Molecular-level comparison of dissolved organic matter in 11 major lakes in Japan by Orbitrap mass spectrometry

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ABSTRACT

Dissolved organic matter (DOM) causes organic pollution in lakes, resulting in the occurrence of off-flavour etc. when lake water is used as a drinking water source. In this study, DOM in 11 major lakes in Japan was characterised by high-resolution Orbitrap mass spectrometry. Molecular formulas were assigned to 845–1,451 components per sample. Among them, 555 components were commonly found in all lakes. The DOM compositions of the 11 lakes were clustered into four groups. Correlation analysis could extract specific components whose relative intensities were associated with water quality indices such as specific ultraviolet absorbance, specific dissolved chemical oxygen demand ($DCOD_{Mn}$), and specific trihalomethane formation potential ($R = 0.80$–0.93, $p < 0.05$). Although further molecular structural analyses of DOM components are necessary, these results could be informative for exploring key candidates related to specific water quality issues. Pre-treatment of samples with permanganate oxidation was applied to screen components which could contribute to $DCOD_{Mn}$. $DCOD_{Mn}$ components accounted for only 7–30% of total peak intensities, indicating the limited performance of permanganate oxidation. Pre-treatment by permanganate coupled with Orbitrap MS revealed that components with higher molecular weight, higher oxygen-to-carbon ratios (O/C), and lower hydrogen-to-carbon ratios (H/C) could be responsible for $DCOD_{Mn}$.

Key words | chemical oxygen demand, dissolved organic matter, lake, molecular characterisation, Orbitrap mass spectrometry

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INTRODUCTION

Eutrophication in closed water bodies remains a major environmental issue in the world (Le Moal *et al.* 2019). In Japan, 14.6% and 51.2% of lakes met the environmental water quality standards for total nitrogen and total phosphorus concentrations, respectively (Ministry of the Environment in Japan 2018). Due to the chronic state of eutrophication in lake water environments, 53.2% of lakes complied with the environmental water quality standard for chemical oxidation demand determined by potassium permanganate oxidation (COD_{Mn}; Ministry of the Environment in Japan 2018). Intensive countermeasures for the

improvement of water quality and pollutant load control have been implemented in 11 major lakes in Japan under the law concerning special measures for conservation of lake water quality enacted in 1984. However, no designated lakes have ever complied with the COD_{Mn} standard, and little information is available regarding organic matter elevation in these lakes. Increase of dissolved organic carbon (DOC) has also been reported in lakes in the north-eastern USA, which could be associated with many factors including extreme precipitation events, enhanced organic matter production due to climate change (Strock

et al. 2016, 2017). Dissolved organic matter (DOM) is a fraction of the organic matter in aquatic environments that causes various problems in water use such as formation of disinfection by-products (Imai *et al.* 2003). In lake environments, not only various external sources but also internal sources, such as algae and sediment, should be considered as origins of DOM (Jiang *et al.* 2018). Furthermore, DOM composition can be influenced by physicochemical and biological reactions more prominently in lakes with longer retention times (Kawasaki *et al.* 2013; Bittar *et al.* 2015; Maizel *et al.* 2017). These factors make it difficult to understand DOM properties in lake environments.

High-resolution and accurate mass spectrometry, such as Fourier transform ion cyclotron mass spectrometry (FT-ICR MS) and Orbitrap MS, is the first technology to fully resolve the complex composition of DOM, which cannot be achieved by conventional water quality indices such as biochemical oxygen demand (BOD), COD, and total organic carbon (TOC). Recently, FT-ICR MS with the highest resolution has been applied to analyse DOM in lake water (Bai *et al.* 2017; Mostovaya *et al.* 2017). Furthermore, Orbitrap MS has a smaller footprint with equivalent resolution. The DOM in various water environments, including lakes, has been characterised by Orbitrap MS (Urai *et al.* 2014; Hawkes *et al.* 2016; Phungsai *et al.* 2016; Yuthawong *et al.* 2017, 2019). The DOM composition (revealed by FT-ICR MS) of 120 lakes in Sweden indicated the DOM chemodiversity was associated with DOM and nutrient concentrations (Kellerman *et al.* 2014). Other factors such as climate change and watershed land-use patterns could also have impacts on DOM properties in lakes. However, the DOM composition in lakes in Japan has not been compared despite their long-term organic pollution. Thus, this study aimed to compare the DOM composition in all 11 lakes in Japan designated by the law concerning special measures for conservation of lake water quality. Orbitrap MS was applied to resolve DOM composition at the molecular level and find out the relationship between organic pollution indices (ultraviolet absorbance, dissolved COD_{Mn} ($DCOD_{Mn}$) trihalomethane formation potential (THMFP), chlorophyll-a (Chl-a)) and common DOM composition. Moreover, molecular components that can contribute to dissolved COD_{Mn} ($DCOD_{Mn}$) were screened by the combination of permanganate oxidation and Orbitrap MS.

