Effects of the constructed wetland on dissolved organic matter properties in the drainage channel of domestic sewage treatment plant in winter

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Abstract. As a low investment and low energy consumption wastewater treatment technology, the constructed wetland has been gradually accepted by the world. However, there is still a lack of systematic assessment on the impact of the constructed wetland on dissolved organic matter (DOM) properties in the drainage channel of domestic sewage treatment plant in winter. In this study, 3D excitation-emission matrix fluorescence spectroscopy and ultraviolet spectroscopy were combined to reveal the evolution process of DOM properties in the constructed wetland in winter. The results showed that DOC contributed more than 55% of COD in the drainage channels of Shijiazhuang domestic sewage treatment plant in winter, but the COD was significantly decreased after treated by the constructed wetland, which was mainly caused by the more extensive degradation of elements N, H, S and P in DOM. In addition, water DOM in the constructed wetland in winter was mainly contributed by microorganisms, and humus-like components in water DOM were more easily degraded than protein-like components. And humus-like components gradually transformed into protein-like components in the degradation process, and fulvic-like and humic-like components had the same decomposition fate in the constructed wetland in winter.

1. Introduction
Dissolved organic matter (DOM) is a heterogeneous compound composed of aliphatic and aromatic polymers, and it plays a vital role in aquatic ecosystem. The concentration, composition, structure and redox properties, etc of DOM have direct or indirect effects on biology (such as microbial and plankton ecology[1]), chemical processes (such as the morphology and transport of trace heavy metals[2], the toxicity of polycyclic aromatic hydrocarbons[3]) and physical properties (such as optical properties[4]) of the aquatic environment.

The constructed wetland is a water surface similar to a marsh, which is constructed and operated artificially and integrates the physical, chemical and biological functions of soil, artificial medium,
plants and microorganisms. Due to its unique ecological environment, DOM in water has unique properties and evolution process, and has gradually become a research hotspot at home and abroad. In recent years, there have been some reports on the dynamic process of DOM in constructed wetlands[5-8], but there are still many deficiencies. Firstly, the existing research results are mainly based on the constructed wetland simulation device, but this is not necessarily consistent with the constructed wetland in the field. Secondly, due to the single analysis methods adopted by most researchers, there is still a lack of comprehensive and in-depth understanding of the variation characteristics of the concentration, composition, source and structure of water DOM in the constructed wetland. Thirdly, most of the studies on water DOM in the constructed wetland mainly focus on summer and autumn rather than winter.

Therefore, this paper selected a constructed wetland in the field in Hebei Province as the research area, combined with 3D excitation-emission matrix fluorescence spectroscopy and ultraviolet spectroscopy, systematically studied the evolution law of DOM properties in the constructed wetland in winter, so as to provide scientific basis for further revealing the geochemical behavior and ecological environmental effects of DOM in the constructed wetland in winter.

2. Materials and Methods

2.1. Overview of the study area
The constructed wetland of Xiao River, Hebei was built in June 2013, distributed on both sides of the river crossing bridge of Hengjing highway in Shijiazhuang, which is located in the downstream of the drainage channel of Qiaodong domestic sewage treatment plant. The total length of the constructed wetland is 2 km, and the total area is nearly 400 mu, including nearly 250 mu of vegetation. There are about 20 kinds of aquatic plants in the constructed wetland, mainly including Phragmites communis, Kerria japonica, Jasminum nudiflorum, and Nymphaea tetragona.

2.2. Sample collection and pretreatment
In December 2014, surface water samples were collected from the drainage channel of domestic sewage treatment plant and the constructed wetland of Xiao River, including 2 samples collected in the drainage channel of domestic sewage treatment plant and 6 samples collected in the constructed wetland of Xiao River. Immediately after collection, the samples were filtered by Millipore polycarbonate filter with a pore diameter of 0.45 μm. The organic matter in the filtrate was DOM, which was refrigerated away from light for future use.

2.3. Determination of DOC, COD, NO₂⁻ and Fe²⁺ concentrations
DOC concentration was measured using a TOC analyzer (Multi N/C 2100, Analytik Jena AG), and the instrument standard deviation was less than 2%. COD content was determined by potassium dichromate method (GB/T 11913-1989). The content of NO₂⁻ was determined by ion chromatography (DIONEX-ICS 2000) with instrument standard deviation < 5%. The content of Fe²⁺ was determined by phenanthroline spectrophotometry.

