Using stable lead isotopes to trace heavy metal contamination sources in sediments of Xiangjiang and Lishui Rivers in China

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ABSTRACT

Lead isotopes and heavy metal concentrations were measured in two sediment cores sampled in estuaries of Xiangjiang and Lishui Rivers in Hunan province, China. The presence of anthropogenic contribution was observed in both sediments, especially in Xiangjiang sediment. In the Xiangjiang sediment, the lower $^{206}Pb/^{207}Pb$ and higher $^{208}Pb/^{206}Pb$ ratio, than natural Pb isotope signature (1.198 and 2.075 for $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$, respectively), indicated a significant input of non-indigenous Pb with low $^{206}Pb/^{207}Pb$ and high $^{208}Pb/^{206}Pb$. The corresponding concentrations of heavy metals (As, Cd, Zn, Mn and Pb) were much higher than natural values, suggesting the contaminations of heavy metals from extensive ore-mining activities in the region.

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1. Introduction

Located in Hunan province of China, Dongting Lake is the largest interior lake of China, and drains into the Yangtze River, the largest river in China. Dongting Lake is fed by four rivers, which are Xiangjinag, Zishui, Yuanjiang and Lishui (Du et al., 2001). These four rivers cover a large area from south to northwest of the Dongting Lake. China has a long history of metal and non-metal mining activities, and the south China region such as Hunan province is rich in mineral resources including non-ferrous metals (Zaw et al., 2007). Many kinds of ores in Hunan province have been exploited, with mine tailing and wastewater produced and dust emitted, which result in the severe pollution in surrounding environment including rivers and lakes. Phosphate fertilizers were generally regarded as a potential source of Cd, As and Hg contamination of farm fields, and applications of manures and pesticides were found to be a significant non-point source of Cd, Cu, Pb, Zn in the soils (Kachenko and Singh, 2006). This has caused the accumulation of heavy metal in edible part of foods and health risk after human digestion (Zhu et al., 2008; Williams et al., 2009; Li et al., 2011). Mining activities, such as the process of mining exploitation and ore concentrating, are believed to be the major source of metals entering into the environment in Dongting Lake (Liu et al., 2005),

although other sources such as wastewater treatment plant, an industrial area, or runoff may also increase the inputs of heavy metal to rivers. It is important to understand and identify the sources of heavy metals in rivers derived from natural or anthropogenic activities so as to control the river contamination and design sustainable management strategies.

Knowing the total concentrations of lead (Pb) may provide useful information about the extent of contamination. However, it is not sufficient for a precise evaluation of contamination sources. Stable Pb isotopes provide a powerful tool that can be used to separate anthropogenic Pb from natural Pb derived from mineral weathering. Pb present in the environment has four stable isotopes: ^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb. While ^{204}Pb is non-radiogenic with a constant abundance on earth in time (Komarek et al., 2008), isotopes ^{206}Pb, ^{207}Pb, and ^{208}Pb are radiogenic and produced by the radioactive decay of ^{238}U, ^{235}U, and ^{232}Th, respectively. Because the isotopic composition of Pb is not significantly affected by physico-chemical fractionation processes associated with smelting, refining and manufacturing (Ettler et al., 2004), each source of Pb can have distinct or sometimes overlapping isotopic ratio ranges from mixing of local/natural Pb with anthropogenic Pb sources. Investigations of Pb isotope compositions have been well-established in geochemistry and are increasingly used in environmental science (Monna et al., 2000; Komarek et al., 2008). The isotopic composition of Pb has been used as an indicator of anthropogenic contribution in many ecosystems, such as sediments, to investigate the impact of recent Pb smelting and/or

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mining activities on the surrounding environment (Renberg et al., 2002; Monna et al., 1999).

It is probable that in Hunan province, the metallurgical activity is the principal source of soil and river pollution due to many ores exploitation. The studies of Pb and other heavy metal concentrations in river sediments contaminated by mining activities represent the first step in evaluating the extent of pollution (Zhang et al., 1989). To date, no Pb isotopic data are available for river sediments of Hunan province. Tracing contamination sources of heavy metal in river sediments by Pb isotope could be useful for designing sound management strategies to minimize contamination. Therefore, the present study aims to determine the Pb isotopic composition, as well as the contents of heavy metals, of river sediment profiles sampled in the Xiangjiang River, the biggest river and one of the main drinking and irrigation water sources in Hunan Province, and Lishui River, which is believed to be the lightest polluted or unpolluted of the four rivers flowing into the Dongting Lake.