METHODS

Sampling

As shown in Table 1 and Figure S1 in Supplementary Materials, surface water samples were collected from 11 major lakes (Lake Hachiro, Lake Kamafusa (reservoir), Lake Nojiri, Lake Suwa, Lake Kasumigaura, Lake Tega, Lake Inba, Lake Biwa, Lake Nakaumi, Lake Shinji, and Lake Kojima) in Japan in October and November 2017. These lakes have been designated by the government as special lakes that need intensive measures for conserving water quality. Among them, Lake Kamafusa, Lake Kasumigaura, Lake Inba, and Lake Biwa are used as a source for drinking water. Samples were stored in 2 L glass bottles, which had been baked at 550 °C for 6 h to remove residual carbon, and then transported in cooling boxes to the laboratory within 24 h.

Water quality analysis

Unfiltered water samples were directly subjected to analysis of non-purgeable TOC with a TOC analyser (TOC-LCSH, Shimadzu, Japan) and total COD_{Mn} ($TCOD_{Mn}$), according to Japanese Industrial Standards (JIS method K0102). To analyse DOM fraction, water samples were treated with a 0.3 μm glass fibre filter (GF-75, Advantec, Japan). DOC and $DCOD_{Mn}$ were determined. Moreover, ultraviolet absorbance at 254 nm was measured with a visible–UV spectrophotometer (UH3500, Hitachi, Japan) using a quartz cell (1 cm). To determine the THMFP, sodium hypochlorite was added to the filtered samples so that the free chlorine residual after 24 h of incubation in the dark was 1–2 mg/L. After quenching the free chlorine residual with a sodium thiosulfate solution, trihalomethane was determined by headspace gas chromatography (GC-2010 Plus with ECD detector, Shimadzu, Japan). In this analysis, *p*-bromofluorobenzene was used as an internal standard. Chl-a was extracted by 90% (v/v) acetone from algae collected on 1.0 μm glass fibre filters (Whatman, GF/B). The absorbance at 750, 663, 645, and 630 nm of supernatant was measured with a UH3500 in order to calculate Chl-a concentration (Japan Water Works Association 2001).

Orbitrap MS analysis

Orbitrap MS can preferentially detect lower molecular weight DOM compared with FT-ICR MS (Hawkes *et al.*

Table 1 │ Basic specifications of the 11 studied lakes and sampling information

Lake and Reservoir		Volume ($\times$ 1,000 m^3)	Average depth (m)	Sampling site	Sampling date
Lake Hachiro		132,600	2.8	N 39.9253 E 139.9905	8 Nov 2017
Kamafusa Lake (reservoir)		39,300	11.6	N 38.2015 E 140.6953	18 Oct 2017 15 Nov 2017
Lake Nojiri		96,000	21.0	N 36.4930 E 138.1315	11 Oct 2017
Lake Suwa		62,987	4.7	N 36.0497 E 138.0851	11 Oct 2017
Lake Kasumigaura		850,000	4	N 36.0358 E 140.4036	11 Oct 2017
Lake Tega		5,600	0.86	N 35.8604 E 140.0254	23 Oct 2017
Lake Inba		27,700	1.7	N 35.7579 E 140.1987	23 Oct 2017
Lake Biwa	North Lake	27,300,000	43	N 35.2161 E 135.9986	1 Nov 2017
	South Lake	200,000	4	N 35.0672 E 135.9075	
Lake Nakaumi		521,000	5.4	N 35.4680 E 133.1868	1 Nov 2017
Lake Shinji		366,000	4.5	N 35.4488 E 132.9566	1 Nov 2017
Lake Kojima		26,072	2.1	N 34.5752 E 133.9377	21 Nov 2017

2016). The target in this study was low molecular weight DOM ($m/z = 100$–1,000). One litre of the filtrated water sample was subjected to solid-phase extraction using Bond Elut PPL (Agilent, CA; Dittmar et al. 2008). The DOM extracts eluted in 10 mL of methanol were analysed by Orbitrap MS (Exactive, Thermo Fisher Scientific, MA) in flow injection mode. Electrospray ionisation in negative ion mode was selected. Accurate mass data were obtained in the range of m/z 100–1,000. Mass accuracy was maintained below 2 ppm with external and internal mass calibration. While external calibration was performed by Proteomass ESI (Sigma-Aldrich, USA), internal calibration was accomplished by referring to a lock mass peak ($m/z =$ 255.23295) that was detected throughout the analysis. The analytical conditions were the same as in our previous studies (Urai et al. 2014; Phungsai et al. 2016; Yuthawong et al. 2017, 2019; Phungsai et al. 2018).

