

Tracer Application of Several Heavy Metal Isotopes in Environmental Pollution

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Abstract

In recent years, due to the substantial development of scientific measurement technology, stable isotope tracer technology has been increasingly applied to the research and analysis of environmental pollutant sources. According to the isotopic geochemical characteristics of Pb, Cd and Zn elements, the basic theory of tracing heavy metal pollution in atmosphere, water and soil was analyzed. Based on the tracing principle and determination method of the three elements isotopes, a large number of domestic and foreign cases were referred. The application status and deficiency of isotope tracer techniques in the study of environmental heavy metal sources were discussed and the future development prospect was prospected.

Keywords

Heavy metals; Isotope tracing.

1. Preface

Heavy metals such as Pb, Cd, Cu, Zn, Hg and As have been widely introduced into the natural environment and continuously enriched in the environment due to the mining and metal smelting of mines, the rough management development of factories, the development and utilization of fossil energy, and the domestic sewage discharge of residents. Entry into the human body through the food chain poses a serious threat to the health of residents. For example, Pb levels are increasing in the environment and may accumulate in the human body causing Pb poisoning. Pb poisoning is chronic poisoning, and its main influence nerve, blood, digestive, urinary, reproductive and developmental, cardiovascular, endocrine, immune organs, bones, and other kinds of, is the main target organs of the nervous system and hematopoietic system, easy to affect the growth and intellectual development, cognitive function, nerve behavior and the learning and memory and other brain function, serious cause dementia. Acute pneumonia and pulmonary edema can be caused by a single inhalation of Cd dust or Cd compound dust, and pulmonary fibrosis and renal disease can be caused by chronic Cd poisoning. Japan reported "itai-itai disease" is a chronic Cd poisoning caused by long-term ingestion of Cd sulphate contaminated water. Hg poisoning is more common in chronic, which mainly occurs in production activities and is caused by long-term inhalation of Hg vapor and Hg compound dust. The main symptoms are mental-nervous abnormalities, gingivitis, and tremor. Acute Hg poisoning occurs when large doses of Hg vapor inhalation or Hg compound ingestion occurs. It can be seen that heavy metal poisoning is harmful to the human body. In

recent years, more and more heavy metal pollution incidents have been reported. It has aroused widespread concern from the government and all walks of life, and began to spend huge amounts of money on heavy metal pollution control. However, in order to treat regional heavy metal pollution, it is necessary to find out the source of heavy metals in the region before stopping the source of treatment to prevent heavy metal pollution from intensifying over time. At present, the main means of pollution traceability are statistics, which judge the possible sources of pollutants through multivariate statistics. Secondly, other pollution source tracing methods are easily affected in the process of pollutant extraction and analysis, which may cause misjudgment of source identification. Compared with the above methods, due to the geochemical characteristics of stable isotopes, it can be used to trace the source, migration, transformation, and whereabouts of environmental pollutants. As a kind of pollutant, stable isotope of heavy metal has stable composition and reliable discrimination result, which has huge application advantages in pollution tracing. Nowadays, the main elements that can be used to trace heavy metal pollution are Pb, Zn, Cd and so on [1, 2, 3]. Among them, Pb isotope tracing technology is relatively mature and widely used. Zn and Cd are emerging technologies that can be used as supplementary explanations for Pb isotope tracing, and they are beginning to receive attention [4, 5, 6].

2. Isotope Tracer

2.1. Principle and Application of Pb Isotope Tracer

There are four stable isotopes of Pb in nature: ^{204}Pb , ^{206}Pb , ^{207}Pb , and ^{208}Pb . Among them, ^{204}Pb existed before the formation of planets, and its abundance remains unchanged due to non-radioactive origin. The latter three are the final products of ^{238}U , ^{235}U , and ^{232}Th decays, respectively. Its abundance continues to increase with the evolution of time. Pb is a heavy isotope, and the relative mass difference between isotopes is small. Changes in external conditions have little effect on its composition. Unlike light isotopes such as O, S, H, and C and other light isotopes, which are prone to change in the secondary process by the temperature, pressure, pH, Eh and other physical and chemical conditions and biological effects of the system. Therefore, the Pb isotope composition has obvious "fingerprint characteristics", and the Pb isotope composition of environmental pollutants is consistent with that of their source areas, which can be used to study the source of pollution can get ideal results. The variation of Pb isotope composition mainly depends on the content of radioactive elements U and Th, the length of decay time, the content of parent isotope and the mixing of exotic source regions, that is, the time when environmental substances are formed and the ratio of U/Pb and Th/Pb. Due to the different decay constants of ^{238}U , ^{235}U and ^{232}Th , this determines that the ratio of the corresponding daughter isotope ^{206}Pb , ^{207}Pb and ^{208}Pb will change regularly with the positive increase of time; while the ratio of U/Pb and Th/Pb It is the characteristic parameter of the material source area. Together with the material formation time parameter, it can not only reflect the Pb isotope characteristics of the material in the source area of different environmental media, but also determine the Pb isotope that occurs when the material from the external source area is mixed with the original material. The composition changes to different degrees, so the change of Pb isotopic composition not only follows the law of radioactive decay, but is also closely related to the structural environment of its formation.

