinent studies have shown that Cd isotope fractionation was very limited (~0.2‰) during the transfer processes in natural geologic

systems (Wombacher et al., 2003; Scott et al., 2019), while much larger Cd isotope fractionation was observed during high temperature industrial processes (e.g., lead-zinc smelter, coal combustion and glass manufacturing plant) (Shiel et al., 2010; Martinkova et al., 2016; Fouskas et al., 2018; Cloquet et al., 2006; Bridgestock et al., 2017; Salmanzadeh et al., 2017; Wang et al., 2019; Wiggenhauser et al., 2019; Yang et al., 2019 and references therein).

The goal of this review is to summarize the recent progress of using Cd isotopes in environmental studies. The state-of-the art analytical techniques are briefly reviewed, followed by a summary of the Cd isotopic compositions of potential pollutant samples as a "fingerprint". Then, the applications of Cd isotopes as source tracers in environmental systems are focused on, with a special spotlight on river water, sediments, aquatic organism and soils. In particular, anthropogenic activities involving high temperature industrial processes (e.g., lead-zinc smelters and coal-fired power plants) are highlighted.

2. Analytical techniques of Cd isotopic composition

2.1. Chemical separation of Cd

Cadmium has eight stable isotopes: ^{106}Cd (1.25%), ^{108}Cd (0.89%), ^{110}Cd (12.49%), ^{111}Cd (12.80%), ^{112}Cd (24.13%), ^{113}Cd (12.22%), ^{114}Cd (28.73%) and ^{116}Cd (7.49%) (Rehkämper et al., 2012). In order to avoid isobaric and molecular interferences on Cd isotopes from major elements (e.g., Na, Mg, Ca, Fe, Al and Zn) and trace elements (e.g., In, Sn and Pd) (Table S1), it is prerequisite to separate Cd from sample matrix prior to mass spectrometric analysis (Rehkämper et al., 2012).

Chemical separation of Cd is usually achieved by ion-exchange chromatography, using resins such as AG-MP-1 M, AG1-X8 and Eichrom TRU Spec (Table 1). A two-step chromatography method was established for the separation of Cd from meteorites and geological materials (Wombacher et al., 2003). Matrix elements (e.g., Ag, Ca, Zn, Fe, Al, In and Pb) were removed from samples by using Biorad AG1-X8 resin (100–200 mesh) in the first step. Subsequently, Cd was separated from trace elements such as Sn, Nb, Mo and Zr by using Eichrom TRU Spec resin. However, residual Sn is still present in the Cd fraction. A revised three-step chromatography which also used Biorad AG1-X8 (100–200 mesh) and Eichrom TRU Spec resin, was then established by Ripperger and Rehkamper, 2007 for the separation of Cd from seawater. The main difference is that exchange columns (with different sizes) were loaded with AG1-X8 resin, which was used in the first two separation stages to separate Cd from matrix elements. However, this method is not applicable when the Cd concentration in seawater samples is very low (< 0.05 nmol/kg). The column chemistry procedure was further improved via co-precipitation of Cd with a suitable volume of 0.23 N AlCl$_3$

Table 1
Chemical purification methods for Cd isotopes.

Analytical method	Anion-exchange resin	Sample	Reference
Two-stage column/MC-ICP-MS	AG1-X8 (100–200 mesh)/Eichrom TRU Spec	Meteorites/Terrestrial rock and mineral	Wombacher et al. (2003)
One-stage column/MC-ICP-MS	AG-MP-1 M (100–200 mesh)	Soil/Smelter samples	Cloquet et al. (2005a, 2005b)
Three-stage column/MC-ICP-MS	AG1-X8 (200–400 mesh)/ Eichrom TRU Spec	Seawater	Ripperger and Rehkamper, 2007
One-stage column/MC-ICP-MS	AG-MP-1 M (100–200 mesh)	Sediments	Gao et al. (2008)
Two-stage column /TIMS	AG1-X8 (100–200 mesh)	JMC Cd reference standard	Schmitt et al. (2009a)
One-stage column/MC-ICP-MS	AG-MP-1 M (100–200 mesh)	Soils	Zhang et al. (2010)
Three-stage column/MC-ICP-MS	AG1-X8 (100–200/200–400 mesh)/Eichrom TRU Spec	Seawater (Cd content <5 pmol/L)	Xue et al. (2012)
Two-stage column/MC-ICP-MS	Nobias PA-1/AG-MP-1 M (100–200 mesh)	Seawater	Conway et al. (2013)
One-stage column/MC-ICP-MS	AG-MP-1 M (100–200 mesh)	Plants/solution	Wei et al. (2016)
Three-stage column/MC-ICP-MS	AG1-X8 (100–200/200–400 mesh)/Eichrom TRU Spec	Plants/soils	Wiggenhauser et al. (2016)
One-stage column/MC-ICP-MS	AG-MP-1 M (100–200 mesh)	River water	Yang et al. (2019)
Two-stage column/MC-ICP-MS	AG-MP-1 M (100–200 mesh)	Low-Cd geological samples (>20 ng)	Tan et al. (2020)

and NH$_3$ (Xue et al., 2012). Moreover, to separate low levels of Fe, Zn and Cd from seawater simultaneously, a two-stage column chromatography was proposed by Conway et al. (2013). In the first stage, Nobias PA-1 resin was used to extract Fe, Zn and Cd from seawater. In the second stage, AG-MP-1 M resin (100–200 mesh) was employed to elute Fe, Zn and Cd by using 1 N HCl, 2 N HNO$_3$ + 0.1 N HBr and 2 N HNO$_3$, respectively.