The mass data were treated by Sieve Analysis 2.2 (Thermo Scientific, USA) to eliminate background peaks. Components were extracted by integrating isotopologues and different adduct ions. Molecular formulas were assigned to extracted components by compound identification algorithm (Kujawinski & Behn 2006) considering the combination of carbon (0–39), hydrogen (0–72), oxygen (0–20), nitrogen (0–3), and sulphur (0–1). The elemental ratios ($0.2 \leq$ H:C ≤ 3.1; O:C ≤ 1.2; N:C ≤ 1.3), the nitrogen rule, and the range of double-bond equivalent minus oxygen (DBE-O) ($-10 \leq$ DBE-O ≤ 10) were also considered for assignment (Kind & Fiehn 2007; Herzsprung et al. 2014). Elemental compositions of molecular formulas were demonstrated by plotting hydrogen-to-carbon ratios (H/C) and oxygen-to-carbon ratios (O/C) on van Krevelen diagrams. Molecular formulas were categorised based on the elemental composition of biomolecules: lignin ($1.0 \leq$ H/C ≤ 1.4

and $0.35 \leq O/C \leq 0.50$), tannin ($0.75 \leq H/C \leq 1.4$ and $0.35 \leq O/C \leq 0.85$), peptides ($1.60 \leq H/C \leq 1.80$ and $0.35 \leq O/C \leq 0.50$), lipids ($1.75 \leq H/C \leq 2.25$ and $0.02 \leq O/C \leq 0.15$), and carbohydrates ($1.50 \leq H/C \leq 2.00$ and $0.50 \leq O/C \leq 1.00$) (Kim et al. 2003, 2006). Binary data (presence and absence) of DOM composition was subjected to cluster analysis using Ward's method in XLSTAT version 19.7. The unsaturation of assigned molecular formulas was estimated by calculating the DBE-O to eliminate potential double bonds derived from carbonyl functional groups (Yuthawong et al. 2019).

Screening of $DCOD_{Mn}$ components

Following Yuthawong et al. (2019), the components contributing to $DCOD_{Mn}$ were screened. Filtered water samples were oxidised by potassium permanganate under the same condition as the COD_{Mn} analysis (JIS method K0102). After oxidation, DOM was extracted by solid-phase extraction and analysed by Orbitrap MS in the same manner. Non-oxidised and oxidised samples were compared to extract $DCOD_{Mn}$ components that were present in the non-oxidised samples but absent in the oxidised samples. Conversely, the components found in both non-oxidised and oxidised samples were defined as persistent

components, even though some components that were partially oxidised by permanganate were included.

RESULTS AND DISCUSSION

Water quality

Table 2 summarises water quality in the 11 studied lakes. The ranges of TOC and DOC were 1.5–5.8 mg C/L (mean: 3.3 mg C/L) and 1.3–5.0 mg C/L (mean: 2.7 mg C/L), respectively. Lake Kasumigaura had the highest TOC and DOC values, while Lake Kamafusa had the lowest TOC and DOC values. Moreover, DOC was the dominant fraction in all lakes, accounting for 70–105% of TOC (mean: 84%). The ranges of $TCOD_{Mn}$ and $DCOD_{Mn}$ were 1.4–7.8 mg/L (mean: 3.4 mg/L) and 1.2–3.8 mg/L (mean: 2.2 mg/L), respectively. The $DCOD_{Mn}/TCOD_{Mn}$ ratios were in the range of 31–114% (mean: 72%). The lowest ratio was observed in Lake Suwa, where the highest Chl-a concentration was associated with the highest $TCOD_{Mn}$. Furthermore, DOM in Lake Nakaumi ($DCOD_{Mn}/DOC = 1.27$) was more preferably oxidised by permanganate than DOM in Lake Biwa (North; $DCOD_{Mn}/DOC = 0.55$), indicating that the DOM composition contributing to $DCOD_{Mn}$ is dependent on lakes. The specific UV_{254} values

Table 2 │ Water quality in the 11 studied lakes

	TOC (mg C/L)	DOC (mg C/L)	$TCOD_{Mn}$ (mg/L)	$DCOD_{Mn}$ (mg/L)	UV_{254} (1/cm)	SUVA (L/mg C/m)	Chl-a (μg/L)	TTHMFP (μg/L)
L. Hachiro	4.5	3.4	4.6	3.2	0.082	2.41	31.5	85.3
L. Kamafusa in Oct.	1.5	1.4	1.4	1.4	0.034	2.43	NA	43.7
L. Kamafusa in Nov.	1.6	1.3	1.6	1.4	0.034	2.62	3.5	44.7
L. Nojiri	1.9	2.0	1.4	1.6	0.017	0.85	1.7	17.1
L. Suwa	3.2	3.0	7.8	2.4	0.045	1.50	68.7	41.9
L. Kasumigaura	5.8	5.0	5.2	3.8	0.075	1.50	30.1	69.8
L. Tega	4.5	3.2	4.0	1.9	0.037	1.16	52.2	65.6
L. Inba	4.9	3.6	5.0	2.2	0.045	1.25	46.1	67.2
L. Biwa North	2.5	2.2	1.6	1.2	0.023	1.05	3.5	23.8
L. Biwa South	2.3	2.1	1.6	1.2	0.022	1.05	0.9	22.5
L. Nakaumi	2.9	2.2	3.8	2.8	0.044	2.00	4.5	259.6
L. Shinji	2.7	1.9	2.6	1.8	0.043	2.26	14.6	245.4
L. Kojima	4.3	3.5	4.0	3.2	0.066	1.89	18.5	126.7

