Bull Environ Contam Toxicol (2012) 89:1225–1230
DOI 10.1007/s00128-012-0828-z

Distribution and Bioavailability of Metals in Subsidence Land in a Coal Mine China

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Received: 20 June 2012 / Accepted: 12 September 2012 / Published online: 22 September 2012

Abstract Land subsidence in coal mine would change the type of soil so that it influences the distribution and bioavailability of metals. The results show that the total metal concentration was in the range from 0.41 ± 0.26 mg/kg (Cd) to 94.16 ± 12.06 mg/kg (Zn) and Cd was the serious pollution metal. In spatial, the concentration of most metals (except Sb) was highest in perennial waterlogged zone while was lowest in no waterlogged zone, which implied that the perennial waterlogged zone was a sink of metals in coal mine area. However, the bio-available fraction of metals was lowest in perennial waterlogged zone.

Keywords Metals · Bioavailability · Distribution · Subsidence land · Coal mine

With the social-economic development, coal mining has greatly contributed to the development of the economy and society in China. However, 96 % of coal production comes from underground coal mining (Yao et al. 2010). It can result in a lot of ecological and environmental problems, which have severely affected human life, ecological environment and the development of regional economy in mining area (Bian et al. 2007; Yang and Liu 2012). Among those problems, subsidence induced by coal mining is the most serious problem. The area of the subsidence is up to 130 km^2 every year and the subsidence land area has added up to 700,000 km^2 by the end of 2006 (Meng et al. 2009). In the eastern plain of China, there is some shallow groundwater above the coal seams (Meng et al. 2009). When the coal seams were exploited and the surface of coal mining subsidence was lower than the water level of shallow groundwater, the groundwater is gushing up and inundating the surface land, which could form a perennial waterlogged zone in the center of coal mining subsidence land. However, in the edge of the coal mining subsidence land, as the surface land is higher than the groundwater, it is not inundated by groundwater. But when the rainy season sets in, the surface land would also be inundated by the flowing of rainwater and this could form a seasonal waterlogged zone according to the rainy and dry seasons. When the surface lands transform into the perennial or seasonal waterlogged zone, the terrestrial ecosystem transforms into aquatic ecosystem and wetlands ecosystem; and this transformation will influence the environmental factors of ecosystem, such as the land types, physico-chemical properties of soil, community composition and so on (Gong et al. 2009).

Meanwhile, metal pollution was another serious problem in the process of coal mining. Through coal mining, large quantities of coal gangue and other solid wastes were excavated from the underground to the surface of the earth. The metals in those wasters have polluted the surrounding lands (Yao et al. 2010).The long-term accumulation of metals in the soil environment is a concern because they potentially have important consequences for the quality of the human food chain, toxicity to plants and soil microbial processes and once applied they have very long residence times in soil (Stephen 2009). In cola mining subsidence, as the ecosystem had changed, the behavior of metals would be affected by this change. For instance, metal sulfides, especially pyrite, can be oxidized easily during the natural weathering of coal mine spoils. But in the coal mining subsidence land, which is immersed in the water, the

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oxidation process would be slow as there is no enough oxygen. Previous studies also found that the microbiological agents could control the oxidation process of metal sulfides; however, the microbial activity is higher in seasonal waterlogged zone than dry land and it could increase the oxidation process of metal sulfides. In addition, the change of environment also influences the soil pH value, which may influence the release of metals from the solid wastes. In this work, six metals were selected as the object of study. Amongst them, there were 5 frequently studied metals Cd, Cr, Cu, Pb, and Zn and a less studied metal Sb in previous work, which is also toxic to aquatic organisms (Goodyear and McNeill 1999). We explore their distribution and potential bio-availability in different zones of coal mining subsidence land. The relationship between metals of different forms and environmental properties was also discussed. This work will provide a data base for studying the influence of coal mining subsidence land on the physico-chemical properties of soil.

