

# Lead and strontium isotopes as tracers to investigate the potential sources of lead in soil and groundwater: A case study of the Hun River alluvial fan

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## ABSTRACT

Lead (Pb) isotopes and strontium (Sr) isotopes are good combined multiple geochemical tracers to differentiate lead pollution in soil and groundwater due to the characteristic “fingerprints” of Pb isotopes and fractionation of Sr isotopes. Soil, surface water, groundwater, and river sediment samples were investigated for Pb and Sr content and the isotopic ratio was used to determine the potential sources of Pb in soil and groundwater of the Hun River alluvial fan, Liaoning, China. Lead from anthropogenic sources was of high solubility and could translocate, and it was relatively stable after deposition in the soil. Therefore, lead speciation and the isotopic ratio of the acid extraction fraction and the residual fraction in the soil and river sediments were also measured to obtain more information regarding the anthropogenic pollution. The results indicate that most Pb in the soil was of geogenic origin, in particular, ore chemical weathering along the Hun River, while the topsoil was significantly affected by leaded gasoline and coal combustion, sewage irrigation, and other human activities. The geogenic origin of Pb in groundwater was from the carbonate rock aquifer and ore upstream. Shallow groundwater was affected by contaminated surface water through the interaction of groundwater and rivers. The influence of vehicle exhausts and coal combustion on groundwater from municipal wells can be ignored.

## 1. Introduction

Heavy metal contamination in soil and groundwater is an environmental issue. Lead (Pb) is a toxic heavy metal that can enter the human body through inhalation and ingestion from a variety of sources such as contaminated air, water, soil, and food. Geogenic and anthropogenic Pb sources have different isotopic ratios, thus Pb isotopes have been used as “fingerprints” in tracing the contamination sources in soil, groundwater, and other environmental compartments. This method has been applied in research of aerosols (Zheng et al., 2004), urban dust and soil (Galušková et al., 2014), rain (Roy and Négrel, 2001), rime and snow (Cimova et al., 2016), seawater (Reuer et al., 2003), grass (Kylander et al., 2007), tree-rings (Tommasini et al., 1999), lakes (Eades et al., 2002; Graney et al., 1995), river sediments (Ettler et al., 2006), marine sediments (Zhang et al., 2016), and atmospheric deposition and dust (Kumar et al., 2016; Négrel et al., 2015).

Lead isotopes have been widely used to trace the contamination

sources in soil and groundwater by identifying the Pb isotopic value of the original background and regional features (Bove et al., 2011; Reimann et al., 2016; Yu et al., 2016), as well as to trace the landfill leachate plume in shallow groundwater (Vilomet et al., 2003). Lead isotopes have also been applied as tracers for the impacts of human activities on the surface environment to identify the geogenic and anthropogenic sources in groundwater (Grezzi et al., 2011; Landmeyer et al., 2003; Toner et al., 2003) and to investigate drinking water systems (Cheng and Foland, 2005; Sidle, 2007), as well as to study the impact of geological hazards on groundwater resources (Poitrasson et al., 1999).

Since there is no measurable fractionation of strontium (Sr) isotopes during mineral precipitation and chemical weathering, Sr isotopes have often been used to study the water-rock interactions (De Caritat et al., 2005; Petelet-Giraud et al., 2017), groundwater pollution monitoring (Ayuso and Foley, 2016; Siegel et al., 2000), and groundwater recharging and cycling (Dogramaci and Herczeg, 2002). Due to the

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Fig. 1. Study area in Liaoning, China.

complexity of the Pb source in the surface environment, Pb and Sr isotopes can be combined for use as multiple geochemical tracers to differentiate Pb pollution in groundwater.

Moreover, chemical speciation plays an influential role in solubility, potential bioavailability, toxicity, and ability to translocate of heavy metals in soil. Lead of anthropogenic origin is of high solubility and can translocate (Peakall and Burger, 2003; Wong et al., 2002) and is relatively stable after deposition in the soil.

## 2. Sampling and methods

### 2.1. The survey area

The study area was located in the middle of Liaoning, an industrialized city in northeast China (Fig. 1). It is confronted with a series of environmental problems due to the development of metallurgy, pharmaceutical, automobile, and chemical fiber industries. Part of the sample area was a field that had been irrigated by wastewater for a long time, leading to heavy metal and organic contamination of the surface environment. In some areas, high concentrations of Pb were detected in shallow groundwater, thus threatening drinking water safety in the locality.

The study area was located northeast of the Liao river plain where the topography decreases gradually from the northeast to the southwest. Quaternary pore groundwater is recharged by precipitation, the Hun River, and subsurface runoff from the eastern mountain area. The Hun River originates from the north Gunma Mountain in Qingyuan country and flows through Fushun and Shenyang cities. Mixed granite and gold ore deposits in Archean metamorphic rocks are distributed in Qingyuan where the main sulfides are pyrite (FeS), pyrrhotite chalcopyrite (CuS), sphalerite (ZnS), and a small amount of galena (PbS).

### 2.2. Sampling

Soil, surface water, groundwater, and river sediment samples were investigated for their Pb and Sr contents and the isotopic ratio was used to determine the potential sources of Pb in the soil and groundwater of the Hun River alluvial fan.

Soil samples were collected in the study area at intervals of 1 m from the surface to a depth of 5 m in Oct 2011 (Fig. 2). Water samples from domestic wells ( $n = 12$ ;  $n$  is the number of sample sites), municipal wells ( $n = 10$ ), Xi River ( $n = 3$ ), and Hun River ( $n = 2$ ) were collected in Nov 2011. Groundwater samples from municipal wells and domestic wells were not treated and were pumped using a centrifugal pump.

