1 Biogenic emissions and nocturnal ozone depletion events at the
2 Amphitrite Point Observatory on Vancouver Island

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Routine monitoring stations on the west coast of North America serve to monitor baseline levels of criteria pollutants such as ozone (O_3) arriving from the Pacific Ocean. In Canada, the Amphitrite Point Observatory (APO) on Vancouver Island has been added to this network to provide regional baseline measurements. In 2014, McKendry and co-workers reported frequent nocturnal O_3 depletion events (ODEs) at APO that generally correlated with alongshore winds, elevated concentrations of carbon dioxide (CO_2) and stable boundary layer conditions, but whose cause (or causes) has (have) remained unclear.

This manuscript presents results from the Ozone-depleting Reactions in a Coastal Atmosphere (ORCA) campaign, which took place in July, 2015 to further investigate ODEs at APO. In addition to the long-term measurements at the site (e.g., of CO_2 and O_3 mixing ratios), abundances of biogenic volatile organic compounds (BVOC) and aerosol size distributions were quantified. ODEs were observed on the majority of measurement nights and were characterized by a simultaneous increase of CO_2 and BVOC abundances, in particular of limonene, a terpene 2.5× more reactive with respect to oxidation of O_3 than other monoterpenes.

Back trajectory calculations showed that ODEs occurred mainly in air masses that originated from the WNW where the air would have travelled parallel to the coastline and above kelp forests. Head space analyses of sea weed samples showed that bull kelp is a source of gas-phase limonene, consistent with its high relative abundance in air masses from the WNW sector. However, the enhanced terpene and CO_2 content showed that the air likely also came in contact with terrestrial vegetation via mesoscale transport phenomena (such as slope flows and land-sea breeze circulations) that were generally poorly captured by the back trajectories. This absence of aerosol growth during ODEs indicates that dry deposition is likely the primary O_3 loss mechanism.

Keywords: marine boundary layer, ozone depletion, coastal zone, monoterpene emissions, kelp, limonene

1. Introduction

Processes controlling the abundances of ozone (O_3) and fine particulate matter with a diameter smaller than $2.5\ \mu\text{m}$ ($\text{PM}_{2.5}$) continue to be of interest because of the association of high O_3 and $\text{PM}_{2.5}$ concentrations with health impacts such as chronic obstructive pulmonary disease (COPD), heart disease, and lung cancer (e.g., (Lelieveld, Evans, Fnais, Giannadaki, & Pozzer, 2015; Peng et al., 2013; Pope, Ezzati, & Dockery, 2009) and references therein). On the west coast of North America, the budgets of O_3 and, indirectly, the hydroxyl radical (OH) and $\text{PM}_{2.5}$ depend critically on the “background O_3 ” concentration, i.e., the concentration of O_3 entering from the Pacific Ocean (Ambrose, Reidmiller, & Jaffe, 2011; McDonald-Buller et al., 2011). In recent decades, this concentration has slowly been increasing due to long-range transport of continuously rising emissions in Asia (Jaffe, Price, Parrish, Goldstein, & Harris, 2003; Parrish et al., 2010; Parrish et al., 2004). On the other hand, the concentration of O_3 in the layer immediately above the ocean surface, the so-called marine boundary layer (MBL), is frequently depleted relative to atmospheric layers aloft. The principal O_3 depletion mechanisms in the MBL are dry deposition to the sea surface (Gallagher, Beswick, & Coe, 2001; Gallagher, Beswick, McFiggans, Coe, & Choularton, 2001; Ganzeveld, Helmig, Fairall, Hare, & Pozzer, 2009) and photochemical pathways, such as the HO_x driven O_3 destruction in low NO_x environments and catalytic cycles involving reactive halogen species (Galbally, Bentley, & Meyer, 2000; Lee et al., 2009; Read et al., 2008; Singh et al., 1996; Watanabe, Nojiri, & Kariya, 2005).

The Amphitrite Point Observatory (APO) was established on the west coast of Vancouver Island, British Columbia, Canada, in 2010 to serve as a background monitoring site. Recently, McKendry and co-workers (2014) reported observations of rapid nocturnal O_3 depletion events (ODEs) that have not been fully explained to date. Conventionally, nocturnal loss of surface O_3 is interpreted as being due to a

