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Key Points:
- First atmospheric carbonyl sulfide (COS) measurements in a coast redwood forest
- Measurement shows persistent daytime COS depletion and COS:CO_2 linear relationship
- Results support use of COS as a biogeochemical tracer of photosynthesis

Supporting Information:
- Supporting Information S1

Correspondence to:
J. E. Campbell,
elliott.campbell@ucsc.edu

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Plant Uptake of Atmospheric Carbonyl Sulfide in Coast Redwood Forests

J. E. Campbell[1], M. E. Whelan[2], J. A. Berry[3], T. W. Hilton[2], A. Zumkehr[2], J. Stinecipher[2,4], Y. Lu[2], A. Kornfeld[3], U. Seibt[5], T. E. Dawson[6], S. A. Montzka[7], I. T. Baker[8], S. Kulkarni[9], Y. Wang[10], S. C. Herndon[11], M. S. Zahniser[11], R. Commane[12], and M. E. Loik[1]

[1]Environmental Studies Department, University of California, Santa Cruz, CA, USA, [2]Sierra Nevada Research Institute, University of California, Merced, CA, USA, [3]Department of Global Ecology, Carnegie Institution, Stanford, CA, USA, [4]Lawrence Livermore National Laboratory, Livermore, CA, USA, [5]Department of Atmospheric and Oceanic Sciences, University of California, Los Angeles, CA, USA, [6]Department of Integrative Biology, University of California, Berkeley, CA, USA, [7]Global Monitoring Division, NOAA Earth System Research Laboratory, Boulder, CO, USA, [8]Department of Atmospheric Science, Colorado State University, Fort Collins, CO, USA, [9]California Air Resources Board, Sacramento, CA, USA, [10]Department of Atmospheric Science, University of Bremen, Bremen, Germany, [11]Aerodyne Research, Inc., Billerica, MA, USA, [12]School of Engineering and Applied Sciences, Harvard, Cambridge, MA, USA

Abstract The future resilience of coast redwoods (*Sequoia sempervirens*) is now of critical concern due to the detection of a 33% decline in California coastal fog over the 20th century. However, ecosystem-scale measurements of photosynthesis and stomatal conductance are challenging in coast redwood forests, making it difficult to anticipate the impacts of future changes in fog. To address this methodological problem, we explore coastal variations in atmospheric carbonyl sulfide (COS or OCS), which could potentially be used as a tracer of these ecosystem processes. We conducted atmospheric flask campaigns in coast redwood sites, sampling at surface heights and in the canopy (~70 m), at the University of California Landels-Hill Big Creek Reserve and Big Basin State Park. We simulated COS atmosphere-biosphere exchange with a high-resolution 3-D model to interpret these data. Flask measurements indicated a persistent daytime drawdown between the coast and the downwind forest (45 ± 6 ppt COS) that is consistent with the expected relationship between COS plant uptake, stomatal conductance, and gross primary production. Other sources and sinks of COS that could introduce noise to the COS tracer technique (soils, anthropogenic activity, nocturnal plant uptake, and surface hydrolysis on leaves) are likely to be small relative to daytime COS plant uptake. These results suggest that COS measurements may be useful for making ecosystem-scale estimates of carbon, water, and energy exchange in coast redwood forests.

Plain Language Summary The future resilience of coast redwoods (*Sequoia sempervirens*) is now of critical concern due to the detection of a 33% decline in coastal fog that sustains these forests. However, monitoring the potential impacts on redwood forests is challenging because the unique features of the coastal environment interfere with ecological measurement techniques. Here we propose a solution involving a new technique using carbonyl sulfide, an atmospheric chemical that is related to carbon dioxide. We found that the redwoods remove carbonyl sulfide from the atmosphere, which is a critical prerequisite for using this technique to explore redwood resiliency.

1. Introduction

Coast redwoods (*Sequoia sempervirens*) uniquely occur in the California Current upwelling region, suggesting a reliance on coastal fog conditions (Figure 1). Climatological data show a strong statistical relationship between fog and transpiration in coast redwoods (Johnstone & Dawson, 2010). These coastal data also reveal a 33% decline in coastal fog over the 20th century (Johnstone & Dawson, 2010).

The coastal fog decline is of particular concern for redwood forests for multiple reasons. First, coast redwoods are thought to be vulnerable to future changes in fog because they may be poor regulators of water use and may rely on the presence of fog during dry summer months to increase water uptake and reduce evapotranspiration (Dawson, 1998; Simonin et al., 2009). Second, the enormous stature of coast redwoods results in significant interception of fog water, causing fog drip that not only supports coast redwoods but also enhances soil moisture and streamflow for the benefit of coastal ecosystems (Sawaske & Freyberg, 2015). Third, coast

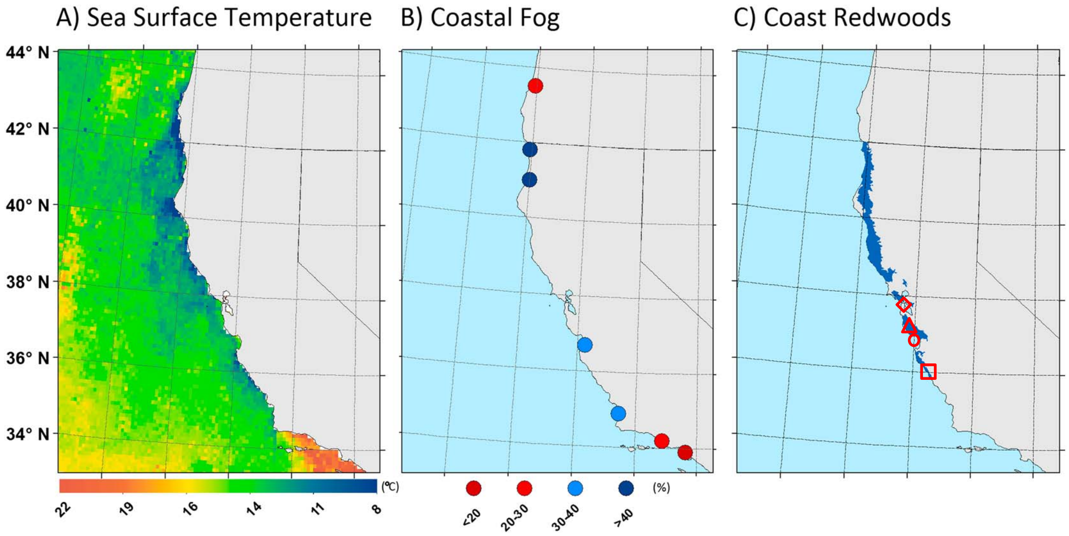

Figure 1. Coastal California domain of upwelling, fog, and coast redwoods. (a) Sea surface temperature from MODIS remote sensing data delineate the coastal upwelling zone of low temperatures(June 2013), (b) summer mean coastal fog frequencies (Johnstone & Dawson, 2010), and (c) coast redwood range along the U.S. Pacific Coast and location of COS measurements (diamond, Sutro; triangle, Big Basin; circle, R/V *Atlantis*; square, Big Creek).

redwoods may play a critical role in coupling the coastal ocean-atmosphere-land system as suggested by more general theoretical work showing positive feedbacks between coastal upwelling and terrestrial ecosystems (Diffenbaugh et al., 2004).