Water samples were stored in acid-rinsed high-density polyethylene bottles and then filtered through 0.45- $\mu\text{m}$  Millipore filters. Samples

were capped and acidified to  $\text{pH} = 2$  using ultra-pure  $\text{HNO}_3$ . River sediment samples were collected from the Hun River ( $n = 2$ ) and Xi River ( $n = 2$ ) at a depth of 5 cm and sealed in wide-mouthed amber bottles in July 2012.

All samples were transported back to the laboratory within 24 h. Soil samples were stored at  $25^\circ\text{C}$ , water samples at  $4^\circ\text{C}$ , and sediment samples at  $-20^\circ\text{C}$  in a refrigerator before pretreatment.

### 2.3. Chemical and isotopes analysis

The lead content of soil samples and the ion concentration of water samples were measured in the Jilin University testing center. The Pb isotopes of soil samples and water samples were measured using an ISOPROBE-T thermal ionization mass spectrometer (TIMS) at the Beijing Research Institute of Uranium Geology. Soil samples (0.1–0.2 g) were leached in a low-pressure sealed tank using a mixture of HF,  $\text{HNO}_3$ , and  $\text{HClO}_4$  for 24 h, then evaporated and dissolved in 6 M HCl. After being evaporated, samples were dissolved in 1 mL of 0.5 M HBr and then centrifuged. The supernatant was separated using anion-exchange resin columns (AG1-X8) and loaded onto a single rhenium filament using phosphoric acid silica gel while isotopic data were collected in static mode. The Pb isotopic composition of water samples was determined using the same procedure. The ratios were corrected for mass fractionation relative to the NBS 981 standard.

Lead content and the isotopic composition of the acid extraction and residual fractions in the soil and river sediments were measured by quadrupole inductively coupled plasma mass spectrometry (Q-ICP-MS) at the National Research Center for Certified Reference Materials, Beijing. The samples were leached in 9 mL of 1.2 M HCl, and then vibrated for 16 h. The residual fraction was leached in a low-pressure sealed tank using a mixture of HF and  $\text{HClO}_4$  for 24 h. The supernatant (acid extraction fraction) was separated using the same procedure as that for the total Pb isotopic composition.

The Sr isotopic composition of water samples was tested using multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) at the National Research Center for Certified Reference Materials. Water samples (1–5 mL) were evaporated and dissolved in 1 mL of 8 M  $\text{HNO}_3$ . After being evaporated, samples were dissolved in 3 mL of 8 M  $\text{HNO}_3$  and then separated through strong base anion-exchange resin columns (AG1-X8).

### 2.4. Quality control

The Pb isotope ratios measured by TIMS and Q-ICP-MS were corrected for the mass fractionation relative to the NBS 981 standard (Table 1).

The Sr isotope ratios tested by MC-ICP-MS were corrected for the mass fractionation relative to the NBS 987 standard and the relative standard deviation was less than 0.0011.

## 3. Results

### 3.1. The isotopic composition of known anthropogenic and geogenic sources

The isotopic composition of known anthropogenic and geogenic sources reported in the essay are significantly different. Isotopic ratios, found by TIMS, of gasoline (leaded and unleaded), diesel, gas, and coal for general use are listed in Table 2.

There listed granite, sedimentary rocks and different kinds of ore deposits in the study area, which provides the research foundation in tracing the potential Pb sources of environmental compartment.

The  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio of leaded gasoline and coal combustion ash ranged from 0.851 to 0.892, and that of unleaded diesel ranged from 0.921 to 0.933. The  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio of ores in the study area varied widely from 0.879 to 1.097.

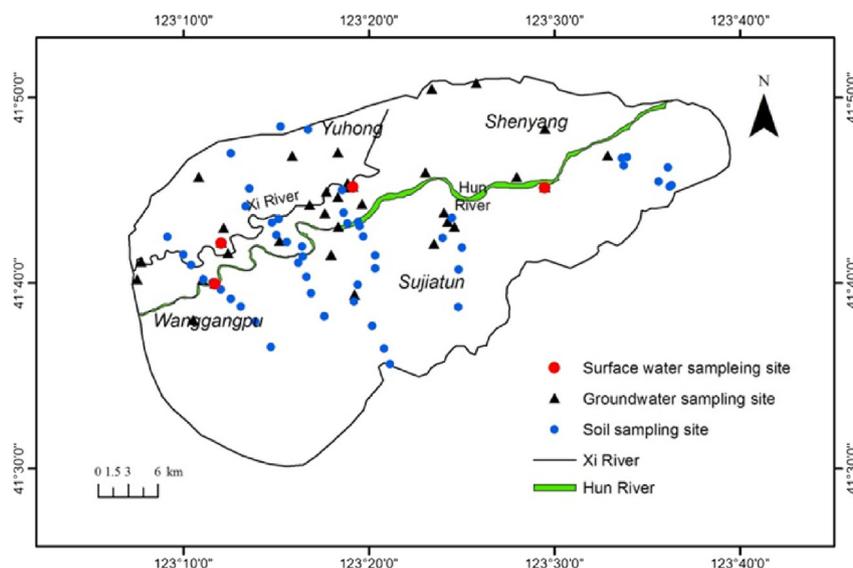


Fig. 2. Location of sampling sites.