combination of dry deposition and chemical titration by nitric oxide (NO) to nitrogen dioxide (NO₂) and by reaction of O₃ with unsaturated biogenic hydrocarbons (Kleinman et al., 1994; Logan, 1989; Neu, Kunzle, & Wanner, 1994; Trainer et al., 1987). At APO, the ODEs are generally associated with along- or onshore flow, stable boundary layer conditions, and an increase in the concentration of carbon dioxide (CO₂) but not with anthropogenic pollution tracers, i.e., NO_x, CO, and SO₂ (McKendry et al., 2014). CO₂ has sinks (photosynthesis) and sources (respiration and combustion) that are much stronger in the continental compared to the marine environment (which is a net CO₂ sink (Gruber et al., 2009)). Hence, elevated concentrations of CO₂ trace continentally influenced air at coastal sites (Parrish, Millet, & Goldstein, 2009). The correlation of ODEs with CO₂ and the absence of correlations with anthropogenic tracers at APO suggest that the upwind air had been in contact with vegetation where O₃ would have been more rapidly deposited than to the ocean surface (Gallagher, Beswick, & Coe, 2001; Wesely & Hicks, 2000). Yet, back trajectories calculated using the Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) (Draxler & Hess, 1998; Draxler & Rolph, 2011) and the "North American Meso" (NAM) meteorological field at 12 km resolution were inconsistent with this interpretation. The back trajectories showed that ODEs were characterized by light onshore or alongshore winds and that the air masses generally originated in the MBL, i.e., had a marine origin. Overall, the evidence indicated that the ODEs at APO are caused by a non-photochemical coastal zone process that extends over a spatial scale of tens of kilometres (McKendry et al., 2014).

One such process could be the natural nocturnal O₃ deposition on near-shore forest vegetation coupled with a nocturnal land breeze that mixes continentally influenced air against the predominant westerly synoptic flow. This process is in all

likelihood poorly captured by the meteorological fields and, hence, HYSPLIT trajectories. Evidence to corroborate this hypothesis would be an enhancement of biogenic volatile organic compound (BVOC) concentrations, in particular of monoterpenes whose emissions have both a light-dependent (photosynthetic) as well as a light-independent fraction which (unlike those of isoprene) continue at night (Fares et al., 2013; Guenther et al., 2012). The tree species in the region are predominantly coniferous and include Western Red Cedar (*Thuja plicata*), Coastal Douglas Fir (*Pseudotsuga menziesii ssp. menziesii*) and Western Hemlock (*Tsuga mertensiana*) (Mason et al., 2015). Monoterpenes ($C_{10}H_{16}$), in particular α - and β -pinene, dominate BVOC emissions from this type of vegetation (Burney & Jacobs, 2012; Copeland, Cape, Nemitz, & Heal, 2014; Drewitt, Curren, Steyn, Gillespie, & Niki, 1998; Geron, Rasmussen, Arnts, & Guenther, 2000; Helmig, Daly, Milford, & Guenther, 2013; Lagalante & Montgomery, 2003; Sakulyanontvittaya, Duhl, et al., 2008).

In this work, mixing ratios of the monoterpenes α - and β -pinene, limonene, carene, and terpinolene, as well as the β -pinene oxidation product nopinone ($C_9H_{14}O$) were quantified at APO for the first time to provide further insight into the cause (or causes) of the nocturnal ODEs during summertime. Nopinone is produced from the reaction of O_3 with β -pinene in ~50% yield (Jenkin, 2004) and is thus a direct tracer of O_3 -monoterpene chemical reactions, though it is also produced (and destroyed) during the daytime from reactions initiated by OH (Barthelmie & Pryor, 1999; Jaoui & Kamens, 2003; Kavouras, Mihalopoulos, & Stephanou, 1999; Larsen et al., 2001). The data set includes measurements of aerosol size distributions as an indirect probe of O_3 -monoterpene chemistry which results in the production of non-volatile material and manifests itself by either new particle formation or growth (Ehn et al., 2014; Griffin, Cocker, Flagan, & Seinfeld, 1999; Sakulyanontvittaya, Guenther, Helmig, Milford, &

Wiedinmyer, 2008). Correlations of ODEs with CO₂ and BVOC concentrations are presented. Sources of BVOCs in the region and implications of the data for the interpretation of ODEs at APO are discussed.