Due to the different material sources, formation mechanisms, formation environment and formation time of the existing different environmental media, they have different Pb isotopic labeling characteristics. Therefore, the organic combination of the Pb isotopic composition of environmental materials, the Pb isotopic structure environmental information, the Pb isotopic mixing model and the calculation results of source area parameters can powerfully trace the source and migration laws of environmental materials.

At present, to identify the source and migration of heavy metal pollution, four Types of Pb isotope ratios ($^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$) are described and analyzed graphically to comprehensively discuss the heavy metal pollution tracing in sediments, soil and atmosphere. The methods of determination of Pb isotope ratio include thermoelectric ionization mass spectrometry (TIMS) and inductively coupled plasma mass spectrometry (ICP-MS), both of which can meet the test accuracy required by the general Pb isotope tracer. However, TIMS method has disadvantages such as long analysis time and complex sample pretreatment. The icP-MS method has the advantages of low detection limit, wide linear range, less interference, high precision and rapid element isotope ratio analysis. In contrast, Mc-icp-ms (multi-receiver inductively coupled plasma mass spectrometry) has more advantages, so it has been widely used in the determination of Pb isotope ratio in recent years, and has become a common environmental monitoring method.

M Kersten studied the severely polluted Elefsis Bay in Athens, Greece, and measured the $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratio by inductively coupled plasma mass spectrometry (ICP-MS) [7]. It was found that the Pb isotope ratio was lower than the local background value and industrial park value because of the influence of Pb ($^{206}\text{Pb}/^{207}\text{Pb} = 1.06$) isotope ratio in gasoline. The Pb pollution in sedimentary samples is mainly from industrial activities (70-80%), and more than 70% of the soluble Pb in the bay is from Pb in gasoline. Gulson studied the source area of Pb in soil of a certain area in southern Australia, and the results showed that orchard spraying, power station and smelter were not the main Pb sources in surface soil, but were polluted by tetraethyl lead in gasoline. Pb contamination does not spread more than 30~40 cm deep, but can spread at least 50 km from the source[8]. Mukai[9] and Zheng[10] measured the Pb isotopic composition of atmospheric aerosol samples by ICP-MS, and pointed out that the main sources of atmospheric Pb pollution in some Chinese cities such as Shanghai include industrial emissions, automobile exhaust and coal burning. Among them, the factors affecting industrial emissions are complex, and there are many sources, mainly including: Pb emissions from metallurgical industry, urban construction and other purposes.

2.2. Principle and Application of Zn Isotope Tracer

Zn is a transition metal element. In nature, Zn is generally distributed in various minerals, rocks, fluids and organisms, and is widely involved in processes such as diagenesis, mineralization, hydrothermal activities, and biological activities. Zn has 5 isotopes: ^{64}Zn , ^{66}Zn , ^{67}Zn , ^{68}Zn and ^{70}Zn , with abundances of 48.63%, 27.90%, 4.10%, 18.75% and 0.62%, respectively. At present, $\delta^{66}\text{Zn} = [(^{66}\text{Zn}/^{64}\text{Zn})_{\text{sample}} / (^{66}\text{Zn}/^{64}\text{Zn})_{\text{standard}} - 1] \times 1000$ is commonly used in environmental scientific research. Although the determination of the isotope composition of Zn began in the 1950s, due to the backward analysis and testing methods at that time, the measured isotope composition changes and the error of the analytical measurement methods are the same order of magnitude, so it is impossible to find the true changes in the isotope composition and its significance. With the emergence and gradual improvement of MC-ICP-MS, the determination and application of Zn isotopic composition as a non-traditional stable isotope have been developed.

