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Contribution of dissolved organic matter to submicron water-soluble organic aerosols in the marine boundary layer over the eastern equatorial Pacific

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Abstract. Stable carbon isotopic compositions of water-soluble organic carbon (WSOC) and organic molecular markers were measured to investigate the relative contributions of the sea surface sources to the water-soluble fraction of submicron organic aerosols collected over the eastern equatorial Pacific during the Tropical Ocean tRoposphere Exchange of Reactive halogens and Oxygenated VOCs (TORERO)/KA-12-01 cruise. On average, the water-soluble organic fraction of the total carbon (TC) mass in submicron aerosols was $\sim$30–35 % in the oceans with the low chlorophyll *a* (Chl *a*) concentrations, whereas it was $\sim$60 % in the high-Chl *a* regions. The average stable carbon isotope ratio of WSOC ($\delta^{13}C_{WSOC}$) was -19.8 ± 2.0 ‰, which was systematically higher than that of TC ($\delta^{13}C_{TC}$) (-21.8 ± 1.4 ‰). We found that in the oceans with both high and low Chl *a* concentrations the $\delta^{13}C_{WSOC}$ was close to the typical values of $\delta^{13}C$ for dissolved organic carbon (DOC), ranging from -22 to -20 ‰ in surface seawater of the tropical Pacific Ocean. This suggests an enrichment of marine biological products in WSOC aerosols in the study region regardless of the oceanic area. In particular, enhanced levels of WSOC and biogenic organic marker compounds together with high values of WSOC / TC ($\sim$60 %) and $\delta^{13}C_{WSOC}$ were observed over upwelling areas and phytoplankton blooms, which was attributed to planktonic tissues being more enriched in $\delta^{13}C$. The $\delta^{13}C$ analysis estimated that, on average, marine sources contribute $\sim 90 \pm 25$ % of the aerosol carbon, indicating the predominance of marine-derived carbon in the submicron WSOC. This conclusion is supported by Lagrangian trajectory analysis, which suggests that the majority of the sampling points on the ship had been exposed to marine boundary layer (MBL) air for more than 80 % of the time during the previous 7 days. The combined analysis of the $\delta^{13}C$ and monosaccharides, such as glucose and fructose, demonstrated that DOC concentration was closely correlated with the concentration levels of submicron WSOC across the study region regardless of the oceanic area. The result implies that DOC may characterize background organic aerosols in the MBL over the study region.

1 Introduction

The ocean surface is a major source of submicron aerosols in both number and mass concentrations (e.g., Spracklen et al., 2008). These aerosols play an important controlling role in the atmospheric radiative budget because they determine the

number of cloud condensation nuclei (CCN) and ice nuclei (IN), particularly over the remote ocean. In general, organic matter (OM) is concentrated in the sea surface microlayer relative to the bulk seawater. OM is further concentrated in aerosols during the bubble-bursting process, which produces primary submicron sea spray aerosol (SSA) that is enriched in OM (O'Dowd and de Leeuw, 2007). It has been recognized that marine microorganisms play a large role in marine aerosol formation and its composition. Marine-derived submicron organic aerosol (OA) can affect marine aerosol optical depth (AOD) as well as CCN and IN concentrations. Nevertheless there is still uncertainty in the chemical signatures of SSA, leading to uncertainty in determining their climate impact.

The oceanic surface chlorophyll *a* (Chl *a*) concentration has been used as a proxy for marine phytoplankton biomass. However, linear source functions based on Chl *a* underpredict organic carbon (OC) enrichments for nascent SSA produced from oligotrophic waters and overpredict OC enrichments for nascent SSA produced from highly productive waters (Long et al., 2011). Recent field and laboratory studies suggest that organic enrichment of SSA might be more closely related to the concentration of oceanic dissolved organic carbon (DOC), rather than to the concentration of Chl *a* in surface seawater (Prather et al., 2013; Quinn et al., 2014).

To assess the impact of marine biological activity on ambient aerosols and the subsequent formation of clouds, it is important to differentiate marine-derived natural aerosols from anthropogenic aerosols over the oceanic regions. For this purpose, methods need to be established to discriminate between ocean- and land-derived aerosols found in marine atmospheres. A method using the isotopic composition of aerosol carbon has been used successfully to determine the contributions of marine and terrestrial sources to aerosol found in the remote marine atmosphere (Chesselet et al., 1981; Cachier et al., 1986; Kawamura et al., 2004; Miyazaki et al., 2011; Ceburnis et al., 2011). The marine-derived OC (δ^{13}C ~ -22 to -18 ‰) is enriched in ^{13}C relative to terrestrial C3 vegetation (which uses the Calvin–Benson cycle as a metabolic pathway for carbon fixation in photosynthesis) and fossil fuel OC (δ^{13}C ~ -30 to -23 ‰ for both) (e.g., Fry and Sherr, 1984). Ocean-derived submicron particles contain a large fraction of water-soluble OC (WSOC), which can significantly alter the hygroscopic property of aerosols (Prather et al., 2013) and act as CCN and IN. Only a few studies have used the ^{13}C of WSOC for source apportionment (Fisseha et al., 2009; Kirillova et al., 2010; Miyazaki et al., 2012). The WSOC-specific ^{13}C analysis in combination with organic molecular markers provides robust tools for the source apportionment of WSOC in marine aerosols.

To better characterize submicron OAs in the marine boundary layer (MBL) and differentiate them from those with terrestrial sources, we investigated the stable carbon isotopic signature of WSOC in submicron aerosols collected over the eastern equatorial Pacific. Primary productivity in that oceanic region accounts for ~ 23 % of the total productivity of the entire Pacific Ocean (Pennington et al., 2006), and the potential of enhanced OM in the surface microlayer is present. Deng et al. (2014) found that long-chain organic molecules and humic-like substances (HULIS) were prevalent in the marine aerosol sampled in a latitudinal cruise over the eastern Pacific. Here we investigated possible sources of submicron WSOC over the oceanic region by the analysis of WSOC-specific ^{13}C combined with several organic molecular markers, such as monosaccharides (glucose and fructose) and low-molecular-weight (LMW) fatty acids (FAs).

2 Experimental

2.1 Submicron aerosol samplings

Aerosol samplings were conducted in the MBL on board the National Oceanic and Atmospheric Administration (NOAA) R/V *Ka'imimoana* during the Tropical Ocean tRoposphere Exchange of Reactive halogens and Oxygenated VOCs (TORERO) field experiment (Coburn et al., 2014; Volkamer et al., 2015). Figure 1 presents the cruise track over the eastern equatorial Pacific between 25 January and 1 March 2012. The cruise originated in Honolulu, Hawaii, and headed to Puntarenas, Costa Rica (KA-12-01), from 157 to 83° W longitude and 21° N to 8° S latitude.

