AN ABSTRACT OF THE DISSERTATION OF

<u>Bharat Rastogi</u> for the degree of <u>Doctor of Philosophy</u> in <u>Forest Ecosystems and Society</u> presented on <u>May 8, 2018.</u>

Title: <u>Ecosystem Photosynthesis and Forest- Atmosphere Interactions Inferred from Carbonyl Sulfide</u>

Abstract approved:

_____
                    Christopher J. Still

An increase in anthropogenic activities since the industrial revolution, primarily due to burning of fossil fuels and changes in land cover, has resulted in a steady increase in the global mean atmospheric CO_2 concentrations. While there is unequivocal scientific evidence on global warming and its multidimensional impacts on natural and human systems, uncertainties on the magnitude of future warming persist, propagating from uncertainties in the response of terrestrial plants to changing climates. This is partially due to our inability to directly measure photosynthesis beyond the leaf level.

Measurements of carbonyl sulfide OCS have recently been shown to provide an independent and direct estimate of plant productivity. OCS is the most abundant reduced sulfur gas present in the atmosphere, with a mean atmospheric concentration of ~ 500 ppt (parts per trillion) and is emitted into the atmosphere from oceans via direct emissions or oxidation of CS_2, and taken up by leaves of actively photosynthesizing leaves.

The focus of this dissertation was to further assess OCS as a proxy for ecosystem-scale stomatal conductance and photosynthesis in a temperate old growth coniferous forest. This dissertation is composed of three studies conducted at the Wind

River Experimental forest located within the Gifford Pinchot National Forest in southwest Washington state, USA (45°49'13.76'' N; 121°57'06.88'' W; 371 m above sea level).

In the first study, co-authors and I find significant ecosystem uptake of OCS using measurements of mixing ratios of this gas within and above the canopy. We find that diurnal patterns of OCS are influenced by a combination of ecosystem uptake and mixing of air from the overlying atmosphere. We quantify the magnitude of mixing and demonstrate how OCS measurements can be used to estimate entrainment and mixing between forests and the atmosphere. We also find that the forest surface and epiphytes consume OCS, and that uptake strength is linked to moisture status.

In the second study, we develop a simple empirical model to predict ecosystem-scale OCS fluxes from mixing ratio measurements at the canopy top. OCS uptake was found to scale with independent measurements of CO_2 fluxes at hourly and monthly timescales across the growing season in 2015. OCS fluxes tracked changes in soil moisture, and were strongly influenced by the fraction of downwelling diffuse light. Fluxes were also strongly affected by sequential heat waves during the growing season.

In the third and final study of this dissertation, OCS flux estimates obtained in the previous study were used to determine GPP for the old growth forest. GPP estimated from OCS flux showed similar seasonal and diurnal patterns as that obtained from flux partitioning of NEE at the site. However, we find that the magnitude of GPP obtained using this method was significantly higher, and similar to independent estimates obtained from measurements of sap flow in trees and the isotopic composition of leaf CO_2, and a process-based model. We conclude that flux partitioning of net ecosystem exchange of CO_2 results in a systematic underestimation of both source and sink terms, likely due to an underestimation of respiratory fluxes.

Our results support the growing body of work that suggests ecosystem-scale OCS uptake is controlled by stomatal dynamics. These studies have implications for carbon cycling in forested ecosystems, particularly in dense and wet forests with extensive epiphyte cover, which are widespread in the humid tropics.

Ecosystem Photosynthesis and Forest- Atmosphere Interactions Inferred from
Carbonyl Sulfide

by
Bharat Rastogi

A DISSERTATION

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Doctor of Philosophy

Presented May 8, 2018
Commencement June 2018

Doctor of Philosophy dissertation of <u>Bharat Rastogi</u> presented on <u>May 8, 2018.</u>

APPROVED:

_____

Major Professor, representing Forest Ecosystems and Society

_____

Head of the Department of Forest Ecosystems and Society

_____

Dean of the Graduate School

I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

_____

Bharat Rastogi, Author

ACKNOWLEDGEMENTS

Being conferred the "highest" conventional academic degree is an honor and a privilege. As such, it is challenging to acknowledge the multiple forms of support I have enjoyed over the years spent in pursuit of this PhD in a manner that is both coherent and concise. However, it must be done!

Funding for this research was acquired through grants to Dr. Christopher Still, Dr. Manish Gupta and Dr. John Kim, through NSF, NASA, USFS and OSU.

Fieldwork was conducted in the Wind River Experimental Forest, operated and funded by the University of Washington and the USFS. Special thanks to Dr. Ken Bible, who excellently managed the site, ensuring that the numerous instruments installed by multiple researchers amassing ginormous datasets provided meaningful numbers. An additional resource was Ken's phenomenal grasp on site dynamics.

An unquantifiable amount of gratitude goes to my PhD advisor, Dr. Christopher Still. Chris has been (and continuous to be) both a dear friend and an excellent mentor. His support and belief in me has been unwavering and (at times) irrational. He has encouraged me to be confident in my analyses and insights. His breadth of knowledge and ability to synthesize amongst different scientific disciplines are commendable and something I have always admired.

My doctoral committee comprised of excellent scientists and advisors, who were involved from day 127, trained me as a scientist, and continue to be role models. Dr. David Noone's brilliance and ability to explain complicated concepts helped in both experimental set-up and improving manuscript drafts.

Dr. Max Berkelhammer's scientific temper, clarity in thought, and timely and critical feedback has tremendously shaped this work. I have always enjoyed reading his papers and comments on various manuscripts. Dr. Frederick Meinzer's expertise in plant physiology, willingness to talk, ability to provide all the right answers all of the time, and share sap flow and stomatal conductance data, made much of this research possible. Moreover, Rick's attitude and saint-like demeanor made sure I looked forward to every meeting I have had

with him in 4 years. Dr. Jeffery Hatten was an excellent Graduate Council Representative. I would also like to acknowledge Dr. Thomas Hilker, who was both a close friend and excellent scientist. He is deeply missed.

Thanks to co-authors and collaborators, namely Dr. Sonia Wharton, Dr. Mary Whelan, Dr. Andreas Schmidt, Dr. Hyojung Kim, Dr. Olaf Menzer, Dr. Youngil Kim, Dr. Yueyang Jiang, Dr. Malcolm Itter, Dr. Chun-Ta Lai, Dr. Mark Gordon and Dr. Brian Leen.

This journey would not have been possible without the support of friends spanning multiple spatiotemporal scales. Prakriti, Ankita and Ritambhara have been in my life since Narega days, and people I knew I could always talk to. Thanks also to Dr. Megha Patnaik, Dr. Kevin Mwenda and SiJie Loo. Richa and Tanveer's support was invaluable and I was very touched that they travelled (without coercion) to attend my defense. Corvallis is kept alive by its community and I have enjoyed the love and friendship of innumerable people here. Thanks in particular to "the veggies", a group of meat-eating and coffee chugging misfits who ensured I remained sane during the last stretch. Specifically, Dr. Franscisco Mauro (Paco) for many shared meals, dil pukares, and running light use efficiency models from Spain, Dr. Dolores Vasquez (Dolo) for being a voice of reason, both loving and firm (and also shared meals) and Serhan Mermer for being Serhan Mermer (also shared meals). A hundred million thanks to Hannah Rolston for taking me to Glacier National Park, introducing me to the rough cuts, putting me on a bike to the top of Mckenzie Pass, listening patiently to my endless irresolvable and circular dilemmas (read Chapter 3), and helping put together a very important document (umm, shared meals?). Thanks also to Franco, Shah, Nike, Jose, Ana and Luciana for being close friends.

Final thanks are reserved for my family. My uncle and aunt Ajay Rastogi and Dr. Ruchi Pant helped me foster a love for nature and the need to care for it from a very young age. My brother Vedant is thanked for being a close friend and a supremely supportive sibling. Finally finally, my parents Sanjay and Anita Rastogi who always let me make my own mistakes and (im)patiently waited for me to finish. The strength of their love poured over oceans and time zones and was a constant source of support and motivation. This dissertation is dedicated to them.

CONTRIBUTION OF AUTHORS

Chapter 2: Bharat Rastogi, Drs. Chris Still, Max Berkelhammer, David Noone and Mary Whelan designed and conducted the study. Drs. Brian Leen and Manish Gupta were involved in instrumentation and maintenance. Dr. Sonia Wharton provided data and guidance. Dr. Malcolm Itter contributed in data analyses. Bharat Rastogi performed the analyses and drafted the paper. All authors contributed to writing the paper.

Chapter 3: Bharat Rastogi designed and implemented the study, performed the analyses and drafted the paper. Drs. Chris Still, Max Berkelhammer, David Noone, Fredrick Meinzer, Sonia Wharton and Mary Whelan provided guidance and contributed to writing the paper.

Chapter 4: Bharat Rastogi designed and implemented the study, performed the analyses and drafted the paper. Dr. Fredrick Meinzer provided data and guidance Drs. Chris Still, Max Berkelhammer, David Noone, Sonia Wharton and Mary Whelan provided guidance and contributed to writing the paper.

TABLE OF CONTENTS

Contents   Page

LIST OF FIGURES

LIST OF TABLES

LIST OF APPENDIX FIGURES

LIST OF APPENDIX TABLES

1   GENERAL INTRODUCTION

An increase in anthropogenic activities since the industrial revolution, primarily due to burning of fossil fuels and changes in land cover, have resulted in a steady increase in the mean atmospheric CO_2 concentration from ~ 280 ppm in the mid-eighteenth century to 390 ppm in 2011 (Ciais et al., 2013). The global mean [CO_2] exceeded 400 pm 5 years later in 2016, was 407 ppm on the day of writing this document (April 23, 2018; ESRL-NOAA), and is now the highest it has been in the last 800,00 years. CO_2 is a greenhouse gas, i.e., it absorbs and re-emits longwave radiation emitted from the earth's surface, and therefore an increase in [CO_2] causes a perturbation in the atmospheric radiation budget resulting in higher global air temperatures (which have increased at ~ 1.4 °C since 1880; Earth Observatory- NASA).

While there is unequivocal scientific evidence (IPCC, 2014) and near-global political consensus (UNFCC, 2015) on global warming and its multidimensional impacts on natural and human systems, uncertainties on the magnitude of future warming persist, propagating from uncertainties in phenomena like the response of terrestrial plants to changing climates. Plants are responsible for removing ~ 25% of anthropogenic CO_2 emissions since 1750 (Le Quéré et al., 2018), and annual variability in CO_2 removal from the atmosphere is highly dependent on the strength of the terrestrial carbon sink (Heimann & Reichstein, 2008). While studies have shown an increase in plant uptake of CO_2 (Ballantyne et al., 2012; Le Quéré et al., 2009), there is lesser certainty on the environmental drivers causing this trend. Positive forcings to the growing terrestrial sink can arise from rising CO_2 levels (CO_2 fertilization; Schimel *et al.*, 2015), nitrogen deposition (Bala et al., 2013), and longer growing seasons in temperate and boreal ecosystems (Forkel et al., 2016). Conversely, increasing temperatures may lead to a decrease in terrestrial carbon sink via a faster increase in respiration than GPP (Li et al., 2018), and greater drought stress (Williams et al., 2013), reducing stomatal conductance (Kimberly A. Novick et al., 2016), the effect of which may be mitigated by increases in water use efficiency in a more CO_2-rich atmosphere (Keeling et al., 2017; Keenan et al., 2014). Consequently, despite large advances in measurement and modeling techniques and increased spatio-temporal measurements of CO_2

concentrations, carbon-climate coupled model intercomparison efforts still fail to converge on even the sign of the shift in the cumulative land sink in response to recent global warming (Huntzinger et al., 2017). This is in part due to our inability to directly measure photosynthesis beyond the leaf level.

The eddy covariance (EC) technique is widely used to measure the net uptake of CO_2 (i.e., net ecosystem exchange, or NEE), at the ecosystem-scale, and has now effectively been adopted as a standard approach to measure this quantity across different ecosystems, even as limitations to application of this method like low turbulence, flow decoupling and advection in tall and/or dense forest canopies, and diverse topographical areas remain (Baldocchi, 2014; Baldocchi et al., 2018; K. A. Novick et al., 2018). An outstanding issue is the lack of a mechanistic approach that partitions NEE into source (respiration) and sink (photosynthesis or GPP) terms (R Wehr et al., 2016).

Measurements of carbonyl sulfide (OCS) have recently been shown to provide an independent and direct estimate of plant productivity (Blonquist et al., 2011; Campbell et al., 2008; Whelan et al., 2017 and references therein). OCS is the most abundant reduced sulfur gas present in the atmosphere, with a mean atmospheric concentration of ~ 500 ppt (parts per trillion; Montzka et al., 2007) and is emitted into the atmosphere from oceans via direct emissions or oxidation of CS_2 (Kettle et al., 2002).

Recent advances in spectroscopic technology have enabled continuous in-situ measurements of OCS on timescales that are relevant to understanding stomatal function at the leaf-scale (Stimler, Montzka, et al., 2010; Stimler, Nelson, et al., 2010), branch scale (Berkelhammer et al., 2014) and the ecosystem-scale (Kooijmans et al., 2017; Richard Wehr et al., 2017). An important distinction between OCS and CO_2 cycling is that there are no reported emissions from actively photosynthesizing leaves. The uptake ratio of OCS:CO_2 is relatively constant at medium to high light levels (Maseyk et al., 2014; Stimler et al., 2010), making it an excellent proxy for quantifying plant productivity (GPP; Asaf et al., 2013; Billesbach et al., 2014; Blonquist et al., 2011). On the other hand, both uptake and emission of OCS from soils have

been identified (Whelan et al., 2016; Sun et al., 2015; Maseyk et al., 2014; Kesselmier et al., 1999). While ecosystem-scale measurements of OCS continue to establish links between OCS uptake and GPP in different ecosystems (for a comprehensive list of ecosystem-scale studies readers are referred to Figure 2 in Whelan et al., 2017), inconsistencies persist. For example, in an oak-savanna woodland in southern France Belviso et al. (2016) found that OCS exchange was strongly influenced by photosynthesis during early morning hours, while meaningful connections between OCS and CO_2 fluxes could be obtained only under very particular conditions. Similarly, Commane et al. (2015) were unable to explain mid-summer emissions of OCS at a mid-latitude deciduous forest. Such uncertainties argue for field-scale measurements of OCS in a variety of ecosystems, particularly as OCS flux predictions have recently been used to inform estimates of plant productivity in global carbon cycle models (Campbell et al., 2017; Hilton et al., 2017; Launois et al., 2015).

The overall focus of this dissertation was to further assess OCS as a proxy for ecosystem-scale stomatal conductance and gross primary production (GPP), in a temperate old-growth coniferous forest. Old-growth forests exhibit dynamics that are very different from those of other forests. These forests often have very tall stature, extremely high aboveground biomass, slow rates of growth (Harmon et al., 2004), and often contain large stores of soil carbon (Luyssaert et al., 2008). In old-growth forests located in the Pacific Northwest (PNW) region of North America, mild temperatures and very wet conditions promote abundant epiphytic vegetation cover on branches and boles of trees, as well as the forest floor, often covering these surfaces in thick mossy carpets. While patterns of CO_2 and H_2O exchange between epiphytic species and the surrounding environment can be very different from those of higher plants, all of these epiphytic species contain the enzyme, carbonic anhydrase (CA), which catalyze OCS exchanges with the atmosphere (Gries et al., 1994; Kuhn et al., 2000; Kuhn & Kesselmeier, 2000).

3

This dissertation is composed of three studies conducted at the Wind River Experimental Forest located within the Gifford Pinchot National Forest in southwest Washington state, USA (45°49'13.76'' N; 121°57'06.88'' W; 371 m above sea level).

The objective of the first study (presented in Chapter 2) was to understand the biotic and abiotic controls on OCS canopy-atmosphere exchange. In this study, co-authors and I sampled canopy air from four different heights in the canopy using a continuous, integrated cavity output spectroscopy analyzer during August-September 2014. Measurements revealed large vertical gradients in OCS, implying significant ecosystem uptake. The diurnal cycle of OCS mixing ratios at all heights exhibited a typical pattern characterized by nighttime drawdown, an early morning minimum, and a midday maximum of OCS concentrations. Daytime increase in OCS in the upper canopy is attributed to entrainment of planetary boundary layer (PBL) air into the canopy. OCS entrainment was quantified using a mass balance approach, assuming that stomatal uptake dominated daytime OCS flux. Moreover, using in-situ and laboratory chamber-based measurements, we found that epiphytes absorb large amounts of OCS, and that such uptake was tightly constrained by available moisture.

In the second study (presented in Chapter 3), I employed a simple empirical model to infer ecosystem-scale OCS uptake from measurements of its mixing ratios made in April – November 2015. OCS uptake was found to scale with independent measurements of CO_2 fluxes at hourly and monthly timescales across the growing season in 2015. OCS fluxes tracked changes in soil moisture, and were strongly influenced by the fraction of downwelling diffuse light. Fluxes were also strongly affected by sequential heat waves during the growing season. Our results bolster previous evidence that ecosystem OCS uptake is strongly related to stomatal dynamics, and measuring this gas relieves constraints on estimating photosynthetic rates at the ecosystem-scale.

In the third and final study of this dissertation (presented in Chapter 4), OCS flux estimates obtained in the previous study were used to determine GPP for the old growth forest. GPP estimated from OCS flux showed similar seasonal and diurnal patterns as those

obtained from standard flux partitioning of NEE at the site. However, we found that the magnitude of GPP obtained using the OCS-based method was significantly higher. A third independent estimate of GPP was calculated using measurements of sap flow in trees of dominant species in the forest, along with the stable carbon isotopic composition of needle tissue from actively photosynthesizing trees (i.e. leaf $\delta^{13}C$). These latter GPP estimates were also higher than those from standard flux partitioning, and the magnitude was comparable to estimates from OCS fluxes. Finally, GPP predictions from a well-known process-based model corroborate these higher GPP findings. We conclude that flux partitioning of NEE results in a systematic underestimation of both source and sink terms, likely due to an underestimation of respiratory fluxes.

These studies have implications for measuring and modeling of carbon cycling in forested ecosystems, particularly dense and very wet forests with extensive epiphyte cover, which are widespread in the humid tropics.

1.1 References

Alden, C. B., Miller, J. B., Gatti, L. V., Gloor, M. M., Guan, K., Michalak, A. M., … Diffenbaugh, N. S. (2016). Regional atmospheric CO2 inversion reveals seasonal and geographic differences in Amazon net biome exchange. *Global Change Biology*, *22*(10), 3427–3443. https://doi.org/10.1111/gcb.13305

Asaf, D., Rotenberg, E., Tatarinov, F., Dicken, U., Montzka, S. A., & Yakir, D. (2013). Ecosystem photosynthesis inferred from measurements of carbonyl sulphide flux. *Nature Geoscience*, *6*(3), 186–190. https://doi.org/10.1038/ngeo1730

Bala, G., Devaraju, N., Chaturvedi, R. K., Caldeira, K., & Nemani, R. (2013). Nitrogen deposition: How important is it for global terrestrial carbon uptake. *Biogeosciences*, *10*(11), 7147–7160. https://doi.org/10.5194/bg-10-7147-2013

Baldocchi, D. (2014). Measuring fluxes of trace gases and energy between ecosystems and the

atmosphere - the state and future of the eddy covariance method. *Global Change Biology*, *20*(12), 3600–3609. https://doi.org/10.1111/gcb.12649

Baldocchi, D., Chu, H., & Reichstein, M. (2018). Inter-annual variability of net and gross ecosystem carbon fluxes: A review. *Agricultural and Forest Meteorology*, *249*(May 2017), 520–533. https://doi.org/10.1016/j.agrformet.2017.05.015

Ballantyne, A. P., Alden, C. B., Miller, J. B., Trans, P. P., & White, J. W. C. (2012). Increase in observed net carbon dioxide uptake by land and oceans during the pst 50 years. *Nature*, *488*(7409), 70–73. https://doi.org/10.1038/nature11299

Belviso, S., Reiter, I. M., Loubet, B., Gros, V., Lathière, J., Montagne, D., … Genty, B. (2016). A top-down approach of surface carbonyl sulfide exchange by a Mediterranean oak forest ecosystem in Southern France. *Atmospheric Chemistry and Physics Discussions*, (June 2012), 1–25. https://doi.org/10.5194/acp-2016-525

Berkelhammer, M., Steen-Larsen, H. C., Cosgrove, A., Peters, A. J., Johnson, R., Hayden, M., & Montzka, S. A. (2016). Radiation and atmospheric circulation controls on carbonyl sulfide concentrations in themarine boundary layer. *Journal of Geophysical Research*, *121*(21), 13,113-13,128. https://doi.org/10.1002/2016JD025437

Berkelhammer, M., Asaf, D., Still, C., Montzka, S., Noone, D., Gupta, M., … Yakir, D. (2014). Constraining surface carbon fluxes using in situ measurements of carbonyl sulfide and carbon dioxide. *Global Biogeochemical Cycles*, *28*(2), 161–179. https://doi.org/10.1002/2013GB004644

Billesbach, D. P., Berry, J. A., Seibt, U., Maseyk, K., Torn, M. S., Fischer, M. L., … Campbell, J. E. (2014). Growing season eddy covariance measurements of carbonyl sulfide and CO2 fluxes: COS and CO2 relationships in Southern Great Plains winter wheat. *Agricultural and Forest Meteorology*, *184*, 48–55. https://doi.org/10.1016/j.agrformet.2013.06.007

Blonquist, J. M., Montzka, S. A., Munger, J. W., Yakir, D., Desai, A. R., Dragoni, D., … Bowling, D. R. (2011). The potential of carbonyl sulfide as a proxy for gross primary production at flux tower sites. *Journal of Geophysical Research: Biogeosciences*, *116*(4), 1–18. https://doi.org/10.1029/2011JG001723

Campbell, J. E., Berry, J., Seibt, U., Smith, S., Nature, S. M.-, & 2017, U. (2017). Large historical growth in global terrestrial gross primary production. *Nature.com*, *544*(7468), 84. Retrieved from https://www.nature.com/articles/nature22030

Campbell, J. E., Carmichael, G. R., Chai, T., Mena-Carrasco, M., Tang, Y., Blake, D. R., … Stanier, C. O. (2008). Photosynthetic control of atmospheric carbonyl sulfide during the growing season. *Science*, *322*(5904), 1085–1088. https://doi.org/10.1126/science.1164015

Čermák, J., Kucera, J., Bauerle, W. L., Phillips, N., & Hinckley, T. M. (2007). Tree water storage and its diurnal dynamics related to sap flow and changes in stem volume in old-growth Douglas-fir trees. *Tree Physiology*, *27*(2), 181–198. https://doi.org/10.1093/treephys/27.2.181

Ciais, P., Sabine, C., Bala, G., Bopp, L., Brovkin, V., Canadell, J., … Thornton, P. (2013). Carbon and Other Biogeochemical Cycles Chapter 6. *Climate Change 2013: The Physical Science Basis. Contribution of Working Group` I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, 465–570. https://doi.org/10.1017/CBO9781107415324.014

Commane, R., Meredith, L. K., Baker, I. T., Berry, J. A., Munger, J. W., Montzka, S. A., … Wofsy, S. C. (2015). Seasonal fluxes of carbonyl sulfide in a midlatitude forest. *Proceedings of the National Academy of Sciences*, *112*(46), 14162–14167. https://doi.org/10.1073/pnas.1504131112

Falk, M., Wharton, S., Schroeder, M., Ustin, S. L., & Paw U, K. T. (2008). Flux partitioning in an

old-growth forest: seasonal and interannual dynamics. *Tree Physiology*, *28*(4), 509–520. https://doi.org/10.1093/treephys/28.4.509

Farquhar, G. D., & Richards, R. A. (1984). Isotopic composition of plant carbon correlates water-use efficiency of wheat genotypes. *Australian Journal of Plant Physiology*, *11*(539–552).

Fessenden, J. E., & Ehleringer, J. R. (2003). Temporal variation in δ13C of ecosystem respiration in the Pacific Northwest: Links to moisture stress. *Oecologia*, *136*(1), 129–136. https://doi.org/10.1007/s00442-003-1260-1

Forkel, M., Carvalhais, N., Rödenbeck, C., Keeling, R., Heimann, M., Thonicke, K., … Reichstein, M. (2016). Enhanced seasonal CO2 exchange caused by amplified plant productivity in northern ecosystems. *Science*, *351*(6274), 696 LP-699. Retrieved from http://science.sciencemag.org/content/351/6274/696.abstract

Granier, A. (1985). A new method to measure the raw sap flux in the trunk of trees. *Ann. For. Sci*, *42*, 193–200.

Gries, C., Nash, T. H., & Kesselmeier, J. (1994). Exchange of reduced sulfur gases between lichens and the atmosphere. *Biogeochemistry*, *26*(1), 25–39.

Guanter, L., Zhang, Y., Jung, M., Joiner, J., Voigt, M., Berry, J. A., … Griffis, T. J. (2014). Global and time-resolved monitoring of crop photosynthesis with chlorophyll fluorescence. *Proceedings of the National Academy of Sciences*, *111*(14), E1327–E1333. https://doi.org/10.1073/pnas.1320008111

Harmon, M., Bible, K., Ryan, M., Shaw, D., Chen, H., Klopatek, J., & Li, X. (2004). Production, Respiration, and Overall Carbon Balance in an Old-growth Pseudotsuga-Tsuga Forest Ecosystem. *Ecosystems*, 498–512. https://doi.org/10.1007/s10021-004-0140-9

HEIMANN, M., & Reichstein, M. (2008). Terrestrial ecosystem carbon dynamics and climate

feedbacks. *Agriculture*, *451*(7176), 289–292. Retrieved from
http://www.nature.com/nature/journal/v451/n7176/full/nature06591.html

Heinsch, F. A., Zhao, M., Running, S. W., Kimball, J. S., Nemani, R. R., Davis, K. J., … Flanagan, L.
B. (2006). Evaluation of remote sensing based terrestrial productivity from MODIS using
regional tower eddy flux network observations. *IEEE Transactions on Geoscience and
Remote Sensing*, *44*(7), 1908–1923. https://doi.org/10.1109/TGRS.2005.853936

Hilton, T., Whelan, M., Zumkehr, A., … S. K.-N. C., & 2017, U. (2017). Peak growing season gross
uptake of carbon in North America is largest in the Midwest USA. *Nature.com*, *7*(6), 450.
Retrieved from https://www.nature.com/articles/nclimate3272

Huntzinger, D. N., Michalak, A. M., Schwalm, C., Ciais, P., King, A. W., Fang, Y., … Zhao, F. (2017).
Uncertainty in the response of terrestrial carbon sink to environmental drivers undermines
carbon-climate feedback predictions. *Scientific Reports*, *7*(1), 1–8.
https://doi.org/10.1038/s41598-017-03818-2

IPCC. (2014). *Climate Change 2013*. *the Fifth Assessment Report* (Vol. 5).

Keeling, R. F., Graven, H. D., Welp, L. R., Resplandy, L., Bi, J., Piper, S. C., … Meijer, H. A. J.
(2017). Atmospheric evidence for a global secular increase in carbon isotopic
discrimination of land photosynthesis. *Proceedings of the National Academy of Sciences*,
201619240. https://doi.org/10.1073/pnas.1619240114

Keenan, T. F., Hollinger, D. Y., Bohrer, G., Dragoni, D., Munger, J. W., Schmid, H. P., &
Richardson, A. D. (2013). Increase in forest water-use efficiency as atmospheric carbon
dioxide concentrations rise. *Nature*, *499*(7458), 324–327.
https://doi.org/10.1038/nature12291

Keenan, T. F., Gray, J., Friedl, M. A., Toomey, M., Bohrer, G., Hollinger, D. Y., … Richardson, A. D.

(2014). Net carbon uptake has increased through warming-induced changes in temperate forest phenology. *Nature Climate Change*, *4*(7), 598–604. https://doi.org/10.1038/nclimate2253

Kettle, A. J., Kuhn, U., Von Hobe, M., Kesselmeier, J., & Andreae, M. O. (2002). Global budget of atmospheric carbonyl sulfide: Temporal and spatial variations of the dominant sources and sinks. *Journal of Geophysical Research: Atmospheres*, *107*(D22).

Klein, T., Rotenberg, E., Tatarinov, F., & Yakir, D. (2016). Association between sap flow-derived and eddy covariance-derived measurements of forest canopy CO2 uptake. *New Phytologist*, *209*(1), 436–446. https://doi.org/10.1111/nph.13597

Knox, S. H., Dronova, I., Sturtevant, C., Oikawa, P. Y., Matthes, J. H., Verfaillie, J., & Baldocchi, D. (2017). Using digital camera and Landsat imagery with eddy covariance data to model gross primary production in restored wetlands. *Agricultural and Forest Meteorology*, *237–238*, 233–245. https://doi.org/10.1016/j.agrformet.2017.02.020

Kooijmans, L. M. J. J., Maseyk, K., Seibt, U., Sun, W., Vesala, T., Mammarella, I., … Chen, H. (2017). Canopy uptake dominates nighttime carbonyl sulfide fluxes in a boreal forest. *Atmospheric Chemistry and Physics*, *17*(18), 11453–11465. https://doi.org/10.5194/acp-17-11453-2017

Kuhn, U., & Kesselmeier, J. (2000). Environmental variables controlling the uptake of carbonyl sulfide by lichens. *Journal of Geophysical Research: Atmospheres*, *105*(D22), 26783–26792.

Kuhn, U., Wolf, A., Gries, C., Nash III, T. H., & Kesselmeier, J. (2000). Field measurements on the exchange of carbonyl sulfide between lichens and the atmosphere. *Atmospheric Environment*, *34*(28), 4867–4878.

Lai, C., Ehleringer, J. R., & Bond, B. J. (2006). Contributions of evaporation, isotopic non-steady

state transpiration and atmospheric mixing on the δ18O of water vapour in Pacific Northwest coniferous forests. *Plant, Cell & Environment*, *29*(1), 77–94.

Lasslop, G., Reichstein, M., Papale, D., Richardson, A., Arneth, A., Barr, A., … Wohlfahrt, G. (2010). Separation of net ecosystem exchange into assimilation and respiration using a light response curve approach: Critical issues and global evaluation. *Global Change Biology*, *16*(1), 187–208. https://doi.org/10.1111/j.1365-2486.2009.02041.x

Launois, T., Peylin, P., Belviso, S., & Poulter, B. (2015). A new model of the global biogeochemical cycle of carbonyl sulfide - Part 2: Use of carbonyl sulfide to constrain gross primary productivity in current vegetation models. *Atmospheric Chemistry and Physics*, *15*(16), 9285–9312. https://doi.org/10.5194/acp-15-9285-2015

Li, W., Ciais, P., Wang, Y., Yin, Y., Peng, S., Zhu, Z., … Piao, S. (2018). Recent Changes in Global Photosynthesis and Terrestrial Ecosystem Respiration Constrained From Multiple Observations. *Geophysical Research Letters*, 1058–1068. https://doi.org/10.1002/2017GL076622

Lloyd, J., & Taylor, J. A. (1994). On the Temperature Dependence of Soil Respiration. *Functional Ecology*, *8*(3), 315–323.

Luyssaert, S., Schulze, E.-D., Börner, A., Knohl, A., Hessenmöller, D., Law, B. E., … Grace, J. (2008). Old-growth forests as global carbon sinks. *Nature*, *455*(7210), 213.

Maseyk, K., Berry, J. A., Billesbach, D., Campbell, J. E., Torn, M. S., Zahniser, M., & Seibt, U. (2014). Sources and sinks of carbonyl sulfide in an agricultural field in the Southern Great Plains. *Proceedings of the National Academy of Sciences*, *111*(25), 9064–9069. https://doi.org/10.1073/pnas.1319132111

McCune, B., Amsberry, K. A., Camacho, F. J., Clery, S., Cole, C., Emerson, C., … Widmer, M.

(1997). Vertical profile of epiphytes in a Pacific Northwest old-growth forest. *Northwest Science*, *71*(2), 145–152. Retrieved from d:%5CArtiklar%5CMcCune et al 1997.pdf

MEINZER, F. C., ANDRADE, J. L., GOLDSTEIN, G., HOLBROOK, N. M., CAVELIER, J., & JACKSON, P. (1997). Control of transpiration from the upper canopy of a tropical forest: the role of stomatal, boundary layer and hydraulic architecture components. *Plant, Cell and Environment*, *20*(10), 1242–1252. https://doi.org/10.1046/j.1365-3040.1997.d01-26.x

Meinzer, F. C., Brooks, J. R., Domec, J., Gartner, B. L., Warren, J. M., Woodruff, D. R., … Sarg, R. (2006). Dynamics of water transport and storage in conifers studied, 105–114.

Meinzer, F. C., Woodruff, D. R., & Shaw, D. C. (2004). Integrated responses of hydraulic architecture, water and carbon relations of western hemlock to dwarf mistletoe infection. *Plant, Cell and Environment*, *27*(7), 937–946. https://doi.org/10.1111/j.1365-3040.2004.01199.x

Miao, G., Guan, K., Yang, X., Bernacchi, C. J., Berry, J. A., DeLucia, E. H., … Masters, M. D. (2018a). Sun-Induced Chlorophyll Fluorescence, Photosynthesis, and Light Use Efficiency of a Soybean Field. *Journal of Geophysical Research: Biogeosciences*. https://doi.org/10.1002/2017JG004180

Miao, G., Guan, K., Yang, X., Bernacchi, C. J., Berry, J. A., DeLucia, E. H., … Masters, M. D. (2018b). Sun-Induced Chlorophyll Fluorescence, Photosynthesis, and Light Use Efficiency of a Soybean Field. *Journal of Geophysical Research: Biogeosciences*, 610–623. https://doi.org/10.1002/2017JG004180

Montzka, S. A., Calvert, P., Hall, B. D., Elkins, J. W., Conway, T. J., Tans, P. P., & Sweeney, C. S. (2007). On the global distribution, seasonality, and budget of atmospheric carbonyl sulfide (COS) and some similarities to CO_2. *Journal of Geophysical Research Atmospheres*, *112*(9), 1–15. https://doi.org/10.1029/2006JD007665

Novick, K. A., Ficklin, D. L., Stoy, P. C., Williams, C. A., Bohrer, G., Oishi, A. C., … Phillips, R. P. (2016). The increasing importance of atmospheric demand for ecosystem water and carbon fluxes. *Nature Climate Change*, *6*(11), 1023–1027. https://doi.org/10.1038/nclimate3114

Novick, K. A., Biederman, J. A., Desai, A. R., Litvak, M. E., Moore, D. J. P., Scott, R. L., & Torn, M. S. (2018). The AmeriFlux network: A coalition of the willing. *Agricultural and Forest Meteorology*, *249*(May), 444–456. https://doi.org/10.1016/j.agrformet.2017.10.009

Oikawa, P. Y., Sturtevant, C., Knox, S. H., Verfaillie, J., Huang, Y. W., & Baldocchi, D. D. (2017a). Revisiting the partitioning of net ecosystem exchange of CO2 into photosynthesis and respiration with simultaneous flux measurements of 13CO2 and CO2, soil respiration and a biophysical model, CANVEG. *Agricultural and Forest Meteorology*, *234–235*, 149–163. https://doi.org/10.1016/j.agrformet.2016.12.016

Oikawa, P. Y., Sturtevant, C., Knox, S. H., Verfaillie, J., Huang, Y. W., & Baldocchi, D. D. (2017b). Revisiting the partitioning of net ecosystem exchange of CO2into photosynthesis and respiration with simultaneous flux measurements of13CO2and CO2, soil respiration and a biophysical model, CANVEG. *Agricultural and Forest Meteorology*, *234–235*, 149–163. https://doi.org/10.1016/j.agrformet.2016.12.016

Parker, G. G. (1997). Canopy structure and light environment of an old growth Douglas-fir/Western hemlock forest. *Northwest Science*, *71*(4), 261–271.

Parker, G. G., Harmon, M. E., Lefsky, M. A., Chen, J., Pelt, R. Van, Weis, S. B., … Frankling, J. F. (2004). Three-dimensional Structure of an Old-growth Pseudotsuga-Tsuga Canopy and Its Implications for Radiation Balance, Microclimate, and Gas Exchange. *Ecosystems*, *7*(5), 440–453. https://doi.org/10.1007/s10021-004-0136-5

Paw U, K. T., Falk, M., Suchanek, T. H., Ustin, S. L., Chen, J., Park, Y.-S., … Matista, A. A. (2004).

Carbon Dioxide Exchange between an Old-Growth Forest and the Atmosphere. *Ecosystems*, *7*(5), 513–524. https://doi.org/10.1007/s10021-004-0141-8

Phillips, N., Bond, B. J., McDowell, N. G., & Ryan, M. G. (2002). Canopy and hydraulic conductance in young, mature and old Douglas-fir trees. *Tree Physiology*, *22*(2–3), 205–211. https://doi.org/10.1093/treephys/22.2-3.205

Protoschill-Krebs, G Wilhelm, C Kesselmeier, J. (1996). Consumption of carbonyl sulphide (COS) by higher plant carbonic anhydrase (CA). *Atmospheric Environment*, *30*(18), 3151–3156. Retrieved from https://www.sciencedirect.com/science/article/pii/135223109600026X

Le Quéré, C., Raupach, M. R., Canadell, J. G., Marland, G., Bopp, L., Ciais, P., … Woodward, F. I. (2009). Trends in the sources and sinks of carbon dioxide. *Nature Geoscience*, *2*(12), 831–836. https://doi.org/10.1038/ngeo689

Le Quéré, C., Andrew, R. M., Friedlingstein, P., Sitch, S., Pongratz, J., Manning, A. C., … Zhu, D. (2018). Global Carbon Budget 2017. *Earth Syst. Sci. Data Etsushi Kato Markus Kautz Ralph F. Keeling Kees Klein Goldewijk Nathalie Lefèvre Andrew Lenton Danica Lombardozzi Nicolas Metzl Yukihiro Nojiri Antonio Padin Janet Reimer*, *1010333739*(10), 405–448. https://doi.org/10.5194/essd-10-405-2018

Reichstein, M., Falge, E., Baldocchi, D., Papale, D., Aubinet, M., Berbigier, P., … Granier, A. (2005). On the separation of net ecosystem exchange into assimilation and ecosystem respiration: review and improved algorithm. *Global Change Biology*, *11*(9), 1424–1439.

Rossini, M., Meroni, M., Migliavacca, M., Manca, G., Cogliati, S., Busetto, L., … Colombo, R. (2010). High resolution field spectroscopy measurements for estimating gross ecosystem production in a rice field. *Agricultural and Forest Meteorology*, *150*(9), 1283–1296. https://doi.org/10.1016/j.agrformet.2010.05.011

Schimel, D., Stephens, B. B., & Fisher, J. B. (2015). Effect of increasing CO_2 on the terrestrial carbon cycle. *Proceedings of the National Academy of Sciences*, *112*(2), 436–441. https://doi.org/10.1073/pnas.1407302112

Schuh, A. E., Denning, A. S., Corbin, K. D., Baker, I. T., Uliasz, M., Parazoo, N., … Worthy, D. E. J. (2010). A regional high-resolution carbon flux inversion of North America for 2004. *Biogeosciences*, *7*(5), 1625–1644. https://doi.org/10.5194/bg-7-1625-2010

Seibt, U., Rajabi, A., Griffiths, H., & Berry, J. A. (2008). Carbon isotopes and water use efficiency: Sense and sensitivity. *Oecologia*, *155*(3), 441–454. https://doi.org/10.1007/s00442-007-0932-7

Seibt, U., Kesselmeier, J., Sandoval-Soto, L., Kuhn, U., & Berry, J. A. (2010). A kinetic analysis of leaf uptake of COS and its relation to transpiration, photosynthesis and carbon isotope fractionation. *Biogeosciences*, *7*(1), 333–341. https://doi.org/10.5194/bg-7-333-2010

Shaw, D. C., Chen, J., Freeman, E. a, & Braun, D. M. (2005). Spatial and population characteristics of dwarf mistletoe infected trees in an old-growth Douglas-fir western hemlock forest. *Canadian Journal of Forest Research*, *35*(4), 990–1001. https://doi.org/10.1139/x05-022

Shaw, D., Franklin, J., Bible, K., Klopatek, J., Freeman, E., Greene, S., & Parker, G. (2004). Ecological Setting of the Wind River Old-growth Forest. *Ecosystems*, *7*(5), 427–439. https://doi.org/10.1007/s10021-004-0135-6

Sjöström, M., Zhao, M., Archibald, S., Arneth, A., Cappelaere, B., Falk, U., … Kutsch, W. (2013). Evaluation of MODIS gross primary productivity for Africa using eddy covariance data. *Remote Sensing of Environment*, *131*, 275–286.

Stimler, K., Nelson, D., & Yakir, D. (2010). High precision measurements of atmospheric

concentrations and plant exchange rates of carbonyl sulfide using mid-IR quantum cascade laser. *Global Change Biology*, *16*(9), 2496–2503. https://doi.org/10.1111/j.1365-2486.2009.02088.x

Stimler, K., Montzka, S. A., Berry, J. A., Rudich, Y., & Yakir, D. (2010). Relationships between carbonyl sulfide (COS) and CO2 during leaf gas exchange. *New Phytologist*, *186*(4), 869–878. https://doi.org/10.1111/j.1469-8137.2010.03218.x

Thum, T., Zaehle, S., Köhler, P., Aalto, T., Aurela, M., Guanter, L., … Markkanen, T. (2017). Modelling sun-induced fluorescence and photosynthesis with a land surface model at local and regional scales in northern Europe. *Biogeosciences*, *14*(7), 1969–1984. https://doi.org/10.5194/bg-14-1969-2017

van der Tol, C., Verhoef, W., Timmermans, J., Verhoef, A., & Su, Z. (2009). An integrated model of soil-canopy spectral radiances, photosynthesis, fluorescene, temperature and energy balance. *Biogeosciences*, *6*, 3109–3129.

Toomey, M., Friedl, M. A., Frolking, S., Hufkens, K., Klosterman, S., Sonnentag, O., … Richardson, A. D. (2015). Greenness indices from digital cameras predict the timing and seasonal dynamics of canopy-scale photosynthesis. *Ecological Applications*, *25*(1), 99–115. https://doi.org/10.1890/14-0005.1

UNFCC. (2015). United nations framework convention on climate change. *Paris, France*.

Wang, Y. P., Baldocchi, D., Leuning, R., Falge, E., & Vesala, T. (2007). Estimating parameters in a land-surface model by applying nonlinear inversion to eddy covariance flux measurements from eight FLUXNET sites. *Global Change Biology*, *13*(3), 652–670. https://doi.org/10.1111/j.1365-2486.2006.01225.x

Warren, J., Meinzer, F., Brooks, J., & Domec, J. (2005). Vertical stratification of soil water

storage and release dynamics in Pacific Northwest coniferous forests. *Agricultural and Forest Meteorology*, *130*(1–2), 39–58. https://doi.org/10.1016/j.agrformet.2005.01.004

Wehr, R., & Saleska, S. R. (2015). An improved isotopic method for partitioning net ecosystem-atmosphere CO2exchange. *Agricultural and Forest Meteorology*, *214–215*, 515–531. https://doi.org/10.1016/j.agrformet.2015.09.009

Wehr, R., Munger, J. W., McManus, J. B., Nelson, D. D., Zahniser, M. S., Davidson, E. A., … Saleska, S. R. (2016). Seasonality of temperate forest photosynthesis and daytime respiration. *Nature*, *534*(7609), 680.

Wehr, R., Commane, R., Munger, J. W., Barry Mcmanus, J., Nelson, D. D., Zahniser, M. S., … Wofsy, S. C. (2017). Dynamics of canopy stomatal conductance, transpiration, and evaporation in a temperate deciduous forest, validated by carbonyl sulfide uptake. *Biogeosciences*, *14*(2), 389–401. https://doi.org/10.5194/bg-14-389-2017

Wharton, S., & Falk, M. (2016). Climate indices strongly influence old-growth forest carbon exchange. *Environmental Research Letters*, *11*(4), 1–11. https://doi.org/10.1088/1748-9326/11/4/044016

Whelan, M. E., Lennartz, S. T., Gimeno, T. E., Wehr, R., Wohlfahrt, G., Wang, Y., … Campbell, J. E. (2017). Reviews and Syntheses: Carbonyl Sulfide as a Multi-scale Tracer for Carbon and Water Cycles. *Biogeosciences Discussions*, (October), 1–97. https://doi.org/10.5194/bg-2017-427

Williams, A. P., Allen, C. D., Macalady, A. K., Griffin, D., Woodhouse, C. A., Meko, D. M., … Grissino-Mayer, H. D. (2013). Temperature as a potent driver of regional forest drought stress and tree mortality. *Nature Climate Change*, *3*(3), 292.

Winner, W., Thomas, S., Berry, J., Bond, B., Cooper, C., Hinckley, T., … Williams, M. (2004).

Canopy Carbon Gain and Water Use: Analysis of Old-growth Conifers in the Pacific

Northwest. *Ecosystems*, *7*(5), 482–497. https://doi.org/10.1007/s10021-004-0139-2

Wohlfahrt, G., Brilli, F., Hörtnagl, L., Xu, X., Bingemer, H., Hansel, A., & Loreto, F. (2012).

Carbonyl sulfide (COS) as a tracer for canopy photosynthesis, transpiration and stomatal

conductance: Potential and limitations. *Plant, Cell and Environment*, *35*(4), 657–667.

https://doi.org/10.1111/j.1365-3040.2011.02451.x

Biotic and abiotic controls on carbonyl sulfide uptake in a temperate old-growth rainforest

Bharat Rastogi[1], Max Berkelhammer[2], Sonia Wharton[3], Mary E Whelan[4] Malcolm S Itter[5], J Brian Leen[6], Manish X Gupta[6], David Noone[7], Christopher J. Still[1]

[1] Department of Forest Ecosystems and Society, Oregon State University, OR 97331, USA
[2] Department of Earth and Environmental Sciences, University of Illinois at Chicago, Chicago, Illinois, USA
[3] Atmospheric, Earth and Energy Division, Lawrence Livermore National Laboratory, 7000 East Avenue, L-103, Livermore, CA 94550, USA
[4] Carnegie Institution for Science, 260 Panama St., Stanford, CA, 94305, USA
[5] Department of Forestry, Michigan State University, East Lansing, Michigan 48824 USA
[6] ABB – Los Gatos Research, 3055 Orchard Drive San Jose, CA 95134
[7] College of Earth, Ocean and Atmospheric Sciences, Oregon State University, OR 97331, USA

2   BIOTIC AND ABIOTIC CONTROLS ON CARBONYL SULFIDE UPTAKE IN A TEMPERATE OLD-GROWTH RAINFOREST

2.1   Abstract

Diurnal and vertical patterns of carbonyl sulfide OCS and CO_2 mixing ratios above and within a 60m tall old-growth temperate forest are presented. Canopy air from four different heights was sampled *in-situ* using a continuous integrated cavity output spectroscopy analyzer during August-September 2014. Measurements revealed large vertical gradients in OCS, implying significant ecosystem uptake that peaked in the early morning. The diurnal cycle of OCS mixing ratios at all heights exhibited a typical pattern characterized by nighttime drawdown, an early morning minimum, and a maximum of OCS around midday. Daytime increase in the upper canopy is attributed to entrainment of planetary boundary layer (PBL) air into the canopy. OCS entrainment was quantified using a mass balance approach, assuming that stomatal uptake dominated daytime OCS flux. The validity of this assumption is discussed, in light of large uptake by epiphytes. The site is characterized by a large amount of epiphytic biomass due to moist conditions and mild temperatures in the understory. While epiphytic uptake of OCS has been studied before, we show for the first time that this may be a dominant component of ecosystem flux under humid or moist conditions, which are most commonly observed during the night. We test this theory using a chamber experiment measuring epiphytic fluxes for two species of lichen and one moss species (in-situ and in a laboratory). We suggest that the role of epiphytes be explicitly considered when using OCS as a tracer of ecosystem-scale photosynthesis in similar forest ecosystems.

2.2   Introduction

Measurements of carbonyl sulfide OCS have recently been shown to provide an independent and direct estimate of plant productivity (Blonquist et al., 2011; Campbell et al., 2008; Whelan et al., 2017 and references therein). OCS is the most abundant reduced sulfur gas present in the atmosphere, with a mean atmospheric concentration of ~ 500 ppt (parts per

trillion; (Montzka et al., 2007) and is emitted into the atmosphere from oceans via direct emissions or oxidation of CS_2 (Kettle et al., 2002). Plant uptake of OCS via stomata follows a pathway that is nearly identical to that of CO_2 assimilation (Berry et al., 2013; Stimler et al., 2010). OCS is irreversibly hydrolyzed inside the leaf in a reaction that is catalyzed by the ubiquitous enzyme, carbonic anhydrase (CA). Observations of leaf-level (Stimler et al., 2010), branch-level (Berkelhammer et al., 2014) and ecosystem-level (Asaf et al., 2013) fluxes indicate that the uptake ratio of OCS:CO_2 is relatively constant at medium to high light levels (leaf and ecosystem relative uptake; LRU and ERU respectively; (Maseyk et al., 2014). Berkelhammer et al. (2014) showed that OCS fluxes were highly correlated with water vapor fluxes at the branch level, implying a strong control of OCS uptake by stomatal dynamics. In a study at Harvard forest (maximum LAI = 5; canopy height = 25 m; Urbanski et al., 2007), values of ecosystem-scale stomatal conductance (i.e., canopy conductance) derived from OCS fluxes were similar to those following traditional approaches using heat fluxes (Wehr et al., 2017), while nighttime OCS uptake was related to incomplete stomatal closure in a northern latitude European forest (Kooijmans et al., 2017). These studies highlight the value of OCS for better understanding leaf gas exchange processes.

The key difference between OCS and CO_2 cycling is the absence of a retroflux from actively photosynthesizing plants, i.e., OCS has a one-way flux from the atmosphere into the leaf. Emissions of OCS from soils have been identified (Kesselmeier et al., 1999; Kuhn et al., 1999; Maseyk et al., 2014; Whelan et al., 2016), although these fluxes are usually an order of magnitude smaller than rates of plant uptake. In a soil incubation study, Whelan et al. (2016) found that soil fluxes of OCS were highly dependent on temperature and soil moisture and that dry and warm soils (soil temperatures exceeding 30°C) were likely to be a net source of OCS. Few OCS measurement studies at the ecosystem level exist (for a comprehensive list of sites readers are referred to Fig. 2 in Whelan et al., 2017). Asaf et al. (2013) showed that gross primary productivity (GPP) derived from OCS flux measurements collected across a few days were overestimated, but in qualitative agreement with those calculated from standard

partitioning of the net ecosystem exchange of CO_2 (NEE) across a range of semi-arid ecosystems. Commane et al. (2015) measured one year of OCS fluxes at a temperate deciduous forest. While seasonal patterns of OCS fluxes were similar to calculated GPP from EC flux tower data, high mid-summer emissions of OCS remain unexplained. Another recent study over an oak-savanna woodland in southern France (Belviso et al., 2016) found that OCS exchange was highly influenced by photosynthesis, but only during early morning hours. While such studies continue to establish links between OCS and ecosystem photosynthesis and stomatal conductance dynamics, there is a corresponding need to better understand the dynamics of OCS canopy exchange driven by photosynthesis and other processes in a range of ecosystem types.

OCS measurements have not been previously reported for old-growth forests, although a recent study using flask samples inferred large OCS uptake in coastal redwood forests of northern California (Campbell et al., 2017). Old-growth forests exhibit dynamics that are very different from those of other forest ecosystems due to a high leaf area index (LAI) and complex forest structure (Hollinger et al., 1994). These forests often have very tall stature, extremely high aboveground biomass, slow rates of growth (Harmon et al., 2004), and often are a large storage of soil carbon (Luyssaert et al., 2008). In old-growth forests such as those located in the Pacific Northwest (PNW) region of North America, mild temperatures and very wet conditions promote abundant epiphytic vegetation cover on branches and boles of trees, as well as the forest floor, covering these surfaces in thick green carpets. For instance, individual Sitka spruce trees (in the rainforests of the Olympic peninsula have been estimated to hold up to 1000 Kg of dry epiphytic matter (Haristoy et al., 2014). While patterns of CO_2 and H_2O exchange between epiphytic species and the surrounding environment can be very different from those of higher plants, these epiphytic species contain CA that catalyze OCS exchanges with the atmosphere (Gries et al., 1994; Kuhn et al., 2000; Kuhn & Kesselmeier, 2000). While these earlier studies documented OCS gas exchange on lichens and other epiphytic plants, their influence on ecosystem cycling of this gas remains understudied. For example, Flanagan et al. (1997) showed

that CA-catalyzed epiphytic activity had significant influence on $CO^{18}O$ cycling in boreal forest canopies, and was highly dependent on surface wetness. This implies a similar potential impact of epiphytes on canopy-atmosphere OCS cycling independent of canopy stomatal pathways.

The unequal distribution and abundance of biomass throughout an old-growth canopy creates strong microclimates (Chen et al., 2002; Chen & Franklin, 1997). For instance, radiation-limited understory remains wet for weeks following precipitation events (Heffernan, 2017). However, the effect of a complex vertical LAI distribution on carbon and water fluxes in old-growth forests remains relatively understudied. Dominant tall trees are known to have low net rates of gas exchange in the overstory owing to high hydraulic resistances, which reduce the transport of water from roots to tree tops (Woodruff et al., 2007), while low light levels should strongly constrain photosynthetic fluxes in the understory. Consequently, eddy flux measurements of NEE from temperate old-growth forests (Desai et al., 2005; Hollinger et al., 1994; Law et al., 2001; Wharton et al., 2012; Wharton & Falk, 2016) report low rates of net carbon sequestration (some site-years have also been reported as a net CO_2 source; Wharton and Falk, 2016). However, flux measurements are typically made only above the canopy, and during times of poor canopy air mixing may only be representative of the fluxes in the upper part of the canopy. The measurement problem is enhanced given that air flow in tall canopies is often decoupled (Pyles et al., 2004), i.e., air parcels measured at the tower top may have no influence of lower canopy processes and vice versa. Since OCS exchange is largely tied to leaf processes, profile measurements within and above the canopy may provide additional information on whole-canopy gas exchange dynamics. By contrast, CA is also present in understory and epiphytic vegetation, which is more frequently wetted, and therefore likely to influence ecosystem OCS cycling. Thus, if there are canopy processes that involve CA catalysis other than those occurring in leaves of dominant trees, OCS exchange may not be tied as closely to stomatal dynamics as in other ecosystems. The overarching objective of this study is to understand biotic and abiotic controls on OCS exchange in a heterogeneous, tall old-growth seasonal rainforest, including a better understanding of the influence of epiphytic vegetation

on canopy OCS exchange. The results should provide information on canopy OCS processes generally, but specifically in old-growth forests, which often show different dynamics compared to younger forests.

2.3 Methods

2.3.1 Site description

Measurements were made at the Wind River Experimental Forest (WR), located within the Gifford Pinchot National Forest in southwest Washington state, USA (45°49'13.76'' N; 121°57'06.88'' W; 371 m above sea level). The climate is classified as temperate oceanic with a strong summer drought. Long-term meteorological data available from nearby climate stations indicate that the mean annual temperature over the last century was 8.8°C and precipitation was ~ 2,200mm, of which less than 10% falls between the months of June and September (Shaw et al., 2004). The forest is 478 ha of preserved old growth evergreen needle-leaf forest, with dominant tree species of Douglas fir (*Pseudotsuga menzesii*) and Western hemlock (*Tsuga hetrophylla*). The tallest Douglas fir trees are between 50 and 60m, while the shade tolerant hemlocks are between 20-40 m high. The forest also features a diverse understory that consists of Pacific yew (*Taxus brevifolia*) and deciduous vine maples, and a large assemblage of shrubs that include salal (*Gaultheria shallon*), Oregon grape (*Mahonia aquifolium*) and red huckleberries (*Vaccinium parvifolium*). This results in a bimodal distribution of LAI (Parker, 1997; reproduced and shown in Fig. 1.a), with peaks centered around 25m and 15m respectively. The cumulative LAI is estimated to be ~8-9 m^2m^{-2}, with little seasonality. Additionally, the ecosystem hosts a large biodiversity of mosses, lichens and other epiphytic material. McCune et al. (1997) quantified the total epiphytic biomass of the forest to be 1.3 metric tonnes ha^{-1}. The soils are from volcanic parent material, and most of the top layer is a well-developed organic matter horizon (Shaw et al., 2004).

2.3.2 CO_2 and H_2O flux measurements

Carbon, water and energy fluxes have been collected since 1998 using the eddy covariance (EC) technique at the Wind River AmeriFlux tower (US-wrc; Wharton and Falk 2016). The most recent EC system consists of a 3-D sonic anemometer (CSAT3, Campbell Scientific, Logan, Utah) and a closed-path infrared gas analyzer (LI-7000, Li-Cor, Lincoln, Nebraska). The EC system is located approximately 10 m above the canopy top at a height of 70 m. Over a period of sixteen years (1999-2015), the ecosystem was a net weak sink of carbon annually (-32 g C m^{-2} yr^{-1} ±84 gC m^{-2} yr^{-1}), with monthly NEE peaking early in the growing season (March-April). Interannual variability in NEE is largely explained by climatic variability associated with major teleconnections such as the Pacific Decadal Oscillation and the El-Niño Southern Oscillation (Wharton and Falk 2016).

NEE was measured using the EC system and partitioned into ecosystem respiration (Re) and GPP by identifying a turbulence (friction velocity) threshold, fitting an exponential temperature response curve to the nighttime NEE, and extrapolating the relationship to calculate daytime Re. GPP is calculated as the residual of NEE and Re. Partitioned data were gap filled using the online tool REddyProc based on procedure described in Reichstein et al. (2005). For full data processing readers are referred to Falk et al. (2008) and Wharton et al. (2012).

2.3.3   OCS measurements

A commercially available off-axis integrated cavity output spectroscopy analyzer (Los Gatos Research Inc., model 914-0028) was deployed at the base of the tower in an insulated and temperature-controlled shed from July 21-September 18, 2014. Data reported in this study comprise measurements between August 1-September 13. The instrument measured mixing ratios of OCS, CO_2, H_2O and CO simultaneously at a maximal scan rate of 5Hz. The system used a 4.87 µm cascade laser coupled to a high finesse 800 cm^3 optical cavity and light transmitted through the cavity is focused into a cooled and amplified HgCdTe detector. OCS was detected at ~2050.40 cm^{-1}, CO_2 at 2050.56 cm^{-1}, CO at ~2050.86 cm^{-1}, and H_2O at

~2050.66 cm^{-1}. Pressure broadening associated with changes in the concentration of water vapor in the samples was corrected for in the analysis routine. An additional test was performed in the lab to check for water vapor cross-interference (Fig. S.1). This test revealed that OCS measurements were marginally sensitive to water vapor and that the magnitude of this sensitivity (0.87 ppt decrease in OCS corresponding to a 1 ppth increase in H_2O) was negligible compared to the magnitude of OCS mixing ratios observed in this study. For detailed information regarding instrumentation and the measurement readers are referred to Berkelhammer et al. (2014) and Belviso et al. (2016). To avoid OCS contamination, stainless steel and PFA (polyfluoroacetate) or PTFE (polytetrafluoroethylene) material was used for all tubing and fittings. Ambient air was sampled from four different heights on the tower (70m; above the canopy, 60m; at the canopy height, 10m and 1m above the ground), through 0.25'' diameter PFA tubing using a diaphragm pump at a flow rate of 2L min^{-1}. An additional line was connected to an automated surface chamber described in Sect. 2.7. A 0.2 µm filter with PTFE membrane, encased in stainless steel housing was installed at the inlet of each sampling line. The 1m- sampling line was installed about 15m away from the base of the tower, in an area representative of the forest ground surface. All sample gases were introduced into the analyzer through a Multiport Inlet Unit (MIU; Los Gatos Research Inc., model 908-0003-9002) a computer-controlled bank of solenoids. The MIU was modified by replacing the default brass valves with stainless steel ones to avoid OCS contamination. To avoid static air in the sampling lines, continuous flow was maintained using an external pump (Gast High-Capacity Vacuum Pump). This pump was installed downstream of the analyzer, to avoid OCS contamination from the pump's gaskets. Each intake line was sampled for 5 minutes, during which measurements were made at a frequency of 0.1 Hz. The first minute of each sampling interval was discarded to avoid any inter-sampling mixing. The remaining data were checked for temperature and pressure fluctuations inside the measurement chamber, and a moving window filter was used to eliminate any sudden outliers in the data (i.e., adjacent data points that were more than 7 ppt apart). Data for all gases was then aggregated to hourly means.

2.3.4 Calibration

A reference gas tank filled with ambient air was used as a reference standard. Tanks were filled to ~2300 psi and stabilized at 2000 psi, once compressed air cooled to ambient temperatures. Tanks were stored in an insulated shed and switched out at pressures ~700 psi. Air was analyzed daily from the calibration tank, through the MIU, for a period of 5 min and processed as described above (see section 2.3). At the beginning of the measurement campaign, a glass flask was filled with air from the reference tank and measured against a NOAA GMD reference standard to be within 3 ppt of the measurement from the analyzer. This difference was well within the reported accuracy of measurement from the manufacturer, as well as the minimum uncertainty of 12.6 pmol mol^{-1} reported by Berkelhammer et al. (2014) who used a similar instrument. We assumed that OCS concentrations in the tanks were stable over the course of the campaign. Data were corrected for drift by detrending against the calibration using native functions in Matlab (v.8.6).

2.3.5 Environmental data

Ancillary environmental data was measured at the site. A full list of variables and measurement methods is provided in supplementary information (Table 6-1).

2.3.6 Estimating Ecosystem Fluxes

Following Lai et al. (2006) and Lai & Ehleringer (2011), and under the assumptions of horizontal homogeneity, incompressible flow the steady state mass balance of OCS within a forest can be expressed as

$$M_c . \frac{dv_c}{dt} = F_{bio} + F_{entrainment} \qquad (1),$$

where Mc represents the number of moles of air in a column of air per unit ground area, v_c is the average mole fraction of OCS in the column, and F$_{bio}$ and F$_{entrainment}$ represent the biotic and

entrainment source/sink strength of OCS within the forest canopy. The left-hand side of (1) is calculated as the integral of concentration changes over height up to the height of the profile system (h$_{EC}$) following Aubinet et al. (2001).

$$M_c \cdot \frac{dv_c}{dt} = \frac{P}{RT_{air}} \int_1^{h_{EC}} \frac{dC_z}{dt} \cdot dz \qquad (2)$$

where P is the atmospheric pressure (Pa), R is the ideal gas constant (Jmol^{-1}K^{-1}), T is the air temperature (K), and C$_z$ is the mixing ratio (of OCS and CO_2, units of ppt and ppm respectively) along a vertical profile from the forest floor to h$_{EC}$. The integral was determined from hourly means of measured profile concentrations at 1, 10, 60, and 70m (Fig. 3) by using trapezoidal areas. It is important to note that the quantity on the right-hand side of equation 2 is routinely estimated at flux tower sites as a storage flux for CO_2. Throughout the rest of this study, we refer to fluxes estimated from Eq (2) as storage.

For the purpose of this study, we assume that vascular plant stomatal uptake dominates daytime biotic uptake of OCS (i.e., is much larger than soil and epiphytic uptake), and therefore $F_{bio} \sim F_{leaf}$. F$_{leaf}$ is the ecosystem-scale 'leaf' flux of OCS, and is estimated using Asaf et al. (2013) as

$$F_{Leaf} = GPP \cdot \frac{OCS}{CO_2} \cdot \frac{1}{LRU} \qquad (3)$$

where OCS and CO2 are the observed tower top mixing ratios, and GPP was estimated from measured EC CO_2 fluxes at the tower top. LRU was inferred following (Seibt et al., 2010), who derived this quantity from the ratio of CO_2 in leaf intercellular spaces to that in ambient air (i.e., the c_i/c_a ratio). We estimated canopy scale ci/ca using a process-based model (E.D. 2.1) that was run using site- level data (Jiang et al., *submitted*). Thus, by inferring F_{leaf} (3) from measurements and model calculations, and estimating the total mass balance (2) directly from measurements, we are then able to solve for $F_{entrainment}$.

2.3.7 Estimating Surface Fluxes

In addition to ecosystem-level sampling of canopy air, we also measured OCS exchange between the forest floor and the atmosphere. An automatically opening and closing Li-Cor soil

chamber was modified as in Maseyk et al. (2014) and installed at a series of three 0.3 m^2 plots from July 6-16, Aug 13-Oct 7, and Nov 6-Dec 2, 2015. Near-surface ambient fluxes were observed when the chamber was open for 5 min. When the chamber was closed for 10 min, OCS concentrations decreased then experienced a relatively stable mixing ratio $\pm$ 8 ppt OCS over at least 2 min. Fluxes were calculated by

$$F_{forest\ floor} = M_c \Delta\chi A^{-1} \tag{4}$$

where M$_c$ is the monitored flow rate into the chamber (mol s^{-1}) using the ideal gas law), $\Delta\chi$ is the difference between mixing ratios of OCS or CO_2 in ambient air and the chamber, and A is the measured area of the chamber. Atmospheric pressure and temperature were monitored in order to convert the flow rate from L min^{-1} to mol s^{-1} using the ideal gas law.

Additionally, we collected measurements on a variety of understory epiphytes in August 2015, by placing them in custom-made Teflon branch bags, adapted from Ortega & Helmig (2008). We first measured various epiphytes in the field, and later brought back samples to the laboratory and measured their gas exchange dynamics. Laboratory measurements were performed in a controlled environment (i.e., not *in situ*), and in the dark. Mixing ratios were converted to fluxes using the following equation:

$$F_{epiphyte} = M_c \cdot \frac{\Delta\chi}{Mass} \tag{5}$$

$F_{epiphyte}$ is the estimated flux, Mc and $\Delta\chi$ are defined the same as in equation (4), *Mass* is the weight of the epiphyte (g). For the epiphyte experiments, the flow rate in to the chamber was held constant at 1.8Lmin^{-1}. Epiphyte fluxes were estimated on a per mass basis. For the in-situ measurements, the mass was the weight of the epiphyte in the chamber under field conditions (i.e., it was not dried). For the laboratory experiment, the mass was calculated as the dry weight of the epiphyte. Blank measurements were made periodically to correct for OCS exchanges in

the empty chamber, following Berkelhammer et al. (2014). For the laboratory experiment, air temperature inside the branch bag was measured using a thermocouple, and it remained approximately constant at 23 ± 0.5°C. All epiphytic materials were measured at both field moisture capacity, after adding additional moisture by spraying, and after desiccation in an oven. Epiphyte relative uptake (EpRU), defined as a ratio of deposition velocities of OCS:CO_2 was calculated as :

$$EpRU = \frac{F_{OCS}}{OCS} \cdot \left(\frac{F_{CO_2}}{CO_2}\right)^{-1} \tag{6}$$

2.4 Results

2.4.1 Meteorological data

The mean daily air temperature during the measurement period was 18°C (mean min= 12°C and mean max 23°C), which is typical for this time of year for this site. Most days were clear and sunny (Fig S.2.a), and of the 43 days of measurement, only 2 days recorded measureable precipitation. Daily mean maximum water vapor pressure deficit (VPD) was ~3kPa, although several days in August recorded max VPD ~ 4 kPa (Fig. S.2.b). The mean diurnal cycles of microclimate variables (air temperature, relative humidity and wind speed) are displayed in Fig. 1 (panels b-d). Soil moisture steadily declined during the measurement campaign from 26% to 19% (measured at 40cm below the soil surface; see Supplemental Figure S.2.c for soil moisture measurements at different depths), but remained well within the range of available water within the root zone and the wilting point (30% and 12% respectively; Wharton et al., 2009). During the measurement period, mean maximum GPP was ~ 10µmol m^{-2}s^{-1} (plotted as a negative quantity in Fig 1.e to show uptake).
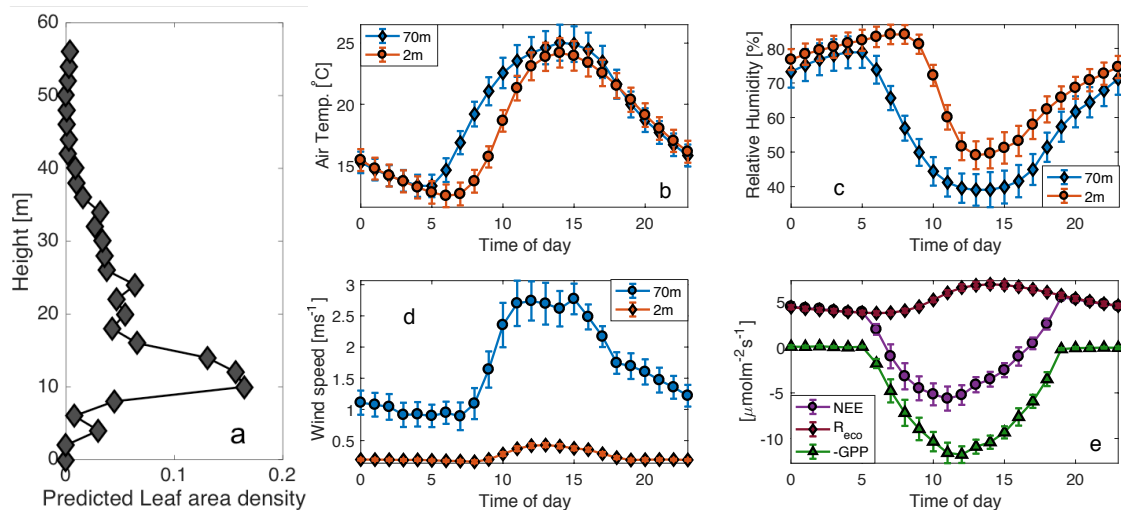
Figure 2-1. Inferred LAI profile at Wind River from Parker (1997) (a), along with mean diurnal cycles of air temperature (b), relative humidity (c), wind speed (d), and carbon fluxes (e). Measurements were made at 70m (above canopy) and 2m (near surface). Carbon fluxes were only measured at 70m. GPP is plotted as a negative quantity indicating gross ecosystem uptake of CO2. Vertical bars represent standard errors. All times are Pacific Standard time (GMT − 7).

2.4.2 Concentration profiles

The mean diurnal cycles of concentration profiles for OCS, CO_2 and H_2O are shown in Fig. 2 (for the complete time series see Fig S.3). Dotted lines indicate local sunrise and sunset times during the measurement period. CO_2 (Fig 2.b) and H_2O vapor (Fig 2.c) concentration profiles show the influence of ecosystem gas-exchange processes on the lower canopy (1, 10 m) and the above canopy (60, 70 m) air space. OCS mixing ratios follow a similar diel pattern at all heights, characterized by a steady nighttime decrease, a minimum in the morning after sunrise, followed by a strong, rapid increase in concentration that peaks during midday (Fig. 2.a). A time lag of one hour is observed for the timing of the minima at the 1m height (near the forest floor) compared to the other heights, likely due to a delay in the warming and drying (Figure 2c) of the air just above the forest floor. The overall mean maximum OCS at 70m was 340 ppt, while the mean maximum OCS at 1m was 260 ppt and the mean minimum at 1m was 152 ppt.
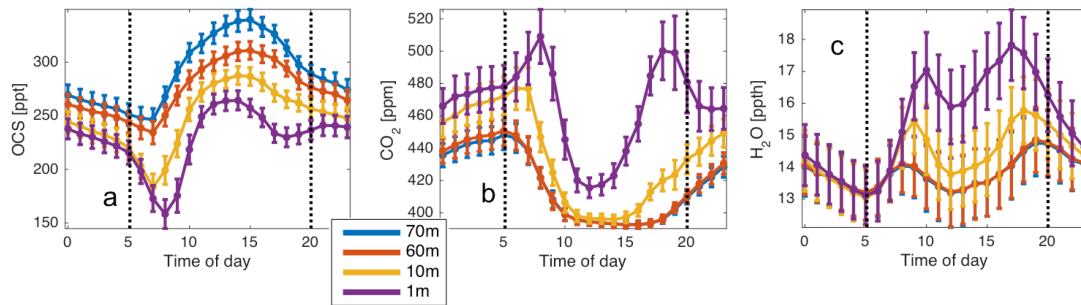
Figure 2-2. Mean diurnal cycles of all measured gases. Vertical bars represent standard errors. Dashed vertical lines indicate approximate times of sunrise and sunset during the study period.

These OCS patterns are distinct from CO_2 and H_2O in at least two ways:

(i) In contrast to CO_2 and H_2O, OCS was always highest at the top of the canopy and lowest just above the forest floor, implying strong forest uptake of OCS. CO_2 and H_2O exhibit profiles characteristic of actively metabolizing plants and microbes, i.e., high CO_2 mixing ratios at the forest surface from heterotrophic and autotrophic respiration. Similarly, evaporation from dew on the surface of the understory species and coarse woody debris in the early morning (Unsworth et al., 2004), transpiration from the understory species, some evaporation of soil water in the late afternoon as the lower canopy heats up (Lai et al., 2006), and abiotic factors influencing gradients in temperature and humidity all contribute to significantly higher H_2O mixing ratios near the forest floor.

(ii) OCS maintained a stronger gradient at all heights throughout the daylight hours while gradients for CO_2 and H_2O above the canopy top (70m and 60m) appear to be unresolved. In contrast, profiles of OCS remain distinct even during times when the top of the canopy is likely coupled to the overlying atmosphere. For all species, the gradient is highest near the forest floor (10m-1m; yellow lines in Fig. 3a-c, although OCS is also characterized by significant height-normalized gradients at the canopy top as well.
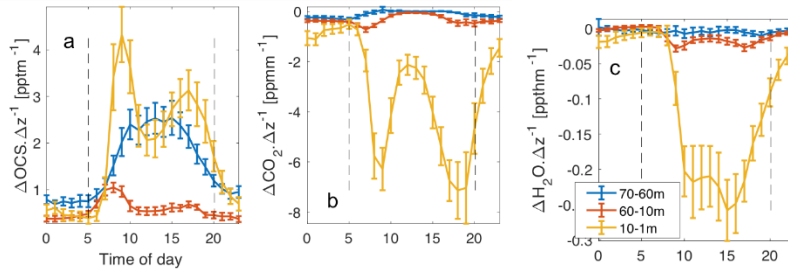
Figure 2-3. Height-normalized gradients of all species (ppt m-1). Vertical bars represent standard errors. Dashed vertical lines indicate times of local sunrise and sunset.

2.4.3 Biotic and Abiotic Fluxes of OCS, CO_2, and H_2O

Storage fluxes reveal large diurnal cycles for OCS and CO_2 (S_{OCS} and S_{CO2} in Fig. 4a-b). OCS mixing ratios decrease throughout the night (Fig. 2a), with a sharp trough shortly after sunrise, followed by a peak before midday. S_{OCS} shows a similar pattern. As inferred by S_{OCS}, OCS is taken up by various components of the ecosystem (i.e., epiphytes, soil organic matter and microbes, and from incomplete stomatal closure) throughout the night. However, a few hours after sunrise, as the canopy air becomes more well-mixed, a spike in S_{OCS} is observed which dissipates through the rest of the day. We infer this as entrainment of background atmospheric OCS. S_{CO2} shows a very similar cycle to that of S_{OCS}, but in the opposite direction. S_{CO2} peaks in the early morning, a few hours after sunrise, as background CO_2 (lower mixing ratios) mixes in with that accumulated throughout the canopy through microbial respiration during the night, resulting in a strong negative storage flux that rapidly approaches zero by midday. This phenomenon is known as flushing and is commonly observed in vegetated ecosystems. S_{OCS} was negatively correlated to both S_{CO2} and S_{H2O} during nighttime and daylight hours and the relationship was stronger between S_{OCS} and S_{CO2} (Fig. S.4a-d). No significant relationship was observed between S_{CO2} and S_{H2O} (Fig. S.4e-f). The tight coupling between S_{OCS} and S_{CO2} indicates that these fluxes are likely the result of common biotic and abiotic processes. During the night, respiration was accompanied by a concomitant uptake of OCS by various components of the ecosystem (i.e. epiphytes, soil, incomplete stomatal closure; discussed in Secs. 3.4-3.6 and

4.2). The early morning maxima S_{OCS} in was the result of entrainment of OCS from the PBL and coincided with a minimum in S_{CO2} due to flushing, since both processes are related to canopy coupling and ventilation. Consequently, the mixing ratio-normalized flux of S_{OCS} and S_{CO2} (calculated by taking the ratio of these fluxes normalized by the canopy top mixing ratio of both species) during nighttime and daylight hours was negative (mean values were -1.39 ± 0.16 and -1.6 ± 0.68 for nighttime and daylight hours, respectively).

NEE and S_{CO2} have the same sign convention (both negative, implying ecosystem uptake), during the morning flushing event, and through most of the day. While we are unable to measure a turbulent (i.e., fast response) OCS flux in this study, vertical profile data (Fig. 2a) suggest high ecosystem uptake of OCS and therefore opposite sign convention for ecosystem uptake (negative) and S_{OCS} during daylight hours. In studies of water vapor isofluxes at Wind River, Lai et al. (2006) and Lai and Ehleringer (2011), observed a very similar signal for entrainment of $\delta^{18}O$ of water vapor into the canopy during morning hours.

Entrainment is not restricted to daylight hours. Storage fluxes of OCS were positive during ~ 17% of nighttime hours and associated with anomalously high friction velocity (Fig. S.5), indicating that entrainment dominated the mass balance of OCS within the ecosystem during these hours, and was characterized by higher turbulence.
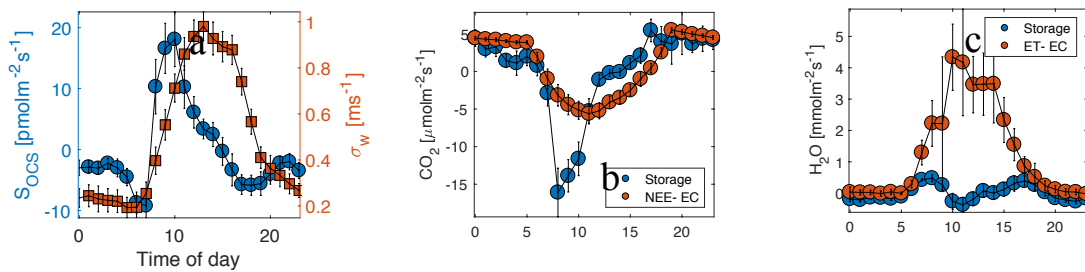
Figure 2-4. Diurnal cycles of storage fluxes integrated over the entire canopy for OCS (blue circles) and σw measured at the tower top (red squares; a), CO_2 (b) and H_2O (c). Vertical bars represent standard errors. Red circles in (b-c) are measured, tower top turbulent fluxes of CO_2 and H_2O. While storage fluxes for CO_2 can account for significant changes in NEE during early morning hours, the effect on H_2O concentrations is comparatively much smaller.

We inferred daytime, ecosystem-scale OCS 'leaf' fluxes (F_{leaf}) using a combination of ecosystem GPP fluxes and a modeled LRU using equation (3). While GPP increased rapidly in the early morning hours, peaked at midday, and declined in the afternoon, F_{leaf} was found to be high in the early morning hours, peaking at noon and declining thereafter. This is a direct consequence of modeled LRU (Fig. 5a), which are higher under lower light levels. LRU is derived from inferred *ci/ca* ratios that are linked to leaf water use efficiency, which has an asymmetric diurnal cycle that peaks in the early morning hours as stomatal conductance during this time is usually high (due to the hydration status of the plant) while photosynthesis is impeded by low light levels.

Entrainment modeled during daylight hours using Eq (1) showed downward fluxes that increased sharply in the early morning hours, and declined slowly during the rest of the day (Fig. 5b). This helps explain observed mixing ratios of OCS (Fig. 2a). Background OCS mixing ratios measured at a nearby mountain-top (Mt. Bachelor, 2731 m a.s.l; ~ 200 Km south of the study site) are ~ 100 ppt higher than those measured at Wind River (Steve Montzka, *pers. comm*). Canopy flushing of atmospheric OCS results in a daytime increase in concentration throughout the canopy, since coupling depths in the canopy are high. Indeed, Pyles et al. (2004) report that vertical patterns of daytime buoyancy driven turbulent mixing diverge usually in the lower 15% of the canopy.
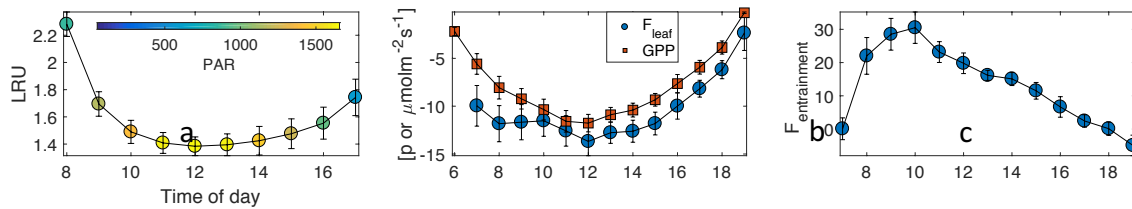
Figure 2-5. Modeled LRU (a), and tower top GPP (red curve in b) are used to infer the ecosystem scale 'leaf- uptake' of OCS (blue curve in b), which is used to calculate the OCS entrainment flux (c).

2.4.4   Near-surface nighttime and early morning OCS exchange

During these hours, the environment is characterized by high relative humidity (mean RH > 80%) and low wind speed (mean u = 0.17ms^{-1}). OCS and CO_2 mixing ratios and gradients were highly correlated through the night and in the early mornings at the near surface (Fig. 6a). This relationship was highly dependent on water vapor. CO_2 build up in the sub-canopy is driven by autotrophic and heterotrophic respiration, and was accompanied by concomitant OCS uptake. Since the forest floor at Wind River is covered by a thick layer of epiphytes, the relationship is likely influenced by understory plant activity, including gas exchange by lichens and bryophytes (liverworts, hornworts, and mosses). At higher temperatures, this relationship is weakened, likely due to enhanced soil activity as well as lower humidity at higher temperatures.
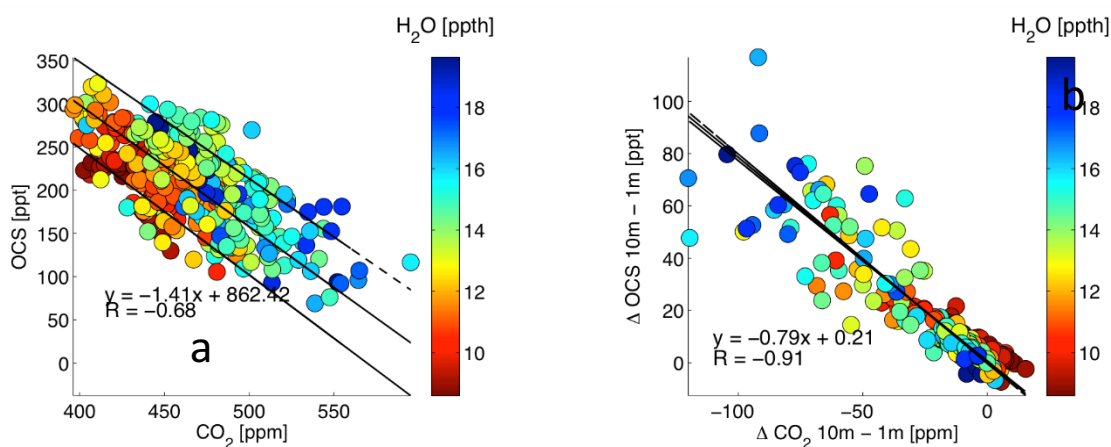
Figure 2-6. CO2 and OCS mixing ratios near the forest floor (1m) are highly correlated during the Nighttime to mid-morning (a), as are OCS and CO2 vertical concentration gradients in the sub-canopy.

2.4.5   Epiphytic uptake

We measured OCS exchange by lichen and moss species that are commonly found in the WR forest understory. In-situ fluxes are summarized in Table 1. In-situ measurements indicated that epiphytic species at the site took up OCS under low-medium light conditions, typically

prevalent in the understory. Across species, OCS fluxes were highly correlated with a proportional CO_2 release (CO_2 flux = $-1.02.10^6$ OCS flux, R^2 = 0.99). Very small emissions were observed from dried out (dormant) epiphytes. *Kindbergia oregona* was additionally measured overnight (Fig.7), and was found to be constant sink of OCS even as CO_2 and H_2O fluxes declined through the course of the night.

Table 2-1. In-situ measurements of epiphytes commonly found in the understory at the study site.

Species	ass (g)	OCS (pmolKg⁻¹s⁻¹)	CO₂ (µmolKg⁻¹s⁻¹)	H₂O (mmolKg⁻¹s⁻¹)	air (°C)	H (%)	PAR (µmolm⁻²s⁻¹)
	5.63	-27.64	25.49	0.35			
Alectoria Sormentosa (live)	7.70	-26.31	25.71	0.35	9	9	381
	8.70	-27.10	26.01	0.40			
Alectoria Sormentosa (dormant)	0.60	0.46	4.98	0.18	1	4	21
	6.40	0.60	1.20	0.09			
Alectoria Sormentosa (wetted)	3.80	-5.90	3.5	0.21	2	3	21
	7.40	-7.07	4.46	0.20			
Kindbergia Oregona (live)	7.40	-1.35	0.40	0.08	2	5	12
	04.60	-1.63	0.34	0.07			
Kindbergia Oregona (dormant)	91.00	0.48	0.12	0.02	0	2	4
	02.00	0.48	0.10	0.02			
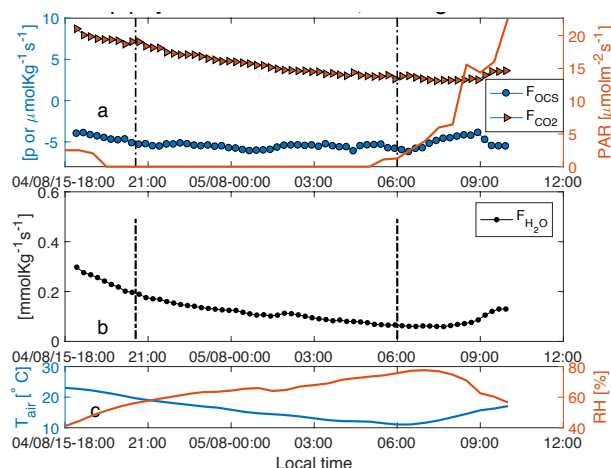
Figure 2-7. Kindbergia oregona OCS and CO2 flux plotted alongside ambient PAR measured at 2m (a), H2O flux (b) and ambient temperature and relative humidity measured at 2m (c).

To examine the effect of moisture on OCS exchange, samples were measured at field *moisture* content, with added moisture, and following dehydration in the lab and in the dark. One of these species, *Lobaria oregana*, was also measured after a second re-wetting, after dehydration. At field moisture, all epiphytic material consumed OCS and emitted CO_2 and H_2O (Fig. 8a-c). Generally, OCS and CO_2 fluxes were tightly coupled for each species, but relative magnitudes of uptake were higher for OCS than for CO_2 (relative, since OCS uptake is six orders of magnitude lower than that of CO_2). Consequently, the Epiphyte relative uptake, (EpRU; defined in section 2.7) was generally negative (except at dehydration) and showed a preferential uptake of OCS that peaked at field moisture content for all measured epiphytic species. Dehydration at temperatures ~40°C drastically reduced subsequent OCS uptake, and yielded very small emissions for *Alectoria sarmentosa* and *Kindbergia oregana*. After rewetting, *Lobaria oregana* resumed OCS uptake, although the flux was ~ 30% of the original value, presumably due to a decrease in microbial and enzymatic activity after dehydration. It is important to note that actual fluxes may be smaller than those observed using the chamber, since the experimental set-up ensured the bag was constantly flushed with ambient air, thereby

minimizing boundary layer resistances. Epiphytes are more commonly found in the understory where wind speeds are low, and therefore the diffusion resistance due to the boundary layer is likely high. Additionally, epiphyte samples were not isolated from their substrates (i.e., small pieces of bark or soil) or other co-occurring fungi, and therefore calculated fluxes likely also were influenced by these entities.
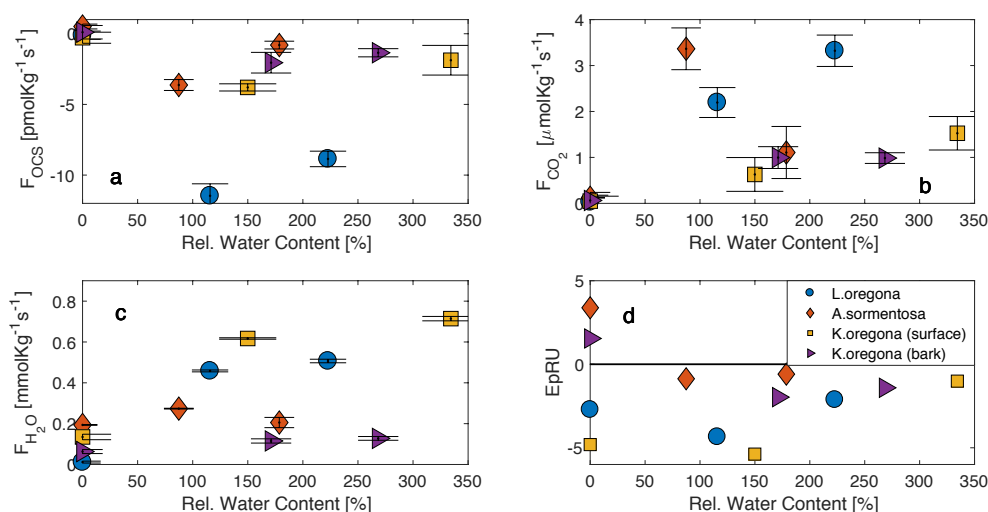
Figure 2-8. Wetness curves for epiphytic vegetation commonly observed in the understory at the study site for OCS (a), CO2 (b), H2O (c), and Epiphytic relative uptake (EpRU), defined as a ratio of deposition velocities for OCS:CO2 (d).

2.4.6 Forest floor OCS exchange

The forest floor was always found to be an OCS sink (mean fluxes are reported in Table 2). Since we were interested in characterizing the response of the forest surface, no surface matter was removed from the chamber locations during air sampling. Three plots were observed in sequence: the latter two plots had a characteristic cryptogamic cover with underlying organic soil. The first plot had a surface cover that looked similar to the other two plots, but was on a buried fallen tree with several decimeters of recognizable woody debris below the surface. This accounts for the difference in sink strength between measurements in July and August, which were only a few weeks apart, but illustrates the scale of heterogeneity

in the forest floor. No discernible diurnal pattern was observed for soil uptake between August and December, but the magnitude of uptake was found to be influenced by soil temperature and moisture during these times, consistent with previous studies of ground surface/soil-atmosphere OCS exchange (Bunk et al., 2017; Kuhn et al., 1999; Maseyk et al., 2014; Sun et al., 2016; Whelan et al., 2016).

*Table 2-2. Mean monthly soil surface OCS fluxes, measured mixing ratios above the canopy, and observed shallow soil moisture and ground surface temperature measured using temperature probes in the upper few cm of the forest floor. *In July, the soil chamber was installed on a plot with significant intact wood litter. Subsequent plots were above a more developed soil organic layer.*

Month	Flux (pmolm^{2}s^{-1})	OCS (ppt)	Mean shallow soil moisture (%)	Mean surface temperature (°C)
Jul*	-22.73 ± 0.74	388.17 ± 11.23	16	20
Aug	-5.83 ± 0.28	385.57 ± 4.66	11	18
Sep	-2.97 ± 0.09	264.24 ± 2.3	15	14
Oct	-3.33 ± 0.13	218.6 ± 1.10	14	13
Nov	-3.99 ± 0.38	309.59 ± 6.03	25	6
Dec	-3.26 ± 0.31	248.82 ± 4.99	27.88	1.25

2.5 Discussion

2.5.1 Daytime ecosystem-scale fluxes of OCS and difference in source-sink estimates

Canopy top gradients for OCS are significantly different from those of CO_2 and H_2O (Fig. 3a-c), even as the exchange of all three gases is controlled by similar biotic and abiotic processes. Calculation of storage fluxes reveal a large positive flux of OCS that peaks before midday and declines thereafter. We inferred ecosystem-scale leaf fluxes using tower top estimates of GPP

and modelled leaf relative uptake. The difference between the leaf sink and storage allowed us to quantify entrainment of OCS in to the canopy. Shortly after sunrise, enhanced mixing transports OCS rich air in to the canopy, some of which is assimilated by various parts of the ecosystem (leaves of dominant trees and understory vegetation, epiphytes, as well as soils), and the remainder is gradually ventilated. At hourly timescales, this results in a persistent increase in OCS mixing ratios of ambient air. At longer timescales, however, the cumulative storage flux (S_{OCS} and S_{CO2}) approaches zero (Fig. S.6a-b), consistent with the assumption of conservation of mass. The measured turbulent flux of CO_2 (i.e. NEE; Fig. S.6c) shows the forest to be a net source of carbon over this time period. Therefore, while storage fluxes are significant over sub-daily timescales, and can be used to study entrainment of boundary layer air that results in an increase in OCS mixing ratios throughout the canopy during the day, these fluxes integrate to zero over larger timescales. However, this approach relies heavily on certain assumptions. These assumptions are addressed below:

1. The very tall and dense nature of the canopy makes it susceptible to advection and decoupling. This results a time lag of ~ one hour in mixing ratios' diurnal cycles of OCS, CO_2 and H_2O between the canopy top and those near the forest floor. Tower top turbulent fluxes of CO_2 (i.e., NEE) are strongly influenced by wind direction and atmospheric stability which determine the measurement footprint (Falk et al., 2008). Since the old growth stand is highly heterogeneous and surrounded by other younger forests mostly to the north, NEE fluxes may not always represent the same footprint that was defined by the concentration profile data. Moreover, there can be issues with partitioning of NEE into source and sink terms. Temperature-based models of respiration may be biased by the selection of driving temperature, i.e., air or soil temperature (Lasslop et al., 2012; Wohlfahrt & Galvagno, 2017) and fail to account for a light inhibition of mitochondrial respiration, known as the Kok effect (Kok, 1949; Wehr & Saleska, 2015). These errors in respiration estimates propagate to errors in GPP inferred from NEE.

2. Leaf relative uptake (LRU) was estimated from ci/ca ratios using relationships that were derived at the leaf-level; however, uncertainties regarding scaling of leaf level ci/ca estimates to canopy scales remain. While modeled canopy-scale ci/ca ratios are in excellent agreement with observed ci/ca ratios of needles collected at the top of a dominant tree at the site (Winner et al., 2004), ci/ca changes strongly through the canopy, owing to lower light, higher ca (e.g. Fig. 2b), leaf acclimation to shading, and species-specific physiology. While individual leaves of dominant trees at the canopy top are known to have higher photosynthetic rates, including at this site (Winner et al., 2004), the LAI profile indicates that most of the leaf area is in fact concentrated at lower heights (Parker, 1997), corresponding to the substantially higher tree density of the shorter hemlocks than the tall Douglas firs (224 tress ha^{-1} and 35 trees ha^{-1} respectively; Shaw et al., 2004). Consequently, it is unclear how much the needles at the canopy top contribute to overall ecosystem photosynthesis and transpiration. Since OCS is more directly a proxy of stomatal conductance than GPP (as leaf OCS uptake is principally controlled by stomata), vertical and temporal offsets in GPP and stomatal conductance are likely to translate into differences between ecosystem-scale uptake of OCS and CO_2.

3. We assumed that daytime biological fluxes of OCS were dominated by actively photosynthesizing needles of the trees. The forest ground surface was found to be an OCS sink, and the sink strength was influenced by the location of the chamber and by environmental conditions. Recent work by Gimeno et al. (2017) found several bryophyte species from temperate forests emit OCS during the day. Epiphytes measured in this study took up OCS in the dark and during daylight hours, with negligible emissions from dormant or dead epiphytes. The abundance of bryophytes, lichens and mosses at our site can affect ecosystem-scale uptake of this gas.

2.5.2 Nighttime uptake due to partial stomatal closure

OCS mixing ratios over natural terrestrial ecosystems are known already to be influenced by a combination of stomatal uptake and soil activity. The mean nighttime storage flux of OCS was -4.2 ± 0.45 pmolm^{-2}s^{-1}, while the forest ground surface flux for August-September 2015 was -3.2 ± 0.21 pmolm^{-2}s^{-1}, demonstrating ecosystem uptake through the night. While a vast proportion of this uptake is by epiphytes, assimilation by leaves of dominant trees due to incomplete stomatal closure likely contributes to this flux. A number of studies report that several coniferous species, including Douglas fir and Western hemlock, exhibit partial stomatal closure during nighttime (Blake & Ferrell, 1977; Dawson et al., 2007; Kavanagh et al., 2007; Running, 1976) This has been speculated to be an ecological adaptation. Daley & Phillips (2006) note that having partially open stomata may enable plants to continue photosynthesis during late evenings and early mornings, when vapor pressure deficits are low. This is certainly true at WR in the summer, when trees can continue assimilating carbon despite high midday VPD, since soil moisture remains reasonably high. Additionally, dominant trees at WR avoid water stress by extracting a greater proportion of their water requirements from deeper soils as the summer drought progresses (Warren et al., 2005). Estimates of individual tree scale conductance (i.e., crown conductance) calculated from sap flow data show that conductance is highest in the early morning hours, and declines steadily as the day progresses - presumably in response to increasing leaf-air vapor pressure deficit (Woodruff et al., 2007). Another study at WR found that sap flow at the base of tall trees continues hours after sunset (Čermák et al., 2007). Much of this is a recharge of water stored in the trunk (of dominant trees) that has been drawn down by daytime transpiration. This recharge has the effect of making water available to needles at the canopy top to start photosynthesis as soon as light is available. Nighttime changes in S$_{OCS}$ driven by a decrease in mixing ratio throughout the canopy profile support the hypothesis that OCS uptake at night is at least partially due to incomplete stomatal closure by trees, as has been shown at a high-latitude European forest (Kooijmans et al., 2017).

2.5.3 Epiphytes

The site is a host to a large diversity and abundance of epiphytes. Using a chamber-based experiment, we found lichen and other epiphytic material to be a strong sink of OCS in low-light conditions and in the dark. This process was found to be highly related to the water content of the epiphyte. This is consistent with previous studies of lichen OCS exchange using chamber measurements (Gimeno et al., 2017; Kuhn et al., 2000; Gries et al., 1994). These plants contain large amounts of CA, and are therefore able to remove OCS from the atmosphere in the dark as long as they have access to moisture. These results indicate the need to continue measurements of OCS exchange for different species of epiphytes, and in differing environmental conditions (moisture content, light, temperature etc.), as well as understand the mechanisms that influence uptake or emission of this gas by epiphytes. This is particularly important given that our results show that endemic epiphytes are able to remove OCS from the atmosphere during the day, contrary to Gimeno et al. (2017), who found several temperate-species of bryophytes in Europe to emit OCS in the light.

We hypothesize that OCS drawdown in the canopy is strongly influenced by epiphytic uptake, which is driven by the water content of the epiphyte. OCS was found to be strongly influenced by relative humidity, both at the canopy top and just above the forest floor (Fig. S.7). Mean diurnal cycles of relative humidity (Fig. 1b) and OCS (Fig. 2a) were negatively correlated. The early morning minimum in OCS occurred when relative humidity near the forest floor was highest (Fig. 2a). Additionally, the decrease in OCS mixing ratios was higher in the sub-canopy than at the canopy top (Fig. 3a). Enhanced atmospheric stability, and high relative humidity, enable OCS uptake by epiphytes like mosses and lichen at night and during early mornings. Epiphytes are present from the surface to heights of 40-50m in the canopy, but their abundance is highest in the understory due to low wind and humid conditions (McCune, 1993). During the day, as relative humidity rapidly declines, epiphytic uptake is reduced. Some epiphytes are able to absorb large volumes of moisture (McCune et al. 1997), including from

44

dew (Gasulla et al., 2012) as well as directly from humid air (Lange et al., 2001), and thus maintain low rates of gas exchange.

Since both mycobiont and photobiont components of epiphytes are known to exhibit high amounts of CA activity (Palmqvist & Badger, 1996), OCS consumption by epiphytes should continue as long as sufficient moisture is available. Indeed, a concomitant decline in mixing ratios of water vapor is clearly observed during these hours (Fig. 2c), as well as a sharp decline in near-surface OCS concentrations, as air and dew point temperatures converge (Fig. S.8). While dew point temperatures rarely equalled air temperatures, the surface temperature of bark and epiphytic material in the understory are likely to be cooler than air temperatures, thereby increasing the likelihood of dew formation at the site (Unsworth et al., 2004). Indeed McDowell et al. (2002) report mid-summer nighttime dew formation being a common occurrence at WR. Therefore, epiphytic vegetation may be a large nocturnal sink for OCS in cool and wet forests, accounting for which is likely to improve estimates of stomatal conductance and CO_2 assimilation inferred from OCS.

2.6   Conclusions

OCS has shown promise as a tracer for ecosystem productivity at multiple scales, since its uptake pathway from the atmosphere in to the leaf nearly mirrors that of CO_2. However, at the ecosystem-scale, there may be differences in the movement of the two gases between the atmosphere and vegetation, an understanding of which is critical if measurement of this gas is to be used to estimate GPP in different ecosystems. Our study site is somewhat atypical (very tall canopy, high biomass, complicated canopy structure and large volume of epiphytes), but is a well-studied temperate coniferous old-growth forest in Pacific Northwest (U.S.A.). We collected continuous in-situ measurements of OCS mixing ratios in ambient air at various heights in the canopy. OCS decreased with height throughout the canopy, but mixing ratios at all heights showed an increase between mid-morning and afternoon. We were unable to identify any within-canopy or surface sources of OCS, except for very small emissions from

dormant epiphytes. Using a mass balance approach, we inferred a strong entrainment signal driving daytime increase in concentrations. Entrainment replenished the canopy air with OCS that was taken up by various parts of the ecosystem at nighttime (incomplete stomatal closure and uptake by epiphytes). Moreover, this approach can provide a method of disentangling biotic and abiotic fluxes of OCS that influence concentration profiles within vegetated canopies (e.g. Belviso et al., 2016). We found that epiphytic material was a moisture dependent sink of OCS in the dark. While previous studies have characterized the role of lichen in OCS exchange, this is the first study that shows that epiphytes may be an important control on OCS exchange in a moist forested canopy. However, questions remain regarding constraints on CA-catalyzed OCS consumption by epiphytes.

While old growth temperate rainforests do not represent a major portion of terrestrial ecosystems, various characteristics of this ecosystem are shared by tropical forests, such as high aboveground biomass, frequent surface wetting, complicated canopy structure with high leaf area, and abundant epiphytic cover. Therefore, this study likely has implications for canopy-atmosphere OCS exchange in tropical forests as well as boreal forests.

2.8   References

Asaf, D., Rotenberg, E., Tatarinov, F., Dicken, U., Montzka, S. A., & Yakir, D. (2013). Ecosystem photosynthesis inferred from measurements of carbonyl sulphide flux. *Nature Geoscience*, *6*(3), 186–190. https://doi.org/10.1038/ngeo1730

Aubinet, M., Chermanne, B., Vandenhaute, M., Longdoz, B., Yernaux, M., & Laitat, E. (2001). Long term carbon dioxide exchange above a mixed forest in the Belgian Ardennes. *Agricultural and Forest Meteorology*, *108*, 293–315.

Belviso, S., Marco Reiter, I., Loubet, B., Gros, V., Lathière, J., Montagne, D., … Genty, B. (2016). A top-down approach of surface carbonyl sulfide exchange by a Mediterranean oak forest ecosystem in southern France. *Atmospheric Chemistry and Physics*, *16*(23), 14909–14923. https://doi.org/10.5194/acp-16-14909-2016

Berkelhammer, M., Asaf, D., Still, C., Montzka, S., Noone, D., Gupta, M., … Yakir, D. (2014). Constraining surface carbon fluxes using in situ measurements of carbonyl sulfide and carbon dioxide. *Global Biogeochemical Cycles*, *28*(2), 161–179. https://doi.org/10.1002/2013GB004644

Berry, J., Wolf, A., Campbell, J. E., Baker, I., Blake, N., Blake, D., … Zhu, Z. (2013). A coupled model of the global cycles of carbonyl sulfide and CO_2 : A possible new window on the carbon cycle. *Journal of Geophysical Research: Biogeosciences*, *118*(2), 842–852. https://doi.org/10.1002/jgrg.20068

Blake, J., & Ferrell, W. K. (1977). The Association between Soil and Xylem Water Potential, Leaf Resistance, and Abscisic Acid Content in Droughted Seedlings of Douglas-fir (Pseudotsuga menziesii). *Physiologia Plantarum*, *39*(2), 106–109.

Blonquist, J. M., Montzka, S. A., Munger, J. W., Yakir, D., Desai, A. R., Dragoni, D., … Bowling, D. R. (2011). The potential of carbonyl sulfide as a proxy for gross primary production at flux tower sites. *Journal of Geophysical Research: Biogeosciences*, *116*(4), 1–18. https://doi.org/10.1029/2011JG001723

Bunk, R., Behrendt, T., Yi, Z., Andreae, M. O., & Kesselmeier, J. (2017). Exchange of carbonyl

    sulfide (OCS) between soils and atmosphere under various CO2concentrations. *Journal of*

    Geophysical Research: Biogeosciences, *122*(6), 1343–1358.

    https://doi.org/10.1002/2016JG003678

Campbell, J. E., Whelan, M. E., Berry, J. A., Hilton, T. W., Zumkehr, A., Stinecipher, J., … Loik, M.

    E. (2017). Plant Uptake of Atmospheric Carbonyl Sulfide in Coast Redwood Forests. *Journal*

    of Geophysical Research: Biogeosciences, *122*(12), 3391–3404.

    https://doi.org/10.1002/2016JG003703

Campbell, J. E., Carmichael, G. R., Chai, T., Mena-Carrasco, M., Tang, Y., Blake, D. R., … Stanier,

    C. O. (2008). Photosynthetic control of atmospheric carbonyl sulfide during the growing

    season. *Science*, *322*(5904), 1085–1088. https://doi.org/10.1126/science.1164015

Čermák, J., Kucera, J., Bauerle, W. L., Phillips, N., & Hinckley, T. M. (2007). Tree water storage

    and its diurnal dynamics related to sap flow and changes in stem volume in old-growth

    Douglas-fir trees. *Tree Physiology*, *27*(2), 181–198.

    https://doi.org/10.1093/treephys/27.2.181

Chen, J., Falk, M., Euskirchen, E., U, K. T. P., Suchanek, T. H., Ustin, S. L., … Bi, R. (2002).

    Biophysical controls of carbon flows in three successional Douglas-fir stands based on

    eddy-covariance measurements. *Tree Physiology*, *22*(2–3), 169–177.

    https://doi.org/10.1093/treephys/22.2-3.169

Chen, J., & Franklin, J. F. (1997). Growing-season microclimate variability within an old-growth

    Douglas-fir forest. *Climate Research*, 21–34.

Commane, R., Meredith, L. K., Baker, I. T., Berry, J. A., Munger, J. W., Montzka, S. A., … Wofsy, S.

    C. (2015). Seasonal fluxes of carbonyl sulfide in a midlatitude forest. *Proceedings of the*

    National Academy of Sciences, *112*(46), 14162–14167.

    https://doi.org/10.1073/pnas.1504131112

Daley, M. J., & Phillips, N. G. (2006). Interspecific variation in nighttime transpiration and

    stomatal conductance in a mixed New England deciduous forest. *Tree Physiology*, *26*(4),

411–419.

Dawson, T., Burgess, S., Tu, K., … R. O.-T., & 2007, U. (2007). Nighttime transpiration in woody plants from contrasting ecosystems. *Tree Physiology*, *27*, 561–575.

Desai, A. R., Bolstad, P. V., Cook, B. D., Davis, K. J., & Carey, E. V. (2005). Comparing net ecosystem exchange of carbon dioxide between an old-growth and mature forest in the upper Midwest, USA. *Agricultural and Forest Meteorology*, *128*(1–2), 33–55. https://doi.org/10.1016/j.agrformet.2004.09.005

Falk, M., Wharton, S., Schroeder, M., Ustin, S. L., & Paw U, K. T. (2008). Flux partitioning in an old-growth forest: seasonal and interannual dynamics. *Tree Physiology*, *28*(4), 509–520. https://doi.org/10.1093/treephys/28.4.509

Flanagan, L. B., Brooks, J. R., Varney, G. T., & Ehleringer, J. R. (1997). Discrimination against C18O16O during photosynthesis and the oxygen isotope ratio of respired CO2 in boreal forest ecosystems. *Global Biogeochemical Cycles*, *11*(1), 83–98.

Gasulla, F., Herrero, J., Esteban-carrasco, A., Ros-barceló, A., Barreno, E., Zapata, J. M., & Guéra, A. (2012). Photosynthesis in Lichen : Light Reactions and Protective Mechanisms. *Advances in Photosynthesis - Fundamental Aspects*, 588. https://doi.org/10.5772/1385

Gimeno, T. E., Ogée, J., Royles, J., Gibon, Y., West, J. B., Burlett, R., … Wingate, L. (2017). Bryophyte gas-exchange dynamics along varying hydration status reveal a significant carbonyl sulphide (COS) sink in the dark and COS source in the light. *New Phytologist*, *215*(3), 965–976. https://doi.org/10.1111/nph.14584

Gries, C., Nash, T. H., & Kesselmeier, J. (1994). Exchange of reduced sulfur gases between lichens and the atmosphere. *Biogeochemistry*, *26*(1), 25–39.

Haristoy, C. T., Zabowski, D., & Nadkarni, N. (2014). Canopy soils of Sitka spruce and bigleaf maple in the Queets River Watershed, Washington. *Soil Science Society of America Journal*, *78*(S1), S118–S124.

Harmon, M., Bible, K., Ryan, M., Shaw, D., Chen, H., Klopatek, J., & Li, X. (2004). Production, Respiration, and Overall Carbon Balance in an Old-growth Pseudotsuga-Tsuga Forest

Ecosystem. *Ecosystems*, 498–512. https://doi.org/10.1007/s10021-004-0140-9

Hollinger, D. Y., Kelliher, F. M., Byers, J. N., Hunt, J. E., McSeveny, T. M., & Weir, P. L. (1994). Carbon dioxide exchange between an undisturbed old-growth temperate forest and the atmosphere. *Ecology*, *75*(1), 134–150.

Kavanagh, K. L., Pangle, R., & Schotzko, A. D. (2007). Nocturnal transpiration causing disequilibrium between soil and stem predawn water potential in mixed conifer forests of Idaho. *Tree Physiology*, *27*(4), 621–629. https://doi.org/10.1093/treephys/27.4.621

Kesselmeier, J., Teusch, N., & Kuhn, U. (1999). Controlling variables for the uptake of atmospheric carbonyl sulfide by soil. *Journal of Geophysical Research: Atmospheres*, *104*(D9), 11577–11584. https://doi.org/10.1029/1999JD900090

Kettle, A. J., Kuhn, U., Von Hobe, M., Kesselmeier, J., & Andreae, M. O. (2002). Global budget of atmospheric carbonyl sulfide: Temporal and spatial variations of the dominant sources and sinks. *Journal of Geophysical Research: Atmospheres*, *107*(D22).

Kok, B. (1949). On the interrelation of respiration and photosynthesis in green plants. *Biochimica et Biophysica Acta*, *3*, 625–631.

Kooijmans, L. M. J., Maseyk, K., Seibt, U., Sun, W., Vesala, T., Mammarella, I., … Chen, H. (2017). Canopy uptake dominates nighttime carbonyl sulfide fluxes in a boreal forest. *Atmospheric Chemistry and Physics*, *17*(18), 11453–11465. https://doi.org/10.5194/acp-17-11453-2017

Kuhn, U., & Kesselmeier, J. (2000). Environmental variables controlling the uptake of carbonyl sulfide by lichens. *Journal of Geophysical Research: Atmospheres*, *105*(D22), 26783–26792.

Kuhn, U., Ammann, C., Wolf, A., Meixner, F. X., Andreae, M. O., & Kesselmeier, J. (1999). Carbonyl sulfide exchange on an ecosystem scale: Soil represents a dominant sink for atmospheric COS. *Atmospheric Environment*, *33*(6), 995–1008. https://doi.org/10.1016/S1352-2310(98)00211-8

Kuhn, U., Wolf, A., Gries, C., Nash III, T. H., & Kesselmeier, J. (2000). Field measurements on the exchange of carbonyl sulfide between lichens and the atmosphere. *Atmospheric Environment*, *34*(28), 4867–4878.

Lai, C. T., & Ehleringer, J. R. (2011). Deuterium excess reveals diurnal sources of water vapor in forest air. *Oecologia*, *165*(1), 213–223. https://doi.org/10.1007/s00442-010-1721-2

Lai, C., Ehleringer, J. R., Bond, B. J., & U, K. T. P. (2006). Contributions of evaparation, isotopic non-stedy state transpiration and atmospheric mixing on the d18O of water vapour in Pacific Northewest coniferous forests. *Plant Cell Environ.*, *29*, 77–94. https://doi.org/10.1111/j.1365-3040.2005.01402.x

Lange, O. L., Green, T. G., & Heber, U. (2001). Hydration-dependent photosynthetic production of lichens: what do laboratory studies tell us about field performance? *Journal of Experimental Botany*, *52*(363), 2033–2042. https://doi.org/10.1093/jexbot/52.363.2033

Lasslop, G., Migliavacca, M., Bohrer, G., Reichstein, M., Bahn, M., Ibrom, A., … Vesala, T. (2012). On the choice of the driving temperature for eddy-covariance carbon dioxide flux partitioning. *Biogeosciences*, *9*, 5243–5259.

Law, B. E., Thornton, P. E., Irvine, J., Anthoni, P. M., & Van Tuyl, S. (2001). Carbon storage and fluxes in ponderosa pine forests at different developmental stages. *Global Change Biology*, *7*(7), 755–777.

Luyssaert, S., Schulze, E.-D., Börner, A., Knohl, A., Hessenmöller, D., Law, B. E., … Grace, J. (2008). Old-growth forests as global carbon sinks. *Nature*, *455*(7210), 213.

Maseyk, K., Berry, J. A., Billesbach, D., Campbell, J. E., Torn, M. S., Zahniser, M., & Seibt, U. (2014). Sources and sinks of carbonyl sulfide in an agricultural field in the Southern Great Plains. *Proceedings of the National Academy of Sciences*, *111*(25), 9064–9069. https://doi.org/10.1073/pnas.1319132111

McCune, B. (1993). Gradients in epiphyte biomass in three *Pseudotsuga-Tsuga* forests of different ages in Western Oregon and Washington. *The Bryologist*, *96*(3), 405–411. https://doi.org/10.2307/3243870

McCune, B., Amsberry, K. A., Camacho, F. J., Clery, S., Cole, C., Emerson, C., … Widmer, M. (1997). Vertical profile of epiphytes in a Pacific Northwest old-growth forest. *Northwest Science*, *71*(2), 145–152.

McDowell, N. G., Phillips, N., Lunch, C., Bond, B. J., & Ryan, M. G. (2002). An investigation of hydraulic limitation and compensation in large, old Douglas-fir trees. *Tree Physiology*, *22*(11), 763–774. https://doi.org/Article

Montzka, S. A., Calvert, P., Hall, B. D., Elkins, J. W., Conway, T. J., Tans, P. P., & Sweeney, C. S. (2007). On the global distribution, seasonality, and budget of atmospheric carbonyl sulfide (COS) and some similarities to CO_2. *Journal of Geophysical Research Atmospheres*, *112*(9), 1–15. https://doi.org/10.1029/2006JD007665

Ortega, J., & Helmig, D. (2008). Approaches for quantifying reactive and low-volatility biogenic organic compound emissions by vegetation enclosure techniques–Part A. *Chemosphere*, *72*(3), 343–364.

Palmqvist, K., & Badger, M. R. (1996). Carbonic anhydrase (s) associated with lichens: In vivo activities, possible locations and putative roles. *New Phytologist*, *132*(4), 627–639.

Parker, G. G. (1997). Canopy structure and light environment of an old growth Douglas-fir/Western hemlock forest. *Northwest Science*, *71*(4), 261–271.

Pyles, R. D., Paw U, K. T., & Falk, M. (2004). Directional wind shear within an old-growth temperate rainforest: Observations and model results. *Agricultural and Forest Meteorology*, *125*(1–2), 19–31. https://doi.org/10.1016/j.agrformet.2004.03.007

Reichstein, M., Falge, E., Baldocchi, D., Papale, D., Aubinet, M., Berbigier, P., … Granier, A. (2005). On the separation of net ecosystem exchange into assimilation and ecosystem respiration: review and improved algorithm. *Global Change Biology*, *11*(9), 1424–1439.

Running, S. W. (1976). Environmental control of leaf water conductance in conifers. *Canadian Journal of Forest Research*, *6*(1), 104–112.

Seibt U, Kesselmeier J, Sandoval-Soto L, Kuhn U, Berry JA. 2010. A kinetic analysis of leaf uptake of COS and its relation to transpiration, photosynthesis and carbon isotope fractionation. *Biogeosciences* 7: 333–341.Shaw, D., Franklin, J., Bible, K., Klopatek, J., Freeman, E., Greene, S., & Parker, G. (2004). Ecological Setting of the Wind River Old-growth Forest. *Ecosystems*, *7*(5), 427–439. https://doi.org/10.1007/s10021-004-0135-6

Stimler, K., Montzka, S. A., Berry, J. A., Rudich, Y., & Yakir, D. (2010). Relationships between carbonyl sulfide (COS) and CO2 during leaf gas exchange. *New Phytologist*, *186*(4), 869–878. https://doi.org/10.1111/j.1469-8137.2010.03218.x

Sun, W., Maseyk, K., Lett, C., & Seibt, U. (2016). Litter dominates surface fluxes of carbonyl sulfide in a Californian oak woodland. *Journal of Geophysical Research G: Biogeosciences*, *121*(2), 438–450. https://doi.org/10.1002/2015JG003149

Unsworth, M., Phillips, N., Link, T., Bond, B., Falk, M., Harmon, M., … Paw U, K. (2004). Components and Controls of Water Flux in an Old-growth Douglas-fir-Western Hemlock Ecosystem. *Ecosystems*, *7*(5), 468–481. https://doi.org/10.1007/s10021-004-0138-3

Urbanski, S., Barford, C., Wofsy, S., Kucharik, C., Pyle, E., Budney, J., … Munger, J. W. (2007). Factors controlling CO2 exchange on timescales from hourly to decadal at Harvard Forest. *Journal of Geophysical Research: Biogeosciences*, *112*(G2).

Warren, J., Meinzer, F., Brooks, J., & Domec, J. (2005). Vertical stratification of soil water storage and release dynamics in Pacific Northwest coniferous forests. *Agricultural and Forest Meteorology*, *130*(1–2), 39–58. https://doi.org/10.1016/j.agrformet.2005.01.004

Wehr, R., & Saleska, S. R. (2015). An improved isotopic method for partitioning net ecosystem-atmosphere CO2exchange. *Agricultural and Forest Meteorology*, *214–215*, 515–531. https://doi.org/10.1016/j.agrformet.2015.09.009

Wehr, R., Commane, R., Munger, J. W., Barry Mcmanus, J., Nelson, D. D., Zahniser, M. S., … Wofsy, S. C. (2017). Dynamics of canopy stomatal conductance, transpiration, and evaporation in a temperate deciduous forest, validated by carbonyl sulfide uptake. *Biogeosciences*, *14*(2), 389–401. https://doi.org/10.5194/bg-14-389-2017

Wharton, S., & Falk, M. (2016). Climate indices strongly influence old-growth forest carbon exchange. *Environmental Research Letters*, *11*(4), 1–11. https://doi.org/10.1088/1748-9326/11/4/044016

Wharton, S., Schroeder, M., Bible, K., Falk, M., & Paw U, K. T. (2009). Stand-level gas-exchange responses to seasonal drought in very young versus old Douglas-fir forests of the Pacific

Northwest, USA. *Tree Physiology*, *29*(8), 959–974.

https://doi.org/10.1093/treephys/tpp039

Wharton, S., Falk, M., Bible, K., & Schroeder, M. (2012). Old-growth CO_2 flux measurements
reveal high sensitivity to climate anomalies across seasonal, annual and decadal time
scales. *Agricultural and Forest Meteorology*, *161*, 1–14.

Whelan, M. E., Lennartz, S. T., Gimeno, T. E., Wehr, R., Wohlfahrt, G., Wang, Y., … Campbell, J.
E. (2017). Reviews and Syntheses: Carbonyl Sulfide as a Multi-scale Tracer for Carbon and
Water Cycles. *Biogeosciences Discussions*, (October), 1–97. https://doi.org/10.5194/bg-
2017-427

Whelan, M. E., Hilton, T. W., Berry, J. A., Berkelhammer, M., Desai, A. R., & Elliott Campbell, J.
(2016). Carbonyl sulfide exchange in soils for better estimates of ecosystem carbon
uptake. *Atmospheric Chemistry and Physics*, *16*(6), 3711–3726.
https://doi.org/10.5194/acp-16-3711-2016

Winner, W., Thomas, S., Berry, J., Bond, B., Cooper, C., Hinckley, T., … Williams, M. (2004).
Canopy Carbon Gain and Water Use: Analysis of Old-growth Conifers in the Pacific
Northwest. *Ecosystems*, *7*(5), 482–497. https://doi.org/10.1007/s10021-004-0139-2

Wohlfahrt, G., & Galvagno, M. (2017). Revisiting the choice of the driving temperature for eddy
covariance CO2 flux partitioning. *Agricultural and Forest Meteorology*, *237*, 135–142.

Woodruff, D. R., Mcculloh, K. A., Warren, J. M., Meinzer, F. C., & Lachenbruch, B. (2007).
Impacts of tree height on leaf hydraulic architecture and stomatal control in Douglas-fir.
Plant, Cell and Environment, *30*(5), 559–569. https://doi.org/10.1111/j.1365-
3040.2007.01652.x

ECOSYSTEM FLUXES OF CARBONYL SULFIDE IN AN OLD-GROWTH FOREST: TEMPORAL DYNAMICS AND RESPONSES TO DIFFUSE RADIATION AND HEAT WAVES

Bharat Rastogi[1], Max Berkelhammer[2], Sonia Wharton[3], Mary E Whelan[4] Frederick C. Meinzer[5], David Noone[6], and Christopher J. Still[1]

[1] Department of Forest Ecosystems and Society, Oregon State University, OR 97331, USA
[2] Department of Earth and Environmental Sciences, University of Illinois at Chicago, Chicago, Illinois, USA
[3] Atmospheric, Earth and Energy Division, Lawrence Livermore National Laboratory, 7000 East Avenue, L-103, Livermore, CA 94550, USA
[4] Carnegie Institution for Science, 260 Panama St., Stanford, CA, USA, 94305

[5] USDA Forest Service, PNW Research Station, Corvallis, OR 97331, USA

[6] College of Earth, Ocean and Atmospheric Sciences, Oregon State University, OR 97331, USA

3   ECOSYSTEM FLUXES OF CARBONYL SULFIDE IN AN OLD-GROWTH FOREST: TEMPORAL
      DYNAMICS AND RESPONSES TO DIFFUSE RADIATION AND HEAT WAVES

3.1   Abstract

Carbonyl sulfide (OCS) has recently emerged as a tracer for terrestrial carbon uptake.
While physiological studies relating OCS fluxes to leaf stomatal dynamics have been established
at leaf and branch scales and incorporated in global carbon cycle models, the quantity of data
from ecosystem-scale field studies remains limited. In this study we employ established
theoretical relationships to infer ecosystem-scale OCS uptake from concentration
measurements. OCS uptake was found to scale with independent measurements of CO_2 fluxes
over a 60-m-tall old-growth forest in the Pacific Northwestern U.S. (45°49'13.76'' N;
121°57'06.88'') at hourly and monthly timescales across the growing season in 2015. OCS fluxes
tracked changes in soil moisture, and were strongly influenced by the fraction of downwelling
diffuse light. Fluxes were also strongly affected by sequential heat waves during the growing
season. Our results bolster previous evidence that ecosystem OCS uptake is strongly related to
stomatal dynamics, and measuring this gas improves constraints on estimating photosynthetic
rates at the ecosystem scale.

3.2   Introduction

Carbonyl Sulfide (OCS) is the most abundant sulfur gas in the atmosphere, with a mean
atmospheric concentration of ~500 ppt (parts per trillion), and therefore a significant part of
the tropospheric and stratospheric sulfur cycles, with implications for the global radiation
budget and ozone depletion (Johnson et al.,1993; Notholt et al., 2003). The dominant sink of
atmospheric OCS is vegetation (Kesselmeier and Merk, 1993; Kettle et al., 2002; Montzka et al.,
2007 and references therein), through rapid and irreversible hydrolysis by the ubiquitous
enzyme carbonic anhydrase (Protoschill-Krebs, Wilhelm, & Kesselmeier, 1996; Protoschill-Krebs
and Kesselmeier, 1992). Recent advances in spectroscopic technology have enabled continuous
in-situ measurements of OCS on timescales that are relevant to understanding stomatal

function at the leaf-scale (Stimler et al., 2010a, 2010b), branch scale (Berkelhammer et al., 2014) and the ecosystem scale (Kooijmans et al., 2017; Wehr et al., 2017). An important distinction between OCS and CO_2 cycling is that there are no reported emissions from actively photosynthesizing leaves. However, the normalized leaf uptake ratio of OCS:CO_2 (LRU; Sandoval-Soto et al., 2005) is relatively constant at medium to high light levels (Maseyk et al., 2014; Stimler et al., 2010), making it an excellent proxy for quantifying plant productivity (GPP; Asaf et al., 2013; Billesbach et al., 2014; Blonquist et al., 2011). On the other hand, both uptake and emissions of OCS from soils have been identified (Whelan et al., 2016; Sun et al., 2015; Maseyk et al., 2014; Kesselmier et al., 1999). While ecosystem-scale measurements of OCS continue to establish links between OCS uptake and GPP in different ecosystems (for a comprehensive list of ecosystem scale studies readers are referred to Figure 2 in Whelan et al., 2017), inconsistencies persist. For example, in an oak-savanna woodland in southern France Belviso et al. (2016) found that OCS exchange was strongly influenced by photosynthesis during early morning hours, while meaningful values of LRU could only by calculated for a few days in the early afternoons. Commane et al. (2015) were unable to explain mid-summer emissions of OCS at a mid-latitude deciduous forest. Uncertainties highlighted above argue for field-scale measurements of OCS in a variety of ecosystems, particularly as OCS flux predictions have recently been incorporated to inform estimates of plant productivity in global carbon cycle models (Campbell et al., 2017a; Hilton et al., 2017; Launois et al., 2015).

OCS fluxes have not been previously reported for old-growth forests, although a recent study using flask samples inferred large uptake of OCS in coastal redwood forests in northern California (Campbell et al., 2017b). Rastogi et al. (in revision) found large drawdowns in mixing ratios of OCS at an old growth forest in the pacific northwestern U.S., and significant uptake of this gas by various components of the ecosystem (leaves, soils, and epiphytes). In this study we report estimates of OCS fluxes from an old-growth forest and place them in the context of ecosystem carbon and water cycling. Additionally we investigate the response of CO_2, H_2O and OCS fluxes to changes in the fraction of downwelling diffuse radiation, as well as heat wave

events through the growing season. Technological constraints posed limitations in measuring fast-response OCS fluxes so instead we combine continuous in-situ measurements of OCS mixing ratios above and within the canopy with established theoretical equations for OCS uptake (see Berry et al., 2013; Commane et al., 2015; Seibt et al., 2010) to characterize OCS fluxes using a simple empirical model and compare them with ecosystem uptake of CO_2 from co-located eddy covariance measurements.

3.3 Methods

3.3.1 Site Description

Measurements were made at the Wind River Experimental Forest (WR), located within the Gifford Pinchot National Forest in southwest Washington state, USA (45°49′13.76′′ N; 121°57′06.88′′; 371 m above sea level). The site is well studied and described in great detail (Paw U et al., 2004; Shaw et al., 2004; Wharton and Falk, 2016; Winner et al., 2004). The climate is classified as temperate oceanic with a strong summer drought. The forest is 478 ha of preserved old-growth evergreen needle-leaf forest, with dominant tree species of Douglas fir (*Pseudotsuga menziesii*) and Western hemlock (*Tsuga heterophylla*). The tallest Douglas fir trees are between 50 and 60m, while the shade-tolerant hemlocks are typically between 20-30 m high. Maximum rooting depth is 1–2 m for the tallest, dominant Douglas-fir trees although most of the root biomass is concentrated in the first 0.5 m (Shaw et al., 2014). The cumulative LAI is estimated to be 8-9 $m^2\,m^{-2}$ (Parker et al., 2004). Additionally, the ecosystem hosts a large diversity of mosses, lichens and other epiphytic plants, which play an important role in canopy OCS dynamics (Rastogi et al., in revision). The soils are volcanic in origin, although most of the forest surface is comprised of decaying organic matter (Shaw et al., 2004).

3.3.2 Study period

Measurements reported here are between April 18- Dec 31, 2015. However, in early November an intake line at the top of the canopy was damaged after a rainstorm.

Measurements continued at the other intake heights (see sections 2.4 and 2.9). Therefore ecosystem fluxes and related analyses in this study cover 136 days between April 18 and October 31, while chamber based soil fluxes are reported for the months of August-December. Gaps in the time series due to analyzer maintenance correspond to Jun 26-28, July 6-17, August 4-7, August 24 and October 4-7. April-October roughly corresponds to most of the growing season, although at this site GPP usually peaks early in March-April, when soil moisture is high and ecosystem respiration flux is low, while plant productivity is typically severely light and temperature limited in the months of November-December (Wharton and Falk, 2016). Environmental conditions during the measurement campaign are shown in Figure 1 are represent a typical Mediterranean-type climate, with temperature peaking in July and minimal to no measured rainfall between June and September. This results in high summertime atmospheric vapor pressure deficit (VPDa), and soil moisture declines steadily through the summer period, with some recharge following rare precipitation events in September and then more commonly in October. The measurement period also encompasses three distinct heat waves, characterized by anomalously high air temperatures and mid-day VPDa values (often exceeding 4 kPa). We examine the response of OCS and CO_2 fluxes during these heat waves.
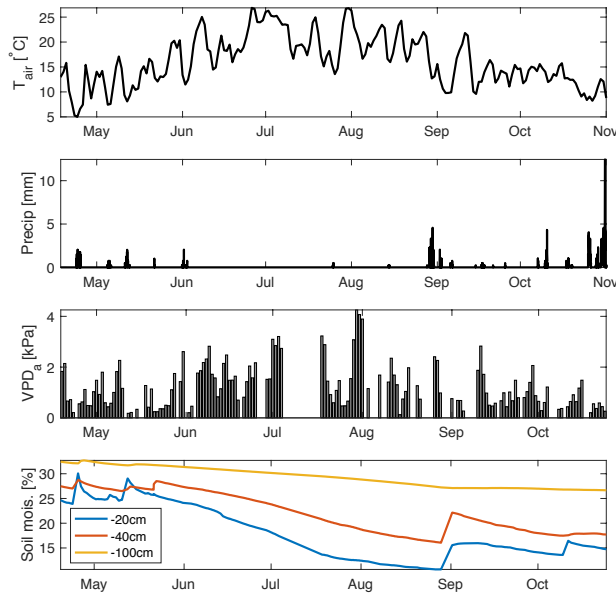
Figure 3-1. Environmental conditions at Wind River during the measurement campaign. Daily mean air temperature (a), precipitation (b) Mid-day VPDa (c) and Soil moisture measured at three depths (d).

3.3.3   CO2 and H2O eddy flux measurements

Carbon, water and energy fluxes have been collected since 1998 at the Wind River AmeriFlux tower (US-wrc; Paw U et al. 2004). For further details readers are referred to Falk et al., (2008; instrumentation and data processing), and Wharton et al., (2012) and Wharton and Falk, (2016) for multi-year carbon and water flux measurements and synthesis.

3.3.4   OCS measurements

A commercially available off-axis integrated cavity output spectroscopy analyzer manufactured by Los Gatos Research Inc., (LGR; model 914-0028) was deployed at the base of the tower in an insulated and temperature-controlled shed. The instrument measures mixing ratios of OCS, CO_2, H_2O and CO simultaneously at a maximal scan rate of 5Hz. The system uses a 4.87 μm cascade laser coupled to a high finesse 800 cm^3 optical cavity and light transmitted through the cavity is focused into a cooled and amplified HgCdTe detector. OCS is detected at

60

~2050.40 cm^{-1}, CO_2 at 2050.56 cm^{-1}, CO at ~2050.86 cm^{-1}, and H_2O at ~2050.66 cm^{-1}.

Pressure broadening associated with changes in the concentration of water vapor in the

samples is corrected for in the analysis routine. Air was sampled through 0.25'' diameter PFA

tubing using a diaphragm pump at a flow rate of 2L min^{-1}, from inlets located at 70m (at the

height of the eddy flux instrumentation), 60m (canopy top), 20m, 10m, and 1m. The sampling

frequency was 0.1Hz and the sampling interval was 5 minutes. The first minute of each

sampling interval was removed to avoid any inter-sampling mixing. The remaining data were

checked for temperature and pressure fluctuations inside the measurement chamber, and a

moving window filter was used to eliminate any sudden outliers in the data. Mixing ratios were

aggregated to provide hourly means. For detailed information regarding instrumentation and

the measurement readers are referred to Rastogi et al (in revision), Berkelhammer et al. (2014)

and Belviso et al. (2016).

3.3.5   Calibration

Calibration was performed using ambient air stored in insulated tanks as a secondary

reference. Air was sampled into the analyzer daily, and tank pressure was routinely monitored

to check for leaks. Glass flasks were randomly sampled form calibration tanks and measured

against a NOAA GMD reference standard. Cross-referencing revealed that the accuracy of the

measurement was within the reported minimum uncertainty of the instrument (of 12.6 pmol

mol^{-1}; Berkelhammer et al., 2016).

3.3.6   Thermal Camera measurements

Leaf temperatures were measured from October 28, 2014 to January 28, 2016 using a

FLIR A325sc thermal camera (FLIR System Inc., Wilsonville, OR), in which a FLIR IR 30-mm lens

(focal length: 30.38 mm; field of view: 15°×11.25°) was installed. The thermal camera has a

pixel resolution of 320×240. Within the field of view (FOV), spot sizes of a single pixel are 0.83

cm from 10-m distance and 8.3 cm from 100-m distance. Manufacturer-reported errors in

original measured thermal temperatures are ±2 °C or ±2% of the measurements. The camera model is identical to one used in another study at an AmeriFlux site in central Oregon (US Me-2), and the detailed specifications can be found in Kim et al. (2016). To monitor a larger canopy region, a pan-tilt unit (PTU) was used for motion control, allowing multiple canopy thermal image acquisition within one motion cycle. We used a FLIR PTU-D100E (FLIR System Inc., Wilsonville, OR; (http://www.flir.com/mcs) to move the thermal camera vertically and horizontally at specific pan and tilt angles. We selected five pan-tilt angle (PT) positions representing the upper canopy (i.e., ~40 to 60 m above the forest floor) to estimate leaf temperatures in this study.

3.3.7 Diffuse light measurement and analyses

An SPN1 Sunshine Pyranometer (Delta-T Devices ltd., Cambridge, U.K.) was installed at the top of the canopy and collected direct and diffuse shortwave downwelling radiation from April- December 2015. Measurements were made every 1 min, and then aggregated to hourly means. We limited our analyses of diffuse radiation data to include only mid-day hours (between 11am-1pm) to minimize the influence of solar angles on diffuse radiation fractions. We defined three distinct periods based on the ratio of diffuse radiation to total incoming solar radiation (*fidff*). Data were characterized as clear if *fdiff* < 0.2; partly cloudy if *fdiff* > 0.2 and *fdiff* < 0.8, and overcast if *fdiff* > 0.8.

3.3.8 OCS flux estimation

Canopy OCS flux was estimated using flux-gradient similarity, following Commane et al., 2015.

$$F_{OCS} = F_{H2O} \cdot \frac{g_{OCS}}{g_{H2O}} \tag{1}$$

where F_{OCS}, F_{H2O}, g_{OCS} and g_{H2O} are the fluxes and gradients of OCS and H_2O, respectively. Following Seibt et al., (2010) and Berry et al., (2013), we assume that OCS is irreversibly and

rapidly consumed inside leaves, such that the gradient between ambient air and the leaf interior effectively reduces to the ambient measured OCS mixing ratio:

$$g_{OCS} = \chi_{OCS}^a - \chi_{OCS}^l = \chi_{OCS}^a \tag{3}$$

where g_{OCS} is defined as he gradient of OCS between ambient air and the leaf intercellular spaces (χ is the mixing ratio of OCS and superscripts a and l refer to ambient and leaf respectively). In our study, χ_{OCS}^a is the measured mixing ratio at the canopy top (60m) instead of above canopy (70m) to account for the boundary layer resistance, the effect of which is likely low in tall and heterogeneous coniferous forests. We use vapor pressure deficit (VPD) as the corresponding gradient for H_2O, under the key assumption that the intercellular leaf surfaces are saturated with water vapor. While VPD is usually calculated using air temperature, a more accurate calculation can be performed with leaf temperatures, which can deviate significantly from air temperatures (Kim et al. 2016), leading to significant differences between the VPD of ambient air and that at the leaf surface (Fig. 2a and 3d in this study). Previously leaf temperatures have been inferred from sensible heat fluxes, wind speed and air temperatures (e.g. Wehr et al., 2017), here we use explicit measurements of leaf skin temperatures to estimate leaf-air VPD (VPD_l). Analogous to Eq (3),

$$g_{H2O} = \chi_{H2O}^l - \chi_{H2O}^a = \frac{(e_s - e_a)}{P} = \frac{VPD_l}{P} \tag{4}$$

where e_s is saturation vapor pressure at the leaf surface (kPa), using leaf skin temperature, ea is the actual vapor pressure (kPa), P is the measured atmospheric pressure (Pa) at the tower top, and $\chi_{H_2O}^l$ and $\chi_{H_2O}^a$ (ppth) are the leaf and ambient H_2O mixing ratios at the canopy top. Finally, since gradients of OCS and H_2O are estimated between ambient air and the leaf intercellular spaces, these are normalized by the ratio of diffusivities of these two species in air (Seibt et al., 2010; Wohlfahrt et al., 2012).

F_{H2O} was measured using eddy covariance at the tower top (70m). In high LAI forests with minimal exposed soil, such as those of the Pacific Northwest, fluxes of F_{H2O} can be treated

as a good proxy for transpiration, since soil evaporation should be minimal. We excluded rainy days, as well as two days following rainfall, to only capture periods when F_{H2O} can be assumed to be dominated by transpiration. We included nighttime data since several temperate tree species are known to transpire during the night (Dawson et al., 2007). Moreover, in this particular forest OCS is taken up by epiphytes under conditions of high humidity, which are common at nighttime (Rastogi et al., in revision). The first term in right hand side of equation (1) was evaluated only under the condition $F_{H2O} > 0.2$ mmolm^{-2}s^{-1}. When this condition was not met (e.g. at nighttime), fluxes were calculated using by integrating the rate of change in hourly OCS mixing ratios through the entire profile.

Leaf Relative uptake was calculated following Seibt et al (2010).

$$LRU = \frac{F_{OCS}}{GPP} \cdot \frac{\chi CO_2}{\chi OCS} \tag{5}$$

where GPP was estimated from CO_2 fluxes measured at the tower top. Finally, canopy conductance (Gc) was calculated by inverting the Penman Monteith equation (Monteith, 1965), which uses a combination of micrometeorological and eddy flux data collected above the canopy at the tower top. Gc is the canopy-scale equivalent of stomatal conductance, with the assumption that the canopy (or ecosystem) acts as a single big leaf.

$$Gc = \left[\frac{\rho Cp \delta e}{\gamma Le} + \frac{\left(\frac{\Delta}{\gamma}\right)\beta - 1}{Ga} \right]^{-1} \tag{6}$$

where ρ is air density (kg m^{-3}), Cp is specific heat (J kg^{-1}K^{-1}), δe is vapor pressure deficit (kPa), Y is the psychrometric constant (kPa K^{-1}), Δ is the slope of the saturation vapor pressure curve (kPa K^{-1}), β is the Bowen ratio (H:LE), and Ga is the aerodynamic conductance for momentum transfer, calculated as $u*^2.u^{-1}$ (where $u*$ is the friction velocity calculated from the momentum fluxes and u is the horizontal wind speed). Ga provides a measure of how well the canopy top is coupled to the background atmosphere (Wharton et al., 2012).

3.3.9 Surface Fluxes

A long-term automatic soil survey chamber (Li-Cor 8100-104, 20 cm diameter) was installed at three 0.03 m^2 surface sites in series, within 1 meter of each other. All plastic and rubber parts had been removed from the chamber and replaced with materials compatible with OCS measurements: stainless steel, PFA plastic, and Volara foam. Blank measurements were performed in the laboratory before deployment and OCS concentrations in the chamber were found to be indistinguishable from incoming ambient concentrations. The stainless steel chamber top opened and closed automatically on a timer. Gas was drawn through the chamber via a pump downstream of the analyzer, and the 3 $Lmin^{-1}$ flow rate was confirmed with a mass flow meter. When the chamber was open, ambient near-surface air was observed. When the chamber was closed, trace gas concentrations reached a stable state for at least 2 minutes during the 10-minute incubation time. The difference between the ambient concentration and the stable closed-chamber concentration were used to calculate the surface fluxes of OCS and CO_2.

$$F_{forest\ floor} = M_c \Delta\chi . A^{-1} \tag{7}$$

where M_c is the measured flow rate into the chamber (converted from $Lmin^{-1}$ to $mols^{-1}$ using the ideal gas law) and $\Delta\chi$ is the difference between mixing ratios of OCS or CO_2 in ambient air and the chamber and A is the surface area of the chamber. The minimum flux detectable with this method was 1.2 $pmolm^{-2}s^{-1}$ uptake or production.

Care was taken to select sites characteristic of the surface, which was generally springy and covered in a mat of mosses and lichen. Surface flux observations were made at site 1 from July 6 to 16, site 2 from August 13 to October 7, and site 3 from November 6 to December 2, 2015. The first site was visually similar to the subsequent two sites at the surface, though the chamber base of the first site was installed into the moss layer and a barely decomposed fallen tree. When a soil sample was attempted to be extracted from the footprint of the chamber base, several liters of in tact wood litter were removed. The influence of the developed soil on site 1 is therefore considered minimal. Site 2 was selected nearby and observations were made

until a dominant tree fell on the soil chamber. The chamber was repaired and re-installed a month later at site 3 and observations continued without incident until the chamber was removed in advance of the soil freezing.

3.4   Results and Discussion

3.4.1   Ecosystem fluxes

The composite diurnal cycles for CO2, water vapor and OCS and fluxes are shown (Fig. 2a-c). The total ecosystem flux of OCS (F_{OCS}; Fig 2.b.) follows a pronounced diurnal cycle that peaks during daylight hours. The vertical profile of mixing ratios measured throughout the canopy is also shown (right y-axis and orange lines in Fig.2.b). OCS mixing ratios are highest at the canopy top and lowest near the forest floor, but mixing ratios increase from the early morning to mid-afternoon. Together these processes are indicative of ecosystem uptake and downward entrainment of boundary layer air. While entrainment helps explain the diurnal cycle of observed mixing ratios, this flux integrates to zero at daily and longer time scales (Rastogi et al., in revision). The shape of the F_{OCS} curve is very similar to those of net and gross carbon fluxes (Fig 2.b), although F_{OCS} was consistently negative throughout the 24-hour period, implying ecosystem uptake during nighttime and daylight hours. While nighttime uptake of OCS (mean nighttime flux ~ -10 ± 1 $pmolm^{2}s^{-1}$) is likely due to a combination of soil, epiphyte, and vascular plant uptake due from partially closed stomata, daytime uptake is likely dominated by vascular plant stomatal activity. Leaf relative uptake, a ratio of F_{OCS}:GPP normalized by the mean mixing ratios of OCS:CO_2, showed a strong light dependence. High-light, mid-day values ranged between 3-4, which is higher than those observed at other forest systems (Kooijmans et al., 2017; Wehr et al., 2017) but well within the spread of values obtained in a recent meta-analyses of OCS studies for vegetated ecosystems (Whelan et al., 2018). The diurnal cycle was found to be asymmetric, with peak values observed in the early morning, when stomatal conductance is likely to be high (Winner et al., 2004), but GPP is limited by low light levels. It is important to note that LRU is likely influenced by large amounts of epiphyte and understory

vegetation, which assimilate OCS even at times when ecosystem CO_2 uptake is low or zero. Epiphytic assimilation of OCS is highly influenced by moisture content (Gimeno et al., 2017) and is typically higher through the night and in the early mornings at this site (Rastogi et al., in revision). Moreover, in tall old-growth forests, leaf area is vertically distributed over a much larger part of the canopy compared to other forests (Parker et al., 2004). While leaves at the canopy top exercise tight stomatal control to limit water loss and minimize hydraulic failure (Woodruff et al., 2007) leaves lower down in the canopy, including those of understory vegetation, likely impose less stomatal control of transpiration (Winner et al., 2004). Lower-canopy leaves may therefore continue to disproportionately assimilate OCS, even under low rates of carbon assimilation (as CO_2 uptake is additionally light limited).
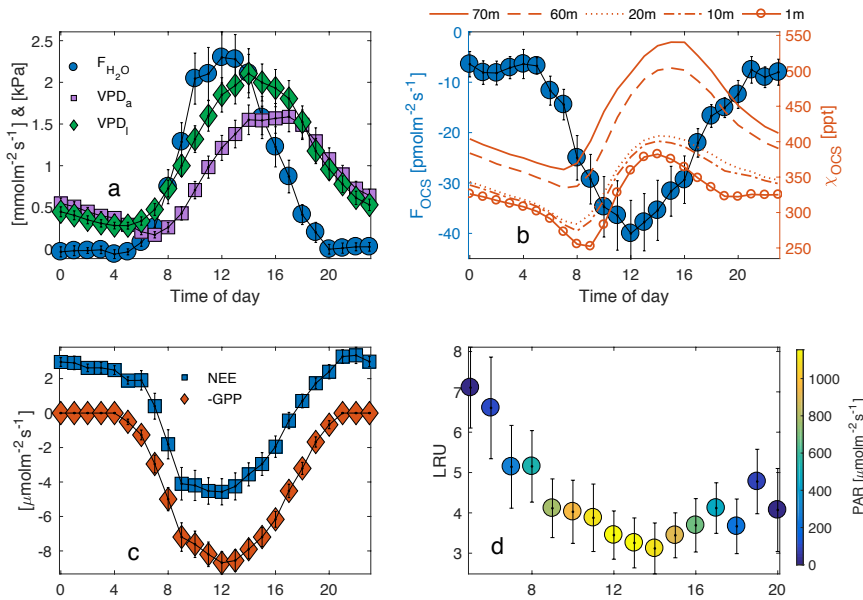
Figure 3-2. Diurnal cycle of H2O flux (blue circles) and VPD estimated from air and leaf temperatures (purple squares and green diamonds respectively; a), estimated OCS flux (circles, left axis) and mixing ratio profile (right axis; b), NEE and GPP (blue squares and red diamonds; c), and leaf relative uptake (calculated only during daylight hours, colors represent Photosynthetically active radiation; d).

3.4.2 Seasonal dynamics

Daytime fluxes of OCS and CO_2 followed similar patterns (Fig. 3a-b). Ecosystem uptake of OCS and CO_2 (as well as GPP) was highest in April, and declined as the soil drought progressed. Mean monthly maximum OCS flux was estimated as -61 ± 6 pmolm^{-2}s^{-1}, while daily mean maximum GPP over this period was estimated as 10 ± 1μmolm^{-2}s^{-1} (plotted as a negative quantity in Fig. 3b to show ecosystem uptake). While the steepest declines in F_{OCS}, NEE and GPP happened between the months of May and June, F_{OCS} continued to decline through the rest of the summer, with a minimum in August, incrementally increasing in September and decreasing again in October. CO_2 fluxes flattened between June-September, before declining again in October. During mid-late summer, water vapor flux declined (Fig.3c), as plants exercised greater control over stomata responding to high VPD (peaking in July; Fig 3d). This can be clearly seen in the seasonal cycle of canopy conductance (Gc; Fig. 3e) calculated using the Penman-Monteith method. Mean monthly Gc was highest in the months of April and May, and then declined precipitously with soil moisture, before increasing again slightly in September and October following soil recharge and decreased VPD due to precipitation events. At the monthly scale, patterns of daytime F_{OCS} were most similar to those of Gc and followed trends in soil moisture. In October, soil water recharge, several rain-free days, and lower VPD (Fig. 1) do not result in increased gas exchange, likely due to downregulation of photosynthesis (Eastman and Camm, 1995), induced by photoprotective changes in the xanthophyll cycle (Adams and Demmig-Adams, 1994).
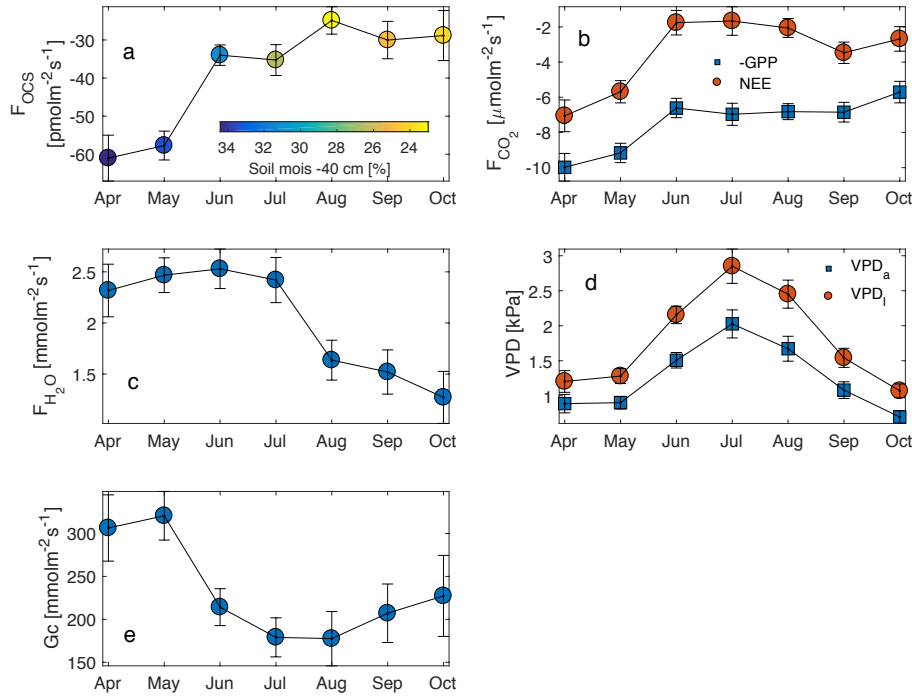
Figure 3-3. Monthly means for daytime FOCS colored according to soil moisture at 40cm depth, NEE and -GPP (red circles and blue squares; b), water vapor flux (c), VPDa and VPDl (blue squares and red circles; d), and canopy conductance (Gc; e).

3.4.3 Nighttime ecosystem and Surface Fluxes

While daytime fluxes of OCS and CO_2 were indicative of seasonal changes in ecosystem productivity and conductance, F_{OCS} and F_{CO_2} were driven by different environmental conditions during the night. Ecosystem respiration is modeled based on temperature and therefore peaked in July (when air temperature was highest). Nighttime F_{OCS} however, was more related to soil moisture status (blue circles in Fig. 4a-b). Nighttime F_{OCS} was highest in April (mean = -12.7± 2.6 $pmolm^{-2}s^{-1}$), lowest between June and August (mean = -5.9± 1.5 $pmolm^{-2}s^{-1}$) and increased again in October (mean = -9.7± 2.2 $pmolm^{-2}s^{-1}$). Nighttime uptake of OCS at the site is likely due to soil (see below), epiphytes (Rastogi et al., in revision; Gimeno et al., 2017), and incomplete stomatal closure (Kooijmans et al., 2017).

Forest floor OCS fluxes were observed from 3 sites in series and within 1 m of each other. Site 1 had approximately twice the OCS uptake compared to the subsequent two sites

and had a substantial layer of intact woody debris under the chamber footprint. Site 2 and 3 had OCS fluxes similar to previous surface fluxes reported for forests (Whelan et al., 2018). For all sites, there was no clear diurnal pattern. For site 2, uptake immediately following chamber installation was higher (~6 pmol $m^{-2}s^{-1}$) than fluxes later on (all <6 pmol $m^{-2}s^{-1}$) when temperatures were lower. Site 3 did not have high uptake after chamber installation, and had consistent fluxes between the detection limit and -6.2 pmol $m^{-2}s^{-1}$ for the first few weeks. When ambient air temperatures dropped below freezing, uptake remained unchanged, except for the largest uptake observed (6 to 12 pmol $m^{-2}s^{-1}$) during two events when average air temperature fluctuated from a cooling to warming trend. Soil temperature never dropped below freezing during the experiment and was generally colder over time. We did not observe any OCS emissions from the chamber based measurements, consistent with recent studies that find that cooler, moist (Maseyk et al., 2014; Sun et al., 2016; Whelan et al., 2016) and radiation limited (Kitz et al., 2017) soils do not emit OCS.

Surface CO_2 emissions exhibited a relationship with temperature, where highest production (~25 μmol $m^{-2}s^{-1}$) corresponded with temperatures ~15°C, and maximum flux values decreased for warmer and colder temperatures. CO_2 emissions had a diurnal pattern, with lowest emissions at night and maximum emissions in late morning to mid afternoon. No obvious relationship emerges from CO_2 emission and OCS uptake, though the high OCS uptake events in late November and early December have a linear relationship with CO_2 emissions. For sites 2 and 3, the ratio of OCS emission to CO_2 production, normalized by the concentration of OCS and CO_2 in the closed chamber, was between -0.25 and -3.5 with a mean of -1. In contrast, the same ratio for site 1 varied from -5 to -19 with a mean of -10.

At the peak of the soil drought (August; Fig. 1d), nighttime ecosystem OCS flux was similar to the chamber-based surface fluxes, after which magnitudes differed by a factor of 2-3. This difference can be explained by epiphytic consumption of OCS. Epiphytes are a moisture dependent sink OCS at the site (Rastogi et al., in revision) and therefore are likely inactive during the warmest and driest part of the year. Surface fluxes of CO_2 on the other hand were

70

much higher than ER estimated from the flux tower (blue circles in Fig. 4b). While there are issues in scaling up chamber-based estimates, these results corroborate earlier work that suggest that flux tower based estimates of ER at this site might be underestimated (Harmon et al., 2004).
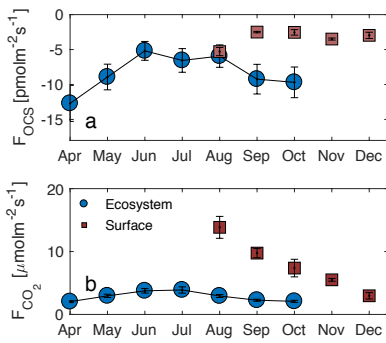
Figure 3-4. Nighttime ecosystem FOCS and FCO2 (blue circles in a-b) and Surface FOCS and FCO2 from chamber measurements (brown squares in a-b) from sites 2 and 3. Site 1 was atypical (see section 2.7) and therefore fluxes are not shown. Values for site 1 FOCS and FCO2 were -22 ± 0.3 pmolm-2s-1 and -83 ± 2 µmolm-2s-1 respectively.

3.4.4 Sensitivity to diffuse light

Mid-day fluxes of OCS and CO_2 were found to be sensitive to changes in the fraction of diffused:total incoming shortwave radiation (*fdiff*; Figure 5a-b). For these analyses, data were separated into three periods corresponding to early summer (DOY 109-180), mid-late summer (DOY 180-240) and early fall (DOY 240-297), and binned into three categories: clear sky conditions, partly cloudy, and overcast, defined in sec. 2.7. Mid-day VPD was highest under clear sky conditions and lowest under overcast skies, but was most different across the three periods, during clear skies (Fig. 5a). Consequently, OCS and CO_2 uptake was highest (most negative fluxes) under overcast conditions during the early summer, and generally declined as *fdiff* decreased across all time periods (Fig. 5b-d). Across the three periods, the rate of decrease was much higher as *fdiff* changed from partially cloudy to clear. During the mid-late summer, however, (red diamonds in Fig. 5a-f), the diffuse light effect resulted in GPP and NEE being

almost as high as during the early summer. F_{OCS} was also highest under partially cloudy skies during this time, and only showed a very weak decline under completely overcast conditions. Overall, the behavior of OCS and CO_2 fluxes was similar during the later time periods. Leaf relative uptake (LRU; calculated according to eq. 5) was lowest under partly clear skies and highest under overcast conditions. This is because under highly diffuse conditions, carbon uptake is additionally limited by light, whereas F_{OCS} is not (Wehr et al., 2017; Maseyk et al., 2014). The shape of the LRU curves can additionally be explained by examining canopy conductance (Gc; Fig. 5f), which was also higher under overcast skies. LRU increased with Gc across all three periods (Fig. 5g), and appeared to be constant for Gc greater than ~400 mmolm$^-$^{2}s^{-1}.

The diffuse light enhancement of stomatal and canopy conductance is well documented across a range of forest ecosystems (Alton et al., 2007; Cheng et al., 2015; Hollinger et al., 2017; Urban et al., 2007; Wharton et al., 2012). Lower VPD (Fig. 5a) and light levels allow plants to keep stomata open at mid-day and continue fixing CO_2. Lower VPD reduces transpirational losses, and the lack of VPD-induced partial stomatal closure reduces the resistance to CO_2 diffusion into the leaf. Correspondingly, the less directional nature of diffuse solar radiation allows greater penetration into the canopy, thus increasing photosynthesis across the entire canopy, even as a reduction in canopy top leaf photosynthesis is observed due to a reduction in total radiation. In a multi-year analysis at Wind River, Wharton et al., (2012) found that cloudy and partly cloudy sky conditions during the peak-growing season lead to an enhancement of NEE. During our study, Gc was generally higher in the early growing season, but increased as sky conditions changed from clear skies to overcast. This increase was similar across the three time periods, even as the response of OCS and CO_2 fluxes was different across these periods. This indicates that declining soil moisture (Fig. 1d) likely limits gas exchange as the summer progresses, even as canopy conductance can be reasonably high under overcast skies.
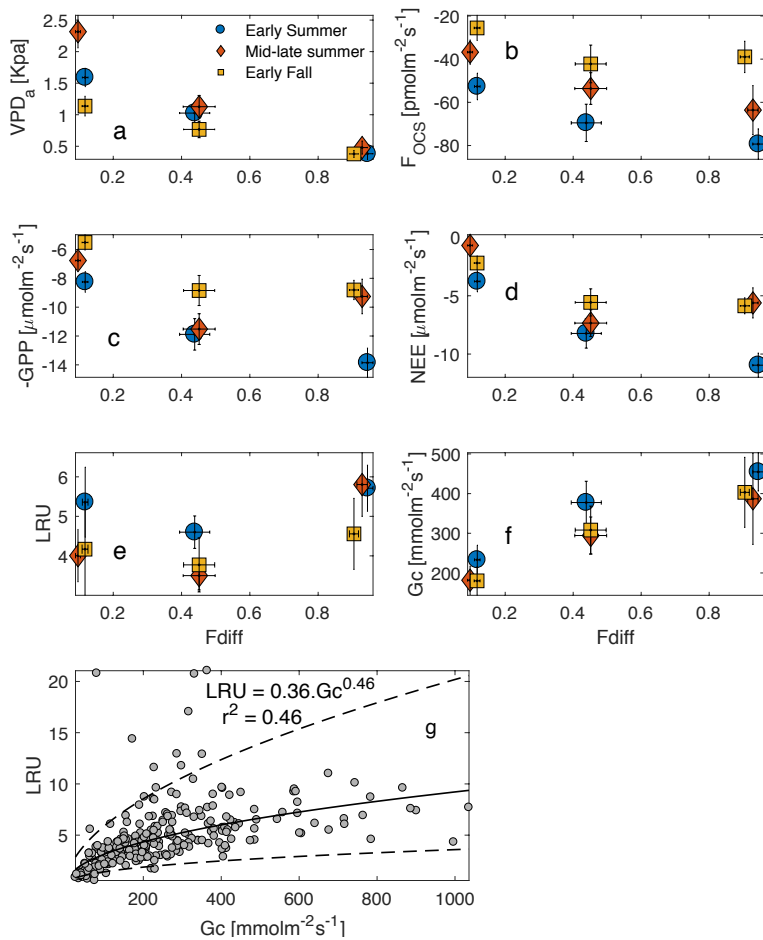
Figure 3-5. Mid-day VPDa, FOCS, NEE and GPP plotted against the fraction of diffuse downwelling shortwave radiation (a-d) for early summer, mid-late summer and early fall of 2015 (these periods are defined in Section 3.4). High values on the x-axis indicate completely overcast or cloudy conditions, whereas as low values indicated clear skies. LRU increases with increasing fdiff during each period but the increase is most pronounced in the early summer (e). Gc increases from clear to partly cloudy conditions across the three periods and plateaus during overcast sky conditions (f). Across the three periods, LRU increased with Gc, and levelled off at Gc values greater than ~ 400 mmolm-2s-1 (g).

3.4.5 Response to heat waves

2015 was the warmest year in large parts of the Pacific Northwest since records began in the 1930s (Dalton et al., 2017). We observed three distinct heat waves during the 2015 summer. These were in early June (DOY 157-160), end of June- early July (DOY 175-188) and

late July-early August (DOY 210-213). The three heat waves are shown as red, yellow and dark purple lines in Fig. 5; the overall time series is shown in blue (mid-day means are plotted for all variables). Mid-day temperatures exceeded 30°C during these heat wave events, while VPD-leaf exceeded 3Kpa during the first heat wave and increased to a maximum of 5.3 kPa during the last event (Fig. 5b). During the first two events, F_{OCS} was similar to days immediately prior (Fig. 5c), but the canopy became a net source of CO_2 during all three events (Fig. 5d). The third events lead to a severe reduction in F_{OCS}, even though the canopy had received some rainfall in the preceding weeks (Fig. 1c). Water vapor fluxes (Fig 5e) increased during the first two heat waves, compared to days immediately prior. The increased water vapor is likely not from increased transpiration, as canopy scale stomatal conductance during these events (Gc; Fig. 5f) is dramatically reduced. The increase is rather due to a flux of water from the soil surface and epiphytes that can store water in the canopy. High temperatures during such events are likely to result in increased evaporation.
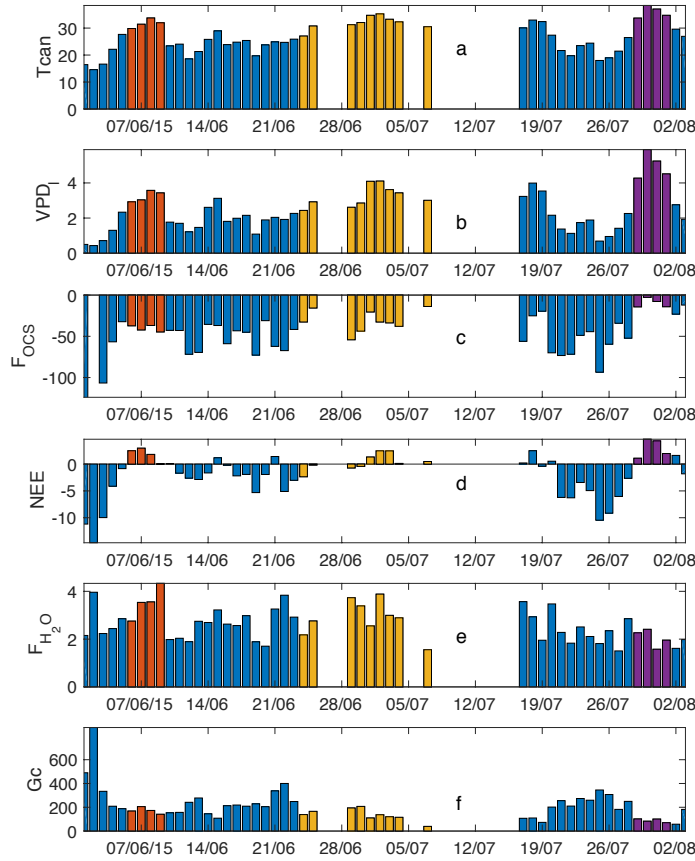
Figure 3-6. Mid-day means (11am-1pm local time) for three heat wave periods (plotted as red, yellow and purple, while the overall time series is shown in blue). Variables displayed are canopy temperature (°C; a), VPD-leaf (b), FOCS (c), NEE (d), water vapor flux (e), and canopy conductance (Gc, f). Units for each panel are the same as specified in previous figures.

3.5   Conclusions

Over hourly and seasonal timescales, estimates of F_{OCS} generally tracked fluctuations in GPP, implying stomatal control of carbon, water, and OCS fluxes at the site. We used continuous in-situ measurements of OCS mixing ratios, collocated measurements of water vapor fluxes, and air and canopy temperatures to calculate OCS uptake. We found the forest to be a large sink for OCS, with sink strength peaking during daylight hours. The mean LRU was ~ 4, and varied in response to changing light conditions and canopy conductance. These LRUs are larger than observed from other ecosystem scale studies, but well within the range of reported

values (Whelan et al., 2018; Sandoval-Soto et al., 2005). The forest surface was found to be a soil moisture dependent sink of OCS, with magnitudes that were roughly half of nighttime ecosystem fluxes, indicating other components of the ecosystem (epiphytes present throughout the canopy and impartial stomatal closure) to also take up OCS during these hours. Ecosystem fluxes of OCS and CO_2 were found to be strongly sensitive to the ratio of diffuse:direct radiation reaching the top of the canopy. Uptake of both OCS and CO_2 increased as sky conditions changed from clear to partly cloudy. A much smaller increase in uptake was observed as sky conditions changed from partly cloudy to overcast, except during the early summer, when soil moisture was not limiting. This change was mediated by the sensitivity of stomata to changing cloudiness and soil moisture, as estimated from canopy conductance calculated according to the inverted Penman-Monteith equation. Finally we examined the response of OCS, CO_2 and H_2O fluxes on heatwaves, and found that sequential heatwaves lead to suppression in stomatal gas exchange of all three fluxes.

Our results support the growing body of work that suggests ecosystem-scale OCS uptake is controlled by stomatal dynamics. While moist old-growth forests in Pacific Northwestern U.S. do not represent a very large fraction of the global terrestrial surface area, results from this study are likely relevant for other old-growth forests, particularly high LAI and very wet forests with extensive epiphyte cover, which are widespread in the humid tropics.

3.6 Acknowledgements

3.7   References

Adams, W. W. and Demmig-Adams, B.: Carotenoid composition and down regulation of photosystem II in three conifer species during the winter, Physiol. Plant., 92(3), 451–458, doi:10.1111/j.1399-3054.1994.tb08835.x, 1994.

Alton, P. B., North, P. R. and Los, S. O.: The impact of diffuse sunlight on canopy light-use efficiency, gross photosynthetic product and net ecosystem exchange in three forest biomes, Glob. Chang. Biol., 13(4), 776–787, doi:10.1111/j.1365-2486.2007.01316.x, 2007.

Asaf, D., Rotenberg, E., Tatarinov, F., Dicken, U., Montzka, S. A. and Yakir, D.: Ecosystem photosynthesis inferred from measurements of carbonyl sulphide flux, Nat. Geosci., 6(3), 186–190, doi:10.1038/ngeo1730, 2013.

Belviso, S., Reiter, I. M., Loubet, B., Gros, V., Lathière, J., Montagne, D., Delmotte, M., Ramonet, M., Kalogridis, C., Lebegue, B., Bonnaire, N., Kazan, V., Gauquelin, T., Fernandez, C. and Genty, B.: A top-down approach of surface carbonyl sulfide exchange by a Mediterranean oak forest ecosystem in Southern France, Atmos. Chem. Phys. Discuss., (June 2012), 1–25, doi:10.5194/acp-2016-525, 2016.

Berkelhammer, M., Asaf, D., Still, C., Montzka, S., Noone, D., Gupta, M., Provencal, R., Chen, H. and Yakir, D.: Constraining surface carbon fluxes using in situ measurements of carbonyl sulfide and carbon dioxide, Global Biogeochem. Cycles, 28(2), 161–179, doi:10.1002/2013GB004644, 2014.

Berkelhammer, M., Steen-Larsen, H. C., Cosgrove, A., Peters, A. J., Johnson, R., Hayden, M. and Montzka, S. A.: Radiation and atmospheric circulation controls on carbonyl sulfide concentrations in themarine boundary layer, J. Geophys. Res., 121(21), 13,113-13,128, doi:10.1002/2016JD025437, 2016.

Berry, J., Wolf, A., Campbell, J. E., Baker, I., Blake, N., Blake, D., Denning, A. S., Kawa, S. R., Montzka, S. A., Seibt, U., Stimler, K., Yakir, D. and Zhu, Z.: A coupled model of the global cycles of carbonyl sulfide and CO $_2$: A possible new window on the carbon cycle, J. Geophys. Res. Biogeosciences, 118(2), 842–852, doi:10.1002/jgrg.20068, 2013.

Billesbach, D. P., Berry, J. A., Seibt, U., Maseyk, K., Torn, M. S., Fischer, M. L., Abu-Naser, M. and Campbell, J. E.: Growing season eddy covariance measurements of carbonyl sulfide and CO2 fluxes: COS and CO2 relationships in Southern Great Plains winter wheat, Agric. For. Meteorol., 184, 48–55, doi:10.1016/j.agrformet.2013.06.007, 2014.

Blonquist, J. M., Montzka, S. A., Munger, J. W., Yakir, D., Desai, A. R., Dragoni, D., Griffis, T. J., Monson, R. K., Scott, R. L. and Bowling, D. R.: The potential of carbonyl sulfide as a proxy for gross primary production at flux tower sites, J. Geophys. Res. Biogeosciences, 116(4), 1–18, doi:10.1029/2011JG001723, 2011.

Campbell, J., Berry, J., Seibt, U., Smith, S., Nature, S. M.- and 2017, U.: Large historical growth in global terrestrial gross primary production, nature.com, 544(7468), 84 [online] Available from: https://www.nature.com/articles/nature22030 (Accessed 29 January 2018a), 2017.

Campbell, J. E., Whelan, M. E., Berry, J. A., Hilton, T. W., Zumkehr, A., Stinecipher, J., Lu, Y., Kornfeld, A., Seibt, U., Dawson, T. E., Montzka, S. A., Baker, I. T., Kulkarni, S., Wang, Y., Herndon, S. C., Zahniser, M. S., Commane, R. and Loik, M. E.: Plant Uptake of Atmospheric Carbonyl Sulfide in Coast Redwood Forests, J. Geophys. Res. Biogeosciences, 122(12), 3391–3404, doi:10.1002/2016JG003703, 2017b.

Cheng, S. J., Bohrer, G., Steiner, A. L., Hollinger, D. Y., Suyker, A., Phillips, R. P. and Nadelhoffer, K. J.: Variations in the influence of diffuse light on gross primary productivity in temperate ecosystems, Agric. For. Meteorol., 201, 98–110, doi:10.1016/j.agrformet.2014.11.002, 2015.

Commane, R., Meredith, L. K., Baker, I. T., Berry, J. A., Munger, J. W., Montzka, S. A., Templer, P. H., Juice, S. M., Zahniser, M. S. and Wofsy, S. C.: Seasonal fluxes of carbonyl sulfide in a midlatitude forest, Proc. Natl. Acad. Sci., 112(46), 14162–14167, doi:10.1073/pnas.1504131112, 2015.

Dalton, M. M., Dello, K. D., Hawkins, L., Mote, P. W. and Rupp, D. E.: The third Oregon climate assessment report, Oregon Clim. Chang. Res. Institute, Coll. Earth, Ocean Atmos. Sci. Oregon State Univ. Corvallis, OR, 2017.

Dawson, T., Burgess, S., Tu, K., … R. O.-T. and 2007, U.: Nighttime transpiration in woody plants from contrasting ecosystems., Tree Physiol., 27, 561–575, 2007.

Eastman, P. A. K. and Camm, E. L.: Regulation of photosynthesis in interior spruce during water stress: changes in gas exchange and chlorophyll fluorescence, Tree Physiol., 15(4), 229–235 [online] Available from: http://dx.doi.org/10.1093/treephys/15.4.229, 1995.

Falk, M., Wharton, S., Schroeder, M., Ustin, S. L. and Paw U, K. T.: Flux partitioning in an old-growth forest: seasonal and interannual dynamics, Tree Physiol., 28(4), 509–520, doi:10.1093/treephys/28.4.509, 2008.

Gimeno, T. E., Ogée, J., Royles, J., Gibon, Y., West, J. B., Burlett, R., Jones, S. P., Sauze, J., Wohl, S., Benard, C., Genty, B. and Wingate, L.: Bryophyte gas-exchange dynamics along varying hydration status reveal a significant carbonyl sulphide (COS) sink in the dark and COS source in the light, New Phytol., 215(3), 965–976, doi:10.1111/nph.14584, 2017.

Harmon, M., Bible, K., Ryan, M., Shaw, D., Chen, H., Klopatek, J. and Li, X.: Production, Respiration, and Overall Carbon Balance in an Old-growth Pseudotsuga-Tsuga Forest Ecosystem, Ecosystems, 498–512, doi:10.1007/s10021-004-0140-9, 2004.

Hilton, T., Whelan, M., Zumkehr, A., … S. K.-N. C. and 2017, U.: Peak growing season gross uptake of carbon in North America is largest in the Midwest USA, nature.com, 7(6), 450 [online] Available from: https://www.nature.com/articles/nclimate3272 (Accessed 29 January 2018), 2017.

Hollinger, A. D. Y., Kelliher, F. M., Byers, J. N., Hunt, J. E., Mcseveny, T. M., Weir, L., Ecology, S. and Jan, N.: Carbon Dioxide Exchange between an Undisturbed Old-Growth Temperate Forest and the Atmosphere Published by : Wiley Stable URL : http://www.jstor.org/stable/1939390 REFERENCES Linked references are available on JSTOR for this article : You may need to log , , 75(1), 134–150, 2017.

Johnson, J. E., Bandy, A. R., Thornton, D. C. and Bates, T. S.: Measurements of

atmospheric carbonyl sulfide during the NASA Chemical Instrumentation Test and Evaluation project: Implications for the global COS budget, J. Geophys. Res., 98(D12), 23443, doi:10.1029/92JD01911, 1993.

Kim, Y., Still, C. J., Hanson, C. V., Kwon, H., Greer, B. T. and Law, B. E.: Canopy skin temperature variations in relation to climate, soil temperature, and carbon flux at a ponderosa pine forest in central Oregon, Agric. For. Meteorol., 226–227, 161–173, doi:10.1016/j.agrformet.2016.06.001, 2016.

Kitz, F., Gerdel, K., Hammerle, A., Laterza, T., Spielmann, F. M. and Wohlfahrt, G.: In situ soil COS exchange of a temperate mountain grassland under simulated drought, Oecologia, 183(3), 851–860, doi:10.1007/s00442-016-3805-0, 2017.

Kooijmans, L. M. J. J., Maseyk, K., Seibt, U., Sun, W., Vesala, T., Mammarella, I., Kolari, P., Aalto, J., Franchin, A., Vecchi, R., Valli, G. and Chen, H.: Canopy uptake dominates nighttime carbonyl sulfide fluxes in a boreal forest, Atmos. Chem. Phys., 17(18), 11453–11465, doi:10.5194/acp-17-11453-2017, 2017.

Launois, T., Peylin, P., Belviso, S. and Poulter, B.: A new model of the global biogeochemical cycle of carbonyl sulfide - Part 2: Use of carbonyl sulfide to constrain gross primary productivity in current vegetation models, Atmos. Chem. Phys., 15(16), 9285–9312, doi:10.5194/acp-15-9285-2015, 2015.

Maseyk, K., Berry, J. A., Billesbach, D., Campbell, J. E., Torn, M. S., Zahniser, M. and Seibt, U.: Sources and sinks of carbonyl sulfide in an agricultural field in the Southern Great Plains, Proc. Natl. Acad. Sci., 111(25), 9064–9069, doi:10.1073/pnas.1319132111, 2014.

Monteith, J. L.: Evaporation and environment, in Symp. Soc. Exp. Biol, vol. 19, p. 4., 1965.

Notholt, J., Kuang, Z., Rinsland, C. P., Toon, G. C., Rex, M., Jones, N., Albrecht, T., Deckelmann, H., Krieg, J. and Weinzierl, C.: Enhanced upper tropical tropospheric COS: Impact on the stratospheric aerosol layer, Science (80-.)., 300(5617), 307–310, 2003.

Parker, G. G., Harmon, M. E., Lefsky, M. A., Chen, J., Pelt, R. Van, Weis, S. B., Thomas, S. C., Winner, W. E., Shaw, D. C. and Frankling, J. F.: Three-dimensional Structure of an Old-growth Pseudotsuga-Tsuga Canopy and Its Implications for Radiation Balance, Microclimate, and Gas Exchange, Ecosystems, 7(5), 440–453, doi:10.1007/s10021-004-0136-5, 2004.

Paw U, K. T., Falk, M., Suchanek, T. H., Ustin, S. L., Chen, J., Park, Y.-S., Winner, W. E., Thomas, S. C., Hsiao, T. C., Shaw, R. H., King, T. S., Pyles, R. D., Schroeder, M. and Matista, A. A.: Carbon Dioxide Exchange between an Old-Growth Forest and the Atmosphere, Ecosystems, 7(5), 513–524, doi:10.1007/s10021-004-0141-8, 2004.

Protoschill-Krebs, G Wilhelm, C Kesselmeier, J.: Consumption of carbonyl sulphide (COS) by higher plant carbonic anhydrase (CA), Atmos. Environ., 30(18), 3151–3156 [online] Available from: https://www.sciencedirect.com/science/article/pii/135223109600026X (Accessed 29 January 2018), 1996.

Protoschill-Krebs, G. and Kesselmeier, J.: Enzymatic pathways for the consumption of carbonyl sulphide (COS) by higher plants, Bot. Acta, 105, 206–212 [online] Available from: http://onlinelibrary.wiley.com/doi/10.1111/j.1438-8677.1992.tb00288.x/full (Accessed 29

January 2018), 1992.

Sandoval-Soto, L., Stanimirov, M., von Hobe, M., Schmitt, V., Valdes, J., Wild, A. and Kesselmeier, J.: Global uptake of carbonyl sulfide (COS) by terrestrial vegetation: Estimates corrected by deposition velocities normalized to the uptake of carbon dioxide, Biogeosciences Discuss., 2(1), 183–201, doi:10.5194/bgd-2-183-2005, 2005.

Seibt, U., Kesselmeier, J., Sandoval-Soto, L., Kuhn, U. and Berry, J. A.: A kinetic analysis of leaf uptake of COS and its relation to transpiration, photosynthesis and carbon isotope fractionation, Biogeosciences 7: 333-341.

Shaw, D., Franklin, J., Bible, K., Klopatek, J., Freeman, E., Greene, S. and Parker, G.: Ecological Setting of the Wind River Old-growth Forest, Ecosystems, 7(5), 427–439, doi:10.1007/s10021-004-0135-6, 2004.

Stimler, K., Nelson, D. and Yakir, D.: High precision measurements of atmospheric concentrations and plant exchange rates of carbonyl sulfide using mid-IR quantum cascade laser, Glob. Chang. Biol., 16(9), 2496–2503, doi:10.1111/j.1365-2486.2009.02088.x, 2010a.

Stimler, K., Montzka, S. A., Berry, J. A., Rudich, Y. and Yakir, D.: Relationships between carbonyl sulfide (COS) and CO2 during leaf gas exchange, New Phytol., 186(4), 869–878, doi:10.1111/j.1469-8137.2010.03218.x, 2010b.

Sun, W., Maseyk, K., Lett, C. and Seibt, U.: Litter dominates surface fluxes of carbonyl sulfide in a Californian oak woodland, J. Geophys. Res. G Biogeosciences, 121(2), 438–450, doi:10.1002/2015JG003149, 2016.

Urban, O., Janouš, D., Acosta, M., Czerný, R., Marková, I., Navrátil, M., Pavelka, M., Pokorný, R., Šprtová, M., Zhang, R., Špunda, V. R., Grace, J. and Marek, M. V.: Ecophysiological controls over the net ecosystem exchange of mountain spruce stand. Comparison of the response in direct vs. diffuse solar radiation, Glob. Chang. Biol., 13(1), 157–168, doi:10.1111/j.1365-2486.2006.01265.x, 2007.

Wehr, R., Commane, R., Munger, J. W., Barry Mcmanus, J., Nelson, D. D., Zahniser, M. S., Saleska, S. R. and Wofsy, S. C.: Dynamics of canopy stomatal conductance, transpiration, and evaporation in a temperate deciduous forest, validated by carbonyl sulfide uptake, Biogeosciences, 14(2), 389–401, doi:10.5194/bg-14-389-2017, 2017.

Wharton, S. and Falk, M.: Climate indices strongly influence old-growth forest carbon exchange, Environ. Res. Lett., 11(4), 1–11, doi:10.1088/1748-9326/11/4/044016, 2016.

Wharton, S., Falk, M., Bible, K., Schroeder, M. and Paw U, K. T.: Old-growth CO 2 flux measurements reveal high sensitivity to climate anomalies across seasonal, annual and decadal time scales, Agric. For. Meteorol., 161, 1–14, doi:10.1016/j.agrformet.2012.03.007, 2012.

Whelan, M. E., Hilton, T. W., Berry, J. A., Berkelhammer, M., Desai, A. R. and Campbell, J. E.: Carbonyl sulfide exchange in soils for better estimates of ecosystem carbon uptake, Atmos. Chem. Phys., 16(6), 3711–3726, 2016.

Whelan, M. E., Lennartz, S. T., Gimeno, T. E., Wehr, R., Wohlfahrt, G., Wang, Y., Kooijmans, L. M. J., Hilton, T. W., Belviso, S., Peylin, P., Commane, R., Sun, W., Chen, H., Kuai, L., Mammarella, I., Maseyk, K., Berkelhammer, M., Li, K.-F., Yakir, D., Zumkehr, A., Katayama, Y., Ogée, J., Spielmann, F. M., Kitz, F., Rastogi, B., Kesselmeier, J., Marshall, J., Erkkilä, K.-M.,

Wingate, L., Meredith, L. K., He, W., Bunk, R., Launois, T., Vesala, T., Schmidt, J. A., Fichot, C. G., Seibt, U., Saleska, S., Saltzman, E. S., Montzka, S. A., Berry, J. A. and Campbell, J. E.: Reviews and Syntheses: Carbonyl Sulfide as a Multi-scale Tracer for Carbon and Water Cycles, Biogeosciences Discuss., (October), 1–97, doi:10.5194/bg-2017-427, 2017.

Winner, W., Thomas, S., Berry, J., Bond, B., Cooper, C., Hinckley, T., Ehleringer, J., Fessenden, J., Lamb, B., McCarthy, S., McDowell, N., Phillips, N. and Williams, M.: Canopy Carbon Gain and Water Use: Analysis of Old-growth Conifers in the Pacific Northwest, Ecosystems, 7(5), 482–497, doi:10.1007/s10021-004-0139-2, 2004.

Wohlfahrt, G., Brilli, F., Hörtnagl, L., Xu, X., Bingemer, H., Hansel, A. and Loreto, F.: Carbonyl sulfide (COS) as a tracer for canopy photosynthesis, transpiration and stomatal conductance: Potential and limitations, Plant, Cell Environ., 35(4), 657–667, doi:10.1111/j.1365-3040.2011.02451.x, 2012.

Woodruff, D. R., Mcculloh, K. A., Warren, J. M., Meinzer, F. C. and Lachenbruch, B.: Impacts of tree height on leaf hydraulic architecture and stomatal control in Douglas-fir, Plant, Cell Environ., 30(5), 559–569, doi:10.1111/j.1365-3040.2007.01652.x, 2007.

4   FLUX PARTITIONING UNDERESTIMATES GPP IN AN OLD-GROWTH CONIFEROUS FOREST: INSIGHTS FROM TWO INDEPENDENT ESTIMATES AND A PROCESS MODEL

4.1   Abstract

Uncertainties in modeling terrestrial climate-carbon feedbacks are driven by our inability to directly measure photosynthesis beyond the leaf-level. The eddy covariance method is widely used to measure net uptake of CO_2 (NEE) across a range of ecosystems but lacks a process-based approach to partition this into source (Respiration) and sink (Gross Primary Productivity or GPP) terms. In this study, we independently estimate ecosystem-scale GPP at a well-studied temperate old-growth coniferous forest using measurements of carbonyl sulfide (OCS), from sap flow and stable isotopes of C in leaves, and a process-based model. GPP inferred from these approaches was found to be higher than that inferred from established flux partitioning of NEE, at sub-daily to seasonal timescales. We discuss limitations of each approach and conclude that eddy flux-based approaches underestimate GPP, likely driven by an underestimation of respiration at the site. We suggest that measurements of trace gases such as OCS, coordinated with physiological and structural measurements, may jointly provide constraints on GPP estimates.

4.2   Introduction

The vegetated terrestrial surface plays an outsized role in global carbon cycling, and annual variability in CO_2 removal from the atmosphere is highly dependent on the strength of the terrestrial carbon sink (Heimann & Reichstein, 2008). However, despite large advances in measurement and modeling techniques and increased spatio-temporal measurements of $[CO_2]$, carbon-climate coupled model intercomparison efforts still fail to converge on even the sign of the shift in the cumulative land sink in response to recent global warming (Huntzinger et al., 2017). This is in part due to our inability to directly measure photosynthesis beyond the leaf level. The eddy covariance (EC) technique is widely used to measure the net uptake of CO_2 (i.e.,

NEE), and has now effectively been adopted as a standard approach to measure this quantity across different ecosystems, even as limitations to application of this method remain, including low turbulence, flow decoupling and advection in tall and/or dense forest canopies, and diverse topographical areas (Baldocchi, 2014; Baldocchi et al., 2018; K. A. Novick et al., 2018). An outstanding issue is the lack of a process-based approach that partitions NEE into source (respiration) and sink (photosynthesis or GPP) terms (R Wehr et al., 2016). The same is true of remote sensing approaches, which typically use an index of "greenness" to relate incoming and Absorbed Photosynthetically Active Radiation (IPAR and APAR respectively) to predict GPP using a parameter called light-use efficiency (ε). Consequently, approaches that rely on EC and/or satellite data often disagree on the response of terrestrial carbon cycling to perturbations in climate and [CO_2]. Cross-site syntheses often show contradictory results, e.g., an increase in carbon uptake due to an increase in the growth period in warmer climates (Keenan et al., 2014), as well as an increase in water-use efficiency (the ratio of carbon fixed to water transpired) due to higher CO_2 concentrations (Keenan et al., 2013). Similarly, variations in terrestrial CO_2 uptake may be driven by a reduction in the land sink strength explained by a faster increase of respiration than GPP (Li et al., 2018) and/or an increase in photosynthesis in northern forests due to recent climate warming (Forkel et al., 2016). Decreases in CO_2 uptake from an increase in the water limitation of photosynthesis due to rising vapor pressure deficits (VPD, the atmospheric demand for moisture) may also be driving these variations (Novick *et al.*, 2016). To an extent this confusion is understandable. since variability in photosynthesis and respiration is regulated by covarying environmental drivers. For instance, an increase in temperature leads to an increase in respiration and photosynthesis (to an extent) based on enzyme kinetics, but rising temperatures are also associated with higher VPD, inducing partial stomatal closure and therefore reduced leaf uptake of CO_2, a feedback that is thought to be mediated to a certain degree by increasing atmospheric CO_2 concentrations. In summary, uncertainty about the principal responses of the biosphere to warming is largely driven by an inability to measure GPP routinely and accurately across a range of ecosystems.

Novel approaches to improve our understanding of GPP include measurements of carbonyl sulfide (OCS; Asaf et al., 2013; Commane et al., 2015; Kooijmans et al., 2017; Maseyk et al., 2014), stable isotopes of CO_2 ($^{13}CO_2$; Oikawa et al., 2017; Wehr & Saleska, 2015), combining sap flow and carbon isotope data (Klein et al., 2016), digital repeat photography (Knox et al., 2017; Toomey et al., 2015), and measurements of solar induced fluorescence (SIF; Guanter et al., 2014; Miao et al., 2018; Rossini et al., 2010). In this study, we focus on constraining GPP using multiple measurement approaches at a well-studied old-growth temperate forest. Finally we compare these GPP estimates to modeled GPP from the mechanistic Soil Canopy Observation Photochemistry and Energy model (SCOPE; van der Tol *et al.*, 2009).

4.3 Methods

4.3.1 Site description

Measurements were made at the Wind River Experimental Forest (WR), located within the Gifford Pinchot National Forest in southwest Washington state, USA (45°49'13.76'' N; 121°57'06.88''; 371 m above sea level). The site is well studied and described in great detail (Paw U et al., 2004; D. Shaw et al., 2004; Wharton & Falk, 2016; Winner et al., 2004). The climate is classified as temperate oceanic with a strong summer drought. The forest is 478 ha of preserved old-growth evergreen needle-leaf forest, with dominant tree species of Douