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Four trace elements contents of water environment of mining subsidence in the Huainan diggings, China

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Abstract Mining subsidence pool is the special waters formed by coal mining, located near the mine. We understand the impact on these waters of the surrounding coal production activities and the electricity plant through research the content and characteristics of harmful trace elements in coal contained in these waters. Pb, Hg, Se and Cr these four trace elements increase 0.52, 0.78, 0.70 and 0.28% respectively in Datong mining subsidence pool from November 2004 to November 2006; the four elements increase 1.52, 1.23, 1.08 and 1.08% respectively in Xie'er mining subsidence pool; the four elements increase 1.01, 1.06, 1.02 and 0.83% respectively in Pansan mining subsidence pool. The absolute value of Pb, Hg, Se and Cr in mining subsidence pool is related with their background value, while the increase in their concentration and their environment of mine and electricity plant surrounded are closely linked.

Keywords Mining subsidence pool · Trace elements · Coal mine

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Introduction

Coal mining subsidence pool is a common environmental geologic hazard, which can not only destroy the construction and vegetation, but also have an such influence on the surface water and groundwater systems that may seriously deteriorate the ecological environment of mining areas. Mining subsidence generally happened in the low-lying area with a relative high groundwater level. And the performance of the mining subsidence is the seeper of basin subsidence which generally form coal mining subsidence pool or seasonal coal mining subsidence pool (Yin 1997).In recent years, with the escalation of environmental protection, the reasonable ecological restoration project of coal mining subsidence area also achieved its initial success. So the study on the water environment of subsidence zone is spewing into the air.

Survey of mining areas, coal mine subsidence district and values of Pb, Hg, Se, Cr in these areas

Survey of mining areas and coal mine subsidence district

Huainan, so called coal base, which covers a total 3,000 square of areas, 100 km long from east to west and about 30 km long from north to south, is very rich in coal resources, There are total 14 pairs of key state-owned coal mines in Huainan. In the process of coal transportation, cleaning, storage, and combustion, the trace element in coal has to happen migration changes. And when the trace element in coal together with main pollutants coming from the harmful element in coal when mined to the ground enter into the water body, they will deteriorate the water environment. Meanwhile, three of the largest thermal power plants of the east China are located in Huainan, including Huainan Tianjia'an power plant with a 80-kW generator set, Huainan Luohe plant with a total of 240 kW generating capacity – four 30-kW generator sets and two 60-kW generator sets, and Huainan Pingwei Power Plant, total of 180 MW generating capacity, three 60-kW units. With the development of coal mining, the expansion of coal mining subsidence zone is also increasing. In 1992, there is 6,709 hm^2 coal mining subsidence zone, while in 2005, the number has increased to 11,800 hm^2.The expanding rate is about 392 km^2. Generally, the depth of mine subsidence district is around 3–10 m, while the subsidence of the old district may up to 20 m deep. Some have formed a large-scale subsidence lakes.

In this paper, water samples were collected from three typical coal mining subsidence pool near Huainan coal mine, including Datong mining subsidence pool, eastern part of Huainan, Xie'er mining subsidence pool, western part of Huainan, and Pansan mining subsidence pool, northern part of Huainan. And some theoretical basis on ecological construction of the mine may be given by analyzing the composition and distribution of the trace element as Pb, Hg, Se, Cr in coal contained in the water samples and analyzing their possible sources.

Profiles of background values of Pb, Hg, Se, Cr in shallow layer underground water of mining areas

The determination of background values is the prerequisite for water quality evaluation and analysis of pollution in hydrochemistry, which has a direct impact on the quality and the extent of exactitude of evaluation on status of water quality and pollution levels (Gui and Hu 2001). Plumbum content in natural water is not high, that the highest concentration in the shallow layer underground water of the western of Huainan City was 0.01461 mg/L, in the northern where Pansan mining subsidence pool located was 0.0073 mg/L. Chromium content In the shallow groundwater of Huainan area is such low, generally less than 0.01 mg/L. Majority samples of shallow underground water in Huainan were not detected Se. Se content in some local areas was 0.001~0.004 mg/L, scattered in the southeast and southwest of Huainan River. While in the southeast the figure is 4.35×10^{-4} mg/L, compare with 9.74×10^{-4} mg/L in the southwest, and 1.69×10^{-4} mg/L in the north. Hg is a kind of quite toxic trace elements. Hg content in the natural water is generally come from industrial wastewater. Few Hg was detected in the samples of shallow underground water in urban areas of Huainan, all of below 0.002 mg/L.