A cascade impactor (CI; Series 230, Tisch Environmental, Cleves, OH, USA) attached to a high-volume air sampler (HVAS; Model 120SL, Kimoto Electric, Osaka, Japan) was used to collect submicron particles (Miyazaki et al., 2012). The sampler was located on the upper deck of the ship. Aerosol samplings were made using quartz fiber filters (25×20 cm) set on the bottom stage of the impactor at a sampling flow rate of ~ 1100 L min^{-1}. The sampling time for each sample was approximately 24 h. The samples were collected on precombusted (450 °C for 3 h) quartz filters, and the average total volume of each sample was 1318.7 m^3. The collected samples were stored individually in glass jars with a Teflon-lined screw top cap at -20 °C prior to analysis. The aerosol data taken during 1–28 February 2012 were used in this study.

To obtain the average size distributions of the WSOC mass, size-segregated aerosol samplings were also performed with an Andersen-type CI running in parallel to the HVAS. The size-segregated aerosol samples were collected on precombusted quartz filters (8 cm ID) every ~ 3 days. The sampling was made according to the 50 % equivalent aerodynamic cutoff diameters, with nine stages between 0.39 and 10.0 µm (Miyazaki et al., 2010). Ambient air was drawn at a flow rate of 120 L min^{-1} per sample without temperature and humidity control. Other data were also obtained using an in situ ozone (O_3) monitor, sonic anemometer and Chl *a* fluorometer along the cruise track.

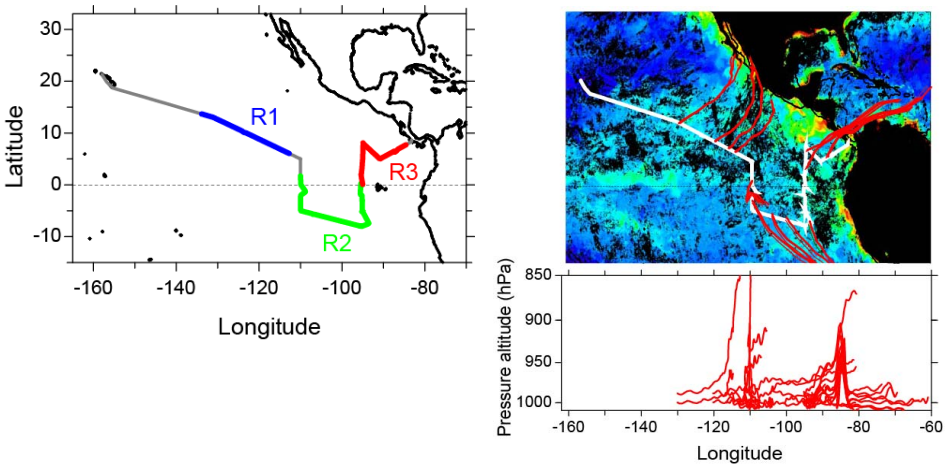

Figure 1. (Left) Cruise track of the National Oceanic and Atmospheric Administration (NOAA) ship *Ka'imimoana* in the eastern equatorial Pacific between 25 January and 1 March 2012 in three categorized oceanic areas (see text). (Right) Typical 5-day back trajectories (red lines) that started along the cruise track, together with monthly averaged concentrations of chlorophyll *a* (Chl *a*) for February 2012. A vertical cross section of the back trajectories is shown in the right bottom panel.

2.2 Aerosol chemical analysis

To determine the WSOC concentration, a portion of each filter sample (19.63 cm^2) was extracted with ultrapure water (> 18 $M\Omega\,cm^{-1}$) using an ultrasonic bath. The ultrapure water was generated by a Sartorius Stedim Biotech arium pro ultrapure water system (Model 611: Sartorius AG, Goettingen, Germany). The extracts were then filtrated with a disc filter (Millex-GV, 0.22 µm, Millipore, Billerica, MA, USA), followed by the injection of the DOC in the extracts into a total organic carbon analyzer (Model TOC-Vcsh, Shimadzu, Kyoto, Japan) (Miyazaki et al., 2011). The WSOC value of a field blank corresponded to less than ∼ 13 % of the WSOC concentration of the ambient samples. All WSOC data presented here were corrected against field blanks.

For the determination of $\delta^{13}C_{WSOC}$, a filter (14.13 cm^2) for each sample was acidified to pH 2 with hydrochloric acid (HCl) to remove inorganic carbon prior to extraction. The decarbonated filter samples were then dried under a nitrogen stream for approximately 2 h. WSOC was extracted from the filters in 20 mL of the ultrapure water using the method as described above for measuring the WSOC concentration. The extracted samples were concentrated by rotary evaporation, and 40 µL of each sample was transferred to be absorbed onto 10 mg of pre-combusted Chromosorb in a pre-cleaned tin cup. The $\delta^{13}C_{WSOC}$ was then measured using an elemental analyzer (EA) (NA 1500, Carlo Erba, Milan, Italy) interfaced to an isotope ratio mass spectrometer (IRMS) (Finnigan MAT Delta Plus, Thermo Finnigan, San Jose, CA, USA). The $\delta^{13}C$ data are reported relative to an established reference of carbon Vienna Pee Dee Belemnite (VPDB). The nitrogen isotope ratio ($\delta^{15}N$) of water-soluble total nitrogen (WSTN) ($\delta^{15}N_{WSTN}$) in aerosols was also measured with basically the same procedure as $\delta^{13}C_{WSOC}$, but without any acidification using HCl. In addition, the concentrations of total carbon (TC) and the $\delta^{13}C$ of TC ($\delta^{13}C_{TC}$) (i.e., without water extraction) were also measured with the EA–IRMS for the same aerosol samples (Miyazaki et al., 2010). Further details of the analytical method used for isotopic analysis are given by Miyazaki et al. (2012).

For the determination of inorganic ions, another filter cut was extracted with ultrapure water. The total extract was filtrated through a membrane disc filter, and major anions including methanesulfonic acid (MSA) and cations were determined using an ion chromatograph (Model 761 compact IC; Metrohm, Herisau, Switzerland) (Miyazaki et al., 2011). The MSA value of field blanks corresponded to less than ∼ 12 % of the concentrations of the ambient samples, whereas the blank values of Na^+, Cl^-, and Mg^{2+} were less than 1 % of the ambient concentrations.