NA: Not available.

(UV_{254}/DOC, SUVA) of Lake Hachiro, Lake Kamafusa, Lake Nakaumi, and Lake Shinji were higher than or equal to 2.00 L/mgC/m. Higher specific UV_{254} values in these lakes demonstrated enrichment of unsaturated DOM. In addition, THMFP was in the range of 17.1–259.6 µg/L. In particular, THMFP in the brackish lakes (Lake Nakaumi and Lake Shinji) and Lake Kojima was more than 100 µg/L due to the predominance of brominated THM. The range of Chl-a concentration was 0.9–68.7 µg/L (mean: 23.0 µg/L). Although the sampling was carried out in October–November, the Chl-a concentration in Lake Hachiro, Lake Suwa, Lake Kasumigaura, Lake Inba, and Lake Tega was more than 30 µg/L. Eutrophication was still apparent in these shallow lakes even in autumn.

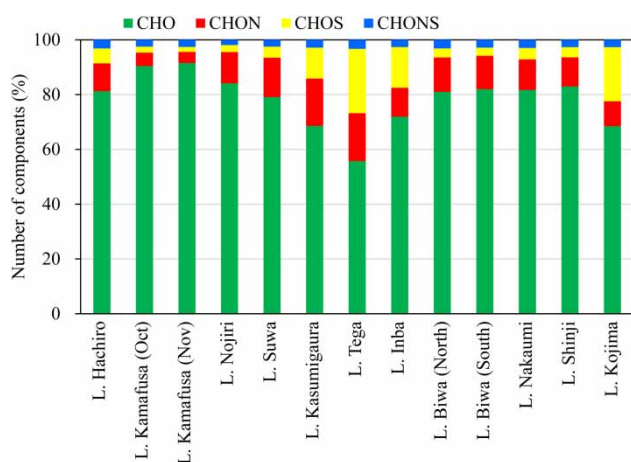**Figure 1** │ Compositions of molecular formulas in the 11 studied lakes.

Characterisation of DOM by Orbitrap MS

Intensity-weighted average *m/z* values were similar among the lakes, ranging from 313.8464 to 337.9052 (mean: 325.2304). Molecular formulas were assigned to 845–1,451 components. The previous study analysing lake DOM by both Orbitrap MS and FT-ICR MS reported that 1,652 formulas were obtained by Orbitrap MS (resolution mode: 100,000), while 6,510 formulas were assigned by 15T FT-ICR MS (Hawkes *et al.* 2016). As shown in Figure 1, more than 50% of the formulas were composed of carbon, hydrogen, and oxygen atoms (CHO) in all the lakes. In particular, more than 90% of molecular formulas were CHO-types in Lake Kamafusa, where DOC was the lowest. The CHOS-type molecular formulas occupied more than 10% in Lake Kasumigaura (11.3%), Lake Inba (14.9%), Lake Tega (23.5%), and Lake Kojima (19.7%). Figure 2 shows van Krevelen diagrams of assigned molecular formulas in the 11 lakes. Most of the CHO-type, CHON-type, and CHOS-type formulas fell in the regions of lignin and tannin. Interestingly, CHONS-types formulas were plotted in the same region ($0.05 \leq H/C \leq 0.25$ and $0.80 \leq O/C \leq 1.30$) in all the lakes. This is the first study to comprehensively compare DOM compositions in 11 major lakes in Japan. Based on this investigation, more data should be accumulated to reveal seasonal variations of DOM compositions in these lakes.