2. Methods

a. Study overview

The APO is located on the west coast of Vancouver Island south of the town of Ucluelet at 48.92° N and 125.54° W (Figure 1) less than 100 m from the high tide line of the Pacific Ocean. It was the location of several recent measurement intensives, and the immediate vicinity of the measurement site has been described comprehensively in the associated manuscripts (Mason et al., 2015; McKendry et al., 2014; Wilson et al., 2015; Yakobi-Hancock et al., 2014). For this study, named the "Ozone-depleting Reactions in a Coastal Atmosphere" (ORCA) campaign, instrumentation was housed in two mobile laboratories separated by a distance of approximately 15 m: one was operated by Environment Canada, British Columbia's Ministry of the Environment, and Metro Vancouver, whose measurement suite (which include a Licor 820 CO₂ monitor) has been described elsewhere (Mason et al., 2015; McKendry et al., 2014; Wilson et al., 2015; Yakobi-Hancock et al., 2014). The other was operated by the University of Calgary, whose measurements are described below. Meteorological parameters were measured at the Amphitrite Lighthouse (located halfway between the main field site and the ocean) and by a weather station (Vaisala WXT520) operated at a height above ground of 5.2 m atop the University of Calgary mobile laboratory. Off-shore meteorological data were collected at a moored buoy (C46206, located at La Perouse Bank 35 km WSW of APO) as described by Mason et al. (2015). Data were collected from July 8 - 31, 2015.

144 *b. Gas phase measurements*

145 Mixing ratios of BVOCs and nopinone were quantified using a commercial gas
146 chromatograph equipped with a cylindrical ion-trap mass analyzer (Patterson et al.,
147 2002; Riter et al., 2002) and electron impact ionization (Griffin 450 GC-MS). This
148 instrument sampled from a 6.5 m long and 0.635 cm outer diameter (o.d.) stainless steel
149 inlet from a height of 4.3 m above ground. A 3 m long section of the inlet was heated to
150 125 °C to remove interference due to O₃ (Hellén, Kuronen, & Hakola, 2012; Pollmann,
151 Ortega, & Helmig, 2005). Air samples were pre-concentrated for 8 minutes at a flow
152 rate of 213 mL min⁻¹ on a dual sorbent trap containing Tenax TA and Carboxen 1017
153 held at 40 °C and were desorbed at a temperature of 240 °C onto a 30 m (length) × 0.25
154 mm (inner diameter) × 0.25 µm (film thickness) DB-5MS column operated with helium
155 carrier gas (Praxair, ECD grade) purified using a triple trap (Restek 22464). The GC
156 oven was programmed as follows: hold at 40° C for 3.00 min, heat at 3° C min⁻¹ to 70°
157 C and hold for 2.00 min, and heat at 15° C min⁻¹ to 200 °C and hold for 2.00 min (total
158 25.67 min). This was followed by a 5.00 min recovery time to allow the oven and
159 preconcentration trap to cool back to 40 °C. Full mass spectra (m/z from 35 to 425 Da)
160 were collected at a rate of ~ 3 Hz. Retention times and indices, quantification ions, and
161 limits of detection of the monoterpenes monitored are summarized in Table S-1.

162 The instrument was calibrated using mass flow controllers and a gas cylinder
163 filled with a standard VOC mixture prepared in-house on July 2, 2015, a week prior to
164 the campaign. This working standard was prepared by quantitatively transferring a 50
165 VOC component calibration mixture (Supelco 49148-U) containing α -pinene, β -pinene
166 and limonene in methanol to an evacuated aluminum cylinder (supplied by Scott-
167 Marrin; internal volume 29.50±0.33 L) which was subsequently pressurized with
168 nitrogen gas to a pressure of 8500±250 kPa. The accuracy of this standard was

compound dependent and calculated from the concentration uncertainties provided by Supelco and uncertainty of the dilution volume and was 9.6% on average (range 8.3% to 12.0%). The uncertainties in the amounts delivered from this cylinder are increased further due to uncertainties in the flow delivered by the mass flow controllers to a total of ~11% on average. This error analysis assumes quantitative delivery of the VOCs through the 2-stage cylinder pressure regulator and the all-metal mass flow controller (a reasonable assumption following a several day long break-in period). Not included in this uncertainty is the potential loss (or production) of terpenes within the cylinder over the course of this campaign, which are expected to be small in a one month old aluminum cylinder but can be substantial, especially over longer time periods (e.g., (Apel et al., 1999; Jones, Kato, Nakashima, & Kajii, 2014; Rhoderick, 2010; Rhoderick & Lin, 2013)).

Between July 16 and 31, 2015, five "full" calibrations, i.e., with ≥ 5 points on the calibration curve measured in random order (including a "blank"), were performed. For the monoterpenes, the slopes of the calibration curves had relative standard deviations in the range of $\pm 3.2\%$ to $\pm 22.6\%$ (average 8.0%) and intercepts whose value ± 1 standard error encompassed zero. The response factors were linearly interpolated between calibration points.

The precision of the GC-MS was determined from the standard deviation of repeated measurements of a small amount of β -pinene evaporated into a 4,000 L smog chamber to an approximate mixing ratio of ~100 pptv and was $\pm 3.4\%$.