Materials and methods

Five sampling points were planted in each pool for taking water samples. One point was in the centre of the pool, and the other four were planted in the North–South and East–West position. Each sampling point was divided into upper, middle and lower layers for sampling. The upper layer was in the place 0.5 m below the surface of water. The middle layer was in middle of the water. And the lower layer was 0.5 m high from bottom of the water. Then equally mixed the water ingested from the three layers as one sample. After been collected, water samples were immediately come into the detection process. Sampling time was from November 2004 to November 2006, a monthly sampling.

Results and discussion

The content and distribution characters of trace elements Pb, Hg, Se, Cr in water environment of coal mining subsidence areas

The content of trace elements Pb, Hg, Se, Cr in water environment of coal mining subsidence areas

Figure 1
Figure 2
Figure 3

The distribution characters of the four harmful trace elements Pb, Hg, Se, Cr in water environment of coal mining subsidence areas

Just take a look at one single mining subsidence pool, the content of Pb, Hg, Se, Cr had an overall wavily

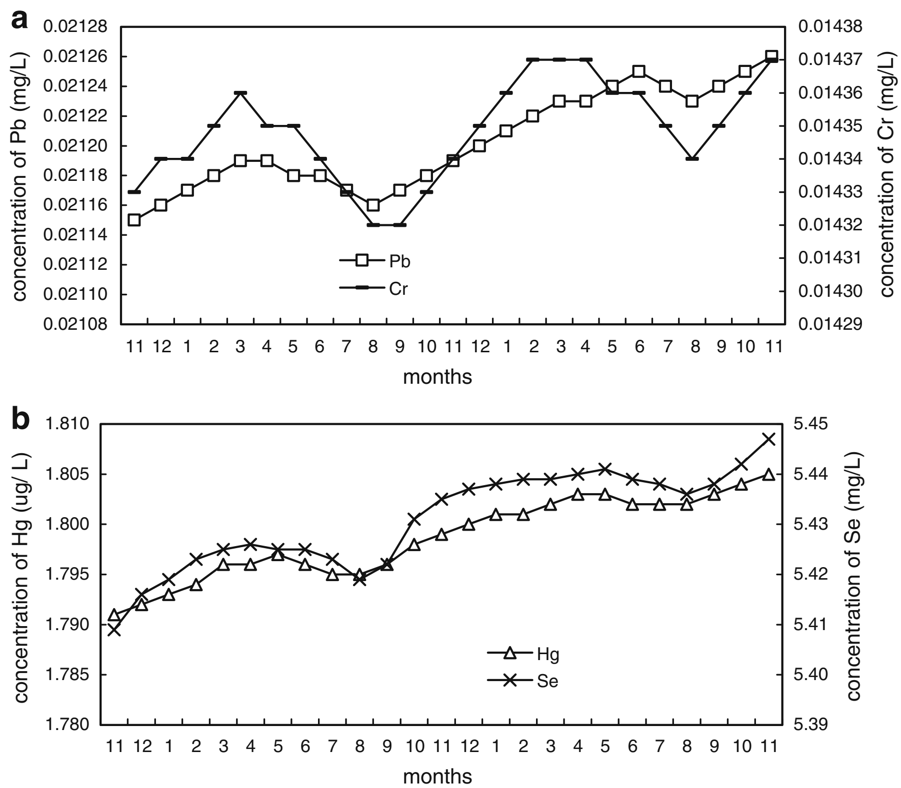

Fig. 1 **a**, **b**. Contents of Pb, Se, Hg, Cr in Datong mining subsidence pool (from November 2004 to November 2006)