While much has been learned about coast redwood ecophysiology at the spatial scale of leaves and individual trees (Ambrose et al., 2009; Burgess & Dawson, 2004; Dawson, 1998; Ewing et al., 2009; Johnstone et al., 2013; Limm et al., 2009; Simonin et al., 2009), we lack measurements at larger spatial scales that are needed for a robust understanding of the interactions between coast redwoods and fog (Fernández et al., 2015; Potter, 2012). In particular, ecosystem-scale measurements of gross primary production (GPP) and stomatal conductance are challenging in redwood forests. GPP estimates using eddy covariance CO_2 measurements face logistical and theoretical challenges due to the complex topography and unstable terrain of redwood forests. Alternatively, regional variation in atmospheric CO_2 cannot be used to infer regional GPP because atmospheric mixing at the regional scale prevents analytical partitioning of the co-located GPP and respiration signals (Campbell et al., 2008). Furthermore, stomatal conductance estimates that are typically based on eddy covariance water vapor measurements are hampered by the presence of coastal fog.

These methodological challenges could potentially be addressed using measurements of atmospheric carbonyl sulfide (COS or OCS). COS is a trace gas that is removed from the atmosphere when it diffuses into plant leaves through stomata and is irreversibly hydrolyzed inside the leaf by the photosynthetic enzyme carbonic anhydrase (Berry et al., 2013; J. Campbell, Kesselmeier, et al., 2017; Campbell et al., 2008; Montzka et al., 2007; Sandoval-Soto et al., 2005; Stimler et al., 2010). The global COS plant sink is largely balanced by COS sources from oceans (Launois et al., 2015) and Asian industry (Campbell et al., 2015). This spatial separation of the dominant source and sink suggests that observed variations in atmospheric COS over terrestrial ecosystems should provide a tracer of plant physiology processes. While other sources and sinks can be large at some points in time and confound the COS approach (Commane et al., 2015; Maseyk et al., 2014), the regional dominance of COS plant uptake over continents during the growing season has led to the use of this tracer for estimating GPP and stomatal conductance at ecosystem to global scales (Asaf et al., 2013; J. E. Campbell, Berry, et al., 2017; Hilton et al., 2017; Wehr et al., 2017).

Unlike CO_2, the land-atmosphere exchange of COS during the growing season is dominated by the plant flux in most ecosystems and other ecosystem sources and sinks are generally less significant. Thus, while regional CO_2 measurements are useful for estimating net ecosystem exchange, COS measurements could be applied to estimate regional GPP and stomatal conductance. Furthermore, while atmospheric water vapor concentrations are influenced by sources from plants and fog, atmospheric COS mixing ratios are more generally

Table 1
Summary of Field Campaigns and Sampling Sites

Campaign	Date	Sample site	Location	Sample elevations (m above surface)
Big Creek 1	24–25 June 2015			
		Coast	36°4′10.10″N, 121°35′54.97″W	2 m
		Redwood	36°3′58.56″N, 121°33′16.42″W	2 m
Big Creek 2	12–13 December 2015			
		Coast	36°2′39.75″N, 121°35′7.37″W	2 m
		Redwood	36°3′23.65″N 121°32′27.93″W	4 m, 34.8 m, 70.5 m
Big Basin	26–27 May 2015			
		Coast	37°05′51.0″N, 122°16′51.1″W	2 m
		Redwood	37°12′46.0″N, 122°13′14.9″W	2 m
		Grassland	37°18′56.7″N, 122°18′23.1″W	2 m

controlled by the COS plant sink (see section 4). In order to explore the potential for the COS approach for coast redwoods, we conducted the first ambient COS observations in Northern California forests. We also collected atmospheric samples from sites adjacent to the redwoods to observe marine boundary layer (coastal) and grassland influences on atmospheric COS. The flask samples were analyzed for COS and CO_2 mixing ratios using a quantum cascade laser spectrometer referenced to the NOAA gas standard. To interpret these measurements, we simulated atmospheric mixing ratios using a high-resolution 3-D model of atmosphere-biosphere exchange and transport. We also used the model to interpret atmospheric COS measurements from a previously conducted survey of coastal California measurements of COS and CO_2 aboard the R/V *Atlantis* during the California Nexus Experiment (CalNex) and NOAA global air-monitoring data from Sutro Tower (San Francisco, CA, USA). We discuss the results with respect to the potential use of COS as a GPP and stomatal conductance tracer for coastal redwoods. Extended methods and results are in the supporting information (Bloem et al., 2012; Li et al., 2007; Vacher et al., 2016).

2. Methods

2.1. Flask Sampling

We conducted three flask sampling campaigns at coast redwood sites in the University of California Natural Reserve System Landels-Hill Big Creek Reserve (Monterey County, CA) and Big Basin State Park (Santa Cruz County, CA). These campaigns included sampling in a Lagrangian framework (upwind coast and downwind forest sites), over diurnal cycles, at a gradient of elevations (near the land surface through near the top of the redwood canopy), and in the summer and winter as summarized in Table 1. During all three campaigns, fog was present in the early morning while the daytime was mostly clear.

These Lagrangian campaigns included sampling in redwood canopy sites and adjacent coast sites, while one of these campaigns included sampling in an adjacent grassland site. The coast sites were within 100 m of the ocean, while the redwood sites were approximately 10 km inland. The predominant northwesterly winds generally created conditions where the coast sites sampled well-mixed, incoming marine background air while the downwind redwood sites sampled continental air. However, other transport regimes were also apparent in the data and are explored in the results. The duration of each campaign was approximately 24 h with a sample collected every 30 min to 2 h.