Composition of zinc isotope fractionation is mainly affected by source area and the thermodynamics and kinetics in the process of geological fractionation effect, depends on mainly include the conditions of temperature, pressure and phase change process of inorganic and organic processes for the biological activity, through mineralogy fractionation, secondary change (again deposition and leaching) and precipitation of three eventually form different fractionation effects.

As a new geochemical tracer, the detailed analysis of the fractionation process and mechanism of Zn isotope is the key to solve scientific problems. Fujii reported the isotopic fractionation of Zn in REDOX reactions, including two isotope effects of mass dependence and mass

independence [11]. Jouvin studied the fractionation of Zn isotopes adsorbed on pure humic acid to better understand the Zn isotopic fractionation mechanism associated with organic matter [12]. Chen measured the $\delta^{66}\text{Zn}$ of suspended particles and floodplain sediments in the Seine Basin, France. According to the $\delta^{66}\text{Zn}$ data obtained, Zn enrichment is mainly formed by the mixing of two main suspended particles, namely natural silicate particles and anthropogenic particles. In addition, according to the range of $\delta^{66}\text{Zn}$, it can be calculated that 70% of Zn in the Seine river in Paris comes from human activities [13]. Juillot measured the $\delta^{66}\text{Zn}$ values of two soil profiles near a lead-zinc processing plant in northern France. The results showed that the $\delta^{66}\text{Zn}$ values at the bottom of the two profiles represented the local geochemical background values, while the larger $\delta^{66}\text{Zn}$ values near the surface were related to anthropogenic Zn. The anthropogenic Zn mainly comes from Zn iron ore grains in the tailings of the lead-zinc smelter [14].

2.3. Principle and Application of Cd Isotope Tracer

There are eight stable isotopes ^{106}Cd , ^{108}Cd , ^{110}Cd , ^{111}Cd , ^{112}Cd , ^{113}Cd , ^{114}Cd and ^{116}Cd with abundances of 1.25%, 0.89%, 12.8%, 12.8%, 24.1%, 12.2%, 28.7% and 7.49%, respectively. $\delta^{114}\text{Cd} = \left(\frac{^{114}\text{Cd}/^{110}\text{Cd}}{^{114}\text{Cd}/^{110}\text{Cd}}_{\text{standard}} - 1 \right) \times 1000$ is commonly used in environmental science research. Is part of the Cd isotope fractionation of outside material is larger, the land material such as rock, soil Cd of isotope fractionation is lesser, but different media can identify the differences still exist, so it is entirely possible that indicates the geochemical processes and Cd source, the isotopic composition of stability and the effect of the fingerprint, not only can effectively analyze source, The relative contribution of various sources can be estimated by isotope mixing model, which is of great scientific significance to the identification of accident pollution sources, the treatment and restoration of contaminated sites and other practical problems. It is also possible to reveal the characteristics of isotopic fractionation in the activation, migration and enrichment of Cd in the epigenetic environment, and as a brand new evidence to reveal the law and enrichment mechanism of Cd in the process of epigenetic migration. Generally speaking, the factors leading to isotope fractionation effect mainly include the following three aspects:

Evaporation/condensation process: Wombacher found that the residue after evaporation is richer in heavy isotopes than the original Cd metal through the experiment of vacuum heating Cd metal, confirming that the evaporation/condensation process can produce larger isotope fractionation. This fractionation feature was also confirmed by Cd isotope data from the flue gas and residue of the Pb-Zn smelter, that is, the flue gas is enriched with light Cd isotope and the residue is enriched with heavy Cd isotope [15].

Adsorption precipitation: Wombacher found in their study of simulated artefact precipitation that the precipitated artefact is enriched in light Cd isotope compared with the remaining solution [15]. Horner through simulating seawater CaCO_3 precipitation experiment, found that CaCO_3 precipitation has a small Cd isotopic composition relative to the remaining solution after precipitation, and the Cd isotopic composition of CaCO_3 precipitation is not affected by temperature, Mg^{2+} concentration and precipitation rate [16]. Thus, the precipitation process makes the sediment richer in light Cd isotopes. Zhang Yuxu studied Cd isotope in the leaching experiment of ore and tailings samples, indicating that the leachate is enriched with heavy Cd isotope in general compared with the residue state, and the dissolution process may lead to the fractionation of Cd isotope [2].