For the analysis of possible tracers of marine DOC, a filter portion was extracted with dichloromethane/methanol. The –COOH and –OH functional groups in the extracts were reacted with N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) to derive trimethylsilyl (TMS) esters and TMS ethers, respectively. The TMS derivatives were then analyzed for α-glucose, β-glucose, α-fructose, β-fructose, and a homologous series of straight-chain fatty acids (C_{12}–C_{19} saturated acids) using a capillary gas chromatograph (GC7890, Agilent, Santa Clara, CA, USA) coupled to a mass spectrometer (5973 MSD, Agilent, Santa Clara, CA, USA) (Fu et al., 2011; Miyazaki et al., 2012). The values of a field blank were less than ∼ 24 % of the concentration of these molecular compounds in the ambient samples.

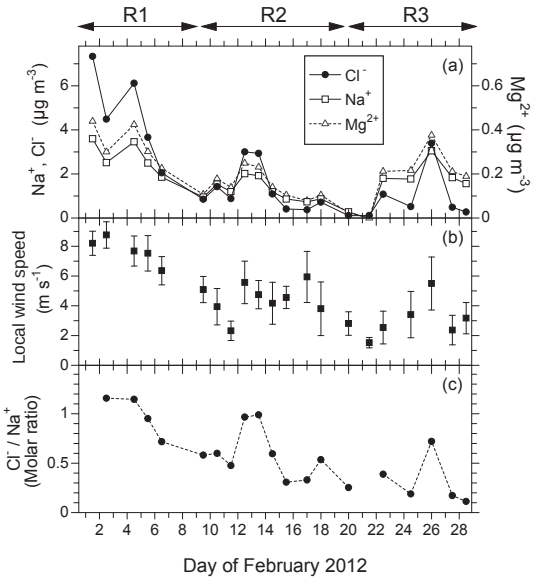

Figure 2. Time series of **(a)** the concentrations of Cl^-, Na^+, and Mg^{2+}; **(b)** local wind speeds measured on the ship; and (c) the Cl^- / Na^+ molar ratios. The local wind speed data were merged into the time interval of each filter sampling, and the average values with the SD over each sampling duration are shown. R1, R2, and R3 denote oceanic regions 1, 2, and 3, respectively, which are defined in the text and shown in Fig. 1.

2.3 Trajectory analysis

To investigate air mass histories along the TORERO cruise track, back trajectories were computed with the Real-time Air Quality Modeling System (RAQMS) (Pierce et al., 2007), which calculated chemical and meteorological forecasts. RAQMS has a horizontal resolution of $1° \times 1°$, with 35 hybrid eta theta vertical levels. Meteorological forecasts are initialized with operational analyses from the National Centers for Environmental Prediction (NCEP) Global Data Assimilation System (GDAS). The RAQMS calculations in conjunction with reverse domain filling (RDF) techniques (Sutton et al., 1994) are based on an analysis of back trajectories initialized along the cruise track. A three-dimensional 7-day back trajectory was calculated using the Langley Trajectory Model (LTM) (Pierce and Fairlie, 1993) and initialized at model hybrid levels along the TORERO cruise tracks.

3 Results and discussion

3.1 Characteristics of sea salt particles

Figure 2 presents a time series of concentrations of Na^+, Cl^-, and Mg^{2+} as tracers of sea spray, together with the daily-averaged local wind speed measured on the ship at each aerosol sampling location. In general, temporal variations of Na^+, Cl^-, and Mg^{2+} in the submicron particles were correlated with variation in local wind speeds with r^2 of 0.41–0.60 ($n = 21$). This is consistent with the wind-driven production of primary marine aerosol particles, whereas the moderate linear correlation can be explained by a power law relationship between sea spray mass and local wind speed (e.g., Ovadnevaite et al., 2012).

In this study, the aerosol sampling regions were classified into three categories according to the differences in oceanic areas and patterns of backward trajectories (Fig. 1). Region 1 (R1), sampled during the period of 1–7 February 2012, corresponded to open oceans at 5–15° N and 112–133° W. Most of Region 2 (R2) covered the oceanic area in the Southern Hemisphere (8° S–2° N and 93–110° W), where the sampling was conducted during 9–19 February. Region 3 (R3) was close to the coastal region at 0–8° N and 84–90° W, where observations were made during 20–28 February. R1 and R2 are characterized by very low anthropogenic impact on marine ecosystem (Halpern et al., 2008) and represent some of the most pristine ocean environments at tropical latitudes with the low Chl *a* concentrations (Fig. 1). According to the back trajectories, the air masses sampled in R1 and R3 (i.e., in the Northern Hemisphere) had been transported over the ocean for at least 48 h prior to aerosol sampling on the ship. The trajectories further indicated that those air masses were not significantly influenced by the land surface for at least 5 days. The air masses sampled in R2 had been transported over the ocean in the Southern Hemisphere for at least 5 days without any significant influence from the land surface or pollution. The relative influence of ocean surface and land on the observed aerosols will be discussed in Sect. 3.3.

In R3, enhanced marine biological activity at the sea surface was observed, with an average Chl *a* concentration of $0.15 \pm 0.04\,mg\,m^{-3}$ (Fig. 1). Because this value is substantially larger than the average concentration in R1 and R2, R3 is characterized as a high-Chl *a* region. The enhancement of the Chl *a* concentration in R3 (up to $0.33\,mg\,m^{-3}$) could be attributed to surface mixing in the Pacific Eastern Boundary Upwelling System (EBUS) (Rossi et al., 2009) and the coastal region (Pennington et al., 2006). R1 was characterized by high concentrations of sea salt particles with the average molar ratio of chloride to sodium (Cl^- / Na^+) close to unity. This is not necessarily expected in submicron aerosols in the tropical oceanic regions, because rapid acidification of sea salt particles occurs on the timescale of seconds (e.g., Pszenny et al., 2004; Keene et al., 2009). The fact that a depletion of Cl^- is apparently less pronounced in R1 indicates that the concentrations of gas species including organic acids (e.g., Laskin et al., 2012) responsible for the Cl^- loss were substantially low in R1. The current results suggest that the submicron particles collected in R1 were more similar to nascent sea spray aerosols compared to those in R2 and R3. The Cl^- / Na^+ ratio tended to decrease from R1 (av 1.06 ± 0.23) to R2 (av 0.60 ± 0.24) and R3 (av 0.32 ± 0.25). In fact, the Cl^- / Na^+ ratio tended to decrease with increasing sulfate concentration (not shown in the figure), whereas this

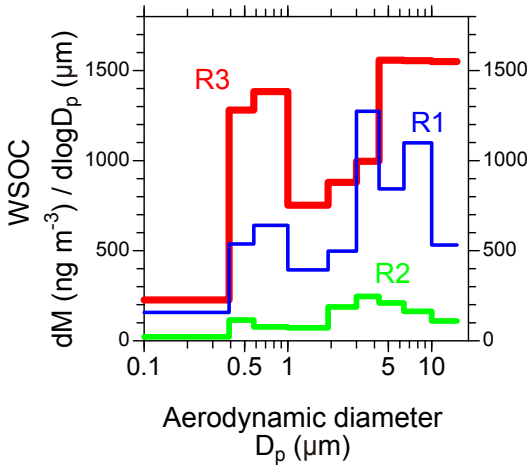

Figure 3. Typical mass size distributions of water-soluble organic carbon (WSOC) in R1, R2, and R3.

trend is not apparent for nitrate. This result suggests the Cl^- depletion by acid substitution in seawater-derived NaCl and indicates production of more chemically aged particles in R3 relative to R1 and R2.

