Molecular transformation of natural and anthropogenic dissolved organic matter under photo-irradiation in the presence of nano TiO$_2$

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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 TiO$_2$) 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 TiO$_2$. 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 TiO$_2$ 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 TiO$_2$; 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 TiO$_2$ 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 TiO$_2$) are the most widely used engineered nanomaterials to date (Troester et al., 2016). Nano TiO$_2$ 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 TiO$_2$ 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 TiO$_2$ 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-TiO$_2$ would exceed 2.5 million tons per year by 2025 (Robichaud et al., 2009). Once released into waters, nano TiO$_2$ 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 TiO$_2$, 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 TiO$_2$ 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 TiO$_2$ in waters.

Another important fact is that TiO$_2$ is a photoactive nanomaterial. Studies have demonstrated that TiO$_2$-based photocatalytic oxidation can induce the destruction of natural organic
Structural characteristics and carbon-functional-group contents in DOMₚ and DOMₘ 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 (Ceaulight, 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 acidic 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 DOMₚ and DOMₘ 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) $\geq 6$, according to stringent criteria with elemental combinations of $C_5=60\ H_{10}=120\ O_{10}=40\ N_0=2\ S_0=2$. 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 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$_{60}$H$_{10}$O$_{10}$N$_0$S$_0$ molecular formulas and 2520 C$_{50}$H$_{50}$O$_{50}$N$_0$S$_0$ 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 (Al$_{mod}$) 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$_s$ and DOM$_p$ 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$_s$ and DOM$_p$. The large amounts of aliphatic compounds in DOM$_s$ were likely due to the strong affinity to solids and the high reactivity of phenol groups, which were preferentially removed and
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 DOMp (4.7%) than in DOMs (1.4%). Solid \(^1\)C 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 DOMs and DOMp. 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 DOMs than DOMp, 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 DOMp than DOMs, obtained from the van Krevelen diagram.

3.2. Photo-bleaching and photo-mineralization of DOM affected by TiO\(_2\)

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 CO\(_2\) (Ward and Cory, 2016). Fig. 2A and B shows that 98.7% of DOMp and 99.8% of DOMs were photo-bleached (quantified by the loss of UV\(_{254}\)), while only 75.3% of DOMp and 66.8% of DOMs were photo-mineralized (quantified by the loss of TOC) after 12 h of photo-irradiation in the presence of nano TiO\(_2\). However, control groups without nano TiO\(_2\) displayed insignificant changes of TOC and UV−Vis absorbance, indicating negligible photo-degradation of DOM in the absence of nano TiO\(_2\). The observed higher percentage of UV\(_{254}\) 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 TiO\(_2\) 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 DOMp and DOMs during photo-irradiation are displayed in Figs. S1 and S2. It seems quite clear that the chemodiversities of DOMp and DOMs were attenuated after photo-irradiation. Fig. 3A shows the decrements of CHO and CHON molecules in DOMp 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 DOMp. Much stronger reduction in molecular diversity was observed for DOM, than for DOMp. About 82.1% of CHO and 84.8% of CHON molecules were degraded in solution compared with molecules in the initial DOMp. 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 DOMs were easily degraded by TiO\(_2\) photocatalytic oxidation.

Fig. 3C and D further display the alteration of molecular components of compounds in DOMp and DOMs, respectively. Fig. 3B shows that the proportion of condensed polycyclic aromatics and polyphenols (compounds in group 1 and 2) in DOMp 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 DOMp 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 photoproduced DOM (Stubbins et al., 2010). Similar to DOMp, the condensed polycyclic aromatics and polyphenols in DOMs (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 DOMs (compounds in group 3) increased from 60.4% to 87.9% (Fig. 3D). In contrast to DOMp, the proportion of aliphatic compounds (compounds in group 4) in DOMs decreased from 30.7% to 12.1%, mainly due to the high amount of CHOS compounds in DOMs. Sixty-five percent of CHOS compounds in DOMs 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 UV\(_{254}\) during TiO\(_2\) photocatalytic transformation of DOMp (A) and DOMs (B) in the presence and absence of TiO\(_2\).](image-url)
3.4. Photochemical alteration of molecular characteristics of DOM

Figs. 4 and 5 further display the detailed molecular transformation of compounds in DOMp and DOMs during photo-irradiation. The percentage of high-molecular-weight compounds decreased, while that of low-molecular-weight compounds increased during photo-irradiation for both DOMp and DOMs, although almost all the CHOS and CHONS compounds in DOMs disappeared after 12 h of photocatalytic transformation (Figs. 4A, E and 5A, 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 DOMp and DOMs were further observed after TiO2 photocatalytic transformation. First, the alterations of molecular weight, H/C, O/C, OSC and DBE of CHON compounds in DOMp during photo-irradiation were consistent

Fig. 3. The relative ratio (FNo/FeNoo) of formulas in DOM after photo-irradiation to the ones in the initial DOMp (A) and DOMs (B); and the percentage of formulas in four groups in DOMp (C) and DOMs (D) after photo-irradiation.

Fig. 4. Relative abundances of m/z (A, E), H/C (B, F) and \( \delta^{13} \)C (C, G), and DBE (D, H) of CHO and CHON compounds in DOMp 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 DOMp was insignificant. In particular, as shown in Fig. 4B and F, the H/C ratio of CHO and CHON compounds in DOMp 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 TiO₂ 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 (OSC) 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 OSC, and a C=O single bond (such as alcohol and ether groups) contributes +1 OSC, while a C−H bond contributes −1 OSC, respectively. As shown in Fig. 4C and G, the average carbon oxidation state (OSC) of CHO and CHON compounds in DOMp decreased with the increase of photo-irradiation time, which implied that compounds with high OSC, especially those containing a C=O double bond, were preferentially degraded during TiO₂ photocatalytic oxidation, for example, by decarboxylation, and transformed to the final product CO₂. As a result, about 75% of the total organic carbon of DOMp was reduced. However, insignificant decrease of the O/C ratio of compounds in DOMp was observed during photo-irradiation (Fig. S3), which indicated the generation of newly formed oxygen-containing groups by TiO₂ 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 OSC, 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 DOMs 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 DOMp, the OSC of CHO, CHON, CHOS and CHONS compounds in DOMs 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 DOMs, which was
different from the molecular transformations of DOMₚ. Compared to DOMₚ, DOMₛ contained less aromatic C and more aliphatic C (as shown by the higher H/Cw and lower DBEₚ in Table S1, and ¹³C NMR results in Table S2) with lower oxidation degree (indicated by the lower O/Cw and ⁰¹⁵Cw in Table S1). Furthermore, the low O/Cw and negative ⁰¹⁵Cw of compounds in DOMₛ implied they contained fewer oxygenic groups, especially carbonyl and/or carboxylic groups, than compounds in DOMₚ, which was further confirmed by ¹³C NMR as shown in Table S2. Therefore, direct decarboxylation induced by TiO₂ photocatalytic oxidation of compounds in DOMₛ 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/Cw and ⁰¹⁵Cw 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 (DOMₚ), a representative of natural DOM) and sludge-derived DOM (DOMₛ, a representative of anthropogenic DOM) under photo-irradiation as affected by nano TiO₂. The results indicated that DOMₛ and DOMₚ had very different chemical and molecular composition. DOMₛ contained more heteroatom formulates with lower aromaticity, higher aliphaticity and lower carbon oxidation state than did DOMₚ. 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 DOMₛ and DOMₚ, 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 DOMₛ (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 DOMₛ but increased in DOMₚ, 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.