It has been reported that monoterpenes can undergo rearrangement reactions during the thermal desorption process following preconcentration on Tenax (Arnts, 2010). In post-campaign experiments, approximately 1.5% of trapped β -pinene was found to isomerize to limonene, α -pinene, and camphene during desorption on our

instrument. Because this process happens during both calibration and ambient measurement of β -pinene, its effect is included in the instrumental response factor. In contrast to β -pinene, no rearrangement products were observed for either limonene or α -pinene.

Assuming that the above uncertainties are independent from each other and neglecting the potential degradation of monoterpenes within the standard gas cylinder, the total uncertainty (at the 1σ level) of the monoterpene measurements presented is $\pm 15\%$, driven by the systematic uncertainty in the preparation of (and delivering a calibrated gas flow from) the standard gas cylinder ($\pm 11\%$), the standard uncertainties in the slopes of the calibration curves ($\pm 8\%$), and the measurement precision ($\pm 3.4\%$).

Not included in this uncertainty estimate are potential systematic errors arising from the interpolation between calibration points.

The response factors for carene and nopinone were determined prior to and after the campaign relative to that of α -pinene; the uncertainty of their mixing ratios was estimated at $\pm 30\%$.

Other gas-phase measurements in the University of Calgary mobile laboratory included a UV absorption O_3 analyzer (Thermo Scientific 49i), a total odd nitrogen (NO_y) chemiluminescence analyzer (Thermo Scientific 42i), and a multi-channel cavity ring-down spectrometer for quantification of NO_2 and NO_x constructed in-house (Odame-Ankrah, 2015; Paul & Osthoff, 2010).

c. Particle phase measurements

Submicron and supermicron size distributions were monitored using a scanning mobility particle sizer (SMPS, TSI 3936L75) operated with butanol and an aerodynamic particle sizer (APS, TSI 3321). The SMPS sampled through a $1\ \mu m$ cut-off impactor (0.071 cm internal diameter) via 3/8" o.d. conductive silicon tubing secured next to the

GC-MS inlet. The APS was operated from the container located on top of the trailer and sampled from a 1.6 m tall ½ o.d. aluminum tube (4.4 m AGL) whose tip was bent into a U-shape to prevent precipitation from entering the inlet. Both instruments were calibrated by the manufacturer but not in the field (e.g., inlet transmission efficiencies were not characterized), such that the aerosol size distributions are semi-quantitative.

d. Photolysis frequencies

Photolysis frequencies were determined by solar actinic flux spectroradiometry (Hofzumahaus, Kraus, & Muller, 1999) using a commercial radiometer with 2π receptor optics and photo diode array (PDA) detector (Metcon; 512 pixels, wavelength range 285 nm - 690 nm) which had been calibrated by the manufacturer. The spectrometer was mounted facing up (zenith view) to measure the down-dwelling radiation. The spectrometer was inverted periodically to determine the up-dwelling radiation. Photolysis frequencies were calculated using reference spectra and quantum yields from the NASA-JPL evaluation (Sander et al., 2010) and updated ClNO₂ cross-sections (Ghosh, Papanastasiou, Talukdar, Roberts, & Burkholder, 2011).

e. Back trajectory calculations

Twelve-hour back trajectories were calculated using the National Oceanic and Atmospheric Administration (NOAA) HYSPLIT online model and the "NAM meteorological field at 12 km resolution. The trajectory calculations were initiated every hour, starting 1 hr prior to the ODEs and ending 1 hr after the ODEs ended, with heights of 10 m, 50 m, and 100 m above ground.

3. Results and analysis

a. Identification of ozone depletion events

Time series of O_3 and CO_2 , the monoterpenes α - and β -pinene, limonene, and carene as well as the β -pinene oxidation product nopinone, NO_2 and odd oxygen ($O_x = O_3 + NO_2$) for the period of July 16 to 31, 2015 are shown in Figure 2. Time series of meteorological parameters are shown in Figure S-1. McKendry et al. (2014) outlined the following criteria to identify ODEs: a drop in O_3 mixing ratio from a starting value of no higher than 32 ppbv (the third monthly quartile O_3 mixing ratio in July), by more than 15 ppbv, and occurring over a time period of 12 hours or less. Using these criteria for the 16 nights shown, 9 nocturnal ODEs were identified. These are indicated as blue bars in Figure 2 and have been summarized in Table 1. The high frequency of ODEs confirms that they are indeed a frequent phenomenon at APO.

b. Correlations of ozone depletion events with chemical tracers

The ODEs were accompanied by an increase in CO_2 mixing ratios (Figures 2A and 5B), as had been reported by McKendry et al. (2014). At the beginning of the ODEs, CO_2 mixing ratios were usually below 380 ppmv. This abundance is less than what was measured at Trinidad Head, California in July, 2015 (396 ± 1 ppmv). (Dlugokencky et al., 2016) Plausible explanations for the lower than expected CO_2 mixing ratios are either a prolonged period of CO_2 oceanic uptake in a decoupled marine boundary layer and/or photosynthetic uptake by vegetation upwind of the measurement location.

