



Change characterization of dissolved organic matter in different subsidence land of a coal mine, China

Ting Li¹, Lai Zhou^{1*}, Yan Zhang² and Bo Gao¹

¹School of Environment Science and Spatial Informatics, China University of Mining and Technology, Xuzhou, China
²Tianjin Academy of Environmental Sciences, Tianjin, China

ABSTRACT

Land subsidence in coal mine would change the type of soil, which may be the result of the change of dissolved organic matter (DOM) characterization in surface land soil. When the subsidence wetland is formed, the 3DEEMs results show that when the subsidence wetland is formed, the protein-like materials decrease and the humic acid materials increase. The UV absorption results imply that the structure of DOM become more complex and the degree of humification of DOM increases. The correlation analysis indicates that changes have significant influence on the bioavailability of metals.

Keywords: Dissolved organic matter, Subsidence land, Fluorescence technique, UV absorbance

INTRODUCTION

In China, 97% of coal is produced by underground mining [1]. After the exploitation of underground coal, the rock mass above the coal seams begins deformation and subsidence, and once the subsidence influences the surface land, the surface ground will subside from the standard elevation to form a low-lying land, generally known as mining induced subsidence land, which is larger than the exploitation of coal seams [2]. In the eastern plain area of China, when the surface of subsidence land is 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. Meanwhile, as the level of ground surface at the edge of mining induced subsidence land is higher than that of shallow underground water, the topsoil can avoid being inundated. However, with the water level going up in the rainy season, the underground water will still inundate the land at the edge, forming a seasonal waterlogged zone.

The formation of waterlogged zone on mining induced subsidence land changes the previous terrestrial ecosystem into aquatic ecosystem, thus changes the physicochemical properties and nutritional conditions of surface land soil such as its volume-weight, organic type, ion exchange adsorption, acid-base neutralization, redox, etc [3]. However, the influence on the environment caused by the change of dissolved organic matter (DOM) cannot be neglected as it can affect the environmental behavior and biological effectiveness of various pollutants [4-5]. And organic matters of different sources can bring different effects owing to their different physicochemical characteristics. For example, the terrestrial organic matter mainly comes from leachate of higher plants and from soil with relatively more carbon double bonds and aromaticity while endogenous organic matter mainly comes from algae of aquatic plant with relatively more fatty substance [6-7]. On mining induced subsidence land, the previous terrestrial organic matter transforms into endogenous organic matter with the shift of terrestrial ecosystem into aquatic ecosystem. Consequently, the transformation of organic matter will definitely affect the environmental behavior of pollutants.

At present, many methods have been widely used to describe the physicochemical characteristics of DOM, including 3-dimensional excitation-emission matrix spectra (3DEEMS), UV absorbance (UVA), nuclear magnetic

resonance, etc [8-10]. Compared with other research methods, the 3DEEMS and UVA with the advantages of higher sensitivity, selectivity, larger information content and fewer samples required are used in a wider scale to reveal the component and composition of DOM. Although many researches on organic matters of various sources have been conducted by using 3DEEMS and UVA, there is no report about the changes of organic matter on subsidence land. As the subsidence is the most serious environmental problem in mining area, a study on the change characteristics of organic matters on subsidence land has great significance for pollutants transportation and management in mining area. In view of the above, the paper takes the mining induced subsidence land in Huaibei as the study object. It analyzes the spectroscopy characterization of DOM in soil and sediments of different type subsidence land using 3DEEMS and UVS, and discusses the component and composition of DOM in different types of subsidence land. This will provide the basic data for revealing the change characteristics of DOM on subsidence land and its influence on the environmental behaviors of other pollutants in coal areas.

EXPERIMENTAL SECTION

Sample collection and treatment

The subsidence land locates in a coal mining subsidence land of the floodplain of Huaife River, which is in the north of Anhui province of China. In this area, the groundwater is shallow and the water level varies between 2.45-4.75 m depth with the precipitation. Investigation and sampling were conducted in April, 2012 and 13 sampling sites were uniformly located in different parts of this subsidence land (Figure 1). Three samplings were located in perennial waterlogged zone (PWZ), four in seasonal waterlogged zone (SWZ) and six 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 collected with a depth of 5-10 cm, which had removed the surfer soil and sediment samples of 0-10cm were collected 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.