2. Methodology

2.1. Sampling of river sediments

Four sediment cores from each river were collected onboard at estuaries of Xiangjiang (28°50'10″N, 112°52′56″E) and Lishui (29°7'31.6″N, 112°12′2″E) Rivers to Dongting Lake (downstream), Hunan province, China (Fig. 1). The cores were taken using a gravity corer consisting of an acrylic pipe with 8-cm inner diameter and 100 cm length, a sediment catcher and a clear vent. With the slow entry of this corer into the sediment, sediment cores with undisturbed sedimentary column were obtained. Immediately after collection, the sediment cores were cut at 1 cm interval and sealed in labeled plastic bags. After every core was taken, the pipe was replaced for collecting a new sample (Lu and Matsumoto, 2005).

2.2. Sample preparation and analysis of heavy metals

The sediments were air-dried to the constant weight, homogenized. The samples were powdered in the agate mortar, passed through 80-mesh sieve, and then digested with concentrated Aristar Ultra nitric acid (VWR International, West Chester, PA, USA) and hydrogen peroxide (30%) (EM Sciences, Gibbstown, NJ, USA) on a hot plate as described (U.S. EPA, 1996. 3050b; Lorentzen and "Skip" Kingston, 1996). For quality controls, two samples of standard reference materials (SRM) NIST 2710 and 2711 (Montana soils), as well as three blanks without solid samples, were prepared at the same time. After digestion, samples were cooled and then diluted to 50 ml with Millipore ultrapure water (Element A10 and Elix 10, Millipore, Billerica, MA, USA). The samples were then analyzed for total heavy metals including As, Cd, Zn, Mn, Pb, Cu, and Cr using an inductively coupled plasma mass spectrometry (ICP-MS, PerkinElmer SCIEX model Elan® DRC II, Waltham, MA, USA). Indium (In) isotope In-115 was used as the internal standard.

2.3. Measurement of Pb isotopes by ICP-MS

A quadrupole-based ICP-MS system (PerkinElmer SCIEX model Elan® DRC II) was used for the isotope ratio measurements according to the reported methods (Margui et al., 2006, 2007). Briefly, the solution digested for total heavy metals were diluted to about 20 μg/kg by high-purity 1% HNO₃ according to the total Pb concentration of samples. For quality controls, two blanks, as well as two United States Geological Survey (USGS) reference materials BCR-2 (Basalt, Columbia River) and AGV-2 (Andesite, Guano Valley), were prepared along with the samples. The standard reference material NIST SRM 981, available in the form of wire, was employed to evaluate the mass bias. Thallium (Tl) isotopes (^{203}Tl and ^{205}Tl) were measured as internal standards. Furthermore, the isobaric interference from ^{204}Hg on ^{204}Pb measurements was monitored. The accuracy of the Pb isotope ratio measurements was evaluated by analyzing USGS SRM BCR-2 and AGV-2. Good agreements were obtained between the lead isotope ratios measured and the certified values for BCR-2 (deviations within 0.2–0.5%) and AGV-2 (deviations within 0.2–0.3%).