Cloquet et al. (2005a) developed a simple and efficient single-stage procedure to separate solid environmental samples using AG-MP-1 M resin (100–200 mesh). The entire purification procedure washed the matrix elements by using only HCl. This procedure can separate Cd from matrix of various elements, but residual Sn remains. Consequently, Zhang et al. (2010) improved this method by adjusting the eluting solution sequence of 0.06 N HCl and 0.012 N HCl. This single-column chemistry procedure has been successfully applied to separate Cd from plants and river water samples (Wei et al., 2016; Yang et al., 2019). Whereas, these single-stage purification methods which have been established for soils, sediments, sphalerite, plants and river water (Cloquet et al., 2005a; Zhang et al., 2010), were mainly designed for samples with high Cd concentrations (>1 μg/g). To separate Cd effectively from large amounts of matrix elements (such as Mo, Zr and In) in low-Cd samples, an improved purification method originally proposed by Cloquet et al. (2005a) was constructed by Tan et al. (2020). This method can greatly promote the application of Cd isotopes in environmental and geological samples with extremely low-Cd concentration such as aerosols, rainwater, igneous rocks, mantle-derived rocks, and living organisms.

In summary, appropriate procedure of column chemistry should be selected according to sample matrix and Cd concentration in samples. Single stage column chemistry is suitable for the solid environmental samples or contaminated water samples with relatively high Cd concentrations (> 1 μg/g). Low-Cd samples with complex matrices, such as aerosols, rainwater, igneous rocks, mantle-derived rocks, and living organisms, can be analyzed by chromatography method with Cd double spike such as ^{106}Cd—^{108}Cd (Schmitt et al., 2009b), ^{110}Cd—^{111}Cd (Ripperger and Rehkamper, 2007; Conway et al., 2013) and ^{111}Cd—^{113}Cd (Xue et al., 2012; Tan et al., 2020) via a two-stage or three-stage column chemistry.

2.2. Determination of Cd isotopic composition by using mass spectrometry

The first attempt to determine the Cd isotopic ratio in terrestrial minerals was carried out by employing thermal ionization mass spectrometry (TIMS), but the fractionation of Cd isotopes was not discovered due to the low analytical precision of TIMS (±2sd = 4.00–16.00 εCd/amu, Table S2) (Rosman and Delaeter, 1975). Since the beginning of the 20th century, MC-ICP-MS has been developed rapidly and achieved high-precision analysis of Cd isotopes (Wombacher et al., 2003; Weiss et al., 2008; Tan et al., 2020 and references therein). The magnitude of Cd stable isotope fractionation is usually expressed as the relative deviation with respect to a standard reference, i.e., the NIST SRM 3108 Cd solution, in parts per 1000 (δ) ^{114}Cd/^{110}Cd as described in Eq. (1) (Rehkämper et al., 2012; Abouchami et al., 2013):

$$\delta^{114/110}\text{Cd} = \left[\left(^{114}\text{Cd}/^{110}\text{Cd} \right)_{\text{sample}} / \left(^{114}\text{Cd}/^{110}\text{Cd} \right)_{\text{NIST SRM 3108}} - 1 \right] \times 10^3 \quad (1)$$

Various laboratories have utilized different commercially available Cd isotope standard solutions, such as Münster Cd, BAM-1012 Cd, Alfa Cd Zürich and NIST SRM 3108. For comparison of Cd isotopic compositions in different studies, the conversion can be calculated by the following equation:

$$\delta^{114/110}\text{Cd}_{\text{X−NIST SRM3108}} \approx \delta^{114/110}\text{Cd}_{\text{X−A}} + \delta^{114/110}\text{Cd}_{\text{A−NIST SRM 3108}} \quad (2)$$

Where X and A represents the actual sample and original laboratory standard, respectively.

High-precision Cd isotope analysis technique using MC-ICP-MS (± 2sd = 0.20–0.80 εCd/amu) was firstly developed by Wombacher et al. (2003), which were then greatly improved by De Baar et al. (2017) and Guinoiseau et al. (2018) (as displayed in Table S2).