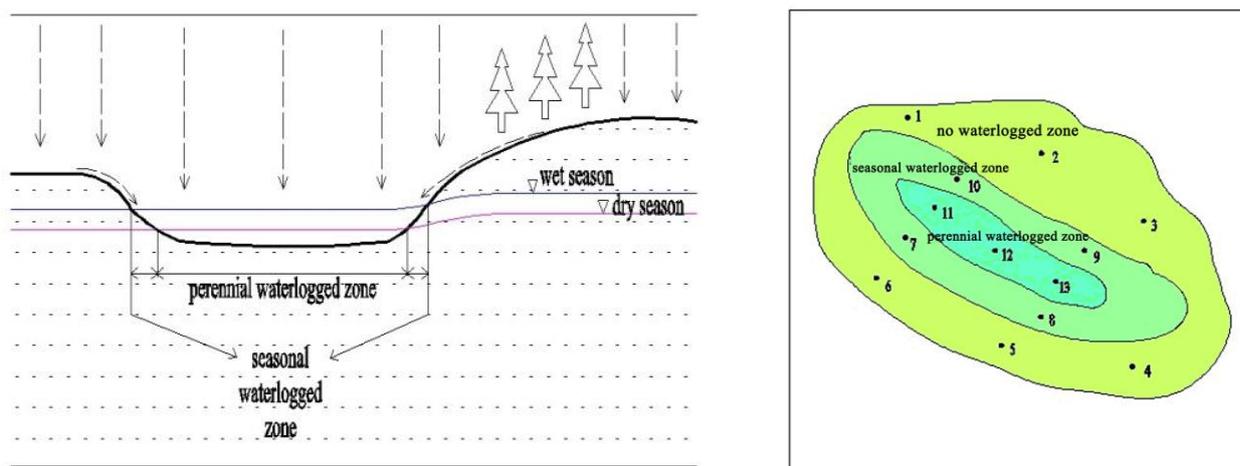


Figure 1: The location of sampling sites

In the laboratory, the samples were air-dried for 3 days and then ground with silica dish. Each ground sample was sieved through 0.5mm nylon sieve and then split into two replicates. The DOM sample in this work was prepared using the soil or sediments. First, the ultra-pure water was added to soil or sediments (water: sediment = 5:1). Then, the suspension was mechanically shaken at 250 r/min for 24h. After shaking, the suspension was centrifuged at 8000 r/min for 10min, and the overlaying solution was filtered through a 0.45 μm Millipore membrane. The extracted solution was DOM.

Analysis and measurement

TOC was tested using TOC analytical instrument (Shimadzu VCPH) with the detection limit of 0.06 mg/L. UV absorbance was measured using UV/VIS spectrophotometer (Shimadzu, UV-2300) with 10cm quartz cell. 3DEEM was analyzed using fluorescence spectra analytical instrument (Hitachi F-4500) with a 150-W Xe arc lamp. Excitation light source: 150W xenon arc light; PMT voltage: 700V; signal-to-noise ratio (SNR)>110; Bandpass: Ex=5nm, Em=5nm; response time was defined automatically; scanning velocity: 1200nm/min; the scan range was 250-550nm for excitation and 200-450nm for emission.

Data manipulation

Each replicate was tested twice for different parameters, thus, all measured data presented in this work were obtained from four replicate measurements. Differences 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 Origin 8.1.

RESULTS AND DISCUSSION

The 3DEEMS characteristics of DOM on different subsidence lands

Through analyzing the 3DEEMS of DOM samplings on different subsidence lands in figure 2, there are mainly two kinds of fluorescence peaks, UV fulvic-like fluorescence peaks (Peak A) and visible fulvic-like fluorescence peaks (Peak C). In addition, some protein-like fluorescence peaks (Peak B) are found in NWZ and SWZ. Generally, Peak A and Peak C show the fluorescence peaks of humic acid and fulvic acid brought by exogenous sources and they are related to the hydroxyl groups and carboxyl groups in fulvic-like and humic composition [11] while Peak B shows the fluorescence peaks of tryptophan caused by biodegradation and it is related to the structure of aromatic amino acid in DOM [12]. So the results imply that when the terrestrial ecosystem changes into aquatic ecosystem, the composition of DOM changes correspondingly and the protein-like matters (peak B) decreases. As is illustrated in Figure 2, the centre of three type peaks is: Peak A: Ex/ Em=250~265/440~445; Peak B; Ex/ Em=270/295; Peak C: Ex/ Em=320~325/415. It can be noticed that there exist little differences between the centre of Peak A and Peak C, that is to say, the humus of DOM in different regions has similar structure and probably the same source. Peak B only exists in NWZ and SWZ but exists in PWZ. In other words, the sediments in PWZ contain little protein-like substance.

