Molecular transformation of natural and anthropogenic dissolved organic matter under photo-irradiation in the presence of nano TiO₂

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ABSTRACT

Photochemical transformation of dissolved organic matter (DOM) plays a very important role in the cycling of organic carbon in aquatic systems. Increasing release of photoactive nanoparticles such as titanium dioxide nanoparticles (nano TiO₂) into surface water may impact this process. The present study employed Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) to examine the molecular transformation of natural DOM (peat DOM, DOM_p) and anthropogenic DOM (sludge-derived DOM, DOM_s) under photo-irradiation as affected by nano TiO₂. Differences in molecular components between DOM_p and DOM_s were observed. DOM_s contained more heteroatom formulas (76%) with low aromaticity and low carbon oxidation state than did DOM_p (22%). The presence of nano TiO₂ resulted in significant decreases in both DOM content and molecular diversity under photo-irradiation. Consistent alterations were observed between DOM_p and DOM_s such that high molecular weight compounds, high aromaticity and/or heteroatom S-containing compounds were more easily photodegraded in the presence of nano TiO₂; whereas the average carbon oxidation state decreased in DOM_p but increased in DOM_s, likely due to the significant differences in O abundance, especially in the contents of carboxyl moieties, between DOM_p and DOM_s. The findings of the present study suggest that the release of nano TiO₂ into aquatic environment will accelerate the consumption of dissolved organic carbon and the attenuation of molecular diversity for both DOM in waters.

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1. Introduction

Among the commercially available engineered nanoparticles (NPs), titanium dioxide nanoparticles (nano TiO₂) are the most widely used engineered nanomaterials to date (Troester et al., 2016). Nano TiO₂ materials have been produced on a large scale for applications in pigments, coatings, and sunscreen cosmetic additives, as well as environmental applications such as removal of various contaminants in water, air and soils by adsorption and/or photo-catalytic degradation (Lee and Choi, 2002; Luo et al., 2010; Pena et al., 2006; Zhang et al., 2007). As a result, the release of nano TiO₂ into the environment is unavoidable, particularly into waters, and the amount will continue to increase (Klaine et al.,

2008; Nowack and Bucheli, 2007). Therefore, the contents of nano TiO₂ in waters are expected to be much higher than other engineered nanoparticles (Gottschalk et al., 2010, 2009). Model studies have predicted that the production of nano-TiO₂ would exceed 2.5 million tons per year by 2025 (Robichaud et al., 2009). Once released into waters, nano TiO₂ will interact with dissolved organic matter (DOM), which universally exists in natural water. In the past few years, many researchers have demonstrated that DOM plays a critical role in the stability and mobility of NPs, including nano TiO₂, in aquatic environments (Domingos et al., 2009; Aiken et al., 2011; Zhu et al., 2014; Adam et al., 2016). These studies have demonstrated that the bond of DOM on nano TiO₂ will significantly reduce the aggregation of nanoparticles in aqueous systems. Therefore, the presence of DOM will not only enhance the mobility but also impact the distribution of nano TiO₂ in waters.

Another important fact is that TiO₂ is a photoactive nanomaterial. Studies have demonstrated that TiO₂-based photocatalytic oxidation can induce the destruction of natural organic

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matters (Eggins et al., 1997; Li et al., 2002; Liu et al., 2008a, 2008b; Wiszniowski et al., 2003). Most of these studies attempted to monitor the changes in concentration and spectral features of dissolved organic carbon (DOC) in waters in the presence of nano TiO₂. Some investigated the changes in the molecular weight and hydrophobic fractions of DOM by using size exclusion chromatography (SEC) and resin fractionation (Liu et al., 2008a, 2008b; Wu et al., 2016). However, these analytical techniques failed to clarify the photocatalytic transformation of DOM at the molecular scale. The great advance in high-resolution mass spectroscopy technique namely electrospray ionization coupled with Fourier transform ion cyclotron resonance mass spectrometry (ESI-FT-ICR-MS) provided the unique opportunity to detect thousands of individual molecules in DOM (Kim et al., 2003), which has greatly improved our understanding of the chemical features of DOM at the molecular level (Reemtsma, 2009; Minor et al., 2014), although it has difficulties with quantitative analysis. Recently, FT-ICR-MS has been used to investigate the molecular transformation of river and ocean DOM induced by sunlight irradiation (Gonsior et al., 2009; Stubbins et al., 2010). The molecular characteristics of photo-resistant, photolabile and photo-produced fractions in Congo River DOM were described by Stubbins et al. (2010).