Materials and Methods

Investigation and sampling were conducted in a coal mining subsidence land in April, 2012. The subsidence land locates in the floodplain of Huaihe River, which is in the north of Anhui province of China. In this area, the groundwater lever varies between 2.45 and 4.75 m depth and the mean annual precipitation is 910.6 mm. 13 sampling sites were located in representative parts of this subsidence land (Fig. 1). Of the sampling sites, three samplings were located in perennial waterlogged zone (PWZ). Four samplings were located in seasonal waterlogged zone (SWZ) and six were located in no waterlogged zone (NWZ). At each sampling site, we collected soil or sediment samples and each sample was collected two replicates near the site. Soil samples were taken with a depth of 5–10 cm, which had removed the surfer soil and sediment samples of 0–10 cm were taken with the corer sampler. Samples were sealed in polythene bags in situ and then taken back to the lab at 0～4°C for further analysis.

In the laboratory, the samples were air-dried for 3 days and then ground with silica dish. Each ground sample was sieved through 0.5 mm nylon sieve and then split into two replicates. All samples (including replicates) were then digested using the National Standard Method (GB/T17140) with HCl-HNO_3-HF-$HClO_4$ acid. The digested solution from each sample was analyzed for the total content of metals. The Bio-available fraction of metals was sequentially extracted using the Tessier method (Tessier et al. 1979). This method divides metals into five fractions using different extracted reagents. In this work, we focused on the former two forms, i.e., exchangeable fraction and acid-extracted fractions; because these two forms are easily released and become bio-available in nature state (Peng et al. 2009). All reagents used in the analysis were analytically pure.

The concentration of metals was analyzed using flame atomic absorbance spectrophotometry method (Hitachi Z-2000, Japan) for Cr, Cu and Zn with the detection limit of <0.007 ppm and using ICP-MS (Agilent 7500CX, USA) for Cd, Sb and Pb with the detection limit of <0.05 ppb. Organic matter was measured using the National standard Method (GB 8834-1988). The pH value was obtained through measuring the extracted solution from the solid samples using pH meter (Model PHS-25). The extracted solution was prepared by adding 50 mL Milli-Q water into 10 g sample and then the mixture was shaken at 250 r/min for 24 h. After shaking, the mixture was centrifuged for 10 min to obtain overlaying water. Then, the water was filtered through a 0.45 μm Millipore membrane for the analysis of pH.

In sample treatment and measurement, the national certified material “Lacustrine Sediment Standard Sample” (GB-W07310, with a known concentration of metal elements) and blank sample processed was synchronously processed and analyzed for quality control. The recovery of the reference material for all metals was 85 %–110 % and

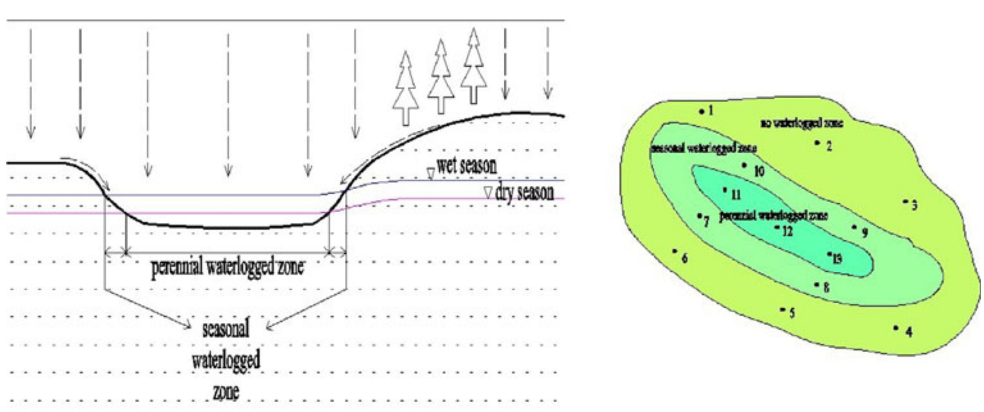

Fig. 1 The location of sampling sites

the relative standard deviation (RSD) of replicates for all metals was <12 %.

Each replicate was tested twice for different parameters and four significant raw data were obtained for all samples. In this work, arithmetic mean was used in this work. Difference between means were tested to be significant through Independent-sample T test, and a confidence level of 0.05 was used. Data calculation and diagram making were performed with SPSS 13.0 and Origin 8.1.