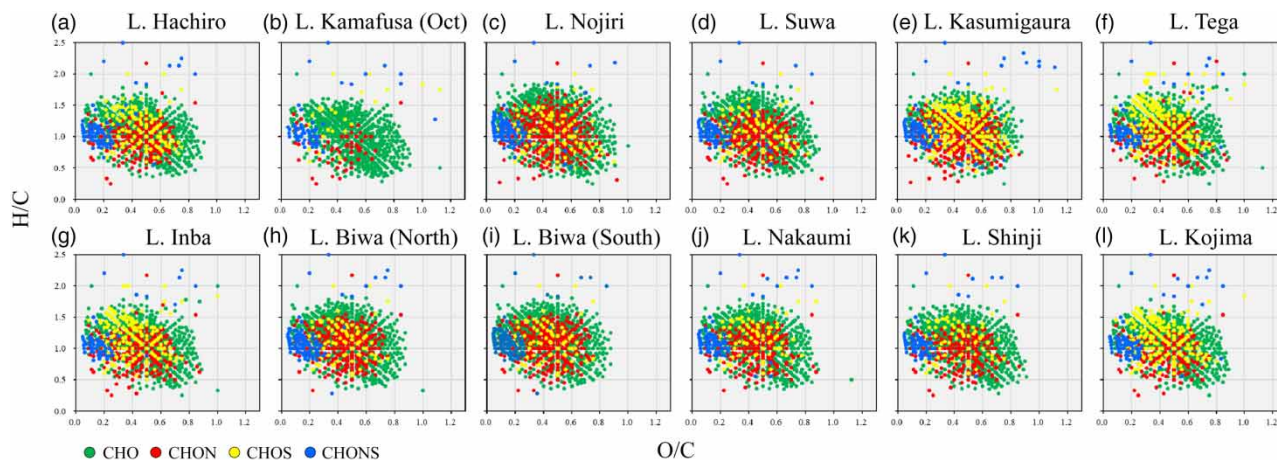Cluster analysis was applied to categorise DOM compositions in the 11 lakes. As shown in Figure 3, DOM

Figure 2 │ Van Krevelen diagrams of components in the 11 studied lakes.

compositions were classified into four clusters: Cluster 1 (Lake Biwa: North and South, Lake Nojiri, and Lake Kasumigaura), Cluster 2 (Lake Kamafusa), Cluster 3 (Lake Inba, Lake Tega, and Lake Kojima), and Cluster 4 (Lake Nakaumi, Lake Shinji, Lake Suwa, and Lake Hachiro). It is reasonable that the two Lake Biwa samples (North and South), two Lake Kamafusa samples (October and November), two closely located lakes in the same watershed (Lake Inba and Lake Tega), and two adjacent brackish lakes (Lake Nakaumi and Lake Shinji) were categorised with each other. However, the clustering pattern was not always attributable to the geological locations of the lakes. Figure S2 shows van Krevelen diagrams of (a) components commonly observed in all the lakes, (b) components commonly observed in Cluster 1, (c) components commonly observed in Cluster 2, (d) components commonly observed in Cluster 3, and (e) components commonly observed in Cluster 4. Many factors should affect the clustering pattern of DOM composition including hydraulic retention time, water temperature, history of lakes, and land-use pattern in the watershed (Kellerman *et al.* 2014). The 555 formulas commonly observed in all the lakes were mainly composed of CHO-type formulas. It is possible that they could derive from the same origins such as common vegetation in their watersheds and common features of DOM derived from internal production. Conversely, it is likely that the same molecular formulas do not always indicate that they are identical compounds since isomers cannot be distinguished only by molecular formulas. Among the common CHOS-type formulas, the identical formulas were

detected from wastewater effluent (Gonsior *et al.* 2011) and a river inflowing to Lake Inba (Yuthawong *et al.* 2017). Some of them were suspected to be biodegradation products (sulfophenyl carboxylic acids: SPC) of linear alkylbenzene sulfonates (LAS) such as $C_{10}H_{12}O_5S$ (C4-SPC) and $C_{11}H_{14}O_5S$ (C5-SPC), suggesting the wide prevalence of surfactant pollution.

Clusters 1 and 4 were characterised by CHON-type formulas while Cluster 3 was characterised by CHOS-type formulas. Lake Inba and Lake Tega in Cluster 3 are among the most polluted lakes in Japan. Some components with CHOS-type formulas could be generated by reaction of sulfide with DOM in anaerobic sediment (Melendez-Perez *et al.* 2018). Conversely, CHO-type formulas were dominant in Lake Kamafusa (Cluster 2). Lake Kamafusa is located in a mountainous region and it showed the highest SUVA values (Table 2). DOM with lignin tannin-like features could be derived from forests in the watershed. A predominance of lignin-like DOM components was also reported in the oligotrophic Lake Superior (Minor *et al.* 2012). Previous studies reported that DOM compositions were unique, depending on water types such as river water, groundwater, and wastewater effluent (Gonsior *et al.* 2011; Urai *et al.* 2014). Establishing a database of molecular-level DOM compositions in lake water and point-sources is required for identifying sources based on DOM composition.

Although Orbitrap MS is a powerful tool to reveal the molecular composition of DOM, several biases such as the solid-phase extraction and ionisation efficiency of molecules affect the results. Furthermore, the analytical window in this study is limited to *m/z* 100–1,000, indicating that molecular ions with a single charge outside of the window are excluded from the analysis.