Characterization of anthropogenic DOM such as the ones derived from wastewater, sewage or farm wastes etc (Meng et al., 2013), at the molecular level using FT-ICR-MS has been very limited (Gonsior et al., 2011; Li et al., 2015; Tseng et al., 2013). In a previous research using FT-ICR-MS, Gonsior et al. (2011) found that DOM in effluent displayed a much more complex molecular diversity than the ones in natural water, notably the presence of an unexpected amount of sulfur-containing molecular formulas. Li et al. (2015) used FT-ICR-MS to further investigate the molecular transformation of DOM in refinery wastewater from water treatment processes. However, clarification of molecular transformation in wastewater- and sludge-derived DOM induced by photochemical or other biogeochemical process has not been achieved.

Sludge is an important sink of engineered nanoparticles. Previous studies have revealed that TiO₂ accumulates in dry sludge at concentrations ranging from 1 to 6 g Ti/kg (Kiser et al., 2009; Gottschalk and Nowack, 2011). Furthermore, organic matters are also prone to sequestration in sludge. As a result, the coexistence of nano TiO₂ and sludge-derived DOM is widespread. The aim of the present study was to investigate the molecular transformations of natural and anthropogenic DOM under photo-irradiation in the presence of nano TiO₂ using ESI-FT-ICR-MS. The results will extend our understanding of the environmental and ecological risk of photoactive nanomaterials such as nano TiO₂ as well as the fate of DOM in the environment.

2. Materials and methods

2.1. Peat and sewage sludge dissolved organic matter

Water-extractable organic matter extracted from a commercially available fen peat (Klasmann, Germany) was selected as the representative of natural DOM (peat DOM, DOM_p), and water-extractable organic matter extracted from sewage sludge (sludge-derived DOM, DOM_s) generated in a wastewater treatment plant in Beijing was selected as the representative of anthropogenic DOM. Briefly, the DOM was extracted by shaking dry peat or sewage sludge with ultrapure water at a ratio of 1:10 for 24 h at room temperature. The leachate was obtained by centrifugation of the above peat or sewage sludge suspensions at 5000 rpm and filtered through 0.22-μm Nylon filters. The extraction procedure was repeated three times. The final DOM_p and DOM_s solutions were kept in the dark at 4 °C until further use.

Structural characteristics and carbon-functional-group contents in DOM_p and DOM_s were measured with solid-state ¹³C NMR using cross-polarization and magic angle spinning (CP/MAS) techniques. Spectra were recorded on a 400 MHz NMR Unity Inova Varian spectrometer using the same method as a previous study (Rodriguez-Zuniga et al., 2008).

2.2. Photochemical experiment

A typical photochemical experimental procedure was adopted in this study. Aqueous solutions of DOM, set at 40 mg L⁻¹ TOC, higher than their normal environmental levels, and commercial-grade TiO₂ (Aeroxide P25, 80% anatase and 20% rutile, 100 mg L⁻¹) were put into a 250-mL glass-lined vessel under constant stirring. The pH of the suspension was adjusted to 7.0 using diluted HCl (0.1 M) and then equilibrated in the dark under stirring for 2 h before illumination. The extent of DOM adsorption onto nano-TiO₂ was found to be insignificant in the dark control (about 1.2% of DOC adsorbed) due to the low ratio of nano-TiO₂ to DOC loaded. Simulated solar irradiation experiments were performed in a CEL-APR photochemical reactor (Cealight, Beijing, China) equipped with a 300 W xenon lamp placed in a quartz cooling well. An AM 1.5 filter was used to best match the total solar spectrum, with average illuminance of about 1.2 × 10⁵ lux. Dark control samples were processed under the same conditions except for photo-irradiation. At given time intervals, a certain amount of suspension solution was collected, centrifuged and filtered through pre-rinsed 0.22 μm Nylon membranes, and the filtered supernatants were used for further analysis. The absorbance spectra of the filtered supernatants from 200–650 were determined using a Shimadzu UV-2600 UV–vis spectrometer. All batch experiments were conducted in triplicate.