3. Results and discussion

3.1. Total Pb and heavy metals in sediment cores

The recoveries in SRM 2710 were As 89%, Cd 81%, Zn 77%, Mn 92%, Pb 83%, Cu 91%, Cr 100% and in SRM 2711 were As 91%, Cd 89%, Zn 96%, Mn 94%, Pb 110%, Cu 96%, Cr 106%. Total metal concentrations in sediment cores from estuaries of Xiangjiang River to Dongting Lake were as follows: As 95.7 mg/kg on average (varied from 48.7 to 153 mg/kg); Cd 12.3 mg/kg (6.3–16.8 mg/kg); Zn 270 mg/kg (123–381 mg/kg), Mn 1806 mg/kg (933–3272 mg/kg) and Pb 133 mg/kg (44.6–257 mg/kg). In contrast, those values for Lishui River are only As 10.8 mg/kg (6.6–16.2 mg/kg), Cd 0.5 mg/kg (0.2–0.7 mg/kg), Zn 85.8 mg/kg (58.7–148 mg/kg), Mn 698 mg/kg
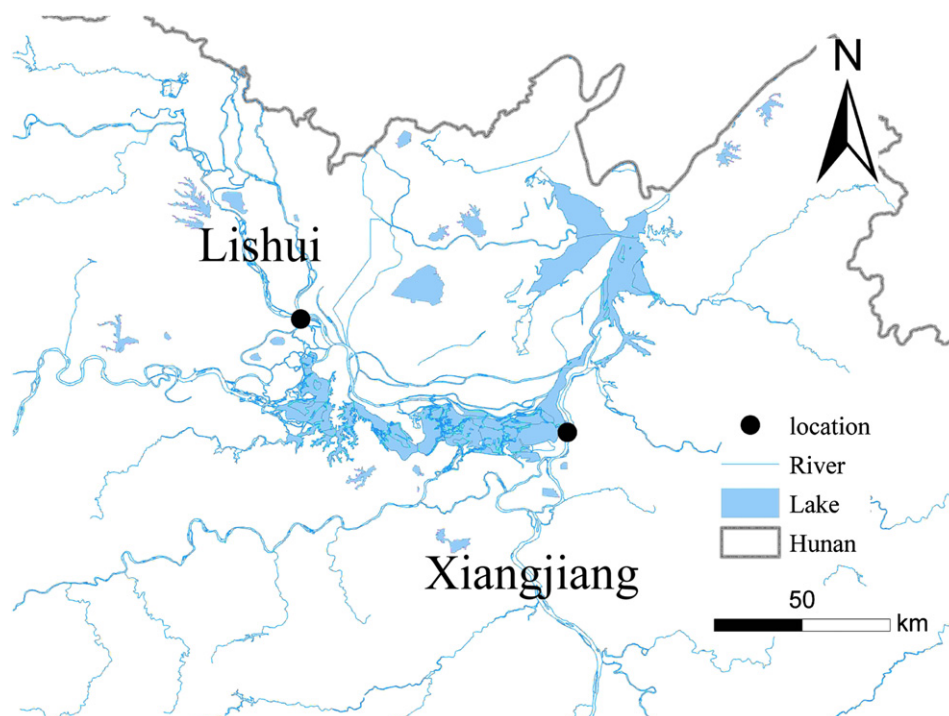

Fig. 1. Location of sampling cores.

Table 1
Descriptive statistics of some elements in sediments of Xiangjing and Lishui.

	Xiangjiang				Lishui			
	Max (mg/kg)	Min (mg/kg)	Median (mg/kg)	Mean (mg/kg)	Max (mg/kg)	Min (mg/kg)	Median (mg/kg)	Mean (mg/kg)
Co	16.7	7.0	13.0	12.7	23.1	9.4	15.0	15.1
Ni	36.0	14.0	24.9	23.8	49.9	25.7	33.5	34.0
Fe	44.8	17.9	32.5	31.9	46.8	12.1	31.9	31.1
Se	2.81	0.32	2.03	1.85	2.87	0.92	1.94	1.94

(376–1038 mg/kg) and Pb 26.5 mg/kg (14.0–34.0 mg/kg). It is obvious that the sediment of Xiangjiang River was seriously contaminated with As, Cd, Zn, Mn, and Pb, in comparison with Lishui River, although both rivers flow into the Dongting Lake. The concentration of Cu and Cr showed similar concentrations in both river sediments. Descriptive statistics of other elements (Table 1) exhibited similar range in both sediments, together with Cu and Cr, indicating their non-contamination.

Previous investigations showed that the surface water and sediment from Xiangjiang River were heavily polluted by heavy metals (Zhang et al., 1989), and the agricultural soils surrounding the Xiangjiang River were contaminated by heavy metals as well (Guo et al., 2008; Wang et al., 2008). Hunan province is regarded as the heartland of Chinese non-ferrous mining. The production of As, Cr, Cd, and Pb were ranked first in China for many years and most ores for mining, and smelting in Hunan is centered in the Xiangjiang valley (Chai et al., 2010). The significant pollution was mainly due to the vicinity of industrial centers, Shuikoushan, Zhuzhou City and Xiangtan (Zhang et al., 1989, 2009). Contamination in Xiangjiang River is much more serious because of its proximity to larger

areas of anthropogenic production. The high concentrations of As, Cd, and Pb found at Xiangjiang sediments indicated that these metals were possibly discharged into the river.

