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Heavy metal pollution and ecological risk assessment of water-based drill cuttings produced in shale gas exploitation in Chongqing, China

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Abstract. Shale gas exploitation is booming in China. Unlike the traditional oil extraction industry, shale gas extraction will generate more solid waste. Water-based drill cuttings (WBDC) as one of them is currently under regulatory vacuum. This article studied the status of heavy metal pollution and evaluated the ecological risk of WBDC. Cd, Cr, Cu, Hg, Mn, Ni, Pb and Zn were selected for the study. The results showed that except for Ni, other heavy metals showed different degrees of pollution, but the leaching toxicity was rather limited. Meanwhile, the ecological risks of all samples were significant, which posed a huge threat to environment. Though its limitation, this article can provide theoretical foundation for regulatory decisions of WBDC.

1. Introduction

Chongqing is a large city with a population of 30 million and it is also an industrially developed city. The development of Chongqing's economy requires more and more energy, and the consumption of coal, natural gas, oil, and electricity is rapidly rising. The contradiction between supply and demand of energy will further intensify and influence economic development. Shale gas, as an unconventional gas resource, has the advantage of little pollution and abundant reserves in Chongqing. The exploitation of shale gas will change the energy structure and consumption composition of Chongqing and even China.

However, the shale gas exploitation process will generate a substantial amount of solid waste, which we usually call drill cuttings. According to a previous study [1], a typical single horizon well in the USA will produce over 200 yd^3 of drill cuttings (1 yd^3=0.764555 m^3). In China, this number is probably higher because Chinese terrain is more complex and the shale gas is buried more deeply. Now, 266 wells have been drilled in Chongqing, and the total amount of drill cuttings was over 53,000 yd^3.

Drill cuttings can be divided into two types: water-based drill cuttings (WBDC) and oil-based drill cuttings (OBDC) according to different demand and conditions. In China, OBDC are classified as hazardous waste because of their oil content, and the government has conducted unified and strict management. However, WBDC has not yet issued a clear policy in China, and it is difficult to effectively supervise it. At present, only a few studies have reported the basic properties and heavy

metal pollution of drill cuttings, but it indeed has posed risk internationally. A high content of Cr, Cu, Ni, Pb Zn and Ba was found in the drill cuttings collected from Northern and Central North Sea [2], and due to the oxidation of metal sulfide complexes, a large amount of heavy metals will enter the water body. In the leaching study of Marcellus Shale drill cuttings, Cd, Cu, Mo, Ni, Sb, U, V and Zn were elevated from the lower portion of the Marcellus Shale [3]. In the Haynessville shale formation, cumulative average weight percentages of some trace metals (V, Cr, Co, Ni, Cu, Zn, Th, Rb, U, Sr, Zr, Mo) was about 0.14% [4]. However, no research that focus on the properties and pollution status of WBDC could be found by the researchers. Therefore, it is of great significance to determine the basic characteristics and pollution status of WBDC, for maintaining public health and providing basic data for management decisions.

For this study, a detailed assessment was conducted on the heavy metal content and leaching toxicity of WBDC. The Pollution Index (PI) and Enrichment Factor (EF) were employed to determine the pollution degree of drilling activities. Finally, the Hakanson method was used to evaluate the ecological hazards under multi-factor combined pollution.

2. Materials and methods

2.1. Sample collection and analysis

According to the drilling stage in drilling field, a total of 5 samples were collected from Jiaoshi Town (29°43' N, 107°35' E), Fuling District, which is located in the mountainous transition zone of the Sichuan Basin. The samples were preserved and transported according to the Technical Specification for Soil Environmental Monitoring of China [5]. All samples were first air-dried until a constant weight was achieved, then pulverized, and well mixed.

For the total heavy metal content test in each sample, 0.1 g of well mixed WBDC was digested by 10 ml of a Leford aqua regia and hydrofluoric acid mixture (volume ratio 7:3), and then digested in a microwave digestion instrument (Mars Model, CEM, Inc). The leaching toxicity was detected using HJ/T 299-2007 [6]. 10 g of the WBDC was immersed in 100 mL of sulfuric acid and nitric acid (mass ratio=2:1, pH=3.20 ± 0.05) solution diluted with ultrapure water. The sample was then shaken for 18 h on an oscillating flip style device. Next, the Cd, Cr, Cu, Mn, Ni, Pb, and Zn content in digestion solutions and leaching solutions were tested by atomic absorption spectroscopy (AAS) (SHIMADZU AA-6300C), and the Hg content was tested using a mercury vaporizer unit (SHIMADZU MVU-1A). Each sample was analysed in triplicate.

2.2. Pollution status

2.2.1. Pollution index.
To determine the pollution status of WBDC, we used the pollution index (PI) to characterize the WBDC.

$$PI = C_i/C_{0i}, \qquad (1)$$

Where: C_i is the concentration of the ith heavy metal in WBDC (mg/kg); C_{0i} is the target concentration of the corresponding metal (mg/kg). In this study, we took the Chinese soil background value as the target concentration.