Results and Discussion

The statistical results of all samples in the coal mine area (1–13) are listed in Table 1. As is shown in the table, the mean values of Zn had the highest content (94.16 ± 12.06 mg/kg) and Cd had the lowest content (0.41 ± 0.26 mg/kg). The average metal content in the cola mine soil/sediment ranked: Cd < Sb < Cr < Cu < Pb < Zn. The total concentration of metals in the soil is correlated to their background value of local soils. The background value of Anhui province soils is also listed in Table 1 (Environmental Monitoring of China 1990). From the results, it can be found that the background value has a similar range with the mean values. However, the mean values were higher than the background values. Especially for Cd, it was 4.22 times higher than the background value. We believe that the elevated content of metals in coal mining land is attributed to the human activities of coaling in this area. This inference can be estimated by comparing the metal concentration in our work with the previous study (Table 1), which reported the metal concentration in this area in 2008 and we found the concentration increased for all metals from 2008 to now. Table 1 also lists the concentration of metals in coal in Anhui province (Yang et al. 2004). We can find that the metal concentration in coal was much higher than the background value. When the coal was exploited from underground, the metals in coal can pollute the soil through dust of coal and leachate from coal (Xavier et al. 2006; Mishra et al. 2008).

Table 1 also exhibits the spatial distribution of all measured metals in the coal mine area. The concentration of most metals (except Sb) was the highest in PWZ and was the lowest in NWZ. It implied that the PWZ was a sink of metals in coal mine area. This was related to the soil erosion and losses in coal mine area (Durán Zuazo et al. 2011; Cantón et al. 2011). When the rainy season is coming, the surfer land is eroded by rain and the particulate matter in soil is flowed into PWZ by surface runoff. In this process, the metals in the soil particle were transported into PWZ, which made the metals concentration in PWZ higher than other areas. In addition, the concentration of metals in SWZ is higher than that in NWZ, which may be because the soil erosion effect of SWZ is significant than that of NWZ.

In this work, we used the "Environmental quality standard for soils" (GB 15618-1995) to evaluate the quality of subsidence land soil. According to the classification of the soil environmental quality in this standard and the application function of soil, we chose Level II as the evaluate quality and the threshold value was listed in Table 1. Comparing this threshold value with our measured values, we found that the overall quality for most metals conformed to Level II of quality standard except Cd, which was beyond the level. This also proved that Cd might be a potential biological toxicity element in this coal mining,

Total concentration of metals in soil or sediments can only reflect pollution degree of environment in general, but not a good indicator to reflect the toxic effect of metals (Gorski et al. 2008), which can directly affect aquatic

Table 1 Comparison of average metal concentrations in subsidence land with local soil background and environmental quality standard for soils (mg/kg)

	Cd	Cr	Cu	Pb	Sb	Zn
NWZ	0.44 ± 0.18	28.51 ± 4.63	40.62 ± 6.18	44.71 ± 7.45	1.91 ± 0.22	94.71 ± 8.74
SWZ	0.31 ± 0.16	20.62 ± 3.18	31.71 ± 5.45	40.52 ± 3.20	1.62 ± 0.31	78.74 ± 8.02
PWZ	0.47 ± 0.22	33.74 ± 5.23	44.61 ± 7.35	51.43 ± 6.36	1.84 ± 0.21	107.32 ± 11.36
Mean values	0.41 ± 0.26	28.16 ± 5.45	39.21 ± 7.71	45.63 ± 7.65	1.80 ± 0.33	94.16 ± 12.06
Background value[a]	0.097 ± 0.061	66.5 ± 20.7	20.4 ± 7.01	26.6 ± 5.37	1.40 ± 0.442	62.0 ± 21.09
Previous study (2008)[b]		25.86 ± 10.7	34.24 ± 2.34	19.59 ± 1.95		37.98 ± 5.41
Metals in coal[c]	1.1	46.5	58.2	38.9	1.52	169
Threshold value[d]	0.3	150	50	250	–	200

[a] Environmental Monitoring of China (1990)

[b] Li et al. (2008)

[c] Yang et al. (2004)