Sources and sinks in the sampling materials are a known challenge for COS measurements. For example, certain plastics in soil chambers have been shown to create a temperature-dependent source (Maseyk et al., 2014). Here we only used sampling equipment that has been demonstrated in previous work to be suitable for COS analysis, including Synflex tubing and flask packages that have been extensively evaluated through field experiments and the NOAA global air-monitoring network (Montzka et al., 2007; Sun et al., 2016).

Ambient air was collected with an automated sampling system consisting of programmable compressor packages (PCPs) and programmable flask packages (PFPs) (High Precision Devices, Inc., Boulder, CO). Software embedded in the PFP automated gas sampling for the diurnal campaigns with minimal intervention, for example, replumbing gas lines for sampling at different canopy heights. Each PFP contained 12 individual 0.7 L glass flasks with elastomer-free glass stoppers on an inlet and outlet. The flasks were first prepared by flushing with nitrogen gas at 15 L min^{-1} for 1 h to prevent contamination and to allow us to detect, postcampaign, flasks that did not fill in the field as programmed. In the field, at preprogrammed intervals, the PCP compressor flushed the external and internal lines with ambient air for a given number of minutes depending on the volume of the sampling line. The sample flask was similarly flushed and then filled to 200–275 kPa. This compressor was powered by an external 12 V battery.

The sampling lines consisted of Synflex tubing that was extended either near the ground surface or into the redwood canopy (Table 1). Particulate matter was excluded using stainless steel filters (2–7 μm), and the lines extended into the canopy had aluminum shields to prevent rain entrainment.

For canopy air sampling, this study adopted a "trees-not-towers" approach, a lower cost method of obtaining samples from different heights within the canopy. In lieu of depending on human-made towers, we were able to sample air in remote locations high in the canopy by climbing the trees and installing sampling lines at various heights. The lines were tied to the tree branches with weatherproof rope and were supported by an aluminum bracket that allowed the gas inlet to be extended away from the tree trunk. This method has the added advantage of avoiding measuring disturbance by other tower instruments, which may be a problem at many sites since COS is outgassed by many common plastics.

2.2. Trace Gas Measurement

Flask samples were analyzed in the laboratory using a quantum cascade laser developed to simultaneously measure COS with parts-per-trillion (ppt) precision and CO_2 to a resolution of 0.1 ppm (Aerodyne Inc., Billerica, Massachusetts; Stimler et al., 2009). The standard system was designed to measure COS on a continuous flow basis. However, to increase the number of replicate measurements that could be performed on a single flask, we developed an automated system that operates on a closed measurement cell (i.e., no flow). We included a magnesium perchlorate water trap upstream of the sample cell to reduce spectral noise introduced in humid samples (Kooijmans et al., 2016). All sample measurements were calibrated by alternating sample measurements with measurements of a secondary standard calibrated to a NOAA certified standard. The uncertainty, taken to be the standard deviation of three repeated measurements on the same flask, was on average ~7 ppt.

2.3. Land-Atmosphere Flux Modeling

We created a high-resolution, atmosphere-biosphere surface flux estimate of COS plant uptake with an hourly, 1 km resolution covering our regional domain. We generated this high-resolution estimate by downscaling our previous global simulations of COS plant uptake with the carbon cycle model SiB3, which is detailed in Berry et al. (2013) and summarized as follows.

The SiB3 model simulates the diffusion of atmospheric COS into leaves based on resistances to diffusion imposed by the stomatal pore and leaf boundary layer (conductance = 1/resistance) using an empirical relationship (Ball et al., 1987; Seibt et al., 2010; Stimler et al., 2010). Once COS has diffused into the leaf, it is irreversibly hydrolyzed at a rate proportional to the COS partial pressure in the chloroplast. The activity rate for this reaction is modeled as a linear function of photosynthetic capacity ($V_{\max}$) with the proportionality constant estimated from leaf gas exchange measurements (Stimler et al., 2010; Stimler et al., 2012).

While the SiB3 model of COS plant uptake has been validated at the global scale using satellite and air-monitoring observations (Berry et al., 2013; Glatthor et al., 2015; Hilton et al., 2015; Kuai et al., 2015; Wang et al., 2016), the SiB3 spatial resolution (1°) is too coarse to resolve regional features such as the coastal forests (Figure S1 in the supporting information). To spatially downscale this global flux we used Moderate Resolution Imaging Spectroradiometer (MODIS) monthly leaf area index (LAI) data (Knyazikhin et al., 1999) at 1 km resolution as a spatial proxy to spatially redistribute the global flux at each hourly time step of the global flux data. We used the global flux to set the sum of the COS flux over the entire model domain, and we used the MODIS LAI to set the spatial distribution of this flux.

2.4. Additional Sources and Sinks

In addition to plant uptake, our simulations also considered the potential for alternative sources and sinks to influence atmospheric COS mixing ratios. Here we used previously reported gridded inventories for anthropogenic emissions and plant uptake (Kettle et al., 2002). Atmospheric analysis suggests that anthropogenic sources in the U.S. are small compared to COS plant uptake (Blake et al., 2008; Campbell et al., 2015; Guo et al., 2010; Zumkehr et al., 2017), suggesting that this inventory could provide a conservative estimate of the anthropogenic signal. While field soil chamber observations show that some soils can switch from a sink to a source at high temperature (Maseyk et al., 2014); lab incubations of soils show a small soil flux in forests that is generally consistent with gridded inventories (Whelan et al., 2016). Biomass burning is another significant global source (Campbell et al., 2015). Although there were fires in our study region in the summer of 2015, there were no significant burning events during the days that we collected air samples. Oceans are thought to be the dominant global source but are not modeled directly in these simulations because our analysis limits the ocean influence by focusing on the difference between the upwind coastal site measurements and downwind redwood site measurements.

2.5. Chemical Atmospheric Transport Modeling

We simulated 3-D, time-varying atmospheric COS mixing ratios using an atmospheric chemical transport model. The transport model is the Sulfur Transport and dEposition Model (STEM) that has been widely applied for analysis of atmosphere-biosphere interactions for the U.S. and other regional domains (Campbell et al., 2007, 2008; Hilton et al., 2015; Sandu et al., 2005). Input to the model includes gridded surface fluxes (sections 2.3 and 2.4) and 3-D meteorological data (see below). STEM is a mesoscale, 3-D Eulerian atmospheric chemical transport model employing a finite differences numerical approach to solve the chemical continuity equation.