2.3. ESI-FT-ICR-MS analysis

Selected samples before and after photo-irradiation were further analyzed by ESI-FT-ICR-MS. Sample entrapment and desalination were performed on all the samples by solid phase extraction (SPE) according to Dittmar et al. (2008) using Varian Bond Elute PPL cartridges (500 mg/6 mL). Briefly, the cartridges were rinsed with 6 mL of methanol (MS grade) and pure water respectively prior to use. The samples were acidified to pH 2 with HCl (32%, ultrapure), and then passed through the cartridges by gravity at a flow rate of approximately 2 mL min⁻¹. Cartridges were rinsed with three volumes of 0.01 M HCl for the removal of salts, dried with a stream of N₂ and immediately extracted with three volumes of methanol (MS grade). Eluted samples were blow-dried with N₂ and kept in the dark at –20 °C. The extraction efficiencies of DOM_p and DOM_s by PPL-based SPE were about 72% and 61% according to their TOC recoveries, respectively. Some highly hydrophilic compounds such as carbohydrates and proteins may be lost during SPE (Riedel et al., 2012); therefore, the identified DOM is actually SPE-DOM. These dried samples were dissolved in 50:50 methanol/water (v/v) for ultrahigh resolution mass spectrometry analysis. Ultrahigh resolution mass spectra were acquired using a Bruker Solarix FT-ICR-MS equipped with a 15.0 T superconducting magnet and an ESI irradiation ion source under the same conditions as the previous report (Cao et al., 2015; Lv et al., 2016).

2.4. Molecular formula assignment

All possible formulas were identified with Bruker Data Analysis software based on the requirement that the mass error for a given chemical formula between measured mass and calculated mass was ≤0.5 ppm. Molecular formulas were assigned to peaks with a

signal-to-noise ratio (S/N) ≥ 6 , according to stringent criteria with elemental combinations of $C_5-60H_{10-120}O_{0-40}N_{0-2}S_{0-2}$. The elemental ratios of $H/C < 2.4$ and $O/C < 1.2$ were used as further restrictions for formula calculation. The following parameters for data analysis were calculated according to previous reports (Hughey et al., 2001; Kellerman et al., 2014; Kim et al., 2003; Koch and Dittmar 2006, Stenson et al., 2003): H/C ratio and O/C ratio, parameters for constructing the van Krevelen diagram (Kim et al., 2003); Kendrick mass (KM) and Kendrick mass defect (KMD) in order to identify CH_2 -homologous molecular formula series (Hughey et al., 2001); and double-bond equivalence (DBE), a measure of the number of double bonds and rings in a molecule (Stenson et al., 2003). The aromaticity index was calculated from formulas according to Koch and Dittmar to estimate the fraction of aromatic and condensed aromatic structures (Koch and Dittmar 2006). Furthermore, four compound groups were delineated by aromaticity index (AI) and H/C cutoffs according to Kellerman et al. (2014): combustion-derived condensed polycyclic aromatics ($AI > 0.66$), vascular plant-derived polyphenols ($0.66 > AI > 0.5$), highly unsaturated and phenolic compounds ($AI \leq 0.50$ and $H/C < 1.5$), and aliphatic compounds ($2.0 \geq H/C > 1.5$).

3. Results and discussion

3.1. Molecular diversity of DOM_p and DOM_s

The molecular characteristics of the initial DOM_p and DOM_s were determined by negative ion ESI-FT-ICR-MS (Fig. 1A–E) and ^{13}C NMR (Fig. 1F). There were 2253 $C_5H_6O_6N_n$ molecular formulas and 2520 $C_5H_6O_6N_nS_s$ molecular formulas ($S/N \geq 6$, in the mass range 200–700 Da) identified in the initial DOM_p and DOM_s , respectively, after quality assurance filtering by ESI-FT-ICR-MS analysis. Considering the remarkably low S content (about 0.45%), the S-containing molecular formulas were not included in the DOM_p . We can see from Fig. 1 that DOM_s contained less CHO formulas (24% for