ascend trend. Since November 2004 to November 2006, the subsidence pool saw an increase of 0.92% of Pb, 0.52% of Hg, 0.70% of Se, 0.28% of Cr. In terms of season, take March 2005 to February 2006 as an example (no special note are the same for the remaining), As shown in Table 1, the content of Pb, the sequence of the content in samples by season from high to low was winter, spring, autumn, summer; Hg and Se in samples was highest in winter and lowest in summer, and almost the same in spring and autumn. For Cr, the sequence of the content in samples by season from high to low was winter = spring, autumn and summer. Xie’er mining subsidence pool also saw an overall wavily ascend trend of content of the elements Pb, Hg, Se, and Cr, Since November 2004–November 2006, the subsidence pool saw an increase of 1.52% of Pb, 1.23% of Hg, 1.08% of Se, 1.08% of Cr. Seasonal change of the content of the elements of Pb and Se from high to low were winter, autumn, summer and spring; For Cr, the sequence of seasonal changes of the content in samples from high to low was winter, spring and summer (autumn was the same as summer); For Hg, the sequence of seasonal changes of the content in samples from high to low was winter, spring (autumn was the same as spring), summer. Pansan mining subsidence pool also saw an overall wavily ascend trend of content of the elements Pb, Hg, Se, and Cr, From November 2005 to November 2006, the subsidence pool saw an increase of 1.01% of Pb, 1.06% of Hg, 1.02% of Se, 0.83% of Cr. Seasonal change of the content of the elements of Se from high to low were winter, autumn, summer and spring; For Cr and Hg, the seasonal changes of the content in samples from high to low was winter, autumn and summer, while spring was the same as summer; For Pb, the seasonal changes of the content in samples from high to low was spring, autumn (winter was the same as autumn), summer.

From contrasting the three mining subsidence pools, as far as the content of Pb, the sequence from high to low was Xie’er mining subsidence pool, Pansan Mining subsidence pool, Datong mining subsidence pool. For Hg, the sequence was Xie’er Mining subsidence pool > Datong mining subsidence pool > Pansan mining subsidence pool. For Se, the sequence was Xie’er Mining subsidence pool > Datong mining subsidence pool > Pansan Mining subsidence pool; For Cr, the sequence was Pansan

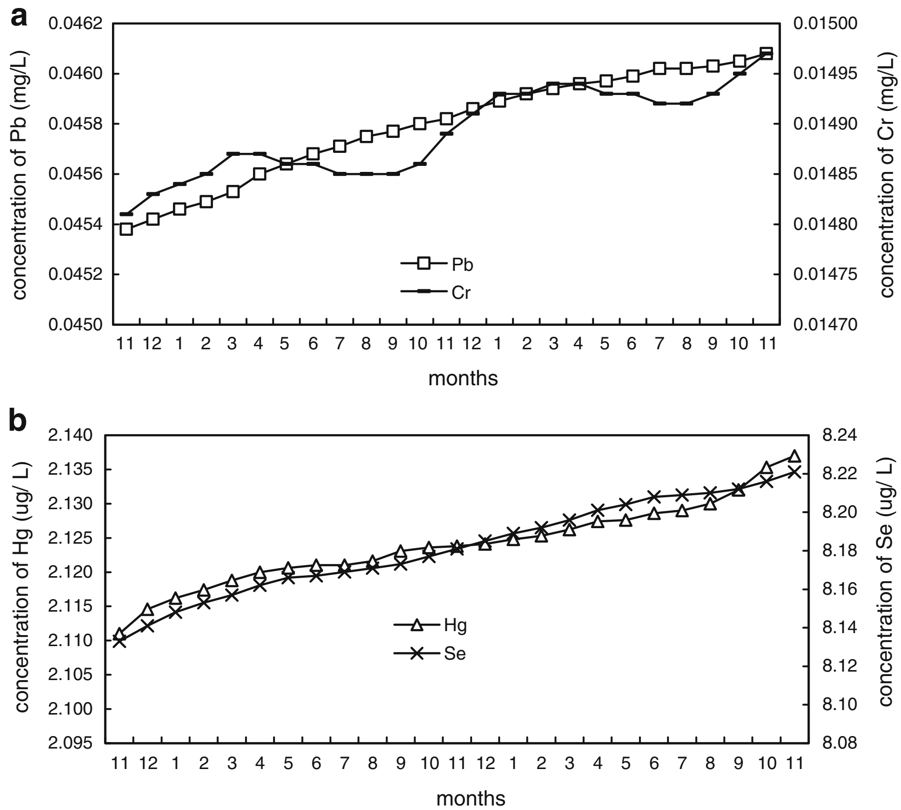

Fig. 2 **a**, **b**. Contents of Pb, Se, Hg, Cr in Xie'er mining subsidence pool (from November 2004 to November 2006)

Mining Subsidence pool > Xie'er Mining subsidence pool > Datong mining subsidence pool.