Once the ODEs started and O_3 mixing ratios decreased, CO_2 mixing ratios increased. Data from all nine ODEs were lumped together in one-hour bins as a function of time of day, with 12:00 (noon) set to the solar zenith angle minimum. The 90th, 75th, 25th, and 10th percentile and median (i.e., 50th percentile) O_3 and CO_2 mixing ratios as

functions of local time of day during the ODEs are shown in Figure 3A. The median O₃ and CO₂ mixing ratios are anti-correlated with a linear correlation coefficient of $r = -0.92$ and slope of (-0.390 ± 0.005) ppbv O₃ / ppmv CO₂.

It is well known that forest vegetation represents a sink of O₃ and, because of the absence of O₃ production, results in a net loss of O₃ at night (Trainer et al., 1987; Turner, Waggoner, & Rich, 1974). The observed anti-correlation can be rationalized by respiration by vegetation, which releases CO₂ into a shallow nocturnal boundary layer; at the same time, O₃ deposition continues, though with reduced deposition velocity (Fan, Wofsy, Bakwin, Jacob, & Fitzjarrald, 1990; Monson & Holland, 2001; Rø-Poulsen, Mikkelsen, Hovmand, Hummelsehoj, & Jensen, 1998; Zeller & Nikolov, 2000).

Since trees continue to emit monoterpenes at night, the nocturnal release of CO₂ from trees is expected to be accompanied by an increase in monoterpene concentration. Accordingly, mixing ratios of monoterpenes were also elevated during ODEs, coinciding with the increase in CO₂ (Figures 2B, 3B and 5B). The highest monoterpene mixing ratios were observed during the ODEs of the nights of July 18/19 and 19/20. Carene and nopinone mixing ratios were elevated on those nights (Figure 2B). The HYSPLIT back trajectories showed that the air masses sampled on those nights originated from the east (Table 1), i.e., had travelled over land covered by dense forests, explaining the higher than average monoterpene mixing ratios and also the presence of the β -pinene oxidation product nopinone.

The linear correlation coefficient of CO₂ and total monoterpene concentrations during ODEs was $r = 0.93$, whereas that of O₃ and total monoterpenes was $r = -0.76$. CO₂ is a more conserved tracer than monoterpenes which are oxidized by O₃ (and the nitrate radical, NO₃). The nopinone mixing ratios (Figure 2B) did not increase during

ODEs (Figure 4B), with exception of the nights of July 18/19 and 19/20, which indicates that titration of O₃ in the gas-phase was a minor O₃ depletion process and suggests that O₃ is lost more by dry deposition than by titration in the gas-phase. This conclusion is supported by the absence of new particle formation and aerosol growth during the ODEs (see section c below).

In polluted areas, O₃ mixing ratios are often depleted due to titration of O₃ by NO, which manifests itself by an anti-correlation of O₃ and NO₂ mixing ratios (Kleinman et al., 1994; Logan, 1989; Neu et al., 1994; Trainer et al., 1987). In contrast to CO₂ and monoterpenes, O₃ mixing ratios only correlated weakly with those of the anthropogenic pollution tracer NO₂ ($r = -0.44$). A scatter plot of O₃ against NO₂ mixing ratios is shown in Figure 5C, where the data points collected during ODEs are colour-coded by CO₂ mixing ratio. The vast majority of data points during ODEs are associated with NO₂ mixing ratios < 2 ppbv. Hence, the contribution of NO-O₃ titration to ozone depletion was minor.

This conclusion is corroborated by considering trends in O_x which parallel those of O₃ (Figure 2C). When O_x (instead of O₃) is correlated with total monoterpenes during ODEs, the anti-correlation becomes more pronounced ($r = -0.78$ compared to -0.76). In contrast, the anti-correlation of O_x with CO₂ changes to $r = -0.81$ (from -0.92), likely because NO₂ and CO₂ are both present in combustion exhaust where they correlate.