[d] Environmental quality standard for soils" (GB 15618-1995), Level II

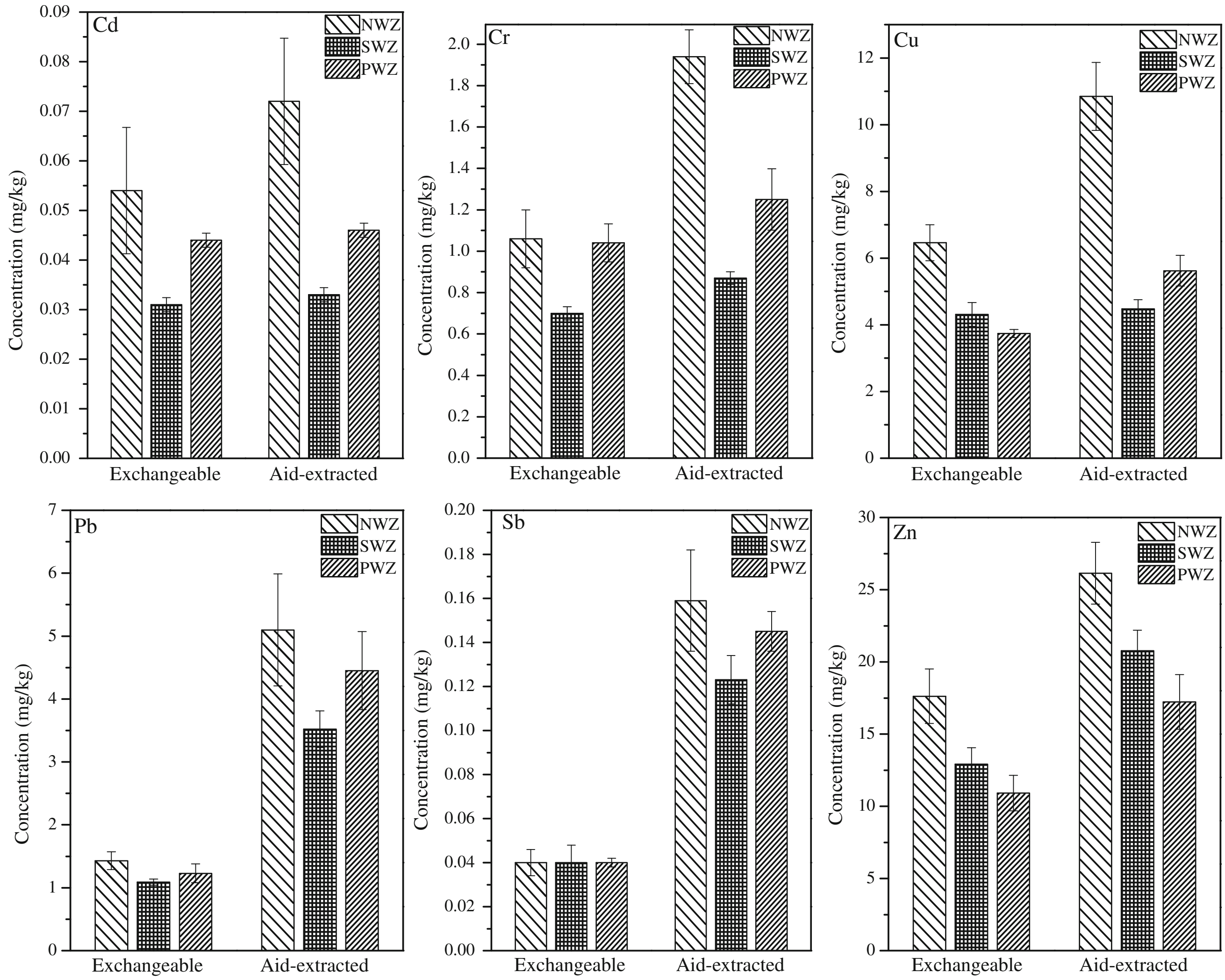

Fig. 2 Concentration of exchangeable and acid-extracted fraction of metals in different subsidence land

organisms. Therefore, the bio-available parts, which included exchangeable fraction and acid-extracted fraction of metals, are discussed in this section. The result is shown in Fig. 2. We discuss the two parts of metals individually as follow.