Relationship between bulk parameters and molecular composition of DOM

The correlation between the relative intensity of the 555 components commonly observed in all the lakes and bulk parameters (SUVA, $DCOD_{Mn}/DOC$, THMFP/DOC, and Chl-a/DOC) in the 11 lakes was evaluated as shown in Figure 4. Similar components ($0.5 \leq H/C \leq 1.5$ and $0.1 \leq O/C \leq 0.8$) showed positive correlations with SUVA, $DCOD_{Mn}/DOC$, and THMFP/DOC, suggesting that these
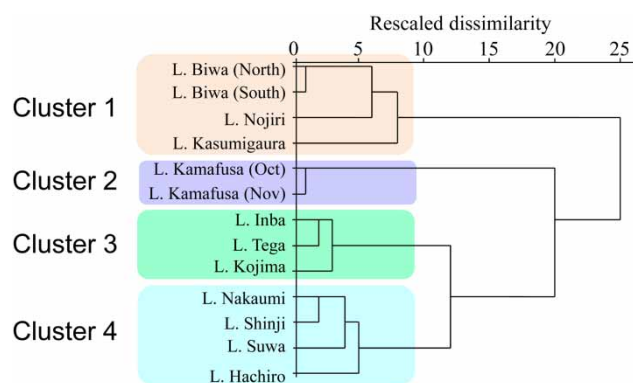

Figure 3 │ Cluster analysis of DOM compositions in the 11 studied lakes. Binary data of components were analysed by Ward's method.
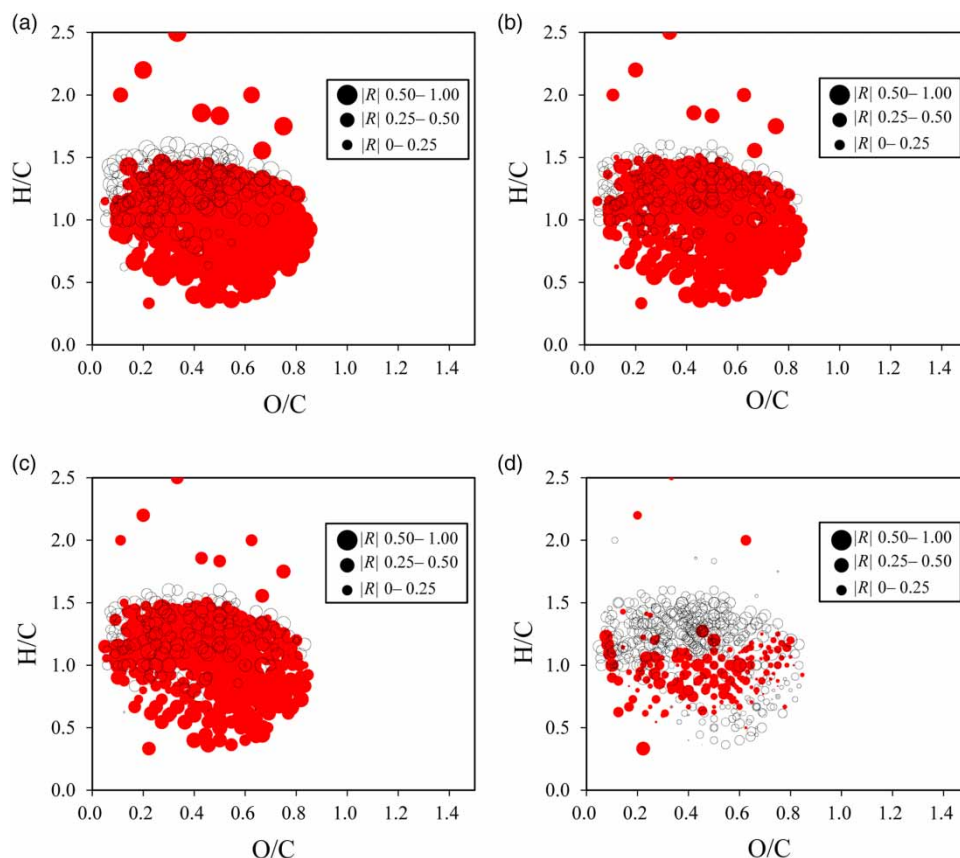
Figure 4 │ Correlation between the relative intensities of 555 common components and bulk parameters: (a) correlation with SUVA, (b) correlation with $DCOD_{Mn}/DOC$, (c) correlation with THMFP/DOC (molar concentration base), and (d) correlation with Chl-a/DOC. Bubble size represents the magnitude of the coefficient of correlation. Closed red circles indicate positive correlations while open circles indicate negative correlations.

components overlapped with the lignin and tannin regions and could contribute to these properties. Conversely, these components showed a moderate positive or negative correlation with Chl-a/DOC. It is possible that algal DOM may not be clearly related to SUVA, $DCOD_{Mn}/DOC$, and THMFP/DOC. Interestingly, some components with $1.0 \leq H/C \leq 1.5$ and $0.1 \leq O/C \leq 0.8$ demonstrated a negative correlation with all parameters.