Overall, the correlations of O₃ with chemical tracers corroborate the notion that ODEs are not driven primarily by anthropogenic pollutants and that ODEs occur in air masses that have been in contact with respiring vegetation.

c. Role of meteorology

The ODEs were generally marked by a reduction in local wind speed (Figures S1 and 5A). The lowest O₃ mixing ratios were observed when the air stagnated (Figure

5A). This suggests that ODEs are caused by a local mechanism and are not representative of a process occurring over a wider scale. There was no correlation of ODEs with tide height (data not shown).

Synoptic conditions during the ODEs, judged from composite sea level pressure and geopotential height and their anomaly maps obtained from the National Oceanic and Atmospheric Administration's Physical Sciences Division's web site (Figure S-2) were similar to those reported by McKendry et al. (2014), in that they show a high pressure region centered north of the Hawaiian Islands in the Pacific Ocean, with a developing high-pressure ridge aligned along the Pacific Northwest coast. Though not as pronounced as shown by McKendry et al. (2014), this high pressure region extends above the measurement site on Vancouver Island. The anticyclonic (i.e., clockwise rotation) conditions (Figure S2) are expected to be associated with predominantly WNW to NW winds in the study region as well as downward advection of warmer, dry air from the upper troposphere in the anticyclone's center, leading to greater temperature inversion and capping of the boundary layer throughout the high-pressure system (Stull & Ahrens, 2000).

McKendry et al. (2014) had based much of their analysis on HYSPLIT back trajectories with the NAM met field. Tables S-2 through S-10 summarize the hourly HYSPLIT back trajectory data for this data set. By and large, the HYSPLIT results were in agreement with local wind direction, with exception of July 27, when the flow reversed (from on-shore to off-shore flow) in the middle of the night which was not captured by the HYSPLIT trajectories. The ends of the ODEs were generally also marked by a change (often a reversal) of local wind direction, which also were not captured by HYSPLIT trajectories (e.g., on July 16, 23, 30). This suggests that the meteorological field only poorly captures the land breeze (which goes against the

synoptic westerly flow), and that the HYSPLIT back trajectories do not capture injections of continentally influenced air into the coastal MBL.

Corroborating this are the relative humidity (RH) data. Often, the RH in HYSPLIT was inconsistent with local observations. For example, during the ODEs on July 18 and 19 and 30, local RH were >80%, whereas those in the simulations were <65%. A lower RH indicates an air mass that has travelled more over (dry) land than over the ocean. Interestingly, the nights of July 18, 19, and 30 had the highest CO₂ and total monoterpene abundances, which is consistent with the air having been in contact with land upwind. In general, RH decreased at the end of the ODEs as the air masses shifted.

The majority of the ODEs were associated with winds from the WNW, i.e., with air that has travelled in parallel to the coast line, consistent with the synoptic conditions. The nights of July 21 and 22 are interesting cases in that on both occasions, local winds and HYSPLIT back trajectories were from the WNW sector and wind speeds decreased (to < 1 m/s on July 22), yet O₃ was conserved on those nights. One can conclude that the HYSPLIT back trajectories by themselves are poor predictors of ODEs. The NOAA ESRL maps show that the high pressure region was located significantly further from the coast on those days ((Figure S-3) than during ODE events and that a low pressure system had formed to the North of the study region.

c. Correlations of ODEs with changes in aerosol size distribution

Reactions of O₃ with monoterpenes are known to yield SOA (Ehn et al., 2014; Griffin et al., 1999; Sakulyanontvittaya, Guenther, et al., 2008). The time series of submicron aerosol size distributions is shown in Figure 6. During the ODEs, the accumulation mode (diameter range 80 to 100 nm) dominated. The highest counts were observed when the predominant wind direction was from the east (nights of July 18/19

and 19/20), whereas much lower aerosol loadings were observed when the winds were from the West. With exception of the night of July 19/20, there was neither noticeable particle growth nor nucleation event during the ODEs. The absence of aerosol growth and new particle formation corroborates that dry deposition is the primary O₃ loss mechanism and that titration of O₃ by gas-phase monoterpenes (which would have yielded SOA and nopinone) was minor. However, new particles were frequently observed after the ODEs ended, usually associated with a wind shift to the east at or after sunrise.