Exchangeable fraction was in a range from 0.043 mg/kg (Cd, SD = 0.026) to 13.81 mg/kg (Zn, SD = 2.84) and this fraction metals varied greatly in different metals. Not only did Zn have the highest total concentration, but also it had the highest exchangeable concentration, accounting for 15.06 % of the total Zn (Table 2). Cu and Cd also had high proportion of this part metal, accounting for 12.66 % and 10.58 %, respectively. In contrast, Cr, Pb and Sb had low proportion of the exchangeable fraction, only accounting for 3.40 %, 2.78 % and 2.26 %, respectively.

It can be seen from Fig. 2 that this fraction for all metals was higher in NWZ than in other parts and it was low in SWZ for Cd, Cr and Pb but was low in PWZ for Cu and Zn.

Table 2 Proportion of exchangeable fraction in different subsidence land (%)

	Cd	Cr	Cu	Pb	Sb	Zn
NWZ	12.21	3.70	15.92	3.21	2.09	18.63
SWZ	10.12	3.42	13.68	2.74	2.63	16.36
PWZ	9.41	3.09	8.37	2.39	2.08	10.20

However, as the total concentration in different subsidence land was various, we calculated the proportion of exchangeable fraction in different subsidence land (Table 2). It can be found that the range of the proportion of exchangeable fraction was always NWZ > SWZ > PWZ for all metals. Generally, the exchangeable fraction of metals in sediments can be in a dynamic equilibrium with the ionic content in water through some typical sorption–adsorptions processes (Peng et al. 2009). So the

Table 3 Proportion of acid-extracted fraction in different subsidence land(%)

	Cd	Cr	Cu	Pb	Sb	Zn
NWZ	16.41	6.82	26.74	11.42	8.31	27.60
SWZ	10.58	4.21	14.10	8.72	7.62	26.41
PWZ	9.39	3.69	12.55	8.66	7.91	16.11

water is important for the mobility of exchangeable fraction of metals. In NWZ, this part metals can only be leached from surface land into subsoil by the rain. But in PWZ, the soil has been immersed for a long time; and this part metals have been released through interstitial water. So the exchangeable fraction of metals was low in PWZ.

Figure 2 shows the result of the acid-extracted fraction of metals. We can find that the concentration of acid-extracted fraction was always higher than that of the exchangeable fractions, especially for Pb and Sb. Similarly, the acid-extracted fraction concentration varied greatly between different metals, accounting for 3.69 % (Cr, PWZ) to 27.60 % (Zn, NWZ) of the total metal in the subside land (Table 3). The proportion of acid-extracted fraction had a range of Cr < Sb < Pb < Cd < Cu < Zn. In spatial, this part metal was higher in NWZ than in other two subsidence land. Especially for Cd, Cr and Cu, the value of NWZ was 1.75, 1.85 and 2.13 times higher than that of PWZ.

The mobility of acid-extracted fraction metals is influenced by pH. With the decreasing of pH value, the solubility and mobility of metals increase significantly (Tessier et al. 1979) and then affects its respective bioavailability and toxicity. In soil or sediments, there is a limit pH controlling their mobility and the metals would be released only low the limit pH value. For Cd, Cu, Pb and Zn, the limit pH is 6.0, 4.5, 4.0 and 6.0–6.5, correspondingly (Peng et al. 2009). We have tested the pH values in the subsidence land and the mean values were 6.75 ± 0.84, 6.21 ± 0.93 and 5.82 ± 0.36 for NWZ, SWZ and PWZ, respectively. We found the pH of PWZ sediments was lower than that of other lands. So in nature state, the acid-extracted fraction metals in PWZ would be released easily into water column, which made the proportion of acid-extracted fraction in PWZ low.

From Fig. 3, it can be found that the sum of the amounts of bio-available fraction for the metals was from 6.78 % (Cr, PWZ) to 46.23 % (Zn, NWZ). Zn had the highest bio-available fraction, accounting for 26.31 %–46.23 % of total metals. Cu had the second highest bio-available fraction, accounting for 20.92 %–42.66 % of total metals. The bio-available fraction of Cd, Pb and Sb was lower than that of Zn and Cu. Cr had the lowest bio-available fraction, accounting for 6.78 %–10.52 % of total concentration Fig. 3.