3.2 Size distribution and time series of WSOC and related parameters

Figure 3 shows the typical mass size distributions of WSOC for each regional category during the TORERO cruise. In general, WSOC displayed a bimodal size distribution, with peaks in the submicron and supermicron particle-size ranges. Bimodal size distributions of WSOC in marine aerosols were also observed in the western North Pacific (Miyazaki et al., 2010), whereas both unimodal and bimodal size distributions of water-soluble organic species were also reported in particles collected at a coastal site facing the eastern North Pacific (Maudlin et al., 2015). The bimodal size observed in this study can be attributed to the difference in the formation processes of WSOC between the two size ranges. The two distinct size modes include (i) direct co-emissions associated with sea salt particles in both size ranges, (ii) aqueous-phase products in the submicron size range, and (iii) partitioning to the surface of coarse particles (i.e., sea salt) and/or heterogeneous reactions in the supermicron size range (Mochida et al., 2002). Although it is difficult to provide a clear explanation by this dataset alone, the observed WSOC size distributions might be explained by some combination of these possible origins and processes. Here we focus on the submicron size of WSOC relevant to its isotope ratios and several chemical tracers.

Figure 4a shows a time series of the mass concentration of WSOC and its ratio to TC in the submicron particles. In R1 and R2, the WSOC concentrations ranged between 50 and 160 ngC m^{-3}, with averages of 130 ± 27 and 85 ± 24 ngC m^{-3} for the two regions, respectively. The

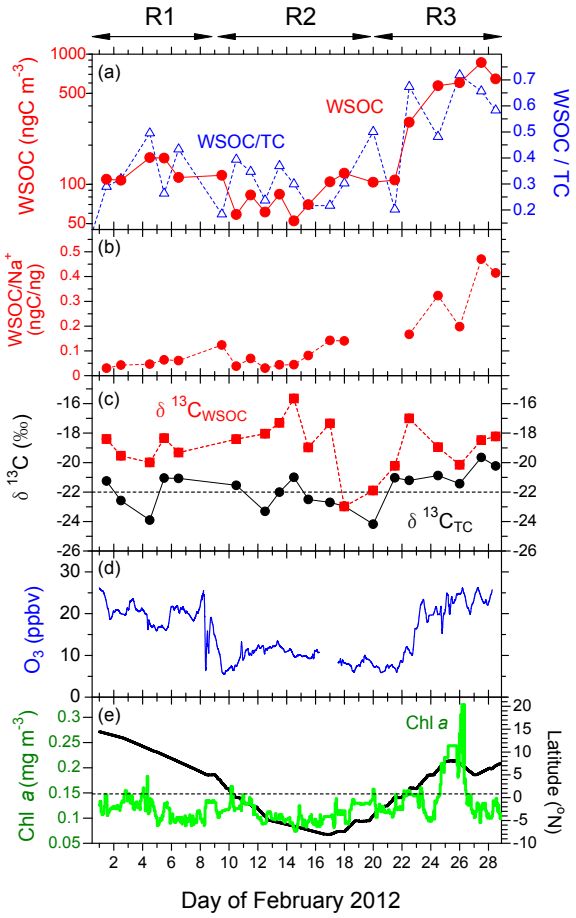

Figure 4. Time series of **(a)** WSOC, WSOC / total carbon (TC); **(b)** the mass ratio of WSOC / Na^+; **(c)** $\delta^{13}C_{TC}$ and $\delta^{13}C_{WSOC}$; **(d)** O_3 mixing ratios; and **(e)** in situ Chl *a* concentrations in surface seawater, along with the ship's position (latitude). The data for the WSOC / Na^+ ratio during 19–21 February are not shown because the Na^+ concentrations were extremely low (< 0.03 μg m^{-3}; Fig. 2a), which substantially increased the ratio.

WSOC / TC ratios ranged between 20 and 50 %, with averages of 36 ± 10 % (R1) and 31 ± 10 % (R2). Although black carbon (BC) concentration in the TC fraction was not measured in this study, most of the TC can be attributed to OC under the assumption of extremely low concentrations of BC (< 2 ng m^{-3}) previously observed over this oceanic region (Shank et al., 2012). The lower WSOC / TC ratios in R1 and R2 can be explained by fresh primary marine aerosols enriched in water-insoluble organic carbon (Facchini et al., 2008).

In contrast, both the WSOC concentrations (515 ± 268 ngC m^{-3}) and the WSOC / TC ratios (62 ± 19 %) were substantially higher in R3 than those in R1 and R2. Further, the correlation of WSOC with Na^+ was strongest in R3 ($r^2 = 0.40$). In the submicron particles, the average WSOC / Na^+ ratio was 0.15 ± 0.14 (Fig. 4b), which is within (though near the lower end of) the OC / Na^+ ratio range (0.1–2.0) pre-

Table 1. Average (± standard deviation) and median concentrations and ratios in the different oceanic areas during the Tropical Ocean tRoposphere Exchange of Reactive halogens and Oxygenated VOCs (TORERO) cruise observation. Values in parentheses show those of the 67th percentile. The precision of each measurement including the blank subtraction is also shown.