3.2. $^{206}Pb/^{207}Pb$ ratio in sediments

Source identification requires a distinction between natural and anthropogenic Pb. $^{206}Pb/^{207}Pb$ ratio is a useful tool for identifying Pb pollution. It is reported that an average $^{206}Pb/^{207}Pb$ ratio of approximately 1.2 by analyzing the Pb composition of the upper continental crust and marine sediments from various regions of the globe (Renberg et al., 2002), although there is some regional variation, such as Swedish lake sediments (Renberg et al., 2002) and sediments from pre-Cambrian provinces (Zhu, 1995). Lead ores largely deviate from the global mean, having $^{206}Pb/^{207}Pb$ ratio below 1.2, since Pb was separated from uranium at the time of formation. The ores ceased to accumulate ^{206}Pb after their formation, while the decay process of ^{238}U to ^{206}Pb continued to occur in the surrounding bedrock, causing the decrease of $^{206}Pb/^{207}Pb$ ratio. Thus, as a general rule, old lead ores are generally characterized by low $^{206}Pb/^{207}Pb$ ratios (Bacon, 2002). The ratio calculated according to the published data of Chinese ores showed that most of the $^{206}Pb/^{207}Pb$ ratios are below the global ratio (~1.2) (Zhu, 1995; Chen et al., 1982).

At the deepest (50–100 cm) of every sediments core we have studied in this work, Pb concentration was the lowest in corresponding core and the $^{206}Pb/^{207}Pb$ ratio remains relatively constant at 1.198 ± 0.002, which was taken as the isotopic composition of geogenic Pb at the site of Xiangjiang River. The $^{206}Pb/^{207}Pb$ ratio of upper sediment (0–50 cm) in Xiangjiang River remains relatively
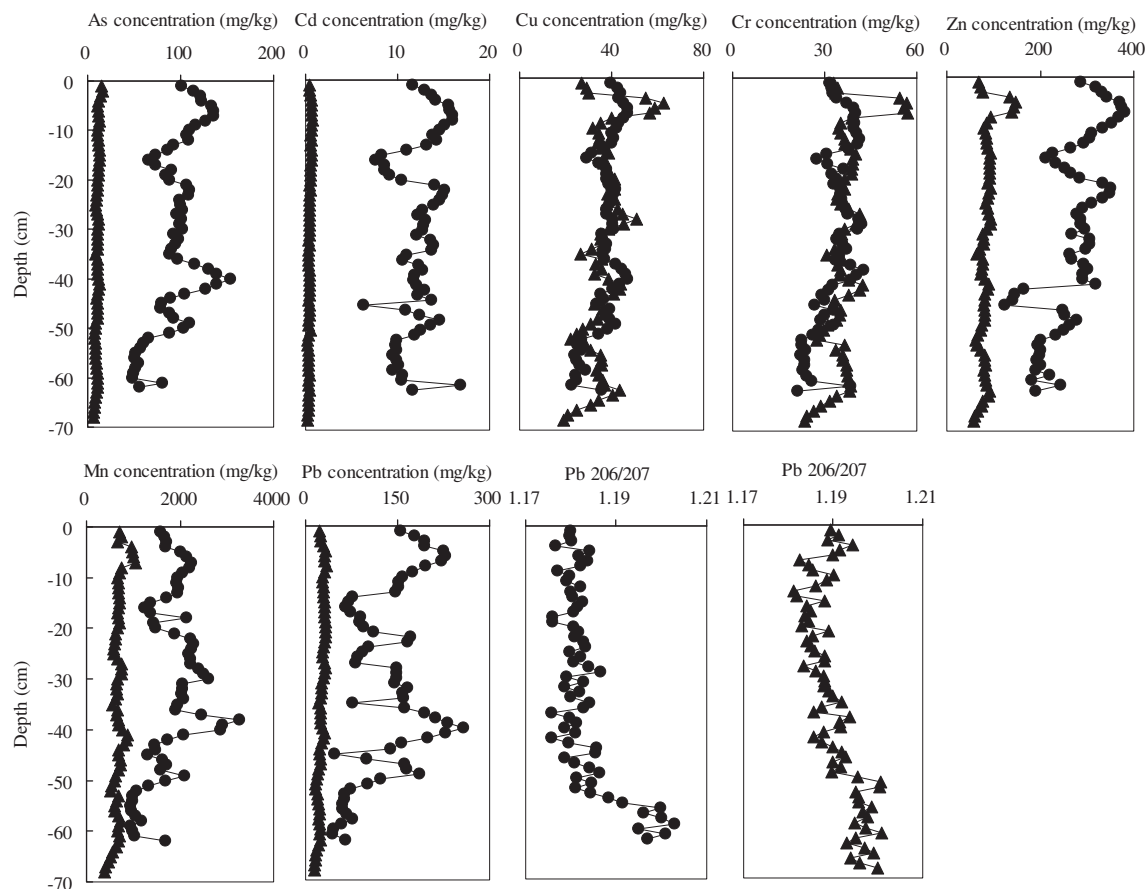
Fig. 2. Profiles of heavy metals concentration (mg/kg) and $^{206}Pb/^{207}Pb$ ratio in the sediment cores of Xiangjiang (●) River and Lishui (▲) River.