### 3.2. Major chemical compositions and content

The Pb content in the topsoil (0.2–1.5 m) ranged from 17.72 to 114.46 mg kg<sup>-1</sup>, with a mean value of 50.01 mg kg<sup>-1</sup>, which is 2.5 times higher than the background value (Table 3). The Pb content in the mid-depth soil (1.5–3 m) ranged from 21.64 to 108.19 mg kg<sup>-1</sup>, with a mean value of 40.60 mg kg<sup>-1</sup>, which is 1.8 times the background value. The Pb content in the deep soil (3–5 m) ranged from 15.16 to 75.7 mg kg<sup>-1</sup>, with a mean value of 30.12 mg kg<sup>-1</sup>.

The proportion of Pb in the acid extraction fraction ranged from 2.34% to 36.78% and decreased with increasing depth while the proportion of Pb in the residual fraction ranged from 63.22% to 97.66% (Table 3).

The pH value of groundwater in the study area was 6.18–7.65, with a lower average pH value of 6.98. The mean Pb concentration of the filtered Hun River and Xi River samples was 0.14 μg L<sup>-1</sup> and 0.37 μg L<sup>-1</sup>, respectively (Table A1 in the Appendix). Groundwater from the municipal wells had low concentrations of Pb ranging from 0.043 to 0.191 μg L<sup>-1</sup>. In contrast, groundwater from domestic wells had higher levels of Pb, ranging from 0.015 μg L<sup>-1</sup> to 19.7 μg L<sup>-1</sup>. Lead concentrations from some domestic wells were several times higher than the groundwater quality standard (0.01 mg L<sup>-1</sup>).

The Sr concentration of groundwater ranged from 0.224 to 0.934 mg L<sup>-1</sup>, with a mean value of 0.520 mg L<sup>-1</sup> (Table A1 in the Appendix) while that of surface water ranged from 0.480 to 0.497 mg L<sup>-1</sup>, with a mean value of 0.488 mg L<sup>-1</sup>. The groundwater has a larger range and a higher mean value of Sr concentration than that of surface water.

### 3.3. Lead isotopic composition in soil and river sediments

The isotopic ratio of Pb has a large range due to the complexity of

the sources in soil and river sediments (Table A2 in the Appendix). The <sup>208</sup>Pb/<sup>204</sup>Pb value ranged from 35.825 to 38.642 of the total Pb, with 35.058–39.518 in the acid extraction fraction and 35.223 to 38.87 in the residual fraction, with a mean value of 37.604, 38.857, and 37.192, respectively. The overall <sup>207</sup>Pb/<sup>204</sup>Pb value ranged from 15.139 to 15.59, with 15.527–15.718 in the acid extraction fraction and 15.082 to 15.666 in the residual fraction, with a mean value of 37.604, 15.601, and 15.365, respectively. The overall <sup>206</sup>Pb/<sup>204</sup>Pb value ranged from 15.84 to 18.586, with 17.759–18.703 in the acid extraction fraction and 15.183 to 18.574 in the residual fraction, with a mean value of 17.524, 18.299, and 16.957, respectively.

### 3.4. Lead and strontium isotopic composition in groundwater

The distribution of the Pb isotopic ratio in groundwater is relatively centralized (Table A3 in the Appendix). The <sup>208</sup>Pb/<sup>204</sup>Pb value ranged from 37.819 to 38.237, the <sup>207</sup>Pb/<sup>204</sup>Pb value ranged from 15.539 to 15.6, the <sup>206</sup>Pb/<sup>204</sup>Pb value ranged from 17.793 to 18.066. The Pb isotopic ratio in the surface water, which is contaminated to some extent, was as follows: the <sup>208</sup>Pb/<sup>204</sup>Pb value ranged from 37.968 to 38.123, the <sup>207</sup>Pb/<sup>204</sup>Pb value ranged from 15.563 to 15.575, and the <sup>206</sup>Pb/<sup>204</sup>Pb value ranged from 17.897 to 18.142; these values are almost within the range of that in groundwater.

The <sup>87</sup>Sr/<sup>86</sup>Sr value of groundwater ranged from 0.710041 to 0.712621, with a mean value of 0.711172 (Table A4 in the Appendix). The mean value of groundwater from municipal and domestic wells was 0.7109 and 0.7113, respectively. The <sup>87</sup>Sr/<sup>86</sup>Sr value of the surface water ranged from 0.710863 to 0.712480, with a mean value of 0.711827.

Table 1

The results and relative standard deviation of NBS-981.

	<sup>206</sup> Pb/ <sup>204</sup> Pb	RSD	<sup>207</sup> Pb/ <sup>204</sup> Pb	RSD	<sup>208</sup> Pb/ <sup>204</sup> Pb	RSD
TIMS	17.0440178	0.0005	15.5949033	0.0005	37.4035045	0.0004
Q-ICPMS	17.0320525	0.0002	15.6274145	0.0003	37.1100183	0.0004
	17.0411698	0.0001	15.6397895	0.0001	37.1399480	0.0001
	17.0427674	0.0005	15.6424622	0.0008	37.1535268	0.0011
	17.0478784	0.0002	15.6498608	0.0003	37.1790368	0.0004