	R1 (1–7 Feb 2012)	R2 (9–19 Feb 2012)	R3 (20–28 Feb 2012)	Precision
Na^+ ($\mu g\,m^{-3}$)	2.78 ± 0.73 2.51 (3.46/2.49)	1.25 ± 0.47 1.19 (1.20/0.95)	2.00 ± 0.60 1.78 (1.83/1.77)	4 %
Cl^- / Na^+ molar ratio	1.06 ± 0.23 1.15 (1.16/0.95)	0.60 ± 0.24 0.58 (0.60/0.54)	0.32 ± 0.25 0.22 (0.25/0.19)	6 %
WSOC / Na^+ (ngC ng^{-1})	0.05 ± 0.01 0.05 (0.06/0.04)	0.08 ± 0.05 0.07 (0.08/0.04)	0.31 ± 0.13 0.35 (0.37/0.32)	16 %
WSOC (ngC m^{-3})	130 ± 27 113 (159/109)	85 ± 24 83 (84/70)	515 ± 268 588 (603/572)	15 %
TC (ngC m^{-3})	380 ± 132 337 (377/324)	322 ± 160 259 (323/238)	978 ± 345 973 (1106/840)	9 %
WSOC / TC (%)	36 ± 10 32 (43/29)	31 ± 10 30 (30/24)	62 ± 19 62 (66/58)	17 %
$\delta^{13}C_{WSOC}$ (‰)	-19.1 ± 0.7 -19.3 ($-18.4/-19.5$)	-19.6 ± 2.2 -18.4 ($-18.0/-19.0$)	-18.8 ± 1.2 -18.7 ($-18.5/-19.0$)	0.7 ‰
$\delta^{13}C_{TC}$ (‰)	-22.0 ± 2.0 -21.3 ($-21.0/-23.9$)	-22.1 ± 1.4 -22.5 ($-22.0/-22.7$)	-20.7 ± 0.7 -21.0 ($-20.9/-21.2$)	0.5 ‰
$\delta^{15}N_{WSTN}$ (‰)	10.1 ± 1.3 10.0 (10.9/9.9)	11.6 ± 1.3 11.4 (11.5/11.3)	12.8 ± 5.4 15.4 (16.5/14.3)	0.8 ‰
Glucose ($ng\,m^{-3}$)	0.11 ± 0.04 0.11 (0.12/0.10)	0.05 ± 0.08 0.03 (0.03/0.02)	1.55 ± 0.66 1.52 (1.89/1.15)	13 %
Fructose ($ng\,m^{-3}$)	0.02 ± 0.01 0.03 (0.03/0.02)	0.01 ± 0.01 0.01 (0.01/0.00)	0.48 ± 0.30 0.34 (0.39/0.28)	13 %
Fatty acids (C_{12}-C_{19}) ($ng\,m^{-3}$)	1.38 ± 0.47 0.97 (1.40/0.69)	3.60 ± 2.20 1.49 (1.58/1.37)	5.82 ± 3.02 3.32 (3.77/2.86)	28 %
MSA ($ng\,m^{-3}$)	92 ± 13 99 (102/82)	141 ± 21 144 (146/131)	123 ± 20 118 (121/114)	18 %
Chl *a* ($mg\,m^{-3}$)	0.112 ± 0.016 0.107 (0.129/0.100)	0.106 ± 0.015 0.101 (0.107/0.097)	0.147 ± 0.037 0.125 (0.127/0.123)	NA

viously reported for submicron marine primary OA (Russell et al., 2010; Frossard et al., 2014). This result is consistent with our understanding that the submicron SSA is enriched in OC relative to seawater (O'Dowd et al., 2004: Keene et al., 2007). The enrichment of water-soluble organics in the submicron particles is particularly significant for R3 (Fig. 4b), where the average WSOC / Na^+ ratio (0.31 ± 0.13) was substantially higher than that in R1 (0.05 ± 0.01) and R2 (0.08 ± 0.05) (Table 1). The enrichment of organics can be attributed to the phytoplankton blooms identified by the increased concentrations of Chl *a* in seawater (up to $0.33\,mg\,m^{-3}$) in R3 (Fig. 4e), together with the spatial distributions measured by the satellite (Fig. 1). Previous studies have shown a linkage between organics and high Chl *a* concentrations on timescales of months (O'Dowd et al., 2004; Sciare et al., 2009). However, Quinn et al. (2014) found no well-defined relationship between instantaneous Chl *a* in seawater and organic-mass enrichment in sea spray, suggesting no significant variability in the OC content of freshly emitted sea spray aerosol, despite significant variability in seawater Chl *a* levels. This point will be discussed in Sect. 3.3. The higher WSOC / Na^+ ratio in R3 can be also interpreted as an indicator of secondary contributions of photochemical products of primary OA and/or marine biogenic organic gas species to the observed aerosols during the ag-

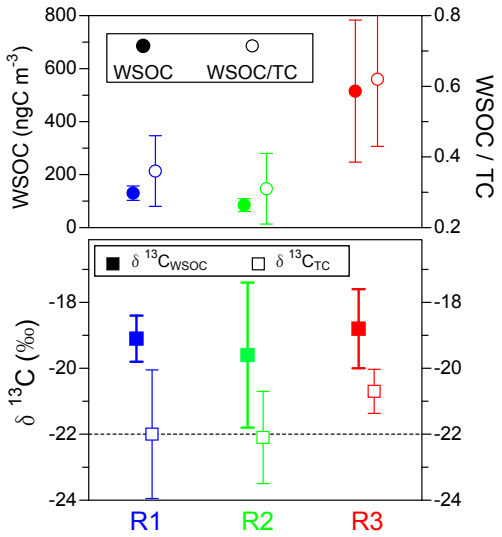

Figure 5. Average values of the WSOC concentration, the WSOC / TC ratio, $\delta^{13}C_{TC}$, and $\delta^{13}C_{WSOC}$ in each oceanic area.

ing, as indicated by the enhanced levels of O_3 (up to 25 ppbv) (Fig. 4d) and the decreased Cl^- / Na^+ ratio (Fig. 2).

3.3 Isotopic characterization of aerosol WSOC and TC

As shown in Fig. 4c, the $\delta^{13}C_{WSOC}$ ranged from −23.0 to −15.7 ‰, with an average of −19.8 ± 2.0 ‰ during the cruise. The $\delta^{13}C_{WSOC}$ values were systematically higher than the $\delta^{13}C_{TC}$ ranging from −25.5 to −19.7 ‰, with an average of −21.8 ± 1.4 ‰ (Fig. 5). On average, WSOC was enriched in ^{13}C by ∼ 2.0 ‰ relative to TC, indicating that ^{13}C-enriched submicron carbonaceous aerosol is preferentially water soluble. Regardless of the oceanic area, the average $\delta^{13}C_{WSOC}$ values of −19.6 to −18.8 ‰ (Table 1) were within the typical range of $\delta^{13}C$ in the DOC pool of seawater (−22 to −18 ‰; Fontugne and Duplessy, 1981). This range is influenced by factors such as local ocean temperatures and phytoplankton species, whereas changes in $\delta^{13}C$ resulting from trophic transfers are minimal (e.g., Guo et al., 2003). In the eastern North Pacific and in tropical oceans, the $\delta^{13}C$ of DOC typically ranges from −22 to −20 ‰ in surface seawater (Bauer and Druffel, 1998). In contrast, relatively few studies have measured the $\delta^{13}C$ signature in aerosol WSOC, which ranges from −25.5 to −23 ‰ at rural and urban sites, and is generally attributable to terrestrial and fossil sources (Kirillova et al., 2010; Wozniak et al., 2012). The $\delta^{13}C_{WSOC}$ measured in this study indicate an enrichment of sea-surface-derived DOC in submicron WSOC aerosols throughout the study region, and the ^{13}C-enriched WSOC over TC cannot be explained by influences of land surface. It should be noted that this enrichment of ^{13}C in WSOC could be partly due to isotopic fractionation throughout the partitioning of semi-volatile organics between the gas and particle phases (Fisseha et al., 2009). In equilibrium, partitioning between the gas and particle phases leads to larger ^{13}C of particle-phase organic compounds than the corresponding gas-phase compounds (Gensch et al., 2014). However, even if this effect (±2.0 ‰) is taken into account, the $\delta^{13}C_{WSOC}$ values were still within the range of $\delta^{13}C$ of DOC.