e. Monoterpene ratios: insights into BVOC sources

An interesting feature of this data set is that the limonene mixing ratio was often greater than those of α - and β -pinene (and sometimes even greater than their sum). Limonene is a factor of 2.5 $\times$ more reactive than the other monoterpenes with respect to oxidation by O₃ and NO₃ (Draper, Farmer, Desyaterik, & Fry, 2015). The high relative concentrations of limonene observed suggest that the air had not been significantly processed ("aged") chemically, which implies that the source (or sources) of limonene was (were) close to the sampling site. Carene and terpinolene were less abundant than the other monoterpenes and accounted for only a small fraction of the total concentration of terpenes observed (Figure 4A). Only one of the common tree species in the area, the Western Red Cedar, emits a greater amount of limonene than other monoterpenes (Drewitt et al., 1998); its emission ratios are most consistent with the observed monoterpene mixtures. In contrast, emissions from Coastal Douglas Firs are expected to have a higher α - and β -pinene content and relatively little limonene (Burney & Jacobs, 2012; Geron et al., 2000), and emissions from Western Hemlock trees have a high α - and β -pinene as well as phellandrene content (Lagalante & Montgomery, 2003), which are less consistent with the relative terpene concentrations observed.

Oddly, there was a dependence of the monoterpene ratios on local wind direction during the ODEs; when local wind speeds were strongest and from the WNW, the ratios of limonene to α - and β -pinene were highest (Figure 5D). The ocean surface is a known (though small) source of a variety of volatile compounds (Carpenter, Archer, & Beale, 2012), including unsaturated compounds such as isoprene (Meskhidze & Nenes, 2006; Yokouchi, Li, Machida, Aoki, & Akimoto, 1999) and monoterpenes (Yassaa et al., 2008). However, one local peculiarity at APO is the presence of kelp forests along the coast line (Watson & Estes, 2011).

f. Kelp forests: an unrecognized source of BVOCs

There is currently very little literature on BVOC emissions from near-shore vegetation. Yassaa and coworkers recently reported evidence for monoterpene emissions from phytoplankton (*Dunaliella tertiolecta*), in which p-ocimene, limonene, and camphene were the dominant monoterpenes emitted (Yassaa et al., 2008). Kelp is known to emit molecular iodine and small molecule halocarbons (e.g., (Ball et al., 2010; Dixneuf, Ruth, Vaughan, Varma, & Orphal, 2009; Nitschke, Dixneuf, Schmid, Ruth, & Stengel, 2015; Weinberg, Bahlmann, Michaelis, & Seifert, 2013)). These iodine emissions and their subsequent chemistry have been linked to near-coastal new particle formation (O'Dowd et al., 2002; O'Dowd & Hoffmann, 2005) though uncertainties remain (e.g., (McFiggans, 2005; O'Dowd et al., 2005).

To investigate whether local sea weed species contributed to BVOC emissions, samples were collected from the intertidal zone, placed in buckets along with sea water, and the head spaces were analyzed by GC-MS.

Total and selected ion chromatograms of the calibration VOC mixture, of ambient air during ODEs with a strong westerly flow, and of the head space above a sample of bull kelp (*Nereocystis luetkeana*) are shown in Figure 7. The selected ion m/z

93(± 1) is a characteristic fragment of monoterpenes ($C_7H_9^+$). The bull kelp head space (Figure 7C) contained ~ 2 ppbv limonene and trace amounts of α - and β -pinene and terpinolene. Terpenes were not elevated when a sample of sea water in the absence of sea flora was analyzed (data not shown). This implies that the kelp forests act as a source of limonene and (at least partially) explains the high relative limonene abundances observed during ODEs where the air originated from WNW sector.

We currently do not have enough information to constrain this source (e.g., size of the kelp forests and their emission rates, which depend on time-of-day, water temperature, light and herbivore exposure, plant age, season, and the extent of desiccation and degradation of kelp deposited near the high tide mark (Bravo-Linares, Mudge, & Loyola-Sepulveda, 2010; Nitschke et al., 2015; Rodgers & Shears, 2016)), though it clearly would be worthwhile to investigate these factors further. Of all the biogenic terpenes, limonene exhibits the highest SOA yield upon photo-oxidation (Griffin et al., 1999; Hoffmann et al., 1997) and upon reaction with O_3 or NO_3 at night (Draper et al., 2015; Fry et al., 2011; Spittler et al., 2006). It stands to reason that emissions of limonene coupled to those of molecular iodine from the same source would have high SOA formation potential.