**Table 2**  
Lead isotopic composition of known anthropogenic and geogenic sources.

Sample type	Sample site	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{207}\text{Pb}/^{206}\text{Pb}$	References
Unleaded diesel	Changchun	–	–	–	2.112	0.921	(Zhongping et al., 2008)
Natural gas		–	–	–	2.146	0.931	
Liquefied gas		–	–	–	2.078	0.931	
Unleaded gasoline		–	–	–	2.117	0.933	
Leaded gasoline	Hangzhou	38.247	15.665	17.772	2.123	0.881	(Haoshou et al., 1998)
		37.723	15.540	18.260	2.110	0.851	
		38.523	15.499	17.376	2.152	0.892	
		37.401	15.648	18.324	2.108	0.854	
		38.631	15.517	18.114	2.118	0.857	
		38.360	15.786	18.461	2.104	0.855	
Coal	Changchun	38.139	15.623	18.032	2.115	0.866	(Tiefu et al., 2005)
		37.989	15.532	17.824	2.131	0.871	
		38.101	15.489	17.965	2.121	0.862	
Granodiorite	Liaoning	37.526	15.534	17.630	2.123	0.881	(Shibing and Liandeng, 1991)
Sedimentary rock	Qingan	38.430	15.570	18.810	2.043	0.828	(Gan et al., 2005)
		38.420	15.560	19.560	1.964	0.796	
		38.490	15.580	19.040	2.022	0.818	
		38.440	15.560	18.950	2.028	0.821	
Pb–Zn ore deposit	Liaoning	38.220	15.640	17.790	2.148	0.879	(CunJie et al., 2010)
Ore deposit	North of Hun River	37.520	15.463	17.339	2.164	0.892	(Shibing and Liandeng, 1991)
Gelenite	Hongtuo mountain	33.498	14.687	13.389	2.502	1.097	
		33.330	14.496	13.545	2.461	1.077	
	Dahuanggou	34.800	14.910	14.020	2.482	1.063	
		33.920	14.820	13.900	2.440	1.066	
	Xianjinchang	37.537	15.592	17.604	2.132	0.886	
		37.541	15.494	17.393	2.158	0.891	
		37.923	15.578	17.588	2.156	0.886	
Pyrite	Dahuanggou	35.983	15.558	16.641	2.162	0.935	
Ore deposit	South of Hun River	36.432	15.260	16.034	2.272	0.952	
Gelenite	Xiadapu	36.671	15.373	16.177	2.267	0.950	
		36.107	15.154	15.912	2.269	0.952	
		36.120	15.186	15.916	2.269	0.954	
	Nuanquan	37.510	15.600	16.510	2.272	0.945	

## 4. Discussion

### 4.1. Lead spatial distribution in soil

The average Pb content of topsoil samples was higher in the north bank of Hun River than that in the south bank and is almost along the downstream of Hun River (Fig. 3).

The Pb content of sand and clay at different depths was measured (Fig. 4). The Pb content in soil decreased gradually with the increasing soil depth and became constant at about 1 m. Due to the high distribution coefficient and stronger adsorption to Pb in soil, heavy metal in topsoil infiltrate slowly and it is difficult for Pb to migrate in soil. However, due to aerial farming or mechanical digging, there were some samples from deep depths with a high Pb content. What's more, the proportion of Pb in the acid extraction fraction decreased with increasing depth (Table 3), which indicates that most of the Pb in the acid extraction fraction was exogenous or anthropogenic.

### 4.2. Source apportionment of Pb in soil

#### 4.2.1. Characteristic of total Pb isotopes

In the study area, the Pb isotope ratios of soil scattered along the Chinese Pb ore and coal line (Cheng and Hu, 2010) (Fig. 5 and Fig. 6). The Pb isotopic ratios of topsoil were concentrated in the range of coal and leaded petrol, which is different to that of unleaded gasoline (Fig. 5). It can be concluded that Pb pollution in topsoil resulting from leaded gasoline still exists even though leaded petrol has been

prohibited since 1998, which reflects the historical accumulation effect of Pb released by automobile exhaust emissions in the surface soil. The Pb isotopic ratios of deeper soil were concentrated in the range of local ore and; therefore, the Pb isotope ratio is mainly controlled by the geochemical background in the study area, while the surface soil was affected by leaded fuel oil and coal.

The Pb isotopic ratios of clay were concentrated in the range of leaded gasoline and coal (Fig. 6) because Pb of anthropogenic origin has high solubility. In addition, high organic contents and a small specific surface area of clay lead to a high  $K_d$  (distribution coefficient). For example, the  $K_d$  of Pb in sandy loam is  $1.53 \times 10^3$  while the  $K_d$  of Pb in clay is  $2.4 \times 10^3$  (Chongjie, 1989), and thus clay adsorbs the exogenous Pb more effectively.

#### 4.2.2. Lead isotopes in the acid extraction and residual fractions

The Pb in the acid extraction fraction is of high solubility and is able to translocate, it is more accurate to trace the anthropogenic sources in the environment. The Pb isotopic ratio of the acid extraction fraction has the same distribution trend with that of leaded gasoline, coal, and surface water, which has relatively low  $^{208}\text{Pb}/^{206}\text{Pb}$  and  $^{207}\text{Pb}/^{206}\text{Pb}$  ratios (Fig. 7). The Pb isotopic ratio of the residual fraction of soil and river sediments are scattered along the Chinese Pb ore and coal line (Fig. 8), which indicates that most Pb in the soil is derived from ore chemical weathering along the Hun River with geogenic origin.

Together, the above data indicate that the topsoil has been impacted by anthropogenic sources, such as vehicle exhausts, coal combustion, and sewage irrigation.