constant at an averaged value of 1.181, much lower than natural isotopic composition of the deeper parts of river sediment (Fig. 2). Lead isotopic ratios are similar in sediment profiles (0−50 cm) as a consequence of long-term temporal trend in depositional sources. This suggested that the sediment were contaminated by anthropogenic Pb, probably from the ore-mining activities; this is consistent with the similar trend of concentration distribution of other heavy metals (As, Cd, Zn, Mn). The ratio in Lishui River only has a little decrease, indicating lighter contamination than Xiangjiang River, which is in agreement with the concentration of heavy metals in sediments of both rivers (Fig. 2).

3.3. Pb isotopic composition

Leachates of Xiangjiang and Lishui River sediments are plotted on diagrams of $^{208}Pb/^{206}Pb$ vs $^{206}Pb/^{207}Pb$. As shown in Fig. 3, these two ratios of ores from Hunan province were calculated according to the reported data (Zhu, 1995; Chen et al., 1982). At the 50−100 cm interval of all sediment cores, the $^{208}Pb/^{206}Pb$ ratio was as the natural isotopic composition at 2.075 ± 0.005 at this site. The Pb isotopic ratios among two rivers were noticeably different from each other. Obviously most $^{208}Pb/^{206}Pb$ ratios of the Xiangjiang sediments were generally higher than those of Lishui sediments, while most $^{206}Pb/^{207}Pb$ ratios of Xiangjiang sediment were generally lower than those of Lishui sediments. The linear relationship of the two isotope ratios was shown, for Lishui River sediment ($R^2 = 0.76$) and Xiangjiang River ($R^2 = 0.81$), which suggested a mixing between two or more components. The results suggested that Xiangjiang River received a considerably larger input of Pb from a distinctively different source than those feeding Lishui River. Overall, the Pb isotopic composition revealed that the contaminated sediments in Xiangjiang River received a significant input of non-indigenous Pb with low $^{206}Pb/^{207}Pb$ and high $^{208}Pb/^{206}Pb$ ratios.