2.2.2. Enrichment factor.
In order to separate human activities from elements from natural origin and to assess the degree of contamination of human activities, an enrichment factor (EF) was introduced for analysis. Table 1 defines the enrichment factor grades.

$$EF = (C_n/C_{ref})_{sample}/(C_n/C_{ref})_{background} \qquad (2)$$

Where: C_n is the heavy metal concentration; C_{ref} is the concentration of reference element for normalization (mg/kg) [7]. This study selected Cr as the reference element, because shale gas operators claimed that the drilling fluid did not contain Cr, which indicating less affected by human activities.

Table 1. The grades of enrichment factors [8]

enrichment factor (EF)	level	degree of enrichment
<2	1	Deficiency to minimal enrichment
2~5	2	Moderate enrichment
5~20	3	Significant enrichment
20~40	4	Very high enrichment
>40	5	Extremely high enrichment

2.3. Ecological risk assessment

The method proposed by Hakanson [9] was used to evaluate the potential ecological risk in this study. Table 2 shows the ecological risk level according to the E_r^i and the RI value. This method is not only suitable for the evaluation of single pollution factors, but also for the evaluation under multiple factor combined pollution.

$$\text{RI} = \sum_{i=1}^{n} E_r^i = \sum_{i=1}^{n} T_r^i \times C_f^i = \sum_{i=1}^{n} T_r^i \times \frac{C_s^i}{C_n^i} \qquad (3)$$

Where: RI is the comprehensive index of ecological risk of multiple pollution factors;

E_r^i is the ith heavy metal ecological risk index

T_r^i is the "toxic-response" factor for the given heavy metal; The factor of Cd, Cr, Cu, Hg, Ni, Pb and Zn were 30, 2, 5, 40, 5, 5 and 1, respectively.

C_f^i is the pollution coefficient of heavy metal i relative reference value;

C_s^i is the measured concentration of heavy metal i;

C_n^i is the evaluation reference value of heavy metal i. In this study, for making the result more realistic, we used the background value as the reference.

Table 2. Indices in assessing potential ecological risk

E_r^i value	RI value	Ecological risk level
$E_r^i < 40$	RI<150	Low
$40 \leq E_r^i < 80$	150≤RI <300	Moderate
$80 \leq E_r^i < 160$	300≤RI <600	Considerable
$160 \leq E_r^i < 320$	RI≥600	High
$E_r^i \geq 320$		Very high

3. Results and discussion

3.1. Heavy metal pollution status in WBDC

The results of heavy metal content, Pollution Index (PI), and Enrichment Factor (EF) are shown in Table 3.

Table 3. Heavy metal pollution in WBDC (mg/kg)

	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Zn
Mean	0.91	164.74	71.30	0.44	25322.11	16.92	101.53	458.69
SD	0.68	43.07	22.65	0.31	8110.61	13.60	48.85	214.24
Background [10]	0.08	79.00	31.10	0.06	657.00	32.60	30.90	86.50
PI	11.52	2.09	2.29	7.33	38.54	0.52	3.29	5.30
EF	5.52	1.00	1.10	3.52	18.48	0.25	1.58	2.54

SD = Standard Deviation

All kinds of heavy metal content except Ni exceed the background value, which indicate that WBDC have been contaminated by heavy metals at different levels. Among them, Mn has the highest content and PI value, and this may be due to the addition of weighting agents to the drilling fluid. Through the ground and downhole circulation, the broken drill cuttings were brought to the surface with the circulating drilling fluid, and this process introduced contaminants in the drilling fluid into the WBDC. It is worth noting that the PI value of Cd (defined as carcinogens) and Hg were both over 6 (a very high contamination index [9]), especially Cd, which was 11.52. This could be a big threat to the wellsite workers and surrounding residents. The PI value of the remaining heavy metal Cr, Cu, Ni, Pb and Zn were 2.09, 2.29, 0.52, 3.29 and 5.30 respectively, which meant moderate ($1 \leq PI < 3$) to considerable ($3 \leq PI < 6$) contamination except for Ni that showed no contamination.

In addition, in a petroleum drill cuttings sample of the UK [11], the content of Cd, Cr, Cu, Mn, Ni, Pb and Zn (no Hg data available) were 21, 106, 44, 345, 38, 150 and 82 mg/kg respectively. Compared to that, the heavy metal contents in our sample were generally lower, except that Cr, Cu and Zn had slightly higher concentrations. However, because of the high background value and high content of Mn, the Mn content could be 73 times higher than the sample of UK.

Although the PI value reflected the status of heavy metal pollution, it is necessary to distinguish between human activities and natural origin by calculating the EF value [12].The enrichment factor (EF) values of heavy metals covered a wide range, from 0.25 to 18.48, which revealed that human activities affected the heavy metal contamination in a different degree. Among them, the EF values of Cr, Cu, Ni and Pb was less than 2 (deficiency to minimal enrichment), Hg and Zn were between 2-5(moderate enrichment) and Cd and Mn were between 5-20 (significant enrichment). The above showed that although shale gas exploitation activities have caused varying degrees of pollution, they were within an acceptable range. However, the high EF values of Cd and Mn need to be brought to the attention of the managers, and the lower pollution can be achieved by optimizing the drilling fluid formulation.