**Table 3**  
The Pb content of soil samples in different profile.

ID	Site	Sampling depth(m)	Pb content(mg/kg)				
			Total	Acids extraction fraction	Proportion(%)	Residual fraction	Proportion(%)
N-2-8-1	Tengfei highway	0.2	39.74	11.27	28.36	28.47	71.64
N-2-8-2		1.3	94.87	2.22	2.34	92.65	97.66
N-2-8-3		2.5	24.68	1.72	6.97	22.96	93.03
N-2-8-4		3.6	25.59	1.32	5.16	24.27	94.84
N-2-9-1	Jingshen highway	0.2	55.17	20.29	36.78	34.88	63.22
N-2-9-2		1.3	32.63	4.40	13.48	28.24	86.55
N-2-9-3		2.4	40.08	3.56	8.88	36.52	91.12
N-2-9-4		3.5	28.51	3.89	13.64	24.62	86.36
N-2-9-5		4.8	27.32	7.47	27.34	19.85	72.66
N-2-7-1	Intersections of new Xi River and Shenliao highway	0.2	40.81	14.69	36.00	26.12	64.00
N-2-7-2		1.3	23.6	2.67	11.31	20.93	88.69
N-2-7-3		2.4	28.91	2.13	7.37	26.78	92.63
N-2-7-4		3.7	28.00	2.06	7.36	25.95	92.68
N-2-7-5		4.8	30.26	4.22	13.95	26.04	86.05
S-2-1-1	Hujia Village southern of Hun River	0.2	80.47	17.64	21.92	62.83	78.08
S-2-1-2		1.4	26.49	3.32	12.53	23.17	87.47
S-2-1-3		2.4	29.12	3.86	13.26	25.26	86.74
S-2-1-4		3.6	33.91	4.75	14.01	29.16	85.99
S-2-1-5		4.6	28.69	8.17	28.48	20.52	71.52
N-2-6-1	Caohou highway	0.2	102.4	–	–	–	–
N-1-2-1	Dazhu Village	0.2	45.59	–	–	–	–
N-1-3-1	Hebei Village	0.2	37.66	–	–	–	–
N-2-1-1	Langjia Village	0.2	65.10	–	–	–	–

4.3. Source apportionment of Pb in groundwater

4.3.1. Source of groundwater solute

There was a positive correlation between Sr and Ca concentration in groundwater ( $r = 0.86$ ,  $P < 0.01$ ), indicating that Sr and Ca in groundwater might share the same origin and hydrogeochemical process (Table A1 in the Appendix).

According to the literature, the value of  $^{87}\text{Sr}/^{86}\text{Sr}$  of silicate and carbonate weathering source ranges from 0.716 to 0.720 and from 0.708 to 0.709, respectively (Yunchao et al., 2005). The mean value of  $^{87}\text{Sr}/^{86}\text{Sr}$  of ground and surface water in the study area was greater than the mean of modern seawater (0.70916), and the difference between the surface water and groundwater was not significant (Fig. 9).

The solute in ground and surface water was mostly affected by weathering and the dissolution of carbonate as well as the modern seawater. The mean value of  $^{87}\text{Sr}/^{86}\text{Sr}$  of surface water was 0.7118 while the mean value of  $^{87}\text{Sr}/^{86}\text{Sr}$  in groundwater from domestic wells and municipal wells was 0.7113 and 0.7109, respectively. We conclude that shallow groundwater from domestic wells has a similar value and distribution trend with that of surface water. There exists a hydraulic connection between shallow groundwater and the surface water to some extent.

The mass ratio of Sr to Na was used to distinguish the chemical weathering source in groundwater, i.e., carbonate, sulfate, or silicate. Groundwater which dissolve amount of carbonate rocks is high in mass ratio of Sr/Na, and low value of  $^{87}\text{Sr}/^{86}\text{Sr}$ . The mass ratio of Sr/Na of

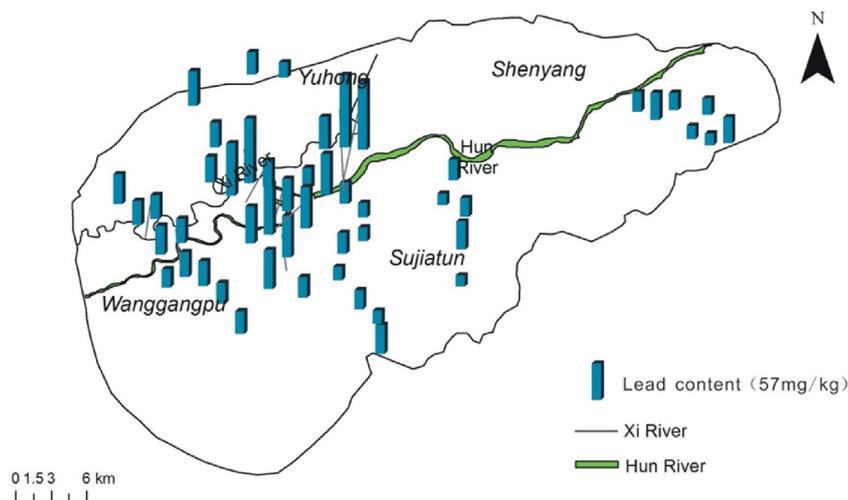


Fig. 3. Distribution of Pb content in soil.

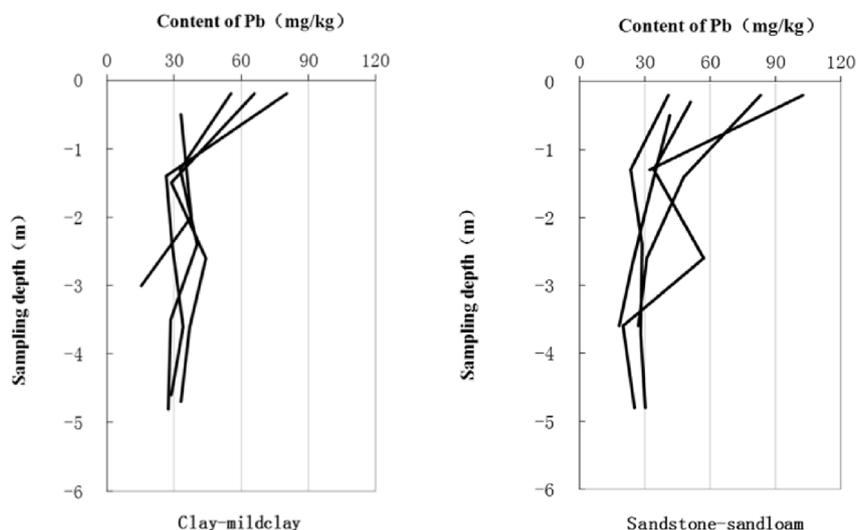


Fig. 4. Lead content in soil profiles at different depths.

most groundwater is greater than 0.01; the value of  $^{87}\text{Sr}/^{86}\text{Sr}$  was under 0.713 in the study area (Fig. 10), which indicates that solutes in the groundwater are derived mainly from chemical weathering of carbonate rocks and that there is a hydraulic connection between the surface water and the shallow groundwater.