DOM_s vs 78% for DOM_p) and more heteroatom formulas (76% for DOM_s vs 22% for DOM_p) than did DOM_p , which were likely ascribable to the contributions of microbial and anthropogenic discharge sources (Michael-Kordatou et al., 2015). The mass spectra showed an irregular distribution of masses in DOM_s compared with those of DOM_p . The intense peaks in the spectra for DOM_s were associated with CHOS formulas. The identified formulas of the most intense peaks in DOM_s corresponded to linear alkyl benzene sulfonates (LAS), which have been found in wastewater at high concentrations, and were also consistent with the molecular characterization of DOM in effluent reported by Gonsior et al. (2011). Magnitude-weighted average formulas of DOM_s contained lower numbers of C and O atoms but higher numbers of H, N and S atoms with higher H/C , lower degree of unsaturation (DBE) and lower O/C than DOM_p (Table S1). The van Krevelen diagram is often used to provide a visual graphic display of compound distribution (Kim et al., 2003). Combining the aromaticity index (AI_{mod}) and H/C , all the identified molecules are divided into four groups according to their location in the van Krevelen diagram (Koch and Dittmar 2006), i.e., condensed polycyclic aromatics (group 1), polyphenols (group 2), highly unsaturated and phenolic compounds (group 3) and aliphatic compounds (group 4) as shown in Fig. 1C–E. The most abundant compounds in DOM_p and DOM_s were located in group 3 (69.8% and 60.4% for DOM_p and DOM_s , respectively); while the second-most abundant compounds were polyphenols (group 2, 21.9%) in DOM_p and aliphatic compounds (group 4, 30.7%) in DOM_s , respectively, which displayed a remarkable difference between DOM_p and DOM_s . The large amounts of aliphatic compounds in DOM_s were likely ascribed to the contributions from anthropogenic discharges such as surfactants, fatty acids and their biodegradation products (Gonsior et al., 2011), as well as lipids produced by aerobic micro-organisms (Angerbaumer et al., 2008). The low abundance of polyphenol compounds in DOM_s was likely due to their strong affinity to solids and the high reactivity of phenol groups, which were preferentially removed and

Fig. 1. Negative ESI-FT-ICR mass spectra of DOM_p (A) and DOM_s (B), pie charts indicate the number distribution of the CHO, CHON, CHOS, and CHONS molecular formulas; van Krevelen diagrams of identified formulas in DOM_p (C) and DOM_s (D), color bar represents the aromaticity index, four groups in van Krevelen diagram are delineated by AI_{mod} and H/C cutoffs; E is the percentage of compounds in each group for DOM_p and DOM_s ; F is solid state ^{13}C NMR spectra of DOM_p and DOM_s . (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

degraded during water treatment processes (Bruno et al., 2002; Lara-Martin et al., 2010; Li et al., 2015). In addition, there were more condensed polycyclic aromatics (group 1) in DOM_p (4.7%) than in DOM_s (1.4%). Solid ¹³C NMR analysis has frequently been used to quantify the relative distributions of C functional groups, especially for aromatic and aliphatic C in DOM, and was therefore conducted on DOM_s and DOM_p. The results (Fig. 1F and Table S2) show the relative distributions, with more aromatic C (18.8% vs 4.0%) and less aliphatic C (17.2% vs 33.4%) in DOM_p than DOM_s, consistent with the results showing the higher molecular abundance distribution of groups 1 and 2 (rich in aromatic C) and lower molecular abundance distribution of group 4 (rich in alkyl C) in DOM_p than DOM_s, obtained from the van Krevelen diagram.