Compared to TIMS, MC-ICP-MS has more advantages in: (1) higher first ionization potential of Cd, (2) more efficient analysis of Cd isotopic measurements, and (3) smaller sample size (Wombacher et al., 2003; Ripperger and Rehkamper, 2007; Yuan et al., 2016; Bao et al., 2020; Tan et al., 2020). Therefore, MC-ICP-MS is widely applied in measurement of Cd isotopic composition (Table S2). Although MC-ICP-MS can generate an instrumental mass discrimination, it can be corrected by various methods, such as sample standard bracketing, external normalization and double spiking (Wombacher et al., 2003; Cloquet et al., 2005a; Ripperger and Rehkamper, 2007; Weiss et al., 2008; Shiel et al., 2009; Gault-Ringold and Stirling, 2012; Zhang et al., 2016; Tan et al., 2020).

3. Isotopic signatures of Cd derived from anthropogenic activities

3.1. Ore signatures

Cadmium contamination is usually generated by industrial activities, which is related to utilization of sulfide minerals, since Cd is often present as an accompanied metal in various sulfide minerals such as sphalerite (ZnS), pyrite (FeS$_2$) and galena (PbS). Signature of Cd isotopes in sulfide-rich ores have been reported by pertinent studies (Schmitt et al., 2009b; Shiel et al., 2010; Zhu et al., 2013; Wen et al., 2015; Chrastny et al., 2015; Martinkova et al., 2016). The δ$^{114/110}$Cd values ranged from −0.19 to 0.16‰ in continental sphalerite (Schmitt et al., 2009b), from −0.18 to 0.13‰ in ore concentrates from Trail smelter, Canada (Shiel et al., 2010). The δ$^{114/110}$Cd values ranged from −0.19 to 0.20‰ in sphalerite and − 1.64 to −0.69‰ in galena from Huize lead-zinc deposits, Guangxi, China, compared with −0.45–0.01‰ in sphalerite from Shanshulin lead-zinc deposits, Guizhou, China (Zhu et al., 2013). The δ$^{114/110}$Cd values ranged from −0.50 to −0.46‰ in sulfide ores from the open-pit Jinding mining area, Yunnan, China (Wen et al., 2015), and sphalerite from Olkusz smelter, Poland, had δ$^{114/110}$Cd values of −0.11‰ (Chrastny et al., 2015). The galena and sphalerite from former Czech smelter site had δ$^{114/110}$Cd values of 0.13‰ and 0.02–0.10‰, respectively (Martinkova et al., 2016). As shown in Fig. 1, except for one galena sample from Huize lead-zinc deposits, which contained very light Cd isotopes (δ$^{114/110}$Cd = −1.64), variations of
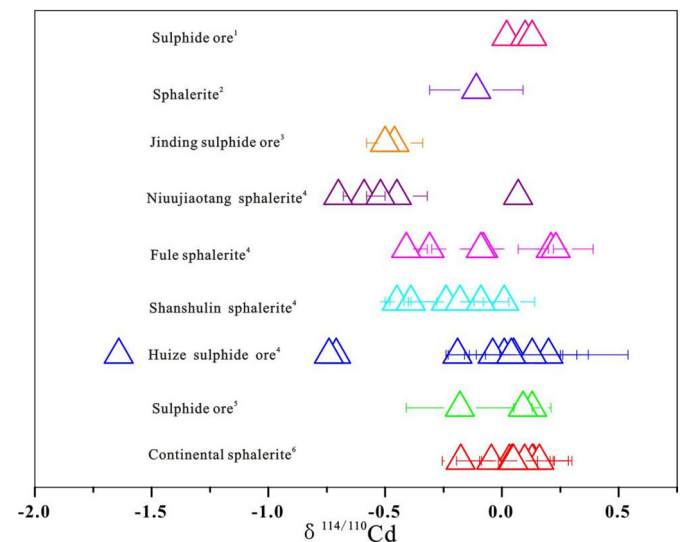

Fig. 1. Cadmium isotopic composition in different sulfide ores. Data based on Martinkova et al. (2016)[1], Chrastny et al. (2015)[2], Wen et al. (2015)[3], Zhu et al. (2013)[4], Shiel et al. (2010)[5] and Schmitt et al. (2009b)[6].

Cd isotopes in sulfide-rich ores ranged from −0.71 to 0.23‰. Moreover, the significant Cd isotopic variation in sulfide ores were mainly from lead-zinc deposits, Southwest China ($\delta^{114/110}$Cd = −1.64–0.23‰), which might be related to different ore forming processes (Zhu et al., 2013; Wen et al., 2015). The $\delta^{114/110}$Cd signatures of ores used in lead-zinc smelters had inconsiderable variation with $\delta^{114/110}$Cd values from −0.18 to 0.13‰ (Shiel et al., 2010; Chrastny et al., 2015; Martinkova et al., 2016).

Cadmium is a metal with low melting point (321 °C) and boiling point (765 °C). Most of Cd compounds are easy to be vaporized during high temperature processes. Lead-zinc smelters and coal-fired power plants, which used Cd-bearing sulfide minerals under high temperature during the production processes, are reported as the main anthropogenic contributors to Cd emissions. Therefore, it is important to understand Cd isotopic variations during these industries.