Figure 5 represents examples of the highest correlations between the relative peak intensities of specific components and water quality parameters. The relative peak intensities of $C_{21}H_{26}O_7$, $C_{24}H_{32}O_{10}$, and $C_{21}H_{28}O_{10}$ were significantly correlated with SUVA ($R = 0.93$, $p < 0.05$), $DCOD_{Mn}/DOC$ ($R = 0.80$, $p < 0.05$), and THMFP/DOC ($R = 0.88$, $p < 0.05$), respectively. Conversely, the correlation coefficient between the relative peak intensities of nitrogen-bearing formula ($C_{15}H_{15}O_9N$) and Chl-a/DOC was not significant

($R = 0.54$, $p > 0.05$). It is possible that Chl-a, which is an indicator of algae, is not directly associated with DOM components. Compounds corresponding to these formulas could be responsible for these specific water quality parameters. It is also possible that compounds other than the 555 common components could contribute to unique water quality in each lake. However, it is likely that a component with a formula contains several isomers. Further studies, including the structural characterisation of components by MS/MS (Merel *et al.* 2017), are necessary to discuss the relationship with water quality parameters.

Screening $DCOD_{Mn}$ components in lake water

Pre-treatment by permanganate oxidation was applied to classify DOM components into $DCOD_{Mn}$ and persistent components (Figure 6, Figure S3). Except for Lake Nakaumi
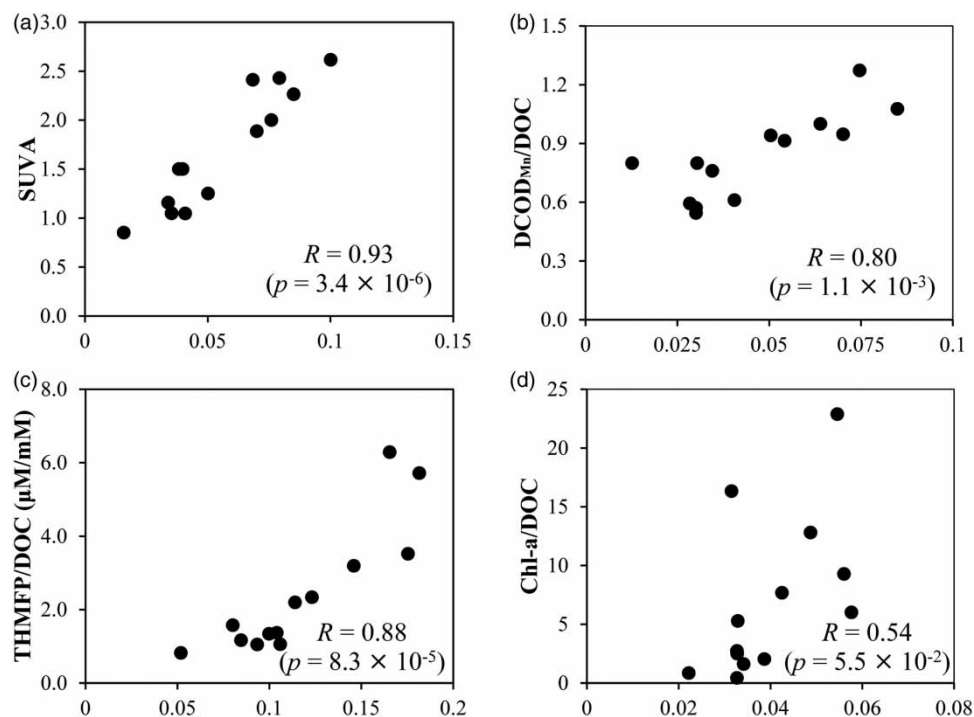
Figure 5 | The highest correlation between relative peak intensities of specific components and water quality parameters: (a) relative peak intensities of $C_{21}H_{26}O_7$ vs SUVA, (b) relative peak intensities of $C_{24}H_{32}O_{10}$ vs $DCOD_{Mn}/DOC$, (c) relative peak intensities of $C_{21}H_{28}O_{10}$ vs THMFP/DOC (µM/mM), and (d) relative peak intensities of $C_{15}H_{15}O_9N$ vs Chl-a/DOC.