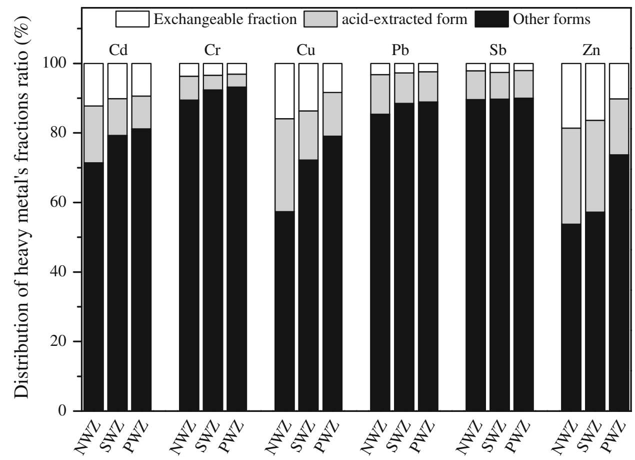

Fig. 3 Proportion of metal forms in different subsidence land

In spatial, the bio-available fraction of most metals in NWZ was always higher than that in PWZ except for Sb, which had no spatial variation in different subsidence land. This is different from the distribution of total metals concentration, which was higher in PWZ than that in NWZ. This may be attributed to the change of the coal mining subsidence land.

The change of total metals is mainly affected by the soil erosion. Ground subsidence significantly changes terrain conditions, such as elevation, slope angle and slope aspect and all these changes greatly affect the rainfall-runoff process (Meng et al. 2012). In this study area, when the surface soil is washed by the rainfall runoff, a great amount of soil particles are carried into subsidence land. Previous study has reported that those soil particles were mainly composed by fine particles, such as silt (<0.064 mm). It is found that in finer particles the concentration of metals is usually higher than in coarse grains due to increased surface area, higher clay minerals and organic matter content in finer grains (Zhang et al. 2007).Therefore, the total metal concentration was high in PWZ. In this paper, we also analyzed the distribution of particle-size in different subsidence land (Table 4). It can be found that the proportion of fine particle in PWZ was higher than that in NWZ. This can give information that the soil in this coal mine has been eroded.

Table 4 Distribution of particle-size of coal mining subsidence land (%)

	<0.064 mm	0.125–0.064 mm	0.25–0.125 mm	0.50–0.25 mm
NWZ	65.29	15.76	8.47	10.48
SWZ	74.38	10.59	6.38	8.65
PWZ	81.65	12.36	3.25	2.74

The pollution transports into subsidence land from coal mining has been a serious concerned problem. Besides the metals, other kind of contamination such as nutrient (nitrogen and phosphor) was also carried into subsidence land by rainfall runoff (Meng et al. 2009). This makes the subsidence land become a sink of pollution. Because the subsidence land environment was a segregated environment, the water in it can not flow away well and its self cleaning capacity was weaker. Although the water in this segregated environment can not transport out, it connected with the groundwater. As a result, the contamination accumulated in subsidence land would cause serious environmental pollution to groundwater.

In subsidence land, the bioavailability of metals was relatively low. This is because the soil of subsidence land was immersed in the water for a long time. The soil of coal mining belonged to terrestrial ecosystems originally. The water content of soil was low and bio-available fraction of metals would not remove in general. Only when the rainy season comes, this part metals will move downward with the infiltration of rain. However, in PWZ, the terrestrial ecosystems have changed into aquatic ecosystem. The soil was immersed in water and the bio-available fraction of metals would be dissolved by water, especially the exchangeable fraction would diffuse into water column through pore water. Thus, it made the proportion of bio-available fraction of metals low, while the metal concentration in water column increased, which brought serious harm and risk to aquatic organisms. At present, the utilizing of perennial waterlogged subsidence land was mainly for excavating into the fish ponds and conducing aquaculture. This made the utilizing of subsidence land obtain a certain economic benefit. However, we should pay attention to the environmental monitoring of water and soil in subsidence land and prevent the metals and others pollution exceed the standard.

Acknowledgments This work was financially supported by the special research funding for the public benefits sponsored by Ministry of Environmental Protection of PRC: "Risk assessment and control technology of groundwater pollution in antiquated mine" (201109011).

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