3.2. Isotopic fractionation of Cd during industrial processes under high temperature

Dust and slag samples collected from Noyelles-Godault lead-zinc refinery plant, Northern France exhibited considerable Cd isotopic fractionation with heavy isotopic signature in slag ($\delta^{114/110}$Cd = 0.26) and light isotopic signature in dust ($\delta^{114/110}$Cd = −0.74) (Cloquet et al., 2006). Obvious variations of Cd isotopes were also observed in materials from Trail lead-zinc smelter in Canada (Shiel et al., 2010). The zinc concentrate (−0.18–0.12‰) was characterised by identical Cd isotopic signatures of the lime-containing clinker (0‰). Both wastewater (0.26–0.41‰) and Cd by-product (0.34–0.47‰) were enriched with heavier Cd relative to the raw material (zinc concentrate). On the contrary, zinc oxide flue gas (−0.57‰) had lighter Cd relative to the raw material (zinc concentrate). The metallurgical slag samples ($\delta^{114/110}$Cd = −0.63 to −0.55‰) collected from Jinding smelter were featured by heavier $\delta^{114/110}$Cd signatures than its smelting material (oxidized ore) ($\delta^{114/110}$Cd = −0.81 to −0.69‰) (Wen et al., 2015). The zinc concentrates ($\delta^{114/110}$Cd = −0.81 to −0.69‰) used as initial material in Jinding smelter were isotopically lighter than zinc concentrates ($\delta^{114/110}$Cd = −0.18– 0.13‰) used in other Lead-zinc smelters. The slag samples from Jinding smelter was also isotopically lighter than the slag from Noyelles-Godault lead-zinc refinery plant and Trail lead-zinc smelter, which might be strongly associated with the initial $\delta^{114/110}$Cd signatures in industrial zinc concentrate. It was suggested that during the smelting process, Cd evaporated from initial Cd-bearing minerals and lighter Cd absorbed into the vapor phase (dust), which was removed from the system, while heavier Cd remained in residual phase (slag).

In a coal-fired power plant from Czech Republic, during coal combustion, ash had lighter isotopic signature (−0.86‰), whereas slag had heavier isotopic signature (5.86‰) with respect to the coal raw materials (−0.23‰) (Martinkova et al., 2016). Like the slag and dust from lead-zinc refinery plant, slag and ash from coal combustion also displayed similar isotopic fractionation directions of Cd. In the glass manufacturing plant from Czech Republic, yellow glass (0.21‰) and red glass (−0.3‰) products displayed significant Cd isotopic fractionation in different directions, compared to their initial material of Cd pigments (−0.01‰). There were differences in the ratio of Cd pigments and temperature settings for producing various coloured glasses, which might lead to the difference in Cd isotopes of yellow and red glasses. The soot (−0.51‰) produced by molten glass had heavier Cd isotopes relative to the glass.

Cloquet et al. (2005b) found that the cold point position in the heat transfer system during municipal waste combustion was quite significant for the degree of Cd isotope fractionation. If the cold point (part of the heat transfer system where the volatile elements condensate) was relatively close to the combustion chamber, which can cause most-fractionated part of the metal to condense again, preventing them from being discharged into the atmosphere (Cloquet et al.,

2005b; Chrastny et al., 2015). In summary, the difference of actual operation and technique in industrial activities may lead to different Cd isotope fractionation between dust/fly ash and slags/bottom ash in industrial process. Moreover, the initial $\delta^{114/110}$Cd signatures in industrial raw materials may also influence the $\delta^{114/110}$Cd signatures in slag and dust.

3.3. Fractionation mechanism during high temperature industrial processes

During the smelting process of lead and zinc ores, the temperature in furnace can be as high as up to 1200 °C, lighter Cd evaporates preferentially into the vapor phase, while heavier Cd remains in residual phase (slag). The Rayleigh fractionation model can describe Cd isotopic evolution of initial ores reservoir from which Cd is continuously extracted and the distinct signature of isotopes between the initial material and the residual fraction providing that it is the closed system:

$$\delta^{114/110}Cd_{residual} - \delta^{114/110}Cd_{initial} \approx 1000\,(\alpha - 1) \times\ \ln f \tag{3}$$

Where $\delta^{114/110}Cd_{residual}$ and $\delta^{114/110}Cd_{initial}$ are the Cd isotopic compositions in initial ores and residual fraction, respectively, α is the Cd isotopic fractionation factor between the vapor phase and initial ores reservoir, f is the ratio of the mass fraction of Cd in the residual fraction. Rayleigh fractionation model can be used to explain the isotopic fractionation behaviour during smelting of sulfide ores: air emissions display lighter signature ($\delta^{114/110}$Cd = −0.74 to −0.57‰), while slags exhibit the heavier signature ($\delta^{114/110}$Cd = 0.23–0.51‰), compared to the initial ore ($\delta^{114/110}$Cd = −0.18–0.13‰).