Meanwhile, by comparing the relative proportions between the standard deviation (SD) and the corresponding heavy metal content, it was found that the content of Cd, Hg, Ni in each sample fluctuated greatly, indicating that the distribution of the heavy metals was not uniform.

3.2. Leaching toxicity in WBDC

To simulate the contamination of groundwater and soil in acid rain conditions when the WBDC were not properly disposed of, we performed a leaching toxicity test using sulphuric acid and nitric acid method [6].

Table 4. Heavy metal leaching toxicity of WBDC (mg/L).

	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Zn
Mean	0.0053	0.2200	0.0440	N.D.	0.0010	N.D.	N.D.	0.0063
SD	0.0034	0.1740	0.0467	N.A.	0.0014	N.A.	N.A.	0.0045
Standard [13]	1.0	15	100	0.1	N.A.	5.0	5.0	100
Leaching ratio (%)	5.861	1.335	0.617	N.A.	0	N.A.	N.A.	0.014

SD = Standard Deviation

N.D. = Not Detected N.A.= Not Available

According to Table 4, the leaching toxicity of each heavy metal was rather low, and the heavy metal content in leaching solution of Hg, Ni, Pb were even lower than the detection limit of the instrument. The leaching toxicity of each element did not exceed the identification standard for extraction toxicity of hazardous wastes in GB 5085.3-2007 [13]. Compared to the acid leaching samples in the UK [3], the leaching concentration of Pb, Cd, Ni and Zn in this study were lower than that in the reference samples, except that Cu was almost the same. Meanwhile, the leaching ratios of

heavy metals were not high, which revealed that even if WBDC are improperly disposed, the leaching toxicity threat of heavy metals to the environment is not significant under acid precipitation.

3.3. Ecologic risk assessment
Due to the lack of "toxic-response" data of Mn, the ecological risk assessment target was focused on Cd, Cr, Cu, Hg, Ni, Pb and Zn.

According to equation (3), the ecologic risks of comprehensive index (RI) and each heavy metal in 5 samples were shown in Figure 1. The uneven distribution of heavy metal in the samples caused the different ecological risk of each sample. In general, RI values of five samples ranged from 465 to 1063, which indicated a considerable ecological risk to very high ecological risk level according to Table 2. Sample 2 and 5 were in the very high risk level (RI≥600), the RI value of which were 1063 and 669 respectively. The remaining samples belonged to considerable risks level (300≤RI <600), and the RI values of sample 1, 3 and 4 were 509, 465 and 522 respectively.
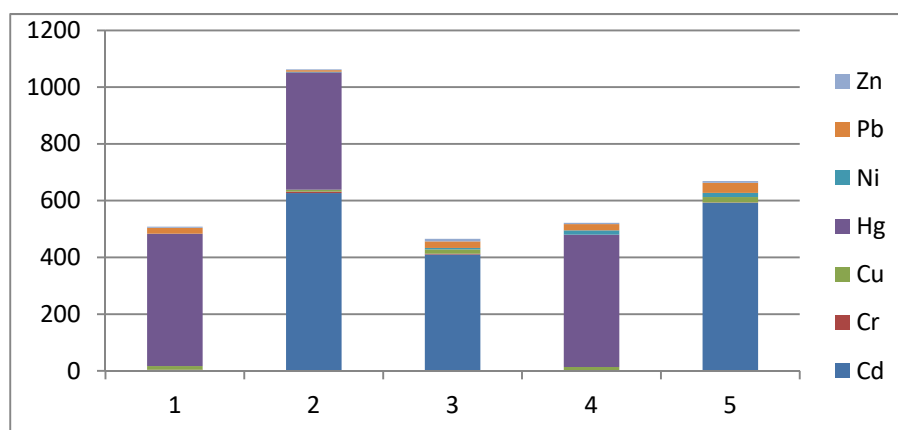

Figure 1. Statistics of ecologic risk of 5 WBDC samples.

Specific to each heavy metal, the ecological risk of Cd and Hg accounted for most of the total risk in each sample (about 90%). This could be explained by the high heavy metal content in WBDC, but related more to the low background value and high toxic-response. The other heavy metals had limited ecological risk

The huge ecological risk of WBDC deserves our attention, especially for the managers and governors. If the content of Cd and Hg can be reduced, the ecological risk of WBDC could be controlled in a low level.

4. Conclusions

In this study, a detailed investigation was conducted to evaluate the heavy metal pollution and ecological risk of WBDC. We believe this is the first time to report contamination information about solid waste produced in shale gas exploitation industry in China. The results showed WBDC was polluted by various heavy metals except Ni, and the degree of pollution (PI value) was: Mn > Cd > Hg > Zn > Pb > Cu > Cr. Meanwhile, the EF value revealed shale gas exploitation has influenced the heavy metal enrichment. Though different heavy metals had different enrichment level, the overall level was acceptable. In addition, the leaching toxicity of WBDC was rather limited that it might pose little threat to the environment. However, the ecologic risk of WBDC was significant, it should attract people's attention.

This article also provided some basic data and evidence for managers and administrators to make decisions for the management of WBDC.

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