3.2. Photo-bleaching and photo-mineralization of DOM affected by TiO₂

Photo-bleaching is caused by the degradation of aromatic and conjugated compounds that have strong light absorbance (Gonsior et al., 2009; Sharpless et al., 2014), while photo-mineralization is due to the complete photooxidation of DOM compounds to CO₂ (Ward and Cory, 2016). Fig. 2A and B shows that 98.7% of DOM_p and 93.8% of DOM_s were photo-bleached (quantified by the loss of UV₂₅₄), while only 75.3% of DOM_p and 66.8% of DOM_s were photo-mineralized (quantified by the loss of TOC) after 12 h of photo-irradiation in the presence of nano TiO₂. However, control groups without nano TiO₂ displayed insignificant changes of TOC and UV–Vis absorbance, indicating negligible photo-degradation of DOM in the absence of nano TiO₂. The observed higher percentage of UV₂₅₄ removal than that of TOC removal indicated that destruction of compounds containing chromophore groups in DOM was easier than the mineralization of DOM, and showed the presence of refractory compounds, either present in the beginning or generated during the photo-degradation (Rodriguez-Zuniga et al., 2008). Similar results were obtained by previous studies on the degradation of DOM by TiO₂ photocatalytic oxidation (Liu et al., 2008a, 2008b). In order to further investigate the molecular characteristics of DOM after photo-irradiation, results obtained from ESI-FT-ICR-MS analysis were used to explain the transformation of the individual molecules in DOM during photo-irradiation.

3.3. Photochemically induced alteration in chemodiversity of DOM

The van Krevelen diagrams of all molecules in DOM_p and DOM_s during photo-irradiation are displayed in Figs. S1 and S2. It seems quite clear that the chemodiversities of DOM_p and DOM_s were

attenuated after photo-irradiation. Fig. 3A shows the decrements of CHO and CHON molecules in DOM_p as a function of photo-irradiation time. The number of identified molecules decreased significantly with the increase of photo-irradiation time. At the end of 12 h, about 52.7% of CHO and 47.3% of CHON molecules were degraded in solution compared to the initial DOM_p. Much stronger reduction in molecular diversity was observed for DOM_s than for DOM_p. About 82.1% of CHO and 84.8% of CHON molecules were degraded in solution compared with molecules in the initial DOM_s. CHONS molecules and especially CHOS molecules, which had high intensities, were almost completely degraded at the end of 12 h (Fig. 3B), implying that S-containing compounds in DOM_s were easily degraded by TiO₂ photocatalytic oxidation.

Fig. 3C and D further display the alteration of molecular components of compounds in DOM_p and DOM_s, respectively. Fig. 3B shows that the proportion of condensed polycyclic aromatics and polyphenols (compounds in group 1 and 2) in DOM_p decreased drastically (from 4.7% to 0% for group 1 and from 21.9% to 1.7% for group 2) within 12 h photo-irradiation, while the proportion of highly unsaturated and phenolic compounds (compounds in group 3) and aliphatic compounds (compounds in group 4) in DOM_p increased (from 69.8% to 88.1% for group 3 and from 3.6% to 10.2% for group 4, respectively). The decreases in the compounds in groups 1 and 2 after photo-irradiation indicated that condensed polycyclic aromatics and polyphenols were more prone to photocatalytic transformation, which is in agreement with the UV–vis absorbance results, since the compounds degraded during photo-irradiation were the condensed polycyclic aromatics and polyphenols that had strong UV absorbance. Similar alterations were observed in Congo River DOM after 57 days of solar radiation, which indicated that aromatic compounds were the most photolabile, while aliphatic compounds dominated the photoproduct DOM (Stubbs et al., 2010). Similar to DOM_p, the condensed polycyclic aromatics and polyphenols in DOM_s (1.4% for group 1 and 7.5% for group 2, respectively) were degraded completely within 12 h of photo-irradiation, while the proportion of highly unsaturated and phenolic compounds in DOM_s (compounds in group 3) increased from 60.4% to 87.9% (Fig. 3D). In contrast to DOM_p, the proportion of aliphatic compounds (compounds in group 4) in DOM_s decreased from 30.7% to 12.1%, mainly due to the high amount of CHOS compounds in DOM_s. Sixty-five percent of CHOS compounds in DOM_s were aliphatics according to the classification based on the van Krevelen diagram mentioned above, however almost all of them were degraded after 12 h of photocatalytic degradation.

Fig. 2. Decreases in DOC and UV₂₅₄ during TiO₂ photocatalytic transformation of DOM_p (A) and DOM_s (B) in the presence and absence of TiO₂.