4. Isotopic compositions of Cd in the industrial-impacted environmental samples

4.1. Water bodies

Mining activities could generate acid mine drainage and release large amount of metal elements into surrounding rivers (Yang et al., 2019). The river water close to the tailing area was strongly enriched in heavier isotopes from 0.64 to 1.03‰ and had very high Cd concentration (181.1–304.2 μg/g). The isotope shifts between upper reach water and sediment ($\triangle^{114/110}Cd_{river\text{-}sediment}$ = 0.91–1.61‰) can indicate that weathering of Cd-bearing minerals in tailings was the main influencing factor (Fig. 2). The adsorption and co-precipitation on minerals can also play a role in this circumstance, because lighter Cd will preferentially adsorb onto manganese oxide or preferentially co-precipitate with sulfide (Wasylenki et al., 2014; Guinoiseau et al., 2018). These factors might explain why the upper reach had large Cd isotopic difference between sediments and river water. Except for the heavier Cd isotopes in the water samples (0.51‰) near the farmland, the $\delta^{114/110}$Cd signatures in the middle and lower reaches of the river varied from 0.21 to 0.35‰, and dissolved Cd concentration decreased with the increasing distance from the tailing area. Moreover, the $\delta^{114/110}$Cd signature of the water near the farmland enhanced drastically with the increase of NH_4^+ and NO_3^- concentrations. This suggested that agricultural activities might be additional source of Cd for pollution in river water downstream of farmland (Fig. 2). Therefore, the Cd contamination sources of stream water can be influenced by mining and agricultural activities.

4.2. Sediments

The sediments collected from downstream the lead-zinc smelter showed significant positive correlationship between Cd isotopic composition and high Cd concentrations, which indicated that the Cd contamination was arised directly from the slag of the lead-zinc smelter (Gao et al., 2013). The sediments were significantly enriched with lighter Cd isotopes and had remarkably high Cd concentrations near electronic waste area, which might be influenced by dust deposition from
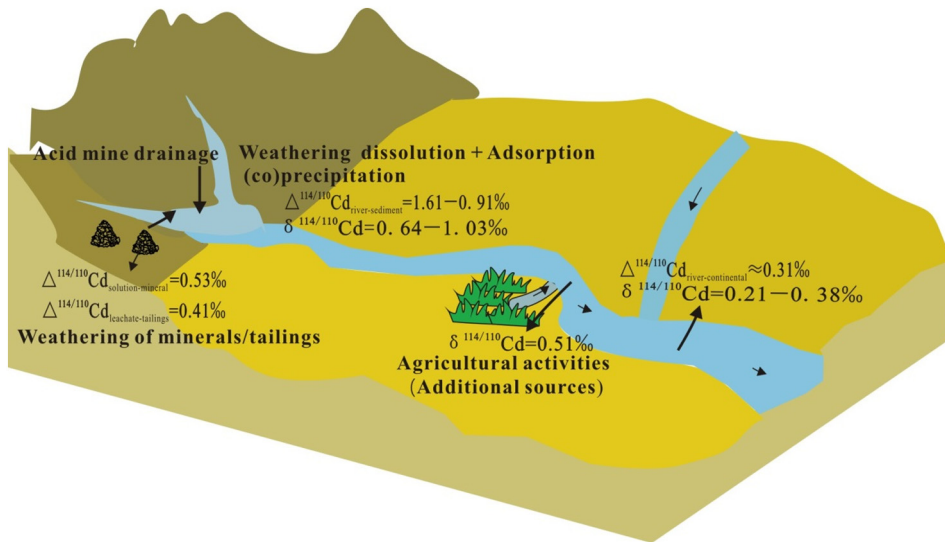
Fig. 2. Cadmium isotopic compositions of water from an acid mine drainage affected river. Databased on Yang et al. (2019) and Zhang et al., 2013.

e-waste dismantling and recycling activities. The $\delta^{114/110}$Cd signatures in stream sediment from the Bijiang River ranged from −0.10 to 0.29‰ at un-contaminated area, from −0.11 to −0.19‰ in the Jinding Pb—Zn mining area where it was considered heavily polluted (Zhang et al., 2016). Re-suspension of particles from slag heap and mining ores might be considered as major Cd contributors to Bijiang River sediments located within 1–5 km radius of smelters and mining site.