Simulations were completed for the field sampling campaign periods including 1 week of spin-up. Constant COS mixing ratio boundary conditions were used to assess the individual contributions of the different sources and sinks to atmospheric COS variation. In addition to constant boundary condition, we also explored the effect of temporal and spatial variations in boundary conditions using output from global chemical transport simulations for COS from the GEOS-Chem model (Wang et al., 2016). Model results were extracted for the times and locations of observations (all observations were within the lowest model vertical layer).

We generated meteorological input data for STEM using the Weather Research and Forecasting version 3.7 (WRF) model. Our WRF runs used a series of nested domains with 36 km, 12 km, and 4 km horizontal resolutions to examine state-level trends as well as a Northern California centered domain with nested 9 km, 3 km, and 1 km subdomains for a detailed investigation of the flask measurements (Figure S2). The STEM simulations used the innermost domain from the WRF runs as meteorological input. We provided boundary conditions to the WRF runs using National Centers for Environmental Prediction final global tropospheric analyses (1° resolution) and WRF options that were consistent with previous WRF studies of coastal California (Angevine et al., 2012).

2.6. Supportive Coastal Observations

We used our field measurements and high-resolution simulations to interpret two additional sets of regional data: CalNex cruise and Sutro Tower air-monitoring data. A COS laser spectrometer was deployed on the R/V *Atlantis* ship during the CalNex experiment in May and June of 2010 (Commane et al., 2013). The R/V *Atlantis* data had a precision of 2 ppt for 50 s averages. The absolute spectroscopic accuracy, determined from analysis of NOAA calibrated standard gas on the ship, was ~5% of the total OCS (~20 pptv). During the morning of 2 June offshore of Santa Cruz, CA (approximately 36°53′60″N, 122°0′36″W), the R/V *Atlantis* data revealed a negative correlation between observed COS and CO_2, and simulated back trajectories suggested the potential for a nocturnal COS sink in the coastal terrestrial ecosystems. The magnitude of this nocturnal sink in relation to the GPP-related daytime sink is unknown. While these offshore measurements were too far from the land to characterize specific ecosystems, they were downwind of a wide expanse of coast redwoods.

Long-term flask observations of atmospheric COS at Sutro Tower (37°45′18.72″N, 122°27′10.08″W) were collected every 12 h as part of the NOAA global air-monitoring network (Montzka et al., 2007). Flask samples are shipped to Boulder (CO) for analysis by gas chromatography and mass spectrometry. The median replicate precision for COS flask samples from the NOAA network is 0.4% (~2 ppt), and 95% of all pairs have a replicate precision of less than 1.3% ($<$6.3 ppt). These observations are designed to characterize broad trends associated with the free troposphere and could provide useful information on the background COS trends for coastal COS experiments.

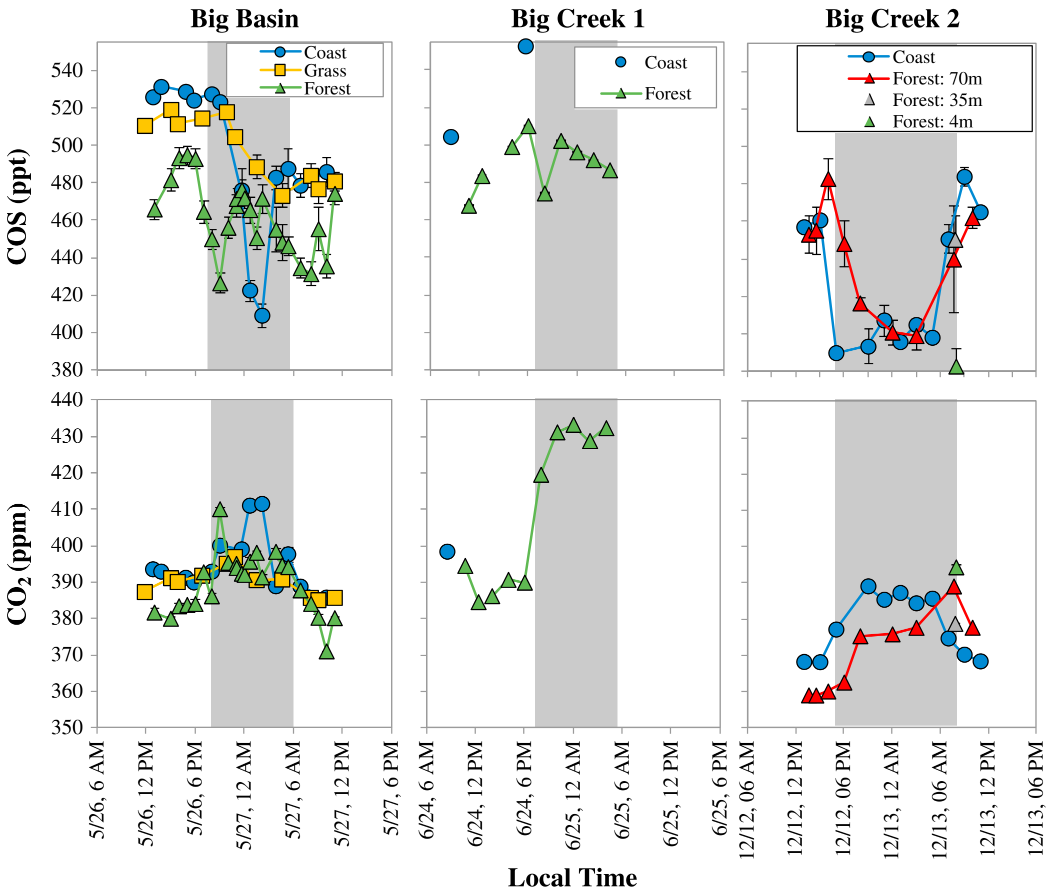

Figure 2. Measurements of COS and CO_2 in ambient air from three field campaigns (Big Basin, Big Creek 1, and Big Creek 2) at coast redwood and adjacent sites. All sample heights are near-surface (2–4 m aboveground level) except for a subset of the forest site samples during the Big Creek 2 campaign, which included samples at 70 m and 35 m aboveground level. Measurement uncertainties are the standard deviation of multiple measurements on each flask; many symbols obscure the error bars. Site locations in Figure 1c and Table 1. The gray shading is nighttime.