4. Summary and conclusions

This study has shown that the ODEs observed at APO occurred in air masses that had been in contact with near-coastal vegetation including kelp forests and trees located near the shore line. Even though this data set was limited to one month during summer, it can be expected that the O_3 -terpene anticorrelation will also be observed during other seasons as terpene emissions continue throughout the year and peak in spring (Helmig et al., 2013). The absence of aerosol growth and new particle formation associated with

ODEs indicates that dry deposition was likely the primary O₃ loss mechanism and that titration of O₃ by gas-phase monoterpenes was a minor pathway. At the same time, more measurements, in particular of terpenoids towards which O₃ is reactive such as the sesquiterpenes (Sakulyanontvittaya, Duhl, et al., 2008), are needed to better constrain their roles in O₃ depletion, especially within the forest canopy. However, the absence of organic aerosol formation during ODEs suggests that reactions of O₃ with biogenic VOCs were of minor importance during this campaign. Back trajectories calculated using HYSPLIT and the NAM meteorology field poorly represented local coastal land-sea breeze effects and hence fell short in explaining how the upwind air at APO came in contact with continentally influenced air masses.

Future studies should focus on a better description of the regional flow patterns and should aim to quantify the relative contributions of terrestrial and oceanic surfaces to O₃ dry deposition, the potential for halogen-catalyzed photochemical destruction of O₃ (e.g., (Huang et al., 2010)), and the exchange of CO₂ with surfaces and vegetation in the region. Future studies should also elucidate whether near-costal oceanic uptake of O₃ is enhanced in the region, for example by elevated iodide surface concentrations (Carpenter et al., 2013; Reeser & Donaldson, 2011). Kelp forests were identified as a novel BVOC source that emits highly reactive terpenes such as limonene. Future work should focus on characterizing the emission factors of BVOCs from kelp and other sea weed species.

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756 Table 1. Summary of ODEs observed.

Date	start time	end time	wind direction (°)		wind speed	ΔO_3	ΔO_x	ΔCO_2	$\Delta\text{Terp.}$
mo/day 2015	hr:min UTC	hr:min UTC	median local	Hysplit NAM12	m/s	ppbv	ppbv	ppmv	ppbv
07/16	09:14	14:00	WNW	WNW	1.1	-15.9	-	20.7	0.10
07/18	03:41	14:46	ESE	E	0.9	-16.0	-15.2	39.0	0.40
07/19	02:50	15:15	W initially, then E	W initially, then E	1.7	-23.3	-19.5	12.0	0.12
07/23	00:02	15:15	WNW	W	1.7	-19.5	-17.1	15.7	0.10
07/24	03:00	09:02	W	W	1.6	-18.1	-17.4	13.8	0.41
07/27	01:39	13:59	W initially, then E	W	1.7	-17.6	-15.6	15.5	0.32
07/28	01:59	14:01	WNW	WNW	2.1	-24.5	-23.8	14.3	0.07
07/30	02:23	10:03	W	W	2.5	-16.8	-16.0	51.7	0.64
07/31	07:04	10:09	WNW	WNW	2.2	-17.2	-16.8	32.4	0.19

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Figure 1. Map of the study region.

Figure 2. Time series of O_3 (left hand side, lhs) and CO_2 mixing ratios (A), monoterpene and nopinone mixing ratios (B), and O_x ($=O_3+NO_2$), NO_2 , NO_y mixing ratios (C). The blue lines indicate O_3 depletion events identified using the criteria by McKendry et al. (2014). The background colouring indicates the NO_2 photolysis frequency. The dates and times are in coordinated universal time (UTC).

Figure 3. (A) O₃ (lhs) and CO₂ (rhs) mixing ratios as functions of (solar) time of day during ODEs. The dashed lines indicate the 90th and 10th percentiles, whereas the shaded areas encompass the 75th and 25th percentiles. The thick solid lines are the median values. Percentiles were calculated over ½ hour bins. The median non-ODE O₃ time series is shown as a blue line. (B) O₃ and terpene mixing ratios as functions of (solar) time of day during ODEs calculated over 1 hour bins.

Figure 4. (A) Median mixing ratios of monoterpenes as functions of time of day. (B) Nocturnal nopinone concentrations during ODE and non-ODE events as functions of time of day.

Figure 5. Correlations of O₃ mixing ratios with (A) wind direction and speed, (B) CO₂ mixing ratios, colour-coded by the sum of α- and β-pinene and limonene mixing ratios, and (C) NO₂ mixing ratios, colour-coded by CO₂ mixing ratios. (D) Dependence of the limonene to (α- plus β-pinene) ratio on wind direction and speed, plotted as their N-S and E-W components.

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Figure 6. Time series of submicron aerosol size distributions.

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Figure 7. Total ion chromatogram (TIC, lhs) and selected (rhs) ion chromatograms of (A) standard VOC calibration mixture, (B) ambient air during an ODE, and (C) headspace above bull kelp (*nereocystis luetkeana*). Et-tol = ethyltoluene, TMB = trimethylbenzene, DCB = dichlorobenzene.