4.3. Aquatic organism

Bivalves are bio-accumulator of heavy metals. The bivalves from USA East coast presented a light Cd isotope ($\delta^{114/110}$Cd = −1.20 to −0.54‰). This might be explained by the developed industrial presence on the USA East coast, emitting Cd pollutants related to light Cd source (Shiel et al., 2012). The bivalves collected from France Atlantic coast were strongly enriched with lighter isotopic signature ($\delta^{114/110}$Cd = −1.08 to −0.62‰) due to its proximity to industrial activity (Shiel et al., 2013). Cadmium concentration in bivalves from Gironde estuary (Atlantic coast) decreased considerably between 1987 and 2005

(129.1 to 28.7 μg/g) corresponding to the shutdown of a Zn smelter in 1987. However, the bivalves still preserved similar $\delta^{114/110}$Cd signatures to the smelting dust, reflecting that Cd contamination in bivalves (Gironde estuary) was strongly influenced by historical Cd emissions from the metallurgical industry (Fig. 3). The bivalves collected from Marennes-Oléron basin where located about 30 km downstream the Gironde estuary, showed similar $\delta^{114/110}$Cd signatures to those bivalves in the Gironde estuary, although the bivalves had a lower concentration of Cd than Gironde estuary. This suggested bivalves at Marennes-Oléron basin and Gironde estuary had a common source of Cd contamination.

4.4. Soils

The air emissions from lead-zinc smelters or coal combustion, and re-suspension of particles from slag heap and mining activities can be considered as major Cd contributors to the soils nearby. Contaminated soils near smelter showed the light $\delta^{114/110}$Cd signatures ranged −0.76–0.10‰, which fell within the range between industrial slag (0.26‰) and dust (−0.74‰) (Cloquet et al., 2006) (Fig. 4). Moreover,
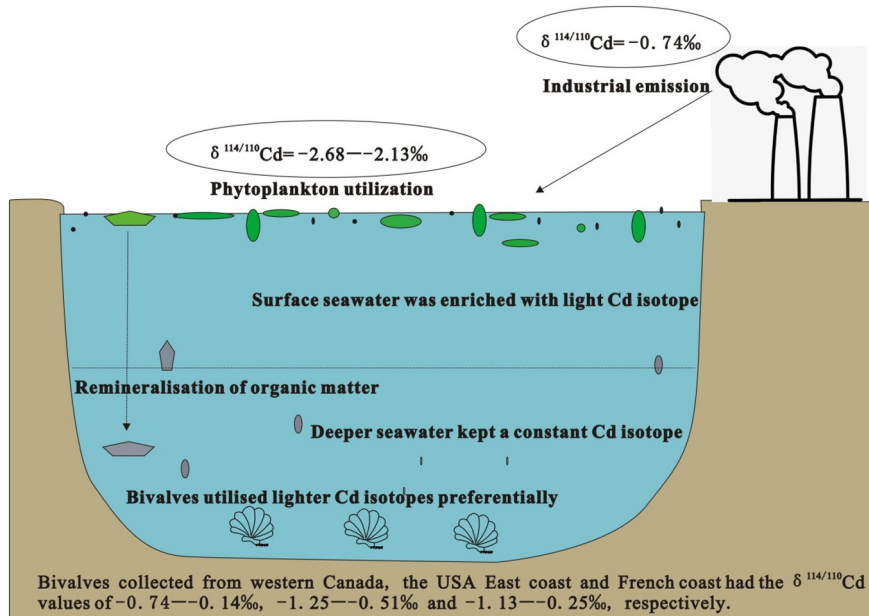

Fig. 3. Cadmium isotopic compositions of bivalves from different areas. Data based on Shiel et al. (2012, 2013), Cloquet et al. (2006) and Lacan et al. (2006).
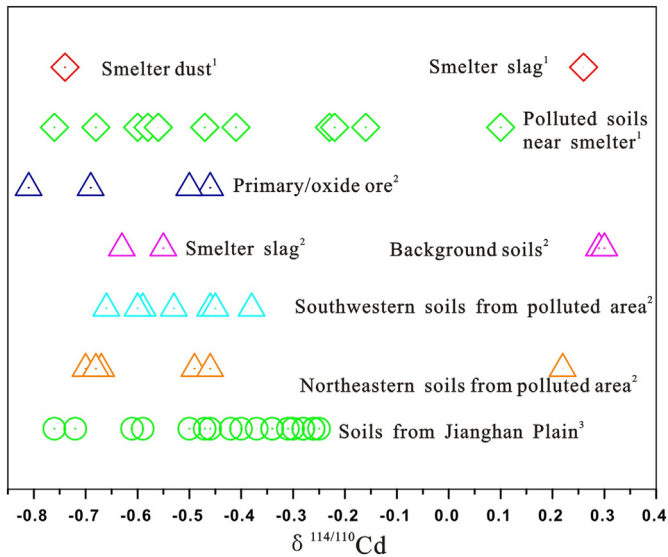
Fig. 4. Cadmium isotopic compositions of various topsoil and smelter samples. Data based on Cloquet et al. (2006)[1], Wen et al. (2015)[2] and Wang et al. (2019)[3].

the $\delta^{114/110}$Cd signatures of contaminated soils close to the smelters displayed lower $\delta^{114/110}$Cd values, which were identical to those of the smelter-derived dust samples. The $\delta^{114/110}$Cd values in contaminated soils were positively correlated to the distance from the smelter (Cloquet et al., 2006). The soils collected within 1–5 km from the Jinding Pb—Zn mine had $\delta^{114/110}$Cd signatures from −0.70 to 0.22‰ (Wen et al., 2015). The Cd concentrations of soils gradually decreased to a background value, while $\delta^{114/110}$Cd values rose with the increased distance from the Jinding Pb—Zn mine (Fig. 4). This might indicate that soils were mainly influenced by the re-suspension of particles from slag heap, mining and smelting activities. Contaminated soils collected from the Jianghan Plain had $\delta^{114/110}$Cd signatures from −0.76 to −0.25‰, which were similar to smelter dust (Fig. 4) and fly ash emitted from coal combustion (Cloquet et al., 2006; Martinkova et al., 2016; Fouskas et al., 2018).