3. Results

3.1. Flask Observations

The field campaigns provide a first view into COS variation in coast redwood forests (Figure 2). COS atmospheric mole fractions at the surface (2 m aboveground level) at the redwood sites are consistently lower than upwind coastal sites for all daytime measurements in the two summer campaigns (Big Basin and Big Creek 1). This persistent horizontal COS drawdown between the coast and the downwind forest site is consistent with a large COS sink in the coast redwoods.

The relatively high temporal resolution measurements during the Big Basin campaign yielded a 45 ± 6 ppt (mean ± SE) horizontal drawdown between the coast and redwood sites during the daytime onshore flow period (Figure 2, left column). The Big Creek 1 campaign had only two observations available for calculating the difference between the redwood and upwind coast sites during the day, but these drawdown measurements were comparable to the Big Basin campaign (42 ppt and 68 ppt; Figure 2, middle column).

While COS mixing ratios during the summer campaigns at the redwood site were significantly lower than the coastal site, the grassland site had similar COS mixing ratios to the upwind coastal site (Figure 2, yellow squares). Our grassland measurements were collected during the end of May, which is climatologically in the dry season but was exceptionally dry during the drought of 2015 (Figure S9). The relatively insignificant depletion of COS over the grassland at the end of May was consistent with the expected low GPP rates and low COS plant uptake previously observed at a coastal grassland field study in this region, which was dormant or senescent (Whelan & Rhew, 2016).

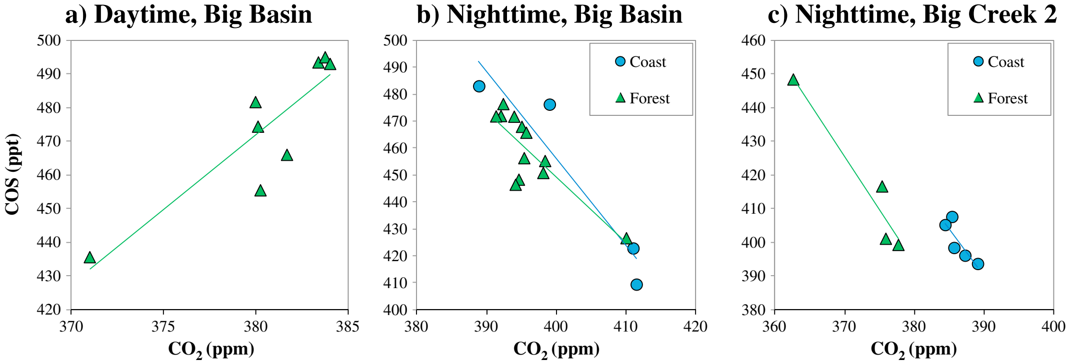

Figure 3. Correlation of COS and CO_2 observations for (a) daytime and (b and c) nighttime ambient samples at coast redwood forest sites (triangles) and on the beach adjacent to the forest (circles). The nighttime coast observations occurred during a period of coastal land breezes. The daytime forest observations occurred during onshore flow. Linear fits are summarized in Table 2.

Diurnal COS trends appear to be associated with the interaction of the land surface flux and atmospheric mixing events. At the Big Basin forest site, the COS minima and CO_2 maxima during the evening and morning coincided with periods of decreased continental boundary layer heights (Figure S6). The correlation between COS and the boundary layer height is consistent with the land surface being a net COS sink. The pulse of low COS air observed at the Big Basin coast site in the evening may be due to katabatic winds that transport continental air to the coast as suggested by the observed shift in wind (Figure S7) and the similarity between the COS:CO_2 correlation at forest and coastal sites described below (Figure 3).

A strong positive correlation between daytime observed COS and CO_2 mole fractions was seen in the relatively high temporal resolution Big Basin measurements (Figure 3a). Similar relationships have also been observed in large-scale observations from continental airborne campaigns (Campbell et al., 2008) and global air-monitoring data (Montzka et al., 2007) (Table 2). The correlation is roughly consistent with the ratio of GPP and net ecosystem CO_2 exchange (NEE) and the regional dominance of COS daytime plant uptake over other terrestrial sources and sinks of COS (Campbell et al., 2008).

While the daytime COS and CO_2 data had a positive correlation, the nocturnal data from the Big Basin forest site were negatively correlated (Figures 3b and 3c). The negative relationship is consistent with a nocturnal ecosystem sink of COS due to nocturnal stomatal conductance and soil uptake and CO_2 source from respiration. Previous work has shown incomplete stomatal closure in redwoods at night (Dawson, 1998), which should lead to a small nocturnal COS plant sink. Nocturnal COS sinks from plants and soils have been observed in other ecosystems to be on the order of 10 to 20% of daily COS uptake (Commane et al., 2015; Kooijmans et al., 2017; Maseyk et al., 2014).

Table 2
Observed Correlation of Atmospheric COS and CO_2 in Daytime and Nighttime Samples

Time	Reference	Site	Slope (ppt COS/ppm CO_2)	R^2
Daytime				
	This study	Big Basin/forest	4.4	0.8
	Campbell et al. (2008)	Continental airborne	5.7	NA
	Montzka et al. (2007)	Northern Hemisphere surface	6	0.9
Nighttime				
	This study	Big Basin/forest	−2.4	0.7
	This study	Big Basin/coast	−3.2	0.9
	This study	Big Creek 2/forest	−3.2	0.9
	This study	Big Creek 2/coast	−2.8	0.7
	Commane et al. (2013)	R/V Atlantis/Monterey Bay	−3.1	0.9

A similar negative COS to CO_2 correlation during the night was also observed at the coastal sites in the Big Basin and Big Creek campaigns. The consistency between the regression slope of the nocturnal measurements from the coastal and inland measurements suggests that a land-breeze may have caused an outflow of continental air to influence the coastal site. Wind observations during the sampling campaigns also show the presence of a land-breeze during the nights and early mornings (Figure S7). Evidence of land-breezes in COS data are also apparent in the ship-based CalNex data (Commane et al., 2013).

No significant daytime correlations of COS and CO_2 were observed from the Big Creek 1 data. This may be due to the limited number of samples collected during this campaign.