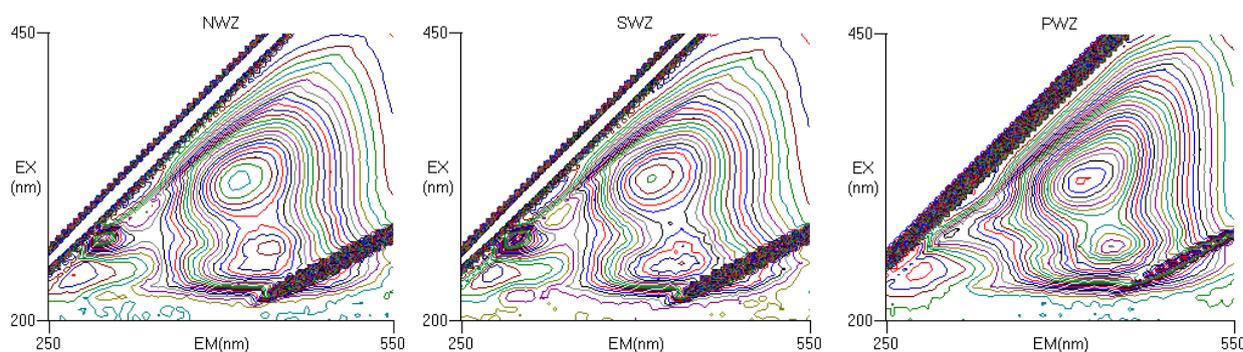


Figure 2: Three-dimensional excitation emission matrix fluorescence spectroscopy of DOM in different subsidence areas

Apart from the analysis of fluorescence peak centers of DOM on different subsidence lands, the peak intensity of DOM was also analyzed. Under the same condition of DOM concentration, the higher peak intensity indicates the more content of this type organic matter. Table 1 shows the distribution characteristics of intensity of different fluorescence peaks. As is illustrated in this table, from NWZ to PWZ, the intensity of Peak A, which indicates the UV fulvic-like substances, increases from 271.5(S.D.=14.56) to 351.7(S.D.=33.26) and the intensity of Peak C, which implies the visible fulvic-like substances, increases from 276.3(S.D.=14.56) to 385.7(S.D.=21.89). Meanwhile, from NWZ to SWZ, the intensity of Peak B decreases from 248.2 (S.D.=31.56) to 216.6(S.D.=24.89) and completely disappears in PWZ. This implies that the protein-like substance decreases when the NWZ changed into PWZ.

Table 1 Characteristic of DOM fluorescence peak intensity in different subsidence areas

	Peak A			Peak B			Peak C		
	Ex	Em	Intensity	Ex	Em	Intensity	Ex	Em	Intensity
NWZ	265	440	271.5±14.56	270	295	208.2±31.56	320	415	266.3±14.56
SWZ	250	440	263.5±21.45	270	295	216.6±24.89	325	415	252.8±33.26
PWZ	265	445	351.7±33.26	-	-	-	325	415	385.7±21.89

The UV characteristics of DOM on different subsidence lands

The characteristic of DOM UV absorption spectrum depends on the complexity rate molecular structure of DOMs [13]. Figure 3 shows the curved line of UV absorption of DOM on different subsidence lands. From NWZ to PWZ, UV absorption strength of DOM keeps increasing within the wavelength of 200nm to 400nm. According to the previous research, with the addition of aromaticity and unsaturated conjugate double bonds of DOM, its UV absorption strength per mole increases [14]. Hence, the curved line and variation trend of UV absorption of DOM on different Subsidence Lands indicate that during the transition from terrestrial ecosystem to aquatic ecosystem, once the mining induced subsidence land comes into being, the aromaticity and degree of unsaturation of humus in DOM will increase with the rising humification, which is consistent with the results obtained by 3DEEMS.