4.3.2. The geogenic origin of Pb in groundwater

The Pb isotope ratios of groundwater are concentrated almost along the Chinese ore Pb line, which covers the ore upstream of the Hun River in the study area (Fig. 11). Lead generally exists in the form sulfide and leaches into groundwater through the interaction of water and rocks. In the study area, Pb sulfide bedrock formation reinforces the oxidation condition and it dissolves into the groundwater and migrates as ions. The groundwater was recharged by precipitation infiltration and lateral leakage from the Hun River stem from the eastern mountains.

There was a positive correlation between Pb and Sr concentration in the groundwater ( $r = 0.571, P < 0.01$ ). In accordance with the interactions of water and rock and weathering sources by Sr isotopic composition, most of the Pb in groundwater is derived mainly from chemical weathering of carbonate rocks and ore upstream.

4.3.3. Source apportionment of Pb in groundwater

The type of shallow groundwater in the study area is

$\text{HCO}_3\text{-SO}_4\text{-Ca}\cdot\text{Mg}$ . It was polluted by industrial and agricultural contamination for a long time. Pollutants, such as acids in industrial wastewater, accelerated the process by which Pb and other ions dissolve into the groundwater. It gradually enriched through groundwater runoff in front of the Hun River alluvial fan. According to the distribution of the Pb isotope ratio in groundwater and surface water (Fig. 11), there was an obvious difference to that of leaded gasoline, which indicates that leaded gasoline has no effect on the groundwater.

The quality of the Xi River is getting worse on account of the discharge of industrial sewage. Lead concentrations are higher in the region downstream of the Xi River. The variation trend of the Pb isotope ratio in the groundwater from domestic wells was direction to acid extraction fraction of river sediments, thus indicating that shallow groundwater is effected by contaminated surface water through the interaction between groundwater and rivers (Fig. 11). According to pollution investigations in the field, most domestic wells in rural areas are used for irrigation only and not for drinking. Therefore, there were scarcely any protective measures for domestic wells. The high Pb concentrations, accompanied by  $\text{NO}_3^-$ , turbidity, and other ionic species (Table A1 in the Appendix), indicate that wastewater and precipitation that infiltrate the municipal refuse flow into domestic wells without shelter directly.

There was no correlation between the Pb isotope ratio of soil in the

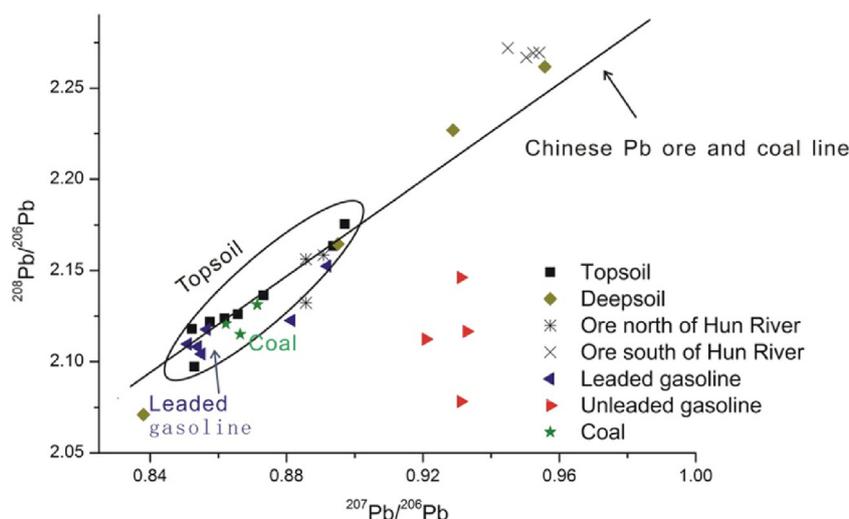


Fig. 5. Lead isotopic ratio in soils of different sampling depths.

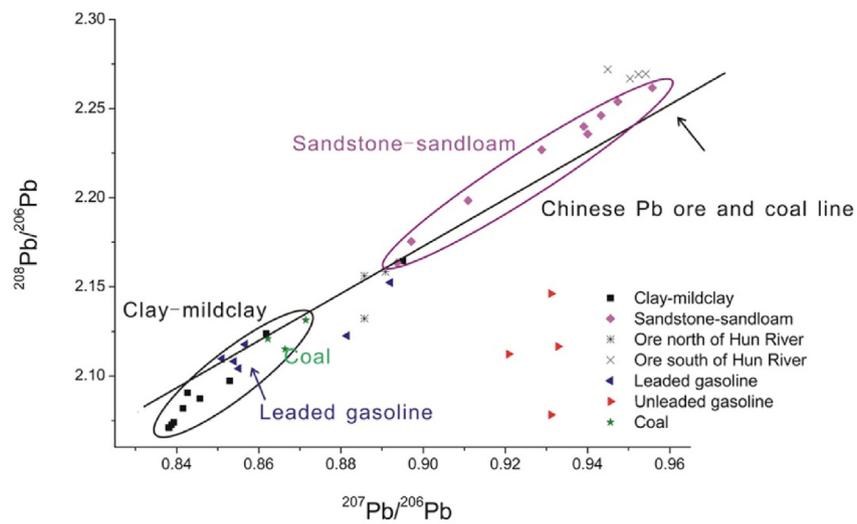


Fig. 6. Lead isotopic ratio in soils of different properties.