Fig. 3. The relative ratio (F.No./F.No.₀) of formulas in DOM after photo-irradiation to the ones in the initial DOM_p (A) and DOM_s (B); and the percentage of formulas in four groups in DOM_p (C) and DOM_s (D) after photo-irradiation.

3.4. Photochemical alteration of molecular characteristics of DOM

Figs. 4 and 5 further display the detailed molecular transformation of compounds in DOM_p and DOM_s during photo-irradiation. The percentage of high-molecular-weight compounds decreased, while that of low-molecular-weight compounds increased during photo-irradiation for both DOM_p and DOM_s, although almost all the CHOS and CHONS compounds in DOM_s disappeared after 12 h of photocatalytic transformation (Figs. 4A, E and 5 A, E, I and M). This alteration of molecular weight was in agreement with the results obtained by Stubbins et al. (2010). Previous study using SEC to fractionate DOM indicated that TiO₂ photocatalytic oxidation preferentially degraded the high-molecular-weight fractions of DOM (Liu et al., 2008b). Similar

results were also obtained by the photochemical alteration of DOM without catalyst using SEC (Brinkmann et al., 2003; Lou and Xie, 2006). However, it is necessary to note that what are detected by SEC are actually the weights of molecular clusters but not of single molecules. Therefore, the molecular weight detected by SEC is much larger than that detected by FT-ICR-MS in this study. Reduction of high-molecular-weight fractions of DOM detected by SEC is more likely ascribed to the breakdown of molecular clusters induced by photo degradation.

Besides the consistent alteration of molecular weight, extensive alterations in molecular characteristics of DOM_p and DOM_s were further observed after TiO₂ photocatalytic transformation. First, the alterations of molecular weight, H/C, O/C, $\overline{OS}_C$ and DBE of CHON compounds in DOM_p during photo-irradiation were consistent

Fig. 4. Relative abundances of m/z (A, E), H/C (B, F) and $\overline{OS}_C$ (C, G), and DBE (D, H) of CHO and CHON compounds in DOM_p before and after photo-irradiation for a period of time.

Fig. 5. Relative abundances of m/z (A, E, I, M), H/C (B, F, J, N) and $\overline{OS}_C$ (C, G, K, O) ratios, and DBE (D, H, L, P) of CHO, CHON, CHON and CHONS compounds in DOM_s before and after photo-irradiation for a period of time.

with those of CHO compounds (Fig. 4), which indicated that the influence of heteroatom N on the photocatalytic transformation of DOM_p was insignificant. In particular, as shown in Fig. 4B and F, the H/C ratio of CHO and CHON compounds in DOM_p increased, while the DBE values of CHO and CHON compounds decreased with the increase of photo-irradiation time, which implied that the carbon unsaturation degree in compounds was decreased by TiO_2 photocatalytic transformation. The decrease in carbon unsaturation degree may be caused by cleavage reactions of rings or double bonds, as supported by the observation of the attenuation of compounds such as condensed polycyclic aromatics and polyphenols during photo-irradiation as mentioned above (Fig. 3). The oxidation state of carbon ($\overline{OS}_C$) is defined as the charge a carbon atom would take if it were to lose all electrons in bonds with more electronegative atoms, but gain all electrons in bonds with less electronegative atoms (Kroll et al., 2011). The electronegativity of atoms follows the order $O > C > H$, in which a $C=O$ double bond (such as carboxyl and carbonyl groups) contributes +2 $\overline{OS}_C$, and a $C-O$ single bond (such as alcohol and ether groups) contributes +1 $\overline{OS}_C$, while a $C-H$ bond contributes -1 $\overline{OS}_C$, respectively. As shown in Fig. 4C and G, the average carbon oxidation state ($\overline{OS}_C$) of CHO and CHON compounds in DOM_p decreased with the increase of photo-irradiation time, which implied that compounds with high $\overline{OS}_C$, especially those containing a $C=O$ double bond, were preferentially degraded during TiO_2 photocatalytic oxidation, for example, by decarboxylation, and transformed to the final product CO_2 . As a result, about

75% of the total organic carbon of DOM_p was reduced. However, insignificant decrease of the O/C ratio of compounds in DOM_p was observed during photo-irradiation (Fig. S3), which indicated the generation of newly formed oxygen-containing groups by TiO_2 photocatalytic oxidation. For example, some compounds with very high O/C and H/C ratios (distributed at the upper right of van Krevelen diagrams), mainly grouped as oxidized polysaccharides, were produced (Fig. S5). The photo-resistant compounds after 12 h photo-irradiation were mainly those with formulas containing high H/C and lower $\overline{OS}_C$, DBE and MW. Because photocatalytic oxidation induced obvious decarboxylation of compounds, the O-containing groups in photo-resistant compounds were thought to be dominated by hydroxyl and ether groups.