Main causes of the four harmful trace elements in the mining subsidence water environment

Huainan is a coal base as well as a thermal power base. The selection of sample coal mining subsidence pool was based on the serviceable life of coal mines next to the pools. Datong mine had been mined in 1921, and abandoned in 1980. Datong mining subsidence pool, lying in the eastern part of Huainan, near the Datong mine, with a history of around 60 years, is the longest time of formation among the three, As coal mining has ceased, the subsidence pool has been so much stable, and no longer sinking, that it has basically been a sealed isolation water, with 2.4 hm^2 subsidence water area, and a maximum depth of 8~10 m Mountains and fields are near it. Xie'er mining subsidence pool, with an over 30-year history, lies in the western of the region where Xie'er mine is in the vicinity. Xie'er mine had been mined in 1957. Till 2006, its annual yield was about 900,000 tons/year. Xie'er subsidence pool began to collapse in late 1960s.Until nowadays, it is with a 14 hm^2 subsidence water area and a 7 m-maximum-depth. Because of water recharging by the Huaihe River, domestic sewage by residents living around and the mine water drained into by the Xie'er mine, the subsidence water areas are still continuing subsidence nowadays. A perennial stacking coal gangue hill with an area of 500 m^2 lies north of Xie'er subsidence pool, 300 m far from it. Pansan mining subsidence pool lies in Northern part of Huainan city, near Pansan coal mine and Pansan coal preparation plant. Pansan coal mine was put into operation in 1992. Nowadays the mine production capacity is 300 million tons/year. With a total area of 1,000 hm^2, 100 m width, 200 m long, and 2–3 m depth, the subsidence areas of Pansan mining subsidence pool are very large, Since Nihe River is the northern neighbor of the mining subsidence pool, it is greatly affected by the water level of the Nehe Rivers. Because it is not a long time since the subsidence, trees and telephone poles can be seen in the pool. Most of the surroundings of the subsidence pool are farmlands while there are several residential buildings

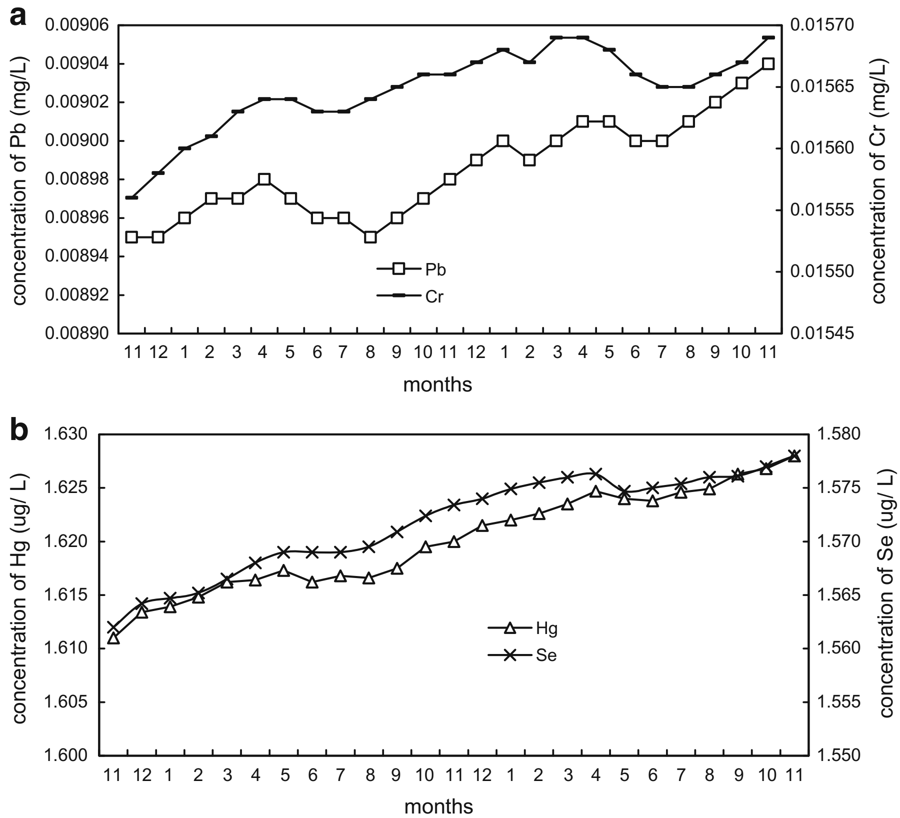

Fig. 3 **a**, **b**. Contents of Pb, Se, Hg, Cr in Pansan mining subsidence pool (from November 2004 to November 2006)

nearby around 1,000 m to the pool. Huainan has three large power plants: Luohe power plant, Tijia'an power plant and Pingwei power plant. Luohe power plant is in the east of Huainan, Tianjia'an power plant is in the centre east of Huainan, and Pingwei power plant is located in the northern Huainan.