2.4. UV spectrum analysis
Uv-Vis spectrophotometer (UV1700, Shimadzu corporation of Japan) was used for UV spectrum analysis. The scanning wavelength range was 200~400 nm, and the scanning interval was 1 nm. The absorbance value a(254) at 254 nm was determined and divided by the DOC concentration, denoted as SUVA₂₅₄ (L/(m·mg)). The absorbance values a(250) and a(365) at 250 nm and 365 nm were determined, and the ratio of a(250) to a(365) was denoted as E₂/E₃. The area integral was performed for the wavelength range from 240 to 400 nm, and the value was denoted as A₂₄₀₋₄₀₀. The absorption spectral slopes within the wavelength range of 275~295 nm and 350~400 nm were calculated, denoted as S₂₇₅₋₂₉₅ and S₃₅₀₋₄₀₀ respectively.
2.5. Fluorescence spectrum analysis and parallel factor analysis

The fluorescence spectrum was determined by a fluorescence photometer (Hitachi F-7000, Hitachi Company). The excitation light source was 150 W xenon arc lamp, the voltage of photomultiplier was 700 V, the signal-to-noise ratio was > 110, the scanning speed was 12000 nm/min, the slit width of the excitation and emission monochromator was 10 nm, and the response time was automatic. The excitation wavelength (Ex) ranged from 200 to 450 nm with an increment of 5 nm. The emission wavelength (Em) ranged from 280 to 550 nm with an increment of 5 nm. When Ex = 370 nm, the fluorescence intensity ratio of Em at 470 nm and 520 nm was denoted as \( r_{470/520} \). When Ex = 310 nm, the ratio of Em fluorescence intensity at 380 nm to 430 nm was denoted as BIX. When Ex = 254 nm, the integral \( \text{Ex} = 435\text{~}480 \text{~nm} \) / [the integral \( \text{Em} = 300\text{~}345 \text{~nm} \) + the integral \( \text{Em} = 435\text{~}480 \text{~nm} \)] was denoted as HIX. The ratio of the fluorescence peak intensity of fulvic-like components \( \text{EX}/\text{EM} = 230\text{~}265 \text{~nm} / 410\text{~}480 \text{~nm} \) to that of humic-like components \( \text{EX}/\text{EM} = 325\text{~}370 \text{~nm} / 420\text{~}480 \text{~nm} \) was denoted as \( r_{(A,C)} \).

The parallel factor analysis of 3D excitation-emission matrix fluorescence spectroscopy was simulated by MATLAB R2100a software with DOMFluor toolbox, and the specific programming and operation steps were described in literature[9].

3. Results and Discussion

3.1. The concentration and variation characteristics of DOC and COD in water in winter

The water DOC concentration in the drainage channel of the domestic sewage treatment plant and the constructed wetland of Xiao River was distributed between 18 mg/L and 30 mg/L (figure 1), which met the V standard of the surface water quality. The water COD concentration in the drainage channel of the domestic sewage treatment plant and the constructed wetland was distributed between 80 mg/L and 120 mg/L (figure 1), which didn’t meet the surface water environmental quality standard V. The drainage channel of the domestic sewage treatment plant was about 5 km from upstream to downstream, but the concentration of DOC and COD in water did not change significantly (as shown in figure 1), indicating that the organic matter in the water of the river cannot be effectively removed in its natural state. When the tail water of the domestic sewage treatment plant entered the constructed wetland of Xiao River through its drainage channel, the concentration of DOC and COD in water showed a gradually decreasing trend along the flow direction (as shown in figure 1), indicating that the constructed wetland had a certain effect on the removal of organic matter in the tail water of the sewage treatment plant.

![Figure 1. DOC concentration and COD value in waters of the drainage channel of the domestic sewage treatment plant and the constructed wetland of Xiao River](image-url)
Using S1 and S6 as the inlet and outlet of the constructed wetland respectively to estimate the removal effect of the constructed wetland on the organic matter in water, it was found that the reduction rate of DOC and COD concentration in constructed wetland could reach about 12% and 30%, respectively. Obviously, this removal effect was significantly lower than that of subsurface flow constructed wetland for organic matter in water[5], indicating that surface flow constructed wetland had less effect on organic matter removal than subsurface flow constructed wetland.

Organic matter (including C, N, H, S, and P elements) and reducing inorganic matter (including nitrite, sulfide and ferrous iron) in water can all contribute to COD. In this study, no sulfide was detected in all water samples. Therefore, we only converted the contents of DOC, nitrite and ferrous iron into the oxygen required for chemical oxidation, so as to estimate the contribution of these reducing substances to COD, and the difference between COD and the total oxygen required for oxidation of these reducing substances was taken as the contribution of N, H, S and P elements in organic matter to the COD. As shown in figure 2, the water COD in the drainage channels of domestic sewage treatment plant and the constructed wetland was mainly contributed by DOC, and its contribution value was basically above 60%, which was greater than the N, H, S, and P elements in organic matter to COD, while the contribution of nitrite and ferrous iron to COD was very small.