Even excluding nocturnal land-breeze periods, significant COS variation was observed during the summer field campaigns in the upwind coastal sites. The COS variation was approximately 50 ppt. These changes in background mixing ratios may be associated with synoptic events (see section 3.3). The significant variation in the coastal measurements suggests that the use of COS as a biogeochemical tracer for coastal systems will require quantification of background variability at a subdaily time resolution.

While the two summer campaigns (Big Creek 1 and Big Basin) were subject to northwesterly flow, the winter sampling during Big Creek 2 was subject to northeasterly flow creating offshore wind conditions. A vertical profile during this campaign was sampled in the early morning when the nocturnal boundary layer was likely still intact. The vertical gradient observed at this time may be due to the effect of a shallow nocturnal boundary layer.

3.2. Atmosphere-Biosphere Simulations

High-resolution simulations of surface fluxes and chemical atmospheric transport were used to interpret the field observations. Atmospheric simulations with the plant uptake, soil uptake, and anthropogenic emissions provide information on the contribution of these alternative components of the regional budget. Simulations show significant reduction in COS mixing ratios over forests due to plant uptake of COS but only small effects on mixing ratios from soil and anthropogenic fluxes (Figure 4).

The relatively high temporal resolution data from the Big Basin campaign provide a point of comparison for these simulations. The horizontal gradients from the inland sites to the coast site show strong similarities between the observations and the simulated mixing ratios extracted for the times and locations of the flask samples (Figure 5). The consistency between the model and measurements suggests that plant uptake may be the dominant driver of the coastal COS drawdown. While future development of modeled canopy mixing and vegetation flux will be needed to infer fluxes from COS measurements, our preliminary simulations suggest that the model can roughly approximate the horizontal spatial trends in the observations.

We also compared our simulations to the R/V *Atlantis* observations of low COS mixing ratios on 2 June in the northern Monterey Bay region. While the consistency between observed COS:CO_2 correlation for the R/V *Atlantis* and our redwood flask measurements provides strong evidence of a forest influence, we find further support of this hypothesis in our model results. The simulations show a coastal land-breeze advecting the redwood air out to sea and cyclonic circulation trapping this air mass in the region of the ship (Figure 6a). This circulation, named the Santa Cruz eddy (SCE), is a climatological feature in this region that occurs in 80% of summer days due to the prevailing northwesterly flow interacting with the Santa Cruz Mountains (Archer et al., 2005; Tseng et al., 2012).

Although the timing of the simulated drawdown during this land-breeze event matches the observations, the simulated drawdown was roughly half the magnitude of the observed drawdown (Figure 6b). The soil sink is unlikely to explain this discrepancy due to its small magnitude. Alternative simulations with the plant sink doubled and the simulated transport resolution increased to 1 km did not improve the model-observation agreement. Uncertainty in the 3-D transport is a likely source of error as the model shows a roughly 5 km horizontal offset in the location of a 30 ppt depletion that is consistent with the magnitude of the observed depletion (also see section S3 in the supporting information).

Two additional STEM modeling sensitivity experiments were run by adjusting the GPP input by 50% (Figure S10). This is a conservative estimate of GPP uncertainty in the region given that North American continental GPP uncertainty is approximately 50% (Huntzinger et al., 2012). The GPP uncertainty propagates to a 30 ppt drawdown uncertainty, which is supportive of the approach because it is considerably larger than the

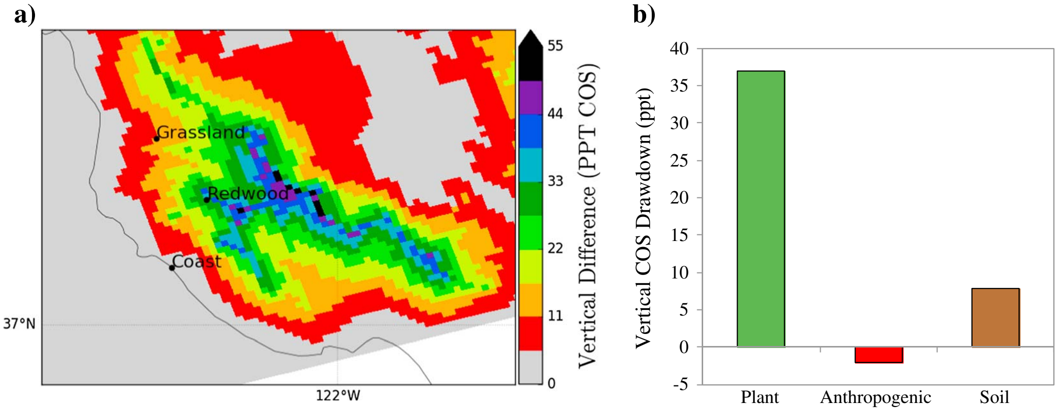

Figure 4. Atmospheric COS mixing ratio drawdown from 3-D regional simulations. (a) Map of midday COS vertical drawdown due to simulated plant uptake and location of three Big Basin field campaign sites. Vertical drawdown is the difference between the COS mixing ratio in the free troposphere and the mixing ratio in the surface model layer. (b) Simulations of average continental COS drawdown from simulations driven by plant uptake (green), anthropogenic emissions (red), and soil uptake (brown).

7 ppt measurement uncertainty. Such sensitivity simulations may also be used to improve the site selection for future work. For example, the region of highest sensitivity was generally to the southeast of the forest field site used in the Big Basin campaign.

3.3. Background Variation

Inferring ecosystem processes from ambient COS mixing ratios at a redwood site will require knowledge of the background variation. During onshore flow conditions, the background signal is associated with the inflowing air to a site, which may be influenced by more distant sources and sinks. Our field campaigns utilized multiple approaches to assess the background variation. First, we obtained coast site measurements that were generally upwind of the forested sites. This is supported by the agreement between the horizontal gradients in the modeled and observed data (Figure 5). Below we also consider the potential for regional tall tower observations and global chemical transport simulations to provide information on background variability.