The linear relationship of the $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios further suggested that Pb in the Xiangjiang and Lishui sediments might be originated from two geological sources. It was plausible to conclude that the non-indigenous Pb was characterized by low $^{206}Pb/^{207}Pb$ and high $^{208}Pb/^{206}Pb$ ratios. In Hunan province, different ores exhibited various isotope signatures (Fig. 3). Although the attribution of different ores to Pb contamination in Xiangjiang sediment could not be assessed exactly, ores seems to be
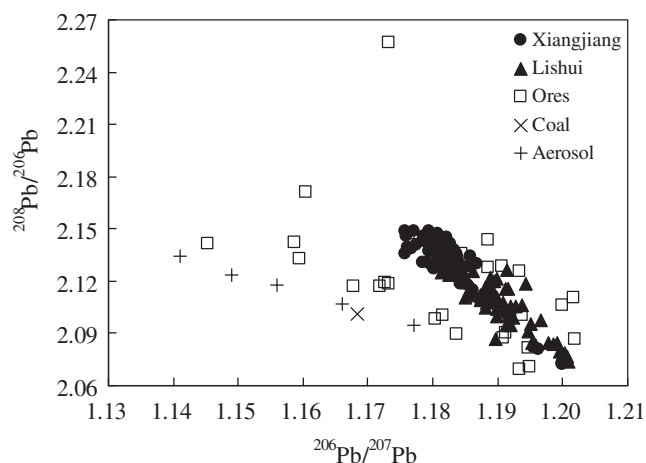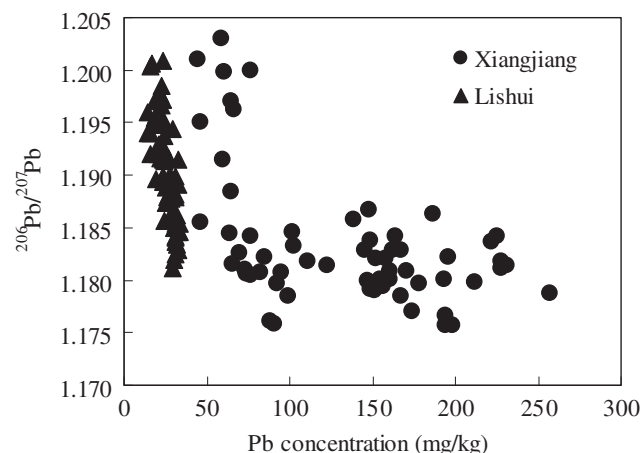
Fig. 4. Scatter plot of $^{206}Pb/^{207}Pb$ ratios versus Pb concentrations of Xiangjiang and Lishui river sediments.

the major contamination sources of heavy metals in Xiangjiang sediments. The reported aerosols and coal of China exhibited lower $^{206}Pb/^{207}Pb$ ratios accompanied by lower $^{208}Pb/^{206}Pb$ ratios (Bollhofer and Rosman, 2001; Mukai et al., 2001; Diaz-Somoano et al., 2009). Lead in aerosols was mainly from industrial emissions (ore smelting), coal combustion, and vehicle exhausts (leaded gasoline). The lower $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios in aerosols (Fig. 3) indicated that automotive lead and coal lead are not the major contamination sources in the sediment after the phase-out of leaded gasoline in China. To our knowledge, this is the first report to trace the heavy metal contamination of rivers in Hunan province using Pb isotopic information.

The relationship between $^{206}Pb/^{207}Pb$ ratios and Pb concentrations demonstrated that, in general, a trend of increasing Pb concentration was accompanied by a shift toward lower isotopic ratios due to higher contents of anthropogenic (excess) Pb (Fig. 4). Lishui samples showed some small-scale variability in Pb concentration reflecting the light contamination. In the upper 50 cm of Xiangjiang sediment, the $^{206}Pb/^{207}Pb$ ratio remained relatively constant with an average value of 1.181 (Figs. 2 and 4), but the Pb concentration increased from 60 to 250 mg/kg (Fig. 4). These data further suggested that the non-indigenous Pb source with high Pb concentration contains a lower $^{206}Pb/^{207}Pb$ ratio than the natural source.

4. Conclusion

Our results showed the serious contamination of As, Cd, Zn, Mn and Pb in the sediments of Xiangjiang River. The anthropogenic pollution of heavy metals was probably from the ore-mining activities, as indicated from the Pb isotope compositions. Heavy metal contamination of the sediments in Xiangjiang River could have significant impacts on the health of the residents and environmental quality of the local and downstream terrestrial and aquatic environment, management strategies should be considered to minimize contamination of rivers.

Fig. 3. The relationship of $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios of the sediments from Xiangjiang and Lishui River sediments with ores from references (Zhu, 1995; Chen et al., 1982), aerosols (Bollhofer and Rosman, 2001; Mukai et al., 2001) and coal (Diaz-Somoano et al., 2009).

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