博士論文(要約)

Investigating Molecular-Level Changes of Dissolved Organic Matter during Drinking and Reclaimed Water Treatment Processes Using Orbitrap Mass Spectrometry

(浄水処理および下水再生水処理における溶存有機物変化の Orbitrap 質量分析計を用いた分子レベルでの評価)

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Dissolved organic matter (DOM) is existed in all water environments and it is one of the most important constituents in raw water of drinking water purification plant (DWTP) and secondary effluent, which is raw water of water reclamation plant (WRP). DOM is generally harmless but it could cause various problems in treatment processes such deterioration of aesthetic quality, organic fouling on membrane filtration, and acting as organic precursors of disinfection by-products (DBPs). As DOM plays a very important role in drinking and reclaimed water treatment plants, many characterization methods such as ultraviolet/visible adsorption spectroscopy (UV-Vis), Fourier-transform infrared (FT-IR) spectroscopy, and 3D fluorescence excitation/emission matrix (3D-EEM) spectroscopy have been applied to understand its behaviours and changes along with treatment processes. However, molecular characteristics of DOM are still evaded from those methods and little is known about DOM at molecular level resulted in difficulty to understand reaction mechanisms of treatment processes or to select the most effective treatment conditions. Recently developed mass spectrometer (MS) namely Orbitrap MS is one of the promising tools with high mass resolution and accuracy enable analysis for wide ranges of DOM. Unknown screening analysis by Orbitrap MS could provide molecular formula determination of each DOM, which is further converted to various molecular characteristics for understanding its properties. However, to our knowledge, only small numbers of study have applied Orbitrap MS in unknown screening analysis of DOM in environmental and urban water or in treatment processes.

The objectives of this study is to (1) to develop methodology for investigating semiquantitative changes of DOM by unknown screening analysis with Orbitrap mass spectrometry, (2) to elucidate differences on molecular characteristics of DOM in environmental and urban water, (3) to investigate changes of DOM during treatment processes of a water reclamation plant and to identify chlorinated DBPs in reclaimed water, (4) to investigate changes of DOM along with water treatment processes in three drinking water treatment plants and to identify chlorinated DBPs in

purified water, and (5) to elucidate effects of oxidation treatments to changes of DOM and to DBP formation potential in post chlorination.

In order to evaluate quantitativeness of the unknown screening analysis of DOM by Orbitrap MS, various water samples from environmental water such as river, and lakes, as well as urban water such as purified waters, secondary effluents and reclaimed water were tested. The dilution series from 10% to 100% (non-diluted) was prepared for each sample, which DOC concentration of the diluted series were ranged from 0.35 to 21 mgC/L. Over 1500 DOM peaks were detected in each non-diluted sample and most of the peaks were also detected in all diluted samples with lower absolute intensity. The peak intensities were decreased along with the sample dilution. The variation of peak intensity in tripicate analyses of all the samples were similarly distributed as bell-curve like with high kurtosis. However, the distributions were not statistically regarded as Gaussian. The degree of variation increased with the increase of sample dilution. In most of the samples, over 95% of DOM peaks varied within the changes range of 30%. Intensity reduction of 30% resulted in actual concentration decreased around 40 to 60%. The results implied possibility to estimate semiquantitative changes of DOM by setting criterion of changes beyond the variation. Intensity changed beyond 30% would be an appropriate criterion for judging changes of DOM after treatment or reaction with high confidence level above 95%.

In addition, molecular formulae of DOM in the environmental and urban water were identified based on mass tolerance, heuristic filtering and functional group relationship considering elements such as carbon, hydrogen, oxygen, nitrogen and sulfur. Over 1000 DOM peaks in all the samples were assigned molecular formulae with mass error below 5 ppm. DOM containing C, H and O (CHO) were most abundant in all water samples and C, H, O and S (CHOS) formulae were rich only in secondary effluents. Molecular formula of each DOM was converted to molecular characteristics such as hydrogen to carbon (H/C), oxygen to carbon (O/C), degree of unsaturation (double bond equivalent minus oxygen (DBE-O)) and degree of oxidation (carbon oxidation state (C_{os})). Abundant CHO formulae in all water samples are lignin-like indicating by plots between H/C and O/C of each formula (=Van Krevelen diagram). Most abundant CHOS formulae in secondary effluent were the same as sulfophenyl carboxylates (SPCs), which are biodegradation products of surfactant. DOM in surface water samples were less hydrogenated (lower H/C), more unsaturated (higher DBE-O), and more oxidized (higher C_{os}) compared to DOM in secondary effluent.