Taking a panoramic view of the content and distribution of the four trace elements in the three mining subsidence pools, the main influencing factors are

> The influence of the storage and transportation of coal and coal gangue on the ground

This is one of main reason. Xie'er mining subsidence pool has the fastest growth trend of the four elements among the three pools. The reason is that this subsidence pool lives both near the mine and the coal gangue hill, As we know that coal was formed in the relative reduction environment, When transported to the surface, because of some changes of physical and chemical conditions, some minerals in coal such as sulfide will decompose and produce a lot of acidic water. This highly acidic water has such a leaching capacity that it can take large quantity of trace elements in coal into the environment. Moreover, under normal circumstances, the atmosphere contains carbon dioxide (about 0.03%).And carbon dioxide can dissolve into rain water to make the rain water pH<7. As for Huainan mining areas mainly in coal and coal-based power generation, large quantities of sulfur dioxide and nitrogen oxide are released in the process of oxidation and combustion of the coal. Generally, this can make rain water pH<5.6 thus so called acid rain. The acid rain has greatly increased the chance of precipitation of the these four kinds of harmful trace elements in coal and coal gangue, and then result in the fastest increase of the content of these four trace elements in Xie'er subsidence pool. Some scholars take immersion as the ultimate state of eluviation to evaluate the impact of trace elements to the environment. Their conclusion is that the impact is not much great (Wu 2004). I believe that immersion experiments are distinguishing with the practical gangue leaching. Firstly, immersion is that all submerged in water and generally the leaching solutions is alkaline. While in fact coal gangue is

Table 1 Content of four trace elements in spring, summer, autumn and winter(from March 2005 to February 2006)

	Spring				Summer				Autumn				Winter			
	Pb	Hg	Se	Cr	Pb	Hg	Se	Cr	Pb	Hg	Se	Cr	Pb	Hg	Se	Cr
	(mg/L)															
Datong mining subsidence pool	0.021900	1.797×10^{-3}	5.426×10^{-3}	0.014335	0.021173	1.796×10^{-3}	5.420×10^{-3}	0.014328	0.021175	1.799×10^{-3}	5.433×10^{-3}	0.014335	0.021215	1.801×10^{-3}	5.438×10^{-3}	0.014355
Xie'er mining subsidence pool	0.045569	2.120×10^{-3}	8.164×10^{-3}	0.014870	0.045700	2.122×10^{-3}	8.170×10^{-3}	0.014855	0.045785	2.122×10^{-3}	$8.179\times 10-3$	0.014855	0.045873	2.125×10^{-3}	8.191×10^{-3}	0.014915
Pansan mining subsidence pool	0.089750	1.617×10^{-3}	1.569×10^{-3}	0.015635	0.08960	1.617×10^{-3}	1.570×10^{-3}	0.015635	0.089650	1.620×10^{-3}	1.573×10^{-3}	0.015655	0.089650	1.622×10^{-3}	1.575×10^{-3}	0.015670

generally in a reduction state. Secondly, the temperature of immersion does not agree with the temperature of the coal gangue in a leaching state. Because the gangue is long open stockpiled, the internal temperature can reach about 1,000°C by natural weathering (Cheng 2001). At this temperature, volatilization, recombination and transformation of the four kinds of trace elements in coal gangue can easily happen. In dry season, recombination and transformation of the trace elements will occur when the exposed gangue hills with high internal temperature are in the weathering and oxidation state. And when the next acid rain comes, the harmful trace elements will be precipitated by the rain. Therefore, I believe that under the condition of long terms of physical and chemical actions, the coal gangue hill in a leaching-weathering – long leaching state, will precipitate much more harmful trace elements.

The influence of power plants

The boiling point of Se is 217°C. And Se will experience transference in the coal burning process. Experiments show (Sun and Jervis 1988) that when get to 750°C, more than 75% Se in coal will volatilize. Selenium dioxide has been released from combustion exists in the air in the state of aerosol. While in humid meta acid environment it may easily be eluviation and migration. And in drought and alkaline environment, the land will enrich in selenium dioxide(Zhang et al. 1999).The boiling point of Hg is 357°C, The mercury in coal will volatilize at 150°C in combustion process. And the majority of mercury gas will get into the atmosphere. Mercury in coal ash is also enriched. Particle size less than 0.125 um of fly ash can enrich over 90% of the mercury. The boiling point of Pb and Cr is 1,740°C and 2,670°C respectively. It will also escape to the outside together with the coal combustion flue gas. And during the migration, it will attach to the surface of fly ashes when the temperature began to low. In the way, it may exist in the atmosphere or down to the soil with rain. From Table 2, the volatilization rate in power plant of Pb, Hg, Se and Cr was 50.1, 90.29, 78.34 and 44.73% respectively. Since the mines near Datong mining subsidence pool has been abandoned since 1980, there won't be the direct coal pollution any longer. However, the content of the four trace elements is still showing a growth trend in the 2 years. Fly ash of the plants is mainly the cause of pollution. Datong