In summary, obvious isotopic fractionation of Cd from high temperature industrial activities (e.g., lead-zinc smelters and coal-fired power plants) can usually preserve its fingerprint characteristics in different environmental compartments. The illustrations of Fig. 5 suggest the feasibility to use $\delta^{114/110}$Cd variations related to industrial activities under high temperatures (e.g., lead-zinc smelters and coal-burning power plant) to trace the Cd contamination.
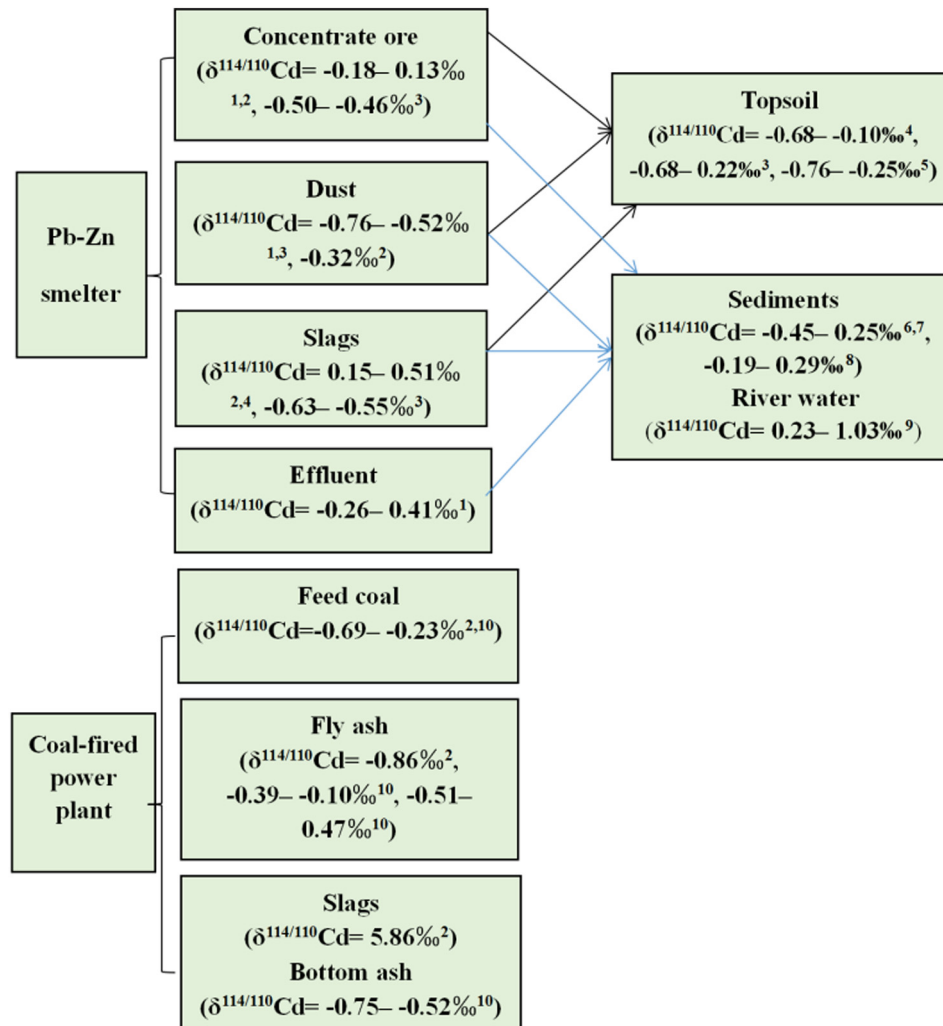

Fig. 5. Cadmium isotopic compositions related to the process materials in Pb—Zn smelter and coal-fired power plant and related data on nearby soil, sediment and river water. Data based on Shiel et al. (2010)[1], Martinkova et al. (2016)[2], Wen et al. (2015)[3], Cloquet et al. (2006)[4], Wang et al. (2019)[5], Gao et al. (2008, 2013)[6,7], Zhang et al. (2016)[8], Yang et al. (2019)[9], and Fouskas et al. (2018)[10].

5. Cadmium isotopic fractionation induced by geochemical process

The extent of fractionation can be greatly varied upon distinctive physiochemical or geochemical processes, e.g., adsorption of metal ions onto Fe-Mn(hydr)oxides, binding to secondary precipitation of carbonates.