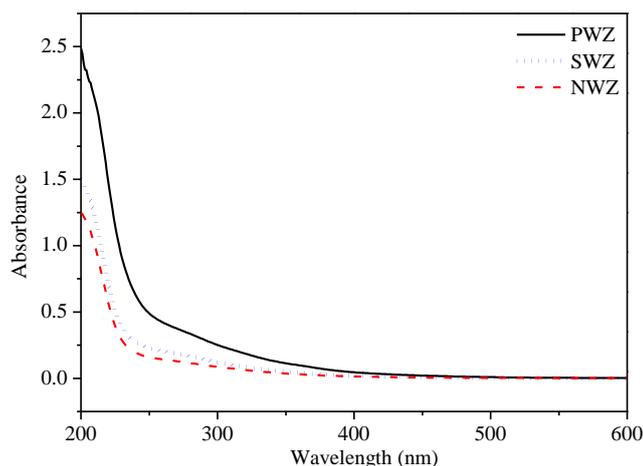


Figure 3: UV absorb curve of DOM in different subsidence areas

The curved line of UV absorption reveals the characteristics of DOM as a whole, and the details of change of DOM can be seen from UV absorption spectra within certain wave bands such as A254 and A280, and the ratio between two absorption strengths at certain wavelength such as A250/A365 and A254/A400. In Table 2, the characteristics of absorption wavelength of DOM in different subsidence lands are listed.

The research conducted by Nishijima *et al.* [15] indicated that at the 254nm wavelength, the absorbance mainly represented the organic matters with unsaturated carbon double bonds including aromatic compounds. With the same DOM concentration, the increasing absorption of 254nm implies the transition of non-humus to humus. During the forming process of subsidence wetland, as is illustrated in Table 2, the UV absorption strength of 254nm keeps rising from 0.152 to 0.457, which explains that the organic matter transforms from non-humus to humus and the aromatic compounds increases.

The absorbance of 280nm generally has a positive correlation with the molecular weight of organic matter. With the greater molecular weight, the absorption value of DOM at the wavelength of 280nm is higher [16]. In Table 2, the A280 shows that as terrestrial soil transforms into water body sediment, the molecular weight of organic matter increases. Generally, with the increase of humification degree or the benzene ring structure, the molecular weight increases correspondingly, so A280 and A254 have the same variation trend. Besides A280 and A254, 250/365 is often used to present the humification degree of DOM [17]. From Table 2, it can be found that the trend of 250/365 changes is similar to the two former UV characteristic parameters. The three characteristic parameter values all together show the increasing humification degree of humus.

Table 2 UV characteristic parameters of DOM in different subsidence areas

	a254	a280	250/365	253/203
NWZ	0.152	0.115	5.71	0.13
SWZ	0.218	0.166	5.87	0.16
PWZ	0.457	0.336	6.11	0.20

Korshin believed that the absorbance ratio of 253nm and 203nm can indicate substituent degree of aromatic ring and the types of substituent groups [18]. When the aliphatic chains in substituent groups of aromatic ring increase, the absorbance ratio decreases, and when the content of hydroxyl groups, carboxyl groups, carbonyl groups and esters in substituent groups of aromatic ring increase, the value increases, too. The value of 253/203 in Table 2 indicates that the aliphatic chains of the organic matter keep reducing from NWZ to PWZ, which may be attributed to easy decomposition of aliphatic chains in benzene ring to functional groups by microorganism in PWZ.

Reason analysis on the transition of DOM during mining subsidence and its environmental significance

From the 3DEEMS and UV characteristic parameters of DOM on different subsidence lands, it can be found that when the subsidence land was formed, the relatively dry terrestrial soil transformed into water body sediment. Correspondingly, the properties of organic matter in soil changed. Protein-like substances of organic matter in previous terrestrial ecosystem started to decrease and the humification degree of humic acid substances became increased. There may be two reasons for such changes. On one hand, as the mining area used to be farmland, the fertilizers used during cultivation usually contain organic fertilizer with organic nitrogen, adding protein-like substances in DOM [19]. However, after the formation of subsidence wetland, the interrupted input of organic

nitrogen results in the decline of protein-like substances in PWZ. On the other hand, due to the long time of immersing in water for sediments in PWZ, microorganism acts actively, degrading many organic matters and consuming easily-deposited protein-like substances [20]. Consequently, the protein-like substances in PWZ is relatively rare.

The organic matter in soil and sediments plays an important role in transporting and transforming heavy metals and other pollutants, which can be considered by the ability of functional groups in organic matter to pollutants. In order to explore the influence of humification degree on the organisms of pollutants, the analysis was made on the correlation between various UV characteristic parameters and the concentration of heavy metals in extracting solution.