![Figure 2. Contributions of reducing substances to COD in waters](image)

### 3.2. The source of water DOM and the variation characteristics of its composition in winter

Fluorescence index $f_{470/520}$ and biological index (BIX) can be used to characterize the source of DOM in water. When $f_{470/520} > 1.9$, DOM was mainly from its own source; when $f_{470/520} < 1.4$, DOM is mainly terrigenous input[10]. When the BIX value was between 0.6 and 0.7, DOM was mainly terrigenous input or affected by human activities. However, when Bix value was greater than 1, DOM was mainly contributed by microorganisms such as bacteria[11]. In this study, the $f_{470/520}$ and BIX values of DOM in the drainage channel of domestic sewage treatment plant and the constructed wetland of Xiao River were greater than 2.0 and 1.0 respectively (figure 3). It can be seen that the two
indexes jointly indicated that DOM in water was mainly contributed by microorganisms. BIX values decreased significantly from S1 to S2 in the constructed wetland (figure 3), which may be caused by human interference. However, from S2 to S6, the values of $f_{470/520}$ and BIX increased gradually (figure 3), indicating that DOM in water was obviously degraded by microorganisms.

According to PARAFAC model, four fluorescence components of DOM in the drainage channel of sewage treatment plant and the constructed wetland of Xiao River were identified. Among them, C1 (240, 300/380) was tryptophan-like component, C2 (230, 275/340) was tyrosine-like component, C3 (250, 275, 350/410) was fulvic-like component, and C4 (225, 260, 360/450) was humic-like component. The relative content of C1, C2 and C3, C4 components in the upstream to downstream of the drainage channel of the domestic sewage treatment plant showed increasing and decreasing trends respectively (figure 4), indicating the humus-like components in water DOM were more easily degraded than the protein-like components, and the humus-like components gradually transformed into protein-like components during the degradation process. This result was consistent with the view that complex organic matter is not difficult to be degraded and utilized by microorganisms[12]. Except for C1 component, the relative content of other three components in the constructed wetland along the flow direction generally showed the same change trend as that in the drainage channel of domestic sewage treatment plant, but the change trend was not obvious in the upstream area of the constructed wetland (figure 4), which was mainly because the water environment had changed after the tail water entered the constructed wetland through the drainage channel of domestic sewage treatment plant, so the microorganisms needed a process in order to adapt to the new environment or perform replacement. $S_{275-295}$ and $S_{350-400}$ can be used for semi-quantitative analysis of the ratio of fulvic-like and humic-like...
components[13]. It can be seen from figure 5 that the fluctuations of $S_{275-295}$ and $S_{350-400}$ in the drainage channel of the domestic sewage treatment plant and the constructed wetland of Xiao River along the water flow direction were not large, indicating that fulvic-like and humic-like components had a consistent degradation trend, which further confirmed that fulvic-like and humic-like components had the same fate during the decomposition process.

![Figure 4. Percentages of C1, C2, C3 and C4 components in waters DOM of the drainage channel of the domestic sewage treatment plant and the constructed wetland of Xiao River](image)

![Figure 5. Indexs of ultraviolet spectrum for waters DOM in the drainage channel of the domestic sewage treatment plant and the constructed wetland of Xiao River](image)
3.3. The degree of humification of DOM and its structural change characteristics in winter

The degree of humification and its structural change characteristics in winter E2/E3, A240-400, r(A,C) and HIX indicators can be used to characterize the degree of humification and molecular weight of DOM under certain conditions[14-18]. r(A,C) is the ratio of the fluorescence peak intensity of fulvic-like components to that of humic-like components in 3D excitation-emission matrix fluorescence spectroscopy of DOM, which has some relationship to the pH of the solution[17]. However, in this paper there was no significant difference in pH value among all water samples. The pH values of all water samples ranged from 7.13 to 7.45. From above analysis, r(A,C) was mainly used as an indicator to characterize the degree of humification in this paper. In the above four indicators about the humification degree, the value of E2/E3 was inversely proportional to the degree of humification and the molecular weight, besides, the other three indicators were in direct proportion to the degree of humification and the molecular weight. From figure 3 to figure 5, the variation trends of E2/E3, A240-400, r(A,C) and HIX indexes from upstream to downstream of the drainage channel of domestic sewage treatment were inconformity, which indicated that further study needs to carried out to select an index to represent the degree of humification of DOM in water in the drainage channel of domestic sewage treatment. Furthermore, in the constructed wetland, the variations of the four indexes along the water flow direction were not large, indicating that the humification degree of DOM in the constructed wetland does not change significantly. When HIX > 8, the humification characteristics of DOM is significantly[15-16]. However, HIX values of all samples in this paper was less than 8 (figure 3), indicating that DOM had a low degree of humification, which was mainly caused by life activities of microbial and its death decomposition.