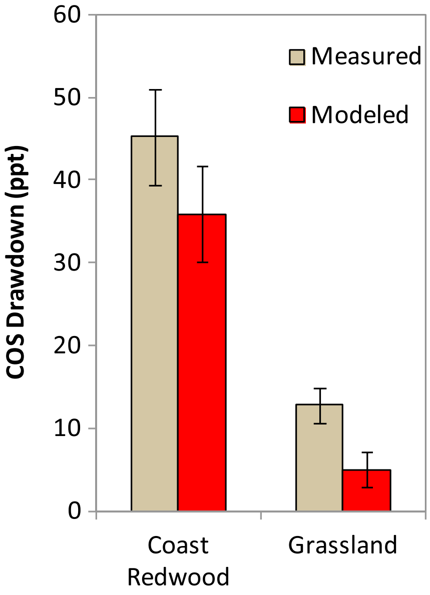

Figure 5. Comparison of simulated (red) and observed (gray) daytime COS drawdown during the Big Basin field campaign. Drawdown is the difference between the inland sites and the coast site. The two inland sites were in the coast redwoods and a coastal grassland. The error bars are standard error of the sample-mean difference.

We compare our coastal observations to ongoing NOAA measurements made at Sutro Tower. Sutro Tower is a coastal observatory within 150 km of our field campaign sites. The Sutro observations have a day to day variation that is roughly consistent with the 50 ppt variation at our coastal sites (Figure 7). Consistent calibration approaches were used in our methods and at the NOAA laboratory. While the data are roughly consistent, some differences could be explained by the large distance between Sutro Tower and our sites.

The R/V *Atlantis* data also show some similarities to Sutro data (Figure 8a). A 50 ppt increase in COS mixing ratios in the R/V record beginning on 16 May, when the ship was still in the Los Angeles basin, was thought to be due to a shift from continental influence to marine influence (Commane et al., 2013). This feature is also observed in the Sutro record, which is consistent with the large spatial extent of background variation. This consistency suggests that Sutro observations may be useful for obtaining background information across the full extent of the coast redwood range.

Alternatively, global atmospheric transport models may provide information on the background signal. Our previously published COS simulations using the GEOS-Chem model (Wang et al., 2016) were consistent with the large-scale temporal trends in the Sutro record (Figure 8b). The model

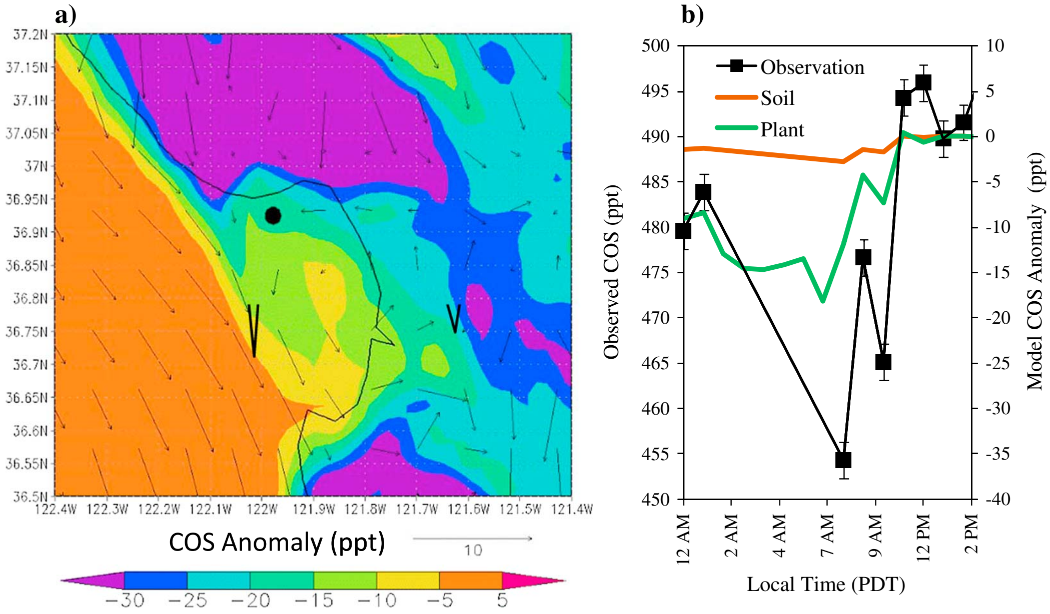

Figure 6. Simulated and observed COS when the R/V *Atlantis* encountered a nocturnal continental outflow on 2 June 2010. (a) Simulations of COS mixing ratio anomaly (colors, defined as the COS drawdown from the free troposphere to the surface), wind vectors (arrows), and ship location (circle) show sampling within the coastal cyclonic circulation known as the Santa Cruz eddy (SCE). (b) Time series of ship-based spectrometer measurements of COS and simulations of the COS model anomaly driven by plant uptake and soil uptake fluxes are shown for the continental outflow plume. Measurement uncertainties are the standard deviation of multiple measurements on each flask.

captures the 50 ppt increase on 16 May as well as the temporary depression on 29 and 30 May that coincided with a low pressure system that caused continental air to reach the coast. Despite the coarse spatial resolution of the global model, the similarities between Sutro and the global model suggest significant model skill in simulating synoptic variation in the background signal.

4. Discussion and Conclusions

We proposed the use of COS as a new biogeochemical tracer for this coastal system to address limitations with existing ecological measurements in coast redwoods. The measurement and model results presented here are encouraging of this tracer approach for multiple reasons. First, measurement error was small relative to observed spatial and temporal variations (Figure 2). While the observed variations were approximately 50 ppt, the measurement reproducibility was less than 5 ppt for most flasks despite known challenges with water vapor spectral effects.

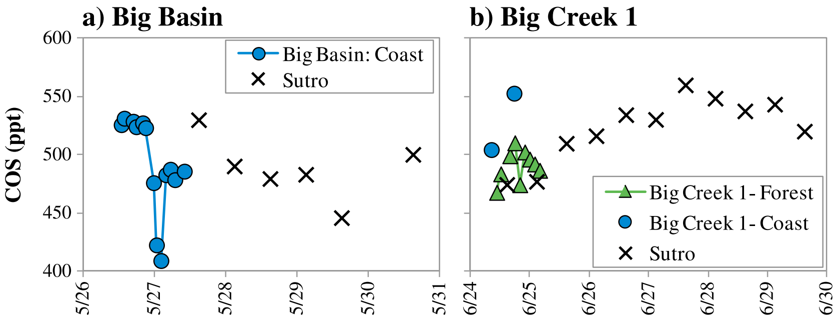

Figure 7. Comparison of field campaign measurements and NOAA background air-monitoring data from Sutro Tower (San Francisco, CA).