A combination of both carbon and nitrogen isotopic signatures can provide better information on the sources of dissolved organic matter (DOM) in marine aerosols than carbon isotopes alone. Figure 6 shows the ranges of the nitrogen isotope ratio of the water-soluble total nitrogen ($\delta^{15}N_{WSTN}$) and $\delta^{13}C_{WSOC}$ in the submicron aerosols for each oceanic region. The $\delta^{15}N_{WSTN}$ ranged between 3.5 and 16.7 ‰, with an average of 11.8 ± 3.1 ‰. The wide range of $\delta^{15}N_{WSTN}$ values was partly due to the fact that WSTN contains inorganic nitrogen, such as NO_3^- and NH_4^+, in addition to water-soluble organic nitrogen (ON). In general, the observed values were similar to the $\delta^{15}N$ values in surface seawater (i.e., 2 m depth). Benner et al. (1997) reported a dataset of $\delta^{15}N$ values for marine high-molecular-weight DOM samples obtained in the Gulf of Mexico and the Pacific and Atlantic oceans, which ranged from 6.6 to 10.2 ‰. The $\delta^{15}N_{WSTN}$ in aerosol also provide evidence of a significant contribution of DOC to the observed submicron aerosols.

Figure 7 shows the percentage exposure (percent of time over 7 days) of the sampled air mass to ocean and land surfaces along the cruise track as functions of altitude and time. The calculated air parcels were initialized at each sampling location along the cruise track. This Lagrangian trajectory analysis showed very low exposure (< 20 %) of air parcels at the sampling points on the ship to boundary layers over land, consistent with the results of the isotopic analysis, and suggested that the majority of submicron WSOC originated from the sea surface during the study period. It is noted that the observed aerosols in R3 had been transported by low-level air flow from the Atlantic, as indicated by the back trajectories (Fig. 1). In fact, the trajectories had passed over the Isthmus of Panama at higher altitudes, followed by descent to the sampling point in R3 as seen in Fig. 1, indicating less influence from the land surface. This is consistent with the results from the isotopic analysis of WSOC, which suggest that the influence of the land surface on the observed WSOC was insignificant.

In R3, the elevated levels of WSOC along the cruise track were not always accompanied by the increase of Chl *a* on a daily timescale. Specifically, the Chl *a* concentrations displayed an insignificant increase on 22 and 27–28 February, whereas the WSOC concentrations increased, ranging from 300 to 900 ngC m^{-3} during the same periods (Fig. 4a and e). Deng et al. (2014) also observed the lack of correlation between organics and Chl *a* over the eastern Pacific. They attributed it to the small variation in Chl *a* and the fact that aerosol composition is only sensitive to major changes in Chl *a*. Rinaldi et al. (2013) observed time lag between Chl *a* and OM enrichment in aerosol, suggesting that biological processes in oceanic surface waters and their timescales

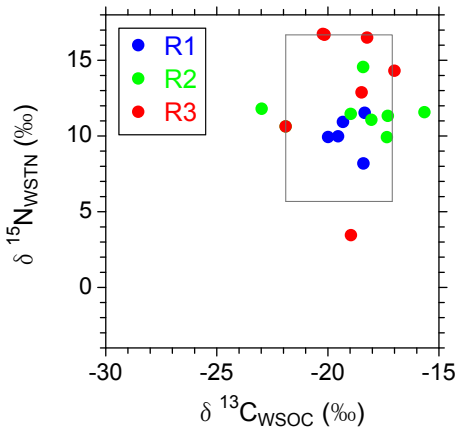

Figure 6. The ranges of the $\delta^{15}N_{WSTN}$ and $\delta^{13}C_{WSOC}$ in the submicron aerosols obtained in each oceanic area. The rectangle in the panel indicates the typical ranges of $\delta^{15}N$ and $\delta^{13}C$ for dissolved organic matter (DOM) in the eastern equatorial Pacific (see text).

should be considered when modeling the production of primary marine OA. Quinn et al. (2014) assessed the relationship between the OC content of seawater and freshly emitted SSA in the presence and absence of phytoplankton blooms in the North Atlantic and the coastal waters of California. They concluded that there is a large reservoir of OC in surface seawater that results in the enrichment of OC in SSA. They also reported that the oceanic source of OC in the region is uncoupled from, and overwhelms any influence of, local biological activity as measured by Chl *a* over large ocean regions. O'Dowd et al. (2015) showed that a correlation between OM in sea salt particles and Chl *a* increased as the timescale increased from daily to monthly intervals and suggested that OM production is closely linked with the decay phase of the bloom and is driven by nanoscale biological processes that release large quantities of transferable OM in surface seawater. The results of our study support those of previous studies in showing that linear source functions based on Chl *a* might not properly predict OC enrichments for SSA on the timescale considered here.

3.4 Monosaccharides, fatty acids, and MSA as marine biogenic tracers

We also used several organic molecular markers to further investigate the contribution of DOC to the submicron organics in concert with the isotope tracers described previously. The analysis of sea surface waters for organics has revealed a significant carbohydrate concentration, including glucose (Aluwihare et al., 1997), whereas primary saccharides (e.g., glucose) in aerosol have been suggested as possible tracers for surface soil dust and/or biomass burning (Simoneit et al., 2004). Electron ionization–mass spectrometry (EI-MS) measurements of marine aerosol in the western Pacific revealed substantial contributions from carbohydrates such as glucose and levoglucosan, and the former is partially attributed to organics from the ocean surface (Crahan et al., 2004). Low-molecular-weight LMW FAs have multiple sources associated with marine microbial activity, vascular plants, and microbes (Mochida et al., 2002; Kawamura et al., 2003). Burrows et al. (2014) introduced a framework for parameterizing the fractionation of marine OM into SSA and partitioned marine OM into different classes, including a polysaccharide-like mixture associated with semilabile DOC, a lipid-like mixture associated with labile DOC, and others. In this study, we investigated the possible contributions of types of DOC to submicron organics using the molecular markers of DOC.