As shown in Fig. 5, the H/C ratio of CHO and CHOS compounds in DOM_s decreased, while it increased for the CHON and CHONS compounds with the increase of photo-irradiation time. The DBE value for CHON and CHONS compounds decreased with the increase of photo-irradiation time, although within a narrow range of DBE value, while little change was observed for the average DBE value of CHO and CHOS compounds. Completely opposite to DOM_p , the $\overline{OS}_C$ of CHO, CHON, CHOS and CHONS compounds in DOM_s increased with the increase of photo-irradiation time, and consistent changes were observed for the O/C of all the compounds (shown in Fig. S3). In summary, alterations in molecular characteristics were consistent for CHO and CHOS compounds and were opposite for CHON and CHONS compounds in DOM_s , which was

different from the molecular transformations of DOM_p. Compared to DOM_p, DOM_s contained less aromatic C and more aliphatic C (as shown by the higher H/C_w and lower DBE_w in Table S1, and ¹³C NMR results in Table S2) with lower oxidation degree (indicated by the lower O/C_w and $\overline{OS}_{Cw}$ in Table S1). Furthermore, the low O/C_w and negative $\overline{OS}_{Cw}$ of compounds in DOM_s implied they contained fewer oxygenic groups, especially carbonyl and/or carboxylic groups, than compounds in DOM_p, which was further confirmed by ¹³C NMR as shown in Table S2. Therefore, direct decarboxylation induced by TiO₂ photocatalytic oxidation of compounds in DOM_s was limited. Instead, unstable moieties such as unsaturated double bonds and alkyl side chains were likely to be oxidized by TiO₂ photocatalytic transformation, resulting in the increase of the O/C_w and $\overline{OS}_{Cw}$ of compounds (Tran et al., 2006).

4. Conclusions

In the present study, ESI-FT-ICR-MS was employed to determine the molecular transformations of peat-derived DOM (DOM_p, a representative of natural DOM) and sludge-derived DOM (DOM_s, a representative of anthropogenic DOM) under photo-irradiation as affected by nano TiO₂. The results indicated that DOM_p and DOM_s had very different chemical and molecular composition. DOM_s contained more heteroatom formulas with lower aromaticity, higher aliphaticity and lower carbon oxidation state than did DOM_p. In the presence of nano TiO₂, photo-irradiation enhanced the consumption of DOC and remarkably reduced the molecular diversity of DOM within several hours. Compounds with high molecular weight and/or aromaticity moieties and/or low O/C ratio were preferentially degraded by TiO₂ photocatalysis in both DOM_p and DOM_s, while some oxidized molecules with low aromaticity were produced. The heteroatom N in compounds had little or no influence on the photocatalytic transformation of both kinds of DOM, while heteroatom S-containing compounds in DOM_s (CHOS and CHONS compounds) were degraded more easily than CHO and CHON compounds. Comparing the two DOM, the average carbon oxidation state was reduced in DOM_p but increased in DOM_s, likely due to the different O abundance in the two types of DOM, especially the contents of carboxyl moieties in compounds in the two DOM. The present study revealed the influences of photoactive nanomaterials such as nano TiO₂ on the molecular transformation of DOM. Such effects are beneficial for the removal of anthropogenic DOM, but they will attenuate the molecular diversity of natural DOM in waters. Considering the fact that more and more photoactive nanoparticles will be released into waters, more attention should be paid to their subsequent impacts on the photocatalytic transformation of DOM in aquatic systems. Particularly, further research is needed to address this issue at environmentally relevant concentrations and conditions, and field studies are highly encouraged.

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Appendix B. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2017.08.051>.

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