Table 3 Correlation between UV characteristic parameters of DOM and heavy metals concentration in different subsidence areas

	Cd	Cr	Cu	Pb	Sb	Zn
a254	0.65(*)	0.56	0.82(**)	0.46	0.75(*)	0.84(**)
a280	0.56	0.67(*)	0.75(**)	0.38	0.63(*)	0.80(**)
250/365	0.82(*)	0.59(*)	0.77(*)	0.31	0.68(*)	0.79(**)
253/203	0.83(*)	0.71(*)	0.82(**)	0.56	0.71(*)	0.83(**)

** Correlation is significant at the 0.01 level (2-tailed); * Correlation is significant at the 0.05 level (2-tailed).

As is illustrated in Table 3, most heavy metals (except Pb) have a significant positive correlation with various UV characteristic parameters, especially for Cu and Zn (except 250/365 and Cu), the significance level was less 0.01. That is to say, with the higher humification degree of DOM, the complex capacity of DOM for metals was strong. During the forming process of subsidence wetland, the humification degree of organic matter increased and the long-chain organic matter was decomposed to hydroxyl groups and carboxyl groups. In general, those functional groups are considered to have strong complex ability for various pollutants [8], so with the higher humification degree, DOM with the same concentration would content more functional groups such hydroxyl groups and carboxyl groups and it will combine more metals. As DOM can exist in the water for a long time in common situation due to its solubility, the soil and sediments with higher humification degree DOM can remove more metals from solid phase to aqueous phase, increasing the risk of metals in aquatic organisms.

CONCLUSION

The results of 3DEEMS reveal that the humic acid substances and the protein-like substances in DOM on different subsidence lands share the same source. However, from NWZ to PWZ, the fluorescence peak of protein-like substances keeps decreasing while the fluorescence peak of humic acid substances keeps increasing, which proves the decreasing content of protein-like substances and the increasing content of humic acid substances in DOM. The characteristics of UV wavelengths also indicate that humification degree of organic matter will be intensified upon the formation of subsidence wetland.

The analysis on the correlation between various UV wavelengths and the concentration of heavy metals demonstrates that the humification degree of DOM can affect the biological effectiveness of heavy metals. The higher the humification degree of organic matter is, the stronger ability of integrating heavy metals will be and the bigger risk of releasing heavy metals from solid phase will take.

Acknowledgments

This study was financially supported by both the Chinese Public Welfare Research Funds for Environmental Protection Industry (201109011) and the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), which we gratefully acknowledge.

REFERENCES

- [1] DX Yao; J Meng; ZG Zhang. *J Coal Sci Eng*, **2010**, 16, 316-319.
- [2] QJ Meng; QY Feng; QQ Wu. *Procedia Earth Plan Sci*, **2009**, 11, 1237-1241.
- [3] SL Gong; C Li; SL Yang. *Environ Geol*, **2009**, 56, 1051-1056.
- [4] JH Park. *Chemosphere*, **2009**, 77, 485-494.
- [5] ML Chen; MP Ren; Y Youhei; J Rudolf. *Appl Geochem*, **2010**, 25, 872-880.
- [6] N Maie; C Yang; T Miyoshi; KJ Parish, R Jaffe. *Limnol Oceanogr*, 2005, 50, 23-35.
- [7] J Hur; G Kim. *Chemosphere*, **2009**, 75, 483-490.
- [8] PQ Fu; FC Wu; CQ Liu; FY Wan. *Appl Geochem*, **2007**, 22, 1668-1679.
- [9] K Maria; K Konstantina; P Ioannis. *J Hazard Mater*, **2009**, 166, 1169-1173.

-
- [10] M Alain; M Anthony. *Geochim Cosmochim Ac*, **2010**, 74, 2556-2580.
[11] FC Wu; E Tanoue. *Environ Sci Technol*, **2001**, 35, 3646-3652.
[12] J Chen; EJ LeBoeuf; S Dai; BH Gu. *Chemosphere*, **2003**, 50, 639-647.
[13] MX Li; XS He; J Liu; BD Xi. *Spectrosc Spect Anal*, **2010**, 30(11), 3081-3085.
[14] J Peuravuori; K Pihlaja. *Environ Inter*, **1997**, 23, 441-451.
[15] W Nishijima; E Gerald; JR Speitel. *Chemosphere*, **2004**, 56, 113-119.
[16] YP Chin; G Aiken; E ÓLoughlin. *Environ Sci Technol*, **1994**, 28, 1853-1858.
[17] LY Wang; FC Wu; RY Zhang. *China Plateau. J Environ Sci*, **2009**, 21, 581-588.
[18] VK Gregory; MB Mark; SS Ronald. *Water Res*, **1997**, 31, 1643-1650.
[19] Y Yan; HB He; Z Bai; HT Xie; XD Zhang. *Chinese J Soil Sci*, **2008**, 39(4), 738-743.
[20] Y Zhang; Y Zhang; T Yu; CM Hu. *Fresen. Environ. Bull*, **2012**, 21, 1118-1126.