Figure 8a–b show a time series of concentrations of glucose, fructose, and LMW FAs (C_{12}–C_{19}) in the submicron particles collected. The concentrations of both glucose and fructose were elevated in R3, with average values of 1.6 ± 0.7 and 0.5 ± 0.3 ng m^{-3}, respectively. The observed concentrations of glucose and LMW FAs were similar to those observed in total suspended particulate matter (TSP) over coastal areas in California and western Mexico (1.0–1.4 and 1.0–6.0 ng m^{-3} for glucose and LMW FAs, respectively) (Fu et al., 2011). The temporal trends of these saccharides were similar to that of WSOC, with r^2 of 0.82 ($n = 21$). The mass ratio of (glucose + fructose) / Na^+ was substantially higher in R3 compared to the other regions, indicating an enrichment of these monosaccharides in submicron sea salt particles over oceanic areas with high biological activity. In contrast, the correlation between LMW FAs and WSOC was less significant ($r^2 = 0.31$). The combined results of the organic molecular tracers and $\delta^{13}C_{WSOC}$ indicate a substantial contribution of saccharide-related DOC associated with sea spray to submicron WSOC. The results also suggest that the monosaccharides detected here might be suitable indicators for the ocean-derived submicron WSOC over the study region.

Russell et al. (2010) used reference Fourier transform infrared (FTIR) spectra of 11 different saccharides, including glucose, and found that a majority of organic component in ambient marine submicron aerosol consisted of organic hydroxyl groups characteristic of saccharides. Frossard et al. (2014) observed a significant amount of monosaccharides and disaccharides in model-generated primary marine aerosols from bubbled seawater, whereas the organic mass hydroxyl group in seawater was mostly characterized by polysaccharides. They attributed this finding to the larger saccharides preferentially remaining in the seawater during the primary OA production. Miyazaki et al. (2014) found lactic and glycolic acids, which are LMW hydroxyacids that can be produced as the major metabolic end products of carbohydrate fermentation, in marine aerosols obtained from biologically active oceanic regions of the western North Pacific. The results of our study on glucose and fructose in the submicron WSOC were consistent with the chemical signatures of marine OA reported in those studies. Moreover, our result is in line with a modeling study by Burrows et al. (2014), who

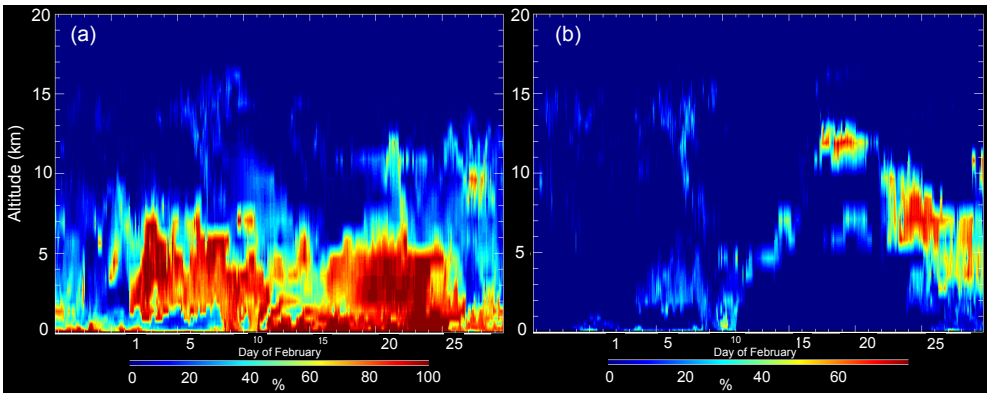

Figure 7. The percentage exposure of the 7-day air mass to the **(a)** maritime and **(b)** continental planetary boundary layer as functions of altitude and time. The calculation was made along the TORERO cruise track with the Real-time Air Quality Modeling System (RAQMS).

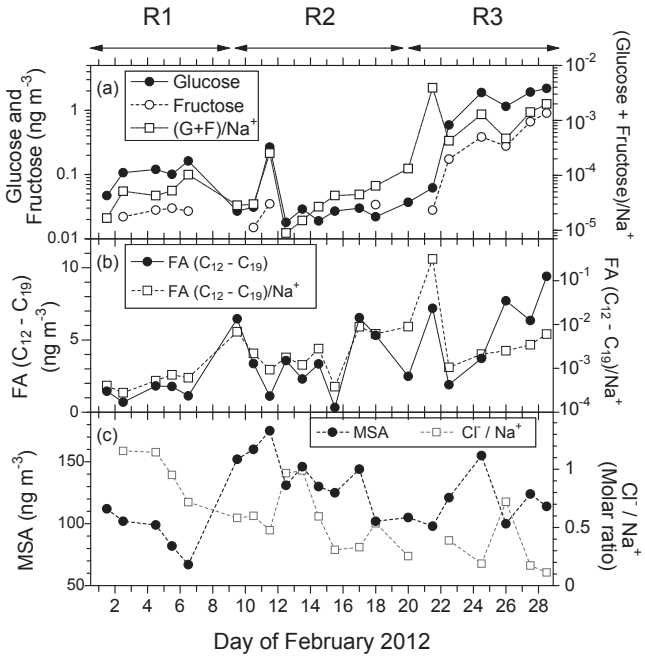

Figure 8. Time series of the concentrations of **(a)** glucose and fructose with their ratios to Na^+, **(b)** fatty acids (C_{12}–C_{19}) with their ratios to Na^+, and **(c)** methanesulfonic acid (MSA) and the Cl^- / Na^+ molar ratios in the submicron aerosol samples collected during the cruise.

simulated that, in regions such as the Southeast Pacific, semi-labile DOM contributes significantly to estimated aerosol organic mass as saccharides and proteins. They also reported an anticorrelation between Chl *a* and OM fraction in their model. Contributions of proteins to the submicron WSOC in the same samples are discussed in Chen et al. (2016) using excitation–emission matrices.

MSA in aerosol is also considered a marker of marine biogenic origin, because it is a major oxidation product of dimethyl sulphide (DMS). The mass concentration of MSA increased in R2, with an average of 141 ng m^{-3}, which was greater than in R3 (123 ng m^{-3}) (Fig. 8c). The increase in the background level of MSA did not necessarily accompany the increase in the background level of WSOC in R2 (Fig. 4a). In fact, a globally coupled ocean–atmosphere model calculation showed a "hot spot" of mean sea surface DMS in the upwelling zones of the eastern equatorial Pacific from December to May whose oceanic area corresponded to R2 (Kloster et al., 2006).