Cadmium isotope fractionation has been found for adsorption of Cd onto oxides or co-precipitation with sulfides. During Cd adsorption onto calcite, Cd isotope fractionation was found between solution and calcite at high ionic strength solution ($\Delta^{114/110}Cd_{seawater-calcite} = 0.45‰$), while not obvious Cd isotope fractionation was observed at low ionic strength (Horner et al., 2011). The marine calcite might be used to record Cd isotopic composition of concomitant seawater, since isotopic fractionation of Cd showed negligible response to temperature and precipitation rate during Cd adsorption onto calcite (Horner et al., 2011). Theoretical calculations showed that different Cd species have different isotopic compositions. Isotopic composition of Cd decreased in the order of cadmium hydroxides > cadmium nitrates > cadmium hydrates > cadmium chlorides > cadmium hydrosulfide (Yang et al., 2015). In high ionic strength, Cd mainly occurred as $CdCl^+$ (47%) and $CdCl_2$ (47%), while almost all Cd occurred as $Cd(H_2O)_6^{2+}$ at low ionic strength (Wasylenki et al., 2014; Guinoiseau et al., 2018). It suggests that the salinity may induce the changes in Cd aqueous speciation at different ionic strength, thereby affecting the extent of isotope fractionation. It was worth noting that the isotopic fractionation between dissolved Cd and sorbed Cd at high ionic strength solution decreased gradually over time, from 0.80‰ ($\Delta^{114/110}Cd_{solution-solid}$) after 1 h to 0.20‰ after 912 h, while the percentage of Cd sorbed to birnessite increased over this interval from 27 to 58% (Wasylenki et al., 2014). The extent of isotopic fractionation between dissolved Cd and sorbed Cd decreased gradually over time might indicated that kinetic effect largely controlled the observed isotopic fractionation at early stage, and then sorbed Cd and dissolved Cd exchanged slowly associated with equilibrium fractionation, decreasing the extent of Cd isotopic fractionation. Thus, it is postulated that the adsorption reactions of Cd onto calcite and oxides (e.g., Mn, Al or Fe oxy (hydr)oxide) can only generate a minor degree of Cd isotopic fractionation in natural settings. Lighter Cd isotopes were evidently enriched in precipitated CdS compared to synthetic seawater or pure water (Guinoiseau et al., 2018). The Cd isotopic fractionation between precipitated CdS and dissolved Cd decreased with increased ionic strength, from 0.61 ($\Delta^{114/110}Cd_{pure\ water-CdS}$) to 0.45‰ ($\Delta^{114/110}Cd_{synthetic\ seawater-CdS}$). In the simulated experiment, Cd isotope fractionation during Cd sulfide co-precipitation is more variable compared to the adsorption reactions of Cd onto oxides.

6. Conclusions

(1) Hitherto, a number of chemical analysis methods for Cd isotopes have been established for purification and subsequent isotope measurement in different types of environmental samples. Cadmium isotopic composition is becoming a useful tool to gain a better understanding of geochemical migration of Cd in the environment. The isotopic fractionation of Cd during high-temperature processes conforms to the Rayleigh fractionation law, which generally leads to the enrichment of lighter Cd isotopes in dust, and heavier isotopes in slags and effluent.

(2) The characteristic Cd isotopic signatures in waste materials (e.g., dusts, slags and effluent) can be used as a very powerful tool to track the potential sources of Cd contamination in different environmental media (waters, sediments, aquatic organisms and soils). For instance, the heavier Cd isotopic signatures in river water near tailing area could be traced to the weathering of sulfide ore in tailing. However, Cd isotopic signatures in aerosol samples are still understudied. The extent of Cd isotopic fractionation induced by other industrial activities (such as electroplating) under high-temperature also remains unclear.

Even though several studies have documented Cd isotopic fractionation during the uptake of Cd by plants (trees, herbs or vegetation), very few have investigated Cd isotopic signatures in different biological samples impacted by smelters.

(3) Therefore, more work should be carried out in the near future to investigate Cd isotopic fractionation during different industrial activities, to identify Cd isotopic composition in aerosols and plants, and to better understand the changes of Cd isotopic signatures in the environment, especially for complex systems affected by multiple metal sources and related processes.

Declaration of competing interests

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.

CRediT authorship contribution statement

Qiaohui Zhong: Investigation, Writing - original draft. **Yuchen Zhou:** Writing - review & editing. **Daniel C.W. Tsang:** Writing - review & editing. **Juan Liu:** Writing - review & editing, Supervision, Project administration. **Xiao Yang:** Writing - review & editing. **Meiling Yin:** Writing - review & editing. **Shijun Wu:** Writing - review & editing. **Jin Wang:** Writing - review & editing, Project administration. **Tangfu Xiao:** Writing - review & editing. **Zhaofeng Zhang:** Writing - review & editing, Supervision.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.139585.

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