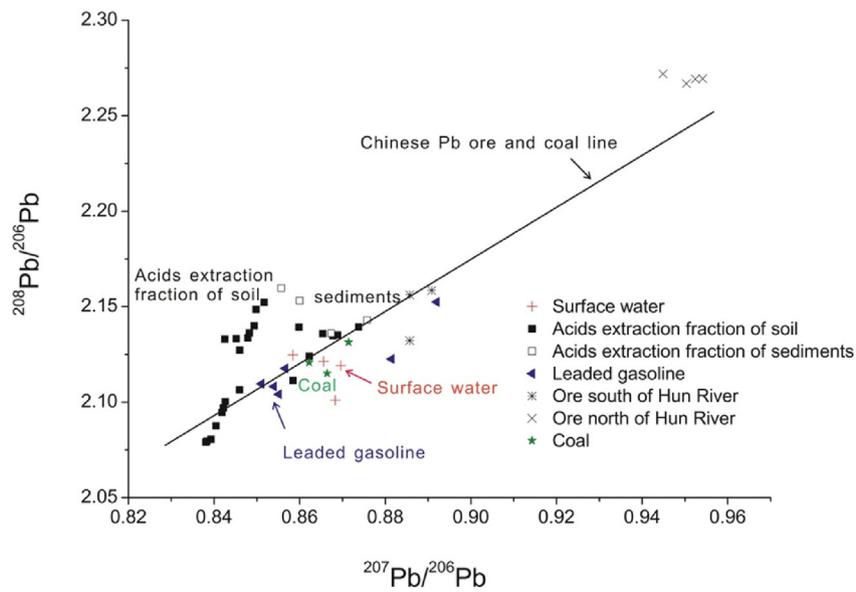


Fig. 7. Lead isotopic ratio of soil and river sediments in the acid extraction fraction.

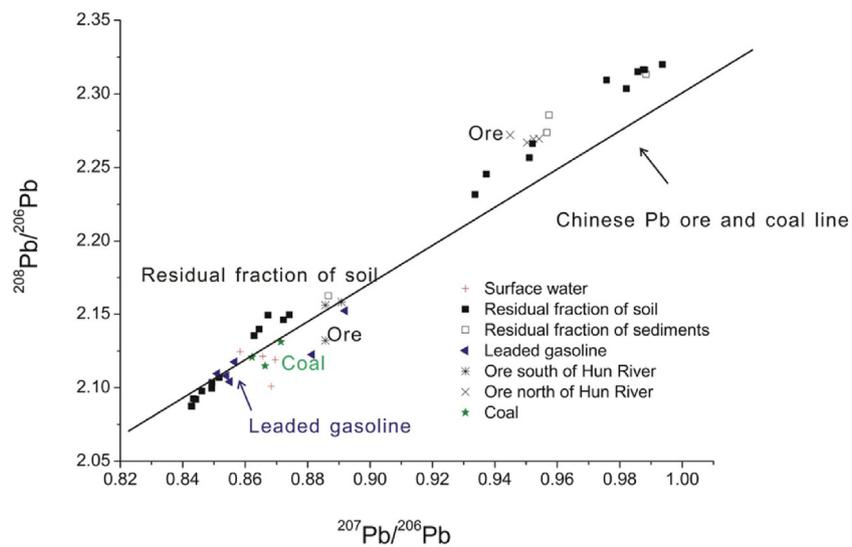


Fig. 8. Lead isotopic ratio of soil and river sediments in the residual fraction.

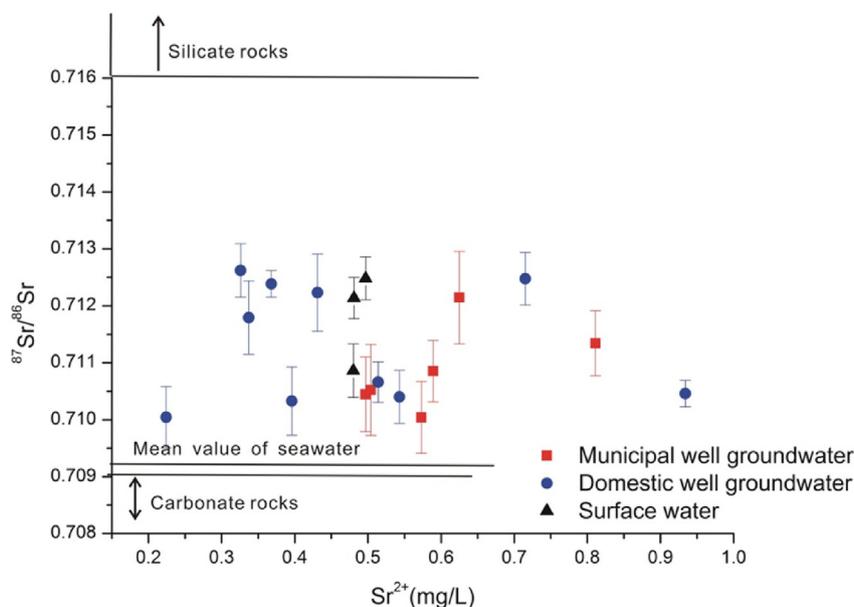


Fig. 9. Relationship of  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\text{Sr}^{2+}$  in the groundwater and surface water.