Changes of DOM along with treatment processes such as biofiltration, ozonation and

chlorination of a water reclamation plant in two different years were elucidated in semiquantitative way using the proposed criterion. Among treatment processes, ozonation induce the largest changes to DOM indicating by hierarchical cluster analysis of peaks in the samples. Intensity of each DOM formula was compared before and after treatment and classified into four groups based on intensity changes after treatment processes; (1) decreased over 30%, (2) unchanged (intensity changed below than 30%), (3) increased over 30% and (4) newly formed formulae for each treatment unit. Biofiltration preferentially removed hundred DOM with relatively hydrogenated (high H/C) and saturated (low DBE-O) character and only small number of DOM were increased or newly formed. Ozonation selectively removed over hundred DOM with relatively unsaturated (high DBE-O) character and produced over two hundred oxidation by-product (OBP) formulae (both increased and newly) with highly saturated (low DBE-O) character. After chlorination, over 168 chlorine-containing formulae (considered as DBPs) were additionally detected with high confidence level by matching isotopic patterns and 26 of them were not previously reported. Putative organic precursors of DBP were identified by both electrophilic substitution and addition reaction. Electrophilic substitution reaction was found to be predominant reaction than addition reaction. Behaviours of 18 putative precursors of DBP formed via electrophilic substitution along with water reclamation processes were investigated. Half of them were increased during ozonation indicating that organic precursors were not only natural compounds but also production by treatment process.

In addition to water reclamation plant, DOM changes in water treatment processes such as coagulation/sedimentation, MIEX® followed by coagulation/sedimentation, oxidation treatments (ozonation and advanced oxidation process using ozone+H_2O_2), biological activated carbon adsorption (BAC) and chlorination of three drinking water purification plants were elucidated. Similar to water reclamation plant, oxidation treatments induced most substantial changes to DOM compared to all treatment processes. Coagulation/sedimentation in Plant A and B and MIEX® in Plant C preferentially removed DOM with highly degree of oxidation (oxygen rich) due to neutral-precipitation reaction and negative ion-exchange mechanisms, respectively. MIEX followed by coagulation/sedimentation in Plant C could remove larger number of DOM compared to coagulation/sedimentation in Plant A and B. Ozonation in Plant A and B preferentially removed unsaturated and produced saturated one similar to observation in ozonation of water reclamation plant. AOP in Plant C could remove smaller number of DOM and produced larger number of OBPs with similar characteristics to OBPs produced in ozonation of Plant A and B. Only BAC in Plant A

effectively in removal over 500 DOM formulae and the latter two could remove around a hundred DOM formulae. DOM with highly saturated (high DBE-O/C) and oxidized (high C_{os}) were refractory to BAC of Plant A. After chlorination, chlorinated and brominated DBPs were additionally detected of all three plants and DBP formulae in chlorinated samples of each plant were unique. By checking on an online database namely ChemSpider, 69 out of 164 DBP formulae were not previously reported. Putative precursors of DBPs formed via electrophilic substitution in all three plant were identified and the similar trends were observed that those compounds were increased during ozonation.

Effects of oxidation treatments such as H_2O_2, ozonation and AOP (O_3+H_2O_2) to DOM and DBP formation potential in chlorination were exemplified in laboratory experiments. A large number of DOM were decreased, increased or newly formed after oxidation by 1 mgO_3/L, 4 mgO_3/L, and AOP while only small number of DOM were changed by H_2O_2 oxidation. When comparing among the oxidation condition, the number of formulae decreased was in the following order: H_2O_2<1 mgO_3/L<4 mgO_3/L<AOP. The number of formulae increased and newly formed was in the following order: H_2O_2<AOP <1 mgO_3/L<4 mgO_3/L. AOP is most effective in removal of DOM and generates lowest number of OBPs. Comparing to ozonation, AOP could remove DOM those removed by ozonation and additionally removed DOM with higher saturated and more oxygenated. After chlorination, number of chlorinated DBPs was in the following order: AOP < 4 mgO_3/L < No oxidation < 1 mgO_3/L. Applying low ozone dosage of 1 mgO_3/L increased formation potential of DBP while using high ozone dosage or addition of H_2O_2 to ozonation to promote AOP before chlorination could minimize formation potential of DBP.

Unknown screening analysis by Orbitrap MS can be applied to elucidate changes of DOM in drinking and reclaimed water treatment processes. Behaviors of thousands of DOM formulae as well as their molecular characteristics can be tracked along with treatment processes. Advance information obtained from the analysis can provide possible modifications of drinking and reclaimed water treatment processes to achieve better treatment efficiency especially in minimization of DBP formation potential.