Table 2 Mass fraction of raw coal, fly ash and bottom ash and its RE and volatilization rate in power plant of the Huainan

	Pb	Hg	Se	Cr
Raw coal ($\times 10^{-6}$)	9.326	0.16	6.4	13.36
Bottom ash ($\times 10^{-6}$)	15.84	0.01	2.6	25.8
Fly ash ($\times 10^{-6}$)	23.74	0.09	7.6	37.5
RE	0.35668	0.01325	0.08531	0.40553
Ve (%)	50.10	90.29	78.34	44.73

RE (Meij 1994)=(bottom ash(or fly ash) concent of element×rate of ash)/concent of one element in coal.

Ve={1−[0.2×*W*(A)×*W*(e bottom ash)+0.8×*W*(A)×*W*(e fly ash)]/(100×*W*(e raw coal)]}×100%.

Ve evaporation rate of element(%), *W*(A) ash productive rate of raw coal(%), *W*(e bottom ash) mass fraction of element in bottom ash (1×10^{-6}), *W*(e fly ash) mass fraction of element in fly ash (1×10^{-6}).

subsidence pool is located in the eastern part of Huainan where it is relative neat to the Tijia'an plant that located in the centre east of Huainan and Luohe plant that located in the east of Huainan.

The influence of climate

Huainan City is belonged to humid climate of cold temperate region. Spring and autumn are short while summer and winter are long. According to the temperature we define that spring is from April to May, summer is from June to September, autumn is from October to November and winter is from December to the next March. The average rainfall of the city is 924.6 mm. Most of the rainfall concentrate in summer (for over 50% of the annual rainfall), followed by spring and fall and winter has the least rainfall(Gui and Hu 2001). Datong mining subsidence pool is mainly affected by fly ash and coal dust ash. But in the summer of 2005 and 2006 (6, 7, 8, 9), the content of these four kinds of trace elements all appeared a descend trend compare with the spring of the year; and then it recovered in the ensuing autumn; and in winter it appeared an upward trend. Because Datong mining subsidence pool is a closed pool, it is greatly influenced by the rainfall. When the output of surrounding plants are in a state, the increased subsidence pool water by precipitation, result in a decrease of the content of the four trace elements. However, this phenomenon did not occurred in the other two mining subsidence pools. The reason is that both of the other two subsidence pools have got peripheral water system replenishment that can keep the water in a basic balance. Another main reason is that since frequent rainfalls in summer can make coal gangue hill precipitating more trace elements. The degree of the concentration of the four trace elements in water is far greater than that of dilution of precipitation. Even water of subsidence pool has increased. So the concentration of four harmful trace elements appears to rise. Xie'er Mining Subsidence pool was most significantly, compared with September 2006 and May 2006, Pb rose 0.28%, Hg rose 0.21%, Se rose 0.10%, and Cr rose 0.06%.

Conclusions

Suffered by coal mining activities and plant ashes, all of the three mining subsidence pools were detected to have Pb, Hg, Se and Cr since November 2004 to November 2006.And the content of these four trace elements were far more than their background values. While for 2 years, their concentration showed a growth trend. The sequence of the extent of the growth trend is Xie'er subsidence pool, Pansan subsidence pool, and Datong subsidence pool.

The increase of the four harmful trace elements in Datong mining subsidence pool is the result of the two nearby power plants. It shows that the concentration of the four elements in summer is below what in spring of the same year. This is because the pool is a closed pool and great influenced by precipitation. The summer rainfall water diluted the concentration. Xie'er mining subsidence pool is great affected by the coal mines and the coal gangue hill nearby. Particularly, because of leaching, weathering of the coal gangue hill and the inflow of storm water together with the elements to the subsidence pool, the content of the four trace elements is in growth quarterly. Pansan mining subsidence pool is mainly affected by the coal mines and coal preparation plant. The yield of Pansan mines and its coal preparation is so much high that the concentration of the four types of harmful trace elements in the growth trend of Pansan mining subsidence pool was after Xie'er mining subsidence pool.

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