The value of SUVA254 was positively correlated with DOM aromaticity degree[19], the value of SUVA254 had declined markedly from upstream to downstream of the drainage channel of domestic sewage treatment (figure 5), which indicated that the aromatic structure of DOM was destroyed in the process of the stream. Nevertheless, the value of SUVA254 showed an increasing trend in the constructed wetland (figure 5), indicating that the constructed wetland environment was conducive to stabilizing the aromatic structure of DOM.

4. Conclusions

The constructed wetland in winter can remove organic matter in water to a certain extent, the rate cutting of the concentration of DOC and COD were 12.0% and 29.6% from the inlet and outlet of the constructed wetland, respectively. 60% COD of the drainage channel of domestic sewage treatment and the constructed wetland of Xiao River origin from DOC, but the reduction of COD value in the constructed wetland was mainly caused by the reduction of N, H, S and P elements, and the contribution rate could reach 65%, and the contribution of the reduction of N, H, S and P elements in organic matter to COD reduction reached 65%.

The DOM of the constructed wetland in winter was mainly contributed by microorganisms, humus-like components in water DOM were more easily degraded than protein-like components. In the degradation process, humus-like components gradually transformed to protein-like components, and the degradation process of the fuli-like acid components and the humin-like acid components were also the same.

Acknowledgments

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References

[1] Maie N, Yamashita Y, Cory R M, Boyer J N, Jaffé R 2012 Appl. Geochem. 27 917-929
[2] Fu P, Wu F, Liu C, Wang F, Li W, Yue L, Guo Q 2007 Appl. Geochem. 22 1668-1679
[3] Diamond S A, Mount D R, Burkhard L P, Ankley G T, Makynen E A, Leonard E N 2000 Environ Toxicol. Chem. 19 1389-1396
[4] Nelson N B, Siegel D A 2013 *Annu. Rev. Mar. Sci.* 5 447-476
[5] Yang C M, Wang M M, Ma R, Li J H 2012 *Spectrosc. Spect. Anal.* 32 708-713
[6] Verhoeven J T A, Meuleman A F M 1999 *Ecol. Eng.* 12 5-12
[7] Mariot M, Dudal Y, Furian S, Sakamoto A, Vallès V, Fort M, Barbiero L 2007 *Sci. Total Environ.* 388 184-193
[8] Hijosa-Valsero M, Sidrach-Cardona R, Martín-Villacorta J, Bécares E 2010 *Chemosphere.* 81 651
[9] Stedmon C A, Bro R 2008 *Limnol. Oceanogr-Meth.* 6 572-579
[10] Mckingt D M, Boyer E W, Westerhoff P K, Doran P T, Kulbe T, Andersen D T 2001 *Limnol. Oceanogr.* 46 38-48
[11] Huguet A, Vacher L, Relexans S 2009 *Org. Geochem.* 40 706-719
[12] Schmidt M W I, Torn M S, Abiven S, Dittmar T, Guggenberger G, Janssens I A, Kleber M, Kögel-Knabner I, Lehmann J, Manning D A C, Nannipieri P, Daniel P, Rasse D P 2011 *Nature* 478 49-56
[13] Careder K L, Steward R G, Harvey G R, Ortner P B 1989 *Limnol. Oceanogr.* 34 68-81
[14] Chin Y P, Aiken G, O'Loughlin E 1994 *Environ. Sci. Technol.* 28 1853-1858
[15] Kimberly P W, Jason C N, George R A 2007 *Ecosystems* 10 1323-1340
[16] Ohno T 2002 *Environ. Sci. Technol.* 36 742-746
[17] Patel-Sorrentino N, Mounier S, Benaim J Y 2002 *Water Res.* 36 2571-2581
[18] Wang L Y, Wu F C, Zhang R Y, Li W, Liao H Q 2009 *J. Environ. Sci-China.* 21 581-588
[19] Shao Z H, He P J, Zhang D Q, Shao L M 2009 *J. Hazard. Mater* 164 1191-1197