The observed MSA is considered to be either produced by gas-phase MSA directly scavenged by aerosols or rapidly produced in aqueous phase from scavenged dimethylsulfoxide (DMSO) and methanesulfinic acid (MSIA) (Zhu et al., 2006), particularly under conditions with high relative humidity typical of the MBL. Assuming a typical average OH concentration of 1×10^6 cm^{-3}, a lifetime of DMS is roughly estimated to be $< \sim 1$ day with respect to oxidation by OH in the MBL (Davis et al., 1999; Kloster et al., 2006). The rapid oxidation of the intermediate reaction products of DMS to produce MSA (on a timescale of hours) and the typical residence time of submicron aerosols in the MBL ($\sim$ 5–7 days) indicate that the measured MSA likely reflects the larger emission of DMS around the sampling locations of R2. Additionally, a large missing source of MSA photolytically enhanced during the daytime has been as suggested by Zhang et al. (2014) and would be consistent with the lowest solar zenith angle in R2 (Coburn et al., 2014). The MSA concentrations generally increased with the decreasing Cl^- / Na^+ ratios (Fig. 8c), which is consistent with the chemical aging of the observed aerosols. Another possible reaction of DMS with species other than OH to produce MSA includes BrO+DMS (Saiz-Lopez et al., 2004). However, BrO in the MBL over this region was extremely low (generally below 0.5 pptv) during the same observational period (Volkamer et al., 2015), indicating that the reaction of BrO+DMS is likely insignificant source for MSA. Gaston et al. (2010) suggested a possible catalytic role of vanadium in MSA formation. The observed increases in the MSA concentrations were most ev-

ident in R2, in which the impacts of anthropogenic sources appeared to be very low. Therefore, the effects of such a catalytic reaction on the increases in MSA concentrations in R2 are likely insignificant. The lack of correlation between MSA and WSOC implies that the presence of DMS in seawater and its subsequent oxidation to MSA were not necessarily linked to the formation of submicron WSOC over this oceanic region. This confirms the difficulties of connecting Chl *a* with DMS concentrations in seawater over subtropical and tropical ocean as previously suggested (Bell et al., 2010).

3.5 Contribution of marine OC sources to the WSOC aerosol

To estimate the relative contribution from marine and terrestrial OC sources to the observed WSOC, an isotopic mass balance equation assuming a two-end-member isotopic mixing was used (e.g., Turekian et al., 2003; Miyazaki et al., 2010). We applied ^{13}C values ranging from −22 to −18 ‰ for marine OC and those ranging from −27 to −26 ‰ for terrestrial OC (e.g., Kirillova et al., 2010) typically found in the Northern Hemisphere. The effect of isotopic fractionation by heterotrophic degradation on OM is considerably small (∼ 1 ‰ for ^{13}C; Shaffer et al., 1999). Our calculation indicates that, on average, marine sources contribute ∼ 90 ± 25 % of the aerosol carbon. As discussed previously, the higher WSOC / Na^+ ratio in R3 indicates some contribution of a secondary, ocean-derived source to WSOC, although it is difficult to quantify their contributions to the WSOC mass.

The results of our study contradict those of Shank et al. (2012), who suggested that there was little to no marine source of submicron OA to the atmosphere in a similar oceanic region (corresponding to R1 and R2 in the current study) over the eastern South Pacific. Shank et al. (2012) reported the average concentrations of non-refractory organics in submicron aerosols to be as low as 70 ng m^{-3} with a maximum of 170 ng m^{-3} at most measured with an Aerodyne high-resolution time-of-flight mass spectrometer (HR-ToF-AMS). Assuming that most of the TC in this study can be attributed to OC in R1 and R2 and given OC-to-OM conversion factors of 1.8 for water-soluble OM and 1.4 for water-insoluble OM reported for the marine OA (Facchini et al., 2008), the average OA concentration in R1 and R2 is estimated to be ∼ 490–580 ng m^{-3} (cf. Table 1). These values are substantially larger than those reported by Shank et al. (2012). One possible explanation for the contradiction between our study and Shank et al. (2012) is that the studies were conducted in different seasons with different meteorological conditions and microbial activity at the sea surface. Another possible explanation is that the AMS could not detect a significant fraction of refractory material (e.g., HULIS) found in primary marine OA over the study region (Deng et al., 2014). Our analysis of $\delta^{13}C_{WSOC}$ and organic molecular markers indicated that DOC in surface seawater contributed substantially to the submicron WSOC levels regardless of the oceanic area of the study region. It is noted that the contribution of anthropogenic sources cannot be negligible although this is indicated by the isotopic analysis. Nevertheless, the present study demonstrates that DOC is closely correlated with the submicron WSOC aerosol concentration and implies that it may characterize background OA in the MBL over the study region.

4 Conclusions

Isotopic and organic molecular characterization of submicron WSOC aerosols provided an evidence of a significant contribution of marine DOC to submicron particles in the MBL during the TORERO/KA-12-01 cruise. On average, the WSOC fraction of the TC mass in submicron aerosols was ∼ 30–35 % in the low-Chl *a* regions, whereas it was ∼ 60 % in the high-Chl *a* regions over the eastern equatorial Pacific. The average $\delta^{13}C_{WSOC}$ (−19.8 ± 2.0 ‰) was systematically higher than $\delta^{13}C_{TC}$ (−22.2 ± 1.9 ‰) during the entire cruise. This was attributed to greater enrichment of planktonic tissues in δ^{13}C in the submicron WSOC. We found that the $\delta^{13}C_{WSOC}$ was close to the typical values of δ^{13}C for DOC in surface seawater throughout the cruise, suggesting enrichment of marine DOC in WSOC aerosols regardless of the oceanic area of the study region.

Enhanced levels of WSOC and monosaccharides (i.e., glucose and fructose) together with an elevated WSOC / TC (∼ 60 %) were observed over the upwelling areas and coastal regions. The δ^{13}C analysis indicated that marine-derived carbon accounted for ∼ 90 % of submicron WSOC. This finding was supported by a Lagrangian trajectory analysis, which suggested little exposure of air parcels at the sampling points to planetary boundary layer air over 7 days prior to the sampling. The lack of correlation between MSA and WSOC implies that the presence of DMS in seawater was not necessarily linked to the formation of submicron WSOC, consistent with the difficulties in connecting Chl *a* with DMS concentrations in seawater over this oceanic region. The combined results of the organic molecular tracers and $\delta^{13}C_{WSOC}$ suggest that the monosaccharide might be a suitable indicator for the ocean-derived submicron WSOC associated with sea salt over this oceanic region. This study provided direct evidence that the contribution of DOC was significantly correlated with the submicron WSOC mass across the study region regardless of the oceanic area.

5 Data availability

The data used in this study is available on request to Y. Miyazaki. The TORERO data is also available at http://data.eol.ucar.edu/master_list/?project=TORERO.

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