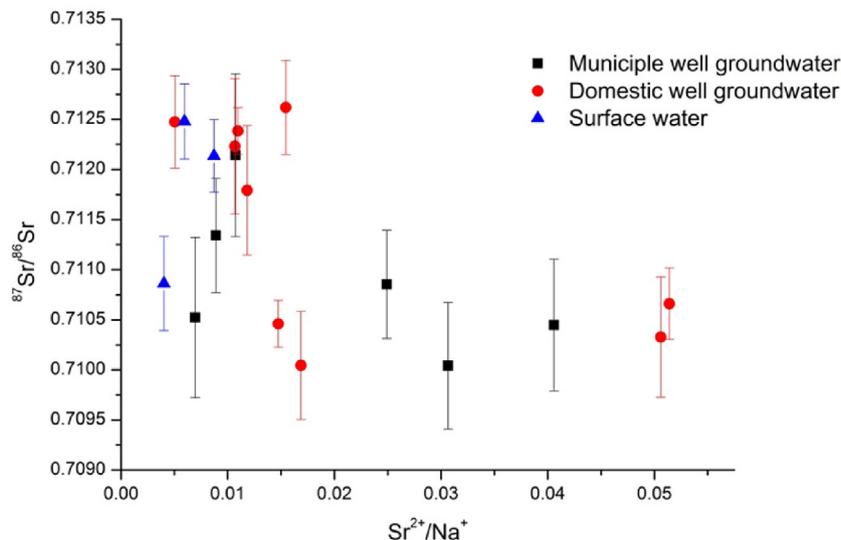


Fig. 10. Correlation of  $^{87}\text{Sr}/^{86}\text{Sr}$  and mass ratio of Sr/Na in the groundwater and surface water.

acid extraction fraction and the groundwater from municipal wells. In addition, the variation trend of the Pb isotope ratio in the domestic well groundwater and that of the surface water was significantly different (Fig. 11). As the sampling depth of municipal well groundwater was 40–50 m, the confined aquifer was overlain by thick sandy loam and, thus, Pb accumulated in the topsoil and surface water and could not infiltrate the confined groundwater directly. The quality of the confined groundwater of municipal wells with protective measures was good and barely polluted.

### 5. Conclusion

(1) Most Pb in soil was derived from ore chemical weathering along the Hun River of geogenic origin, while the topsoil was significantly affected by leaded gasoline and coal combustion, sewage irrigation, and other human activities. The effect decreased gradually with the increasing soil depth. There was no measurable fraction of Pb isotopes from natural environmental processes. Although all vehicles have used unleaded gasoline and fuel additives instead of leaded

petrol since 1998, lead pollution in the topsoil resulting from leaded gasoline still existed, which reflects the historical accumulation effect of Pb released by automobile exhaust emissions in the topsoil.

(2) In accordance with the interactions of water and rock and weathering sources by Sr isotopic composition, high correlation between Pb and Sr concentration in groundwater and the distribution trend along the Chinese ore Pb line which covers the ore in study area, geogenic origin of Pb in groundwater was derived from carbonate rock aquifer and ore upstream. In the front area of the Hun River alluvial fan, horizontal and vertical runoff conditions of groundwater flow became gradually worse. Besides, the discharge of organic acids from industrial wastewater accelerated Pb dissolution into the groundwater from the stratum.

(3) Shallow groundwater was affected by contaminated surface water through the interaction between groundwater and rivers due to the variation trend of the Pb isotope ratio in groundwater from domestic wells was direction to acid extraction fraction of river sediments. Based on pollution investigations in the field, combined with the analysis of Pb,  $\text{NO}_3^-$ , turbidity, and other ionic

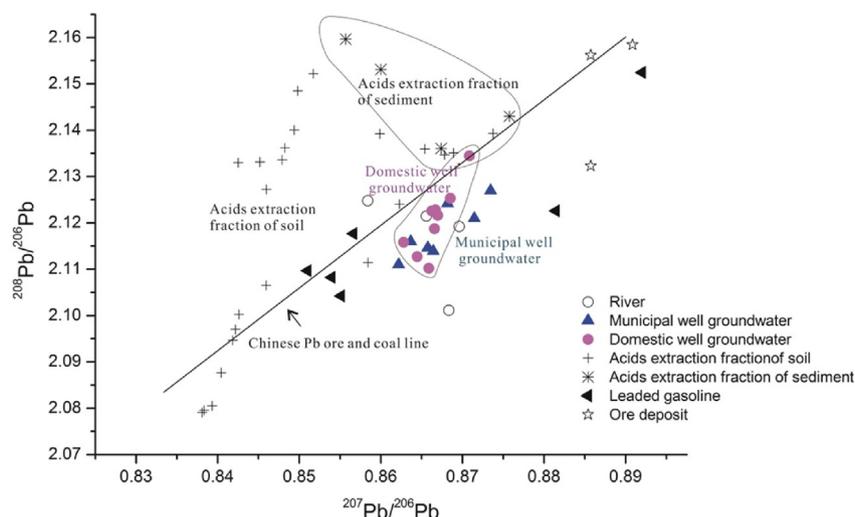


Fig. 11. Lead isotopic ratio in the groundwater and surface water.

concentrations, some domestic wells were polluted by wastewater and municipal refuse leachate directly due to the scarcity of protective measures. The influence of vehicle exhausts and coal combustion to groundwater from municipal wells can be ignored.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.apgeochem.2018.08.022>.

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