Biological effects: Lan can studied seawater samples at different depths and found that the surface seawater had heavier Cd isotope composition than the deep seawater, and the culture experiment of phytoplankton also found that the Cd isotope composition of phytoplankton was significantly lighter than that of culture medium [17]. Therefore, it was believed that phytoplankton preferred to absorb light isotope, resulting in heavier $\delta^{114}\text{Cd}$ in surface seawater.

The fractionation process is similar to the closed system Rayleigh fractionation process. This phenomenon has also been confirmed by later studies [18].

Cloquet analyzed the relationship between $\delta^{114}/^{110}\text{Cd}$ values and Cd concentrations in samples from the lead-zinc smelter in northern France and found that the Cd contribution of contaminated soil came from slag ($\delta^{114}/^{110}\text{Cd} = 0.36\text{‰}$) and dust ($\delta^{114}/^{110}\text{Cd} = -0.64\text{‰}$) [19]. Gao measured the isotopic composition of Cd in sediments from the Beijiang River in southern China, and found that compared with five unpolluted sediments ($\delta^{114}/^{110}\text{Cd} \approx 0\text{‰}$), Two samples from the vicinity of the lead-zinc smelting plant have higher Cd concentration and higher $\delta^{114}/^{110}\text{Cd}$ values ($+0.35\text{‰}$ and $+0.31\text{‰}$, respectively), indicating that Isotope fractionation of Cd occurs during lead-zinc smelting [20]. In 2013, Gao further studied the Cd isotope composition of the sediments in this area, and concluded that the contaminated sediments in this area mainly had three sources of pollution: Metal smelter dust ($\delta^{114}/^{110}\text{Cd} < 0\text{‰}$), smelter slag ($\delta^{114}/^{110}\text{Cd} > 0\text{‰}$) and background and mining activities ($\delta^{114}/^{110}\text{Cd} \approx 0\text{‰}$) [21]. Shiel studied the Cd isotopic composition of a Pb-Zn smelter in Canada at different production stages and found that the Cd isotopic composition of its raw material (Zn concentrate) was $\delta^{114}/^{110}\text{Cd} = -0.13\text{‰} \sim -0.18\text{‰}$. The $\delta^{114}/^{110}\text{Cd}$ value of Zn dust is -0.52‰ , and the slag enriched with heavy Cd isotope is $0.31 \pm 0.07\text{‰}$ and $0.46 \pm 0.08\text{‰}$ after high-temperature culture and firing [22].

3. Existing Problems and Application Prospects

Element isotope tracing is mainly based on the characteristics of isotope fractionation. With the development of testing technology, small changes of isotope ratio in materials can be accurately detected, which provides a firm foundation for the realization of isotope tracing technology. Elements with low isotopic fractionation properties were selected to estimate their sources and relative contributions by isotope mixing model. At present, the most commonly used model is binary hybrid model, but multivariate hybrid model has not been applied in practice. Heavy metal isotope tracing has developed rapidly due to its unique function of traceability and discrimination, but it also has some shortcomings.

1) The tracer of heavy metal isotopes in environmental pollution is mainly applied in atmospheric pollution, which is used to determine the source of gaseous pollutants and study the process of atmospheric particulate matter pollution. In addition to Pb, there are light and stable isotopes of sulfur and carbon. In soil and sediment pollution, stable isotopes such as Pb and carbon have unique advantages as tracers. The Pb isotope ratio can clearly identify its origin. Zn and Cd isotope tracing technology can distinguish the natural and anthropogenic sources of heavy metal pollution in soil and sediment, and calculate the contribution rates of the two with geochemical method, which is beneficial to environmental workers to take different measures to control heavy metal pollution. Therefore, how to better use the characteristics of appropriate elements in the environment to trace the pollution path, pollution rate, pollution mode and contribution rate of specific pollution sources will be the focus of scholars in the study of isotope tracing technology, which is particularly important for the industrial developed areas.

2) In isotope tracing, multiple source analysis methods are used to assist each other, so as to facilitate the interpretation and identification of the sources of heavy metal pollution in sediments, such as the combination of heavy metal element morphology analysis and Pb isotope ratio in the vertical section, isotope tracing, the combination of element geochemical information and multivariate statistics. The establishment of relevant environmental models to explore the spatial and temporal variation of pollution end-member substances in soil and their spatial correlation and dependence with other environmental attributes, and to describe and

predict them, is conducive to more accurate and effective discrimination of the sources of heavy metal pollution in soil.

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