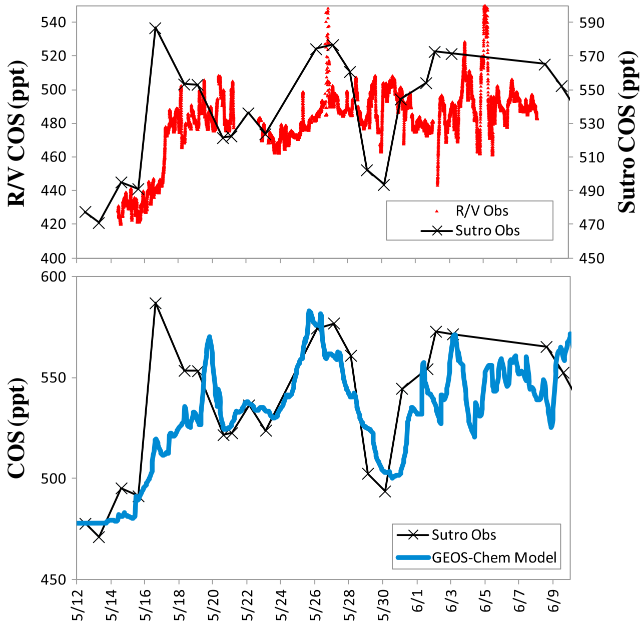

Figure 8. Spatial and temporal atmospheric COS trends during the CalNex period (May/June 2010). (a) Observations along the R/V *Atlantis* ship track (red) and at Sutro Tower (black). (b) Observations at Sutro Tower (black) and global GEOS-Chem simulations interpolated to the location of the Sutro Tower samples (blue). The R/V record is plotted on a different *y* axis in order to highlight the relationship in time trends between these data and the Sutro observations.

Second, the flask sampling campaign suggests that the plant uptake of COS in the redwood forest is generally consistent with our a priori knowledge. In particular, these results provide strong evidence of a close relationship between COS plant uptake, GPP, and stomatal conductance. The first line of evidence is that the daytime COS to CO_2 ratio in the redwoods is also observed in continental and hemispheric observations (Table 2). These large-scale correlations have already been shown to be driven by an approximate relationship between COS plant uptake and GPP and NEE (Berry et al., 2013; Campbell et al., 2008), which implies that the correlation in the redwoods has a similar driver. An additional line of evidence is that our a priori simulation of spatial variation in COS drawdown that is driven by a GPP model is similar to the spatial variation in our flask measurements (Figure 5). While model results will require further investigation of the role of transport errors (e.g., model evaluation with meteorological measurement and multiple chemical tracers), these preliminary model results suggest that the observed spatial variation is consistent with atmospheric COS variation that is driven by known plant uptake processes.

Third, the potentially confounding factors from soil fluxes, anthropogenic emissions, and nighttime uptake are relatively insignificant in this domain. While continental and global applications of the COS tracer are supported by the dominance of plant uptake and the ocean sources, ecosystem scale application can be confounded by the presence of local sources and sinks that are not associated with daytime COS plant uptake (Commane et al., 2015; Maseyk et al., 2014; Wohlfahrt et al., 2012). However, we found no evidence for significant ecosystem sources in the measurements or simulations. In particular, our grassland measurements at Big Basin should be largely influenced by soil fluxes but were similar to coastal inflow measurements suggesting only small soil fluxes. Furthermore, the nocturnal correlation of COS and CO_2 is quantitatively consistent with previous work that shows a relatively small effect from nocturnal COS plant uptake and soils (Maseyk et al., 2014). A rough approximate of the nighttime COS flux can be obtained by combining our measured nighttime correlation of -3 ppt COS/ppm CO_2 with an estimated nighttime CO_2 ecosystem source of 3 μmol CO_2 m^{-2} s^{-1} using the Vegetation Photosynthesis and Respiration Model (VPRM) (Mahadevan et al., 2008), which yields a nighttime COS ecosystem sink that is 9 pmol m^{-2} s^{-1}, only approximately 20% of expected daytime COS plant uptake.

Sources and sinks of COS from fog water also need to be understood and quantified for COS analysis. Our order of magnitude analysis suggests that the influence of fog water will be small relative to plant uptake (see supporting information) (Belviso et al., 1967; Elliot et al., 1989; Mu et al., 2004). Nevertheless, measurements of these processes in redwood forests should be made in future studies to be sure.

Fourth, we found that, although variation in the background signal is significant, it can be characterized by multiple approaches. These approaches include site-level measurements at the coast, NOAA air-monitoring data from Sutro Tower, and global atmospheric chemical transport simulations.

Given the relatively slow pace of the decline in fog, it is unlikely that this measurement technique would be able to detect a response trend in the redwood stomatal conductance and GPP through short-term COS observations. Instead, the COS measurement approach would be better suited to quantify the redwood response to the much larger day-to-day variations in fog. The process knowledge obtained from such measurements could be combined with midcentury fog projections to provide a scenario analysis of potential redwood vulnerabilities.

While these results are encouraging of the biogeochemical tracer approach, they are also supportive of meteorological tracer applications. Continental outflow events observed from the R/V *Atlantis* consistently show 10% to 12% depletions in COS due to the widespread continental sink. In contrast to the COS signal, atmospheric CO_2 in these outflow events varies from a decline of 1% to growth of 4% due to the heterogeneous continental CO_2 sources and sinks. Thus, the large and consistent signal of COS provides a clear indicator of continental influence, which could be used for a variety of applications including filtering out local signals in NOAA's coastal air-monitoring data (De Gouw et al., 2009; Riley et al., 2005).

The use of the COS tracer to support GPP and stomatal conductance estimation in the redwoods may also have broader applications to coastal and continental carbon budgets. North American terrestrial carbon budgets can be inferred using observations of the CO_2 continental inflow on the Pacific coast and outflow on the Atlantic coast. While Pacific coast observations under westerly winds provide a basis for the inflow observation, significant noise is introduced into these measurements from ecosystem sources and sinks that are adjacent to the coastal observatories (Ganguly et al., 2011; Riley et al., 2005). Significant terrestrial CO_2 fluxes in coastal systems have been observed by high-resolution, top-down analysis (Ahmadov et al., 2009; Göckede et al., 2010; Gourdji et al., 2011). In situ COS measurements might characterize Pacific Coast inflow with sharply reduced complications from these varied and co-located coastal CO_2 sources and sinks.

Data Availability

Flask observations of COS and CO_2 mixing ratios are available in the supporting information.

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