(54%) whose $DCOD_{Mn}/DOC$ was the highest (Table 2), only 15%–36% of components were categorised as $DCOD_{Mn}$ components in the other lakes. Intensity-based percentages showed that $DCOD_{Mn}$ components accounted for only 7%–30% (mean: 15%) of total peak intensities. These results clearly demonstrate that only a minor fraction of DOM is monitored as $DCOD_{Mn}$, which was consistent with previous study on the limitation of permanganate oxidation (Geerdink et al. 2017; Yuthawong et al. 2019). The molecular-level analysis clearly demonstrated that COD_{Mn} is not a comprehensive indicator of DOM in lake water.

Table S1 shows the molecular characteristics of $DCOD_{Mn}$ and persistent components. For all lakes, the number-averaged molecular weight and O/C of $DCOD_{Mn}$ components were larger than those of persistent components, while the number-averaged H/C of $DCOD_{Mn}$ components were smaller than those of persistent components. The number-averaged DBE-O of $DCOD_{Mn}$ components were larger than those of persistent components in Lake Kamafusa (October and November), Lake Suwa, Lake Kasumigaura,

Lake Inba, Lake Nakaumi, Lake Shinji, and Lake Kojima, indicating that unsaturated components were preferentially oxidised by permanganate. Conversely, the number-averaged DBE-O of $DCOD_{Mn}$ components in the other lakes were smaller than those of persistent components. These results suggest that the components contributing to $DCOD_{Mn}$ could be dependent on lakes.

CONCLUSIONS

High-resolution Orbitrap MS revealed the DOM composition in the 11 studied lakes were characteristic. However, 38–66% of components in each lake were common among the lakes. The relationship between the relative peak intensities of these common components and water quality parameters such as SUVA, $DCOD_{Mn}/DOC$, and THMFP/DOC could extract key candidates related to specific water quality, which is informative for water quality management. Pre-treatment by permanganate coupled with
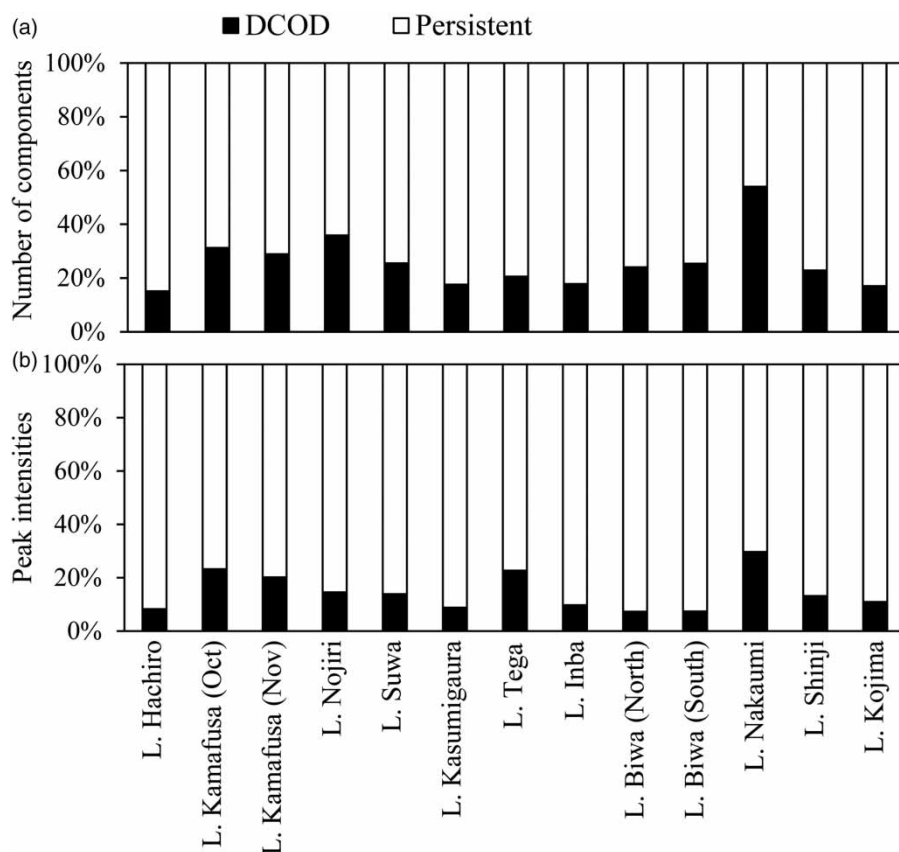
Figure 6 | Classification of DCOD$_{Mn}$ components and persistent components in the 11 studied lakes based on (a) number and (b) relative peak intensities of components.

Orbitrap MS revealed that components with higher molecular weight, higher O/C, and lower H/C could be selectively responsible for DCOD$_{Mn}$, demonstrating clear evidence of the insufficient oxidation performance of permanganate.

SUPPLEMENTARY MATERIAL

The Supplementary Material for this paper is available online at https://dx.doi.org/10.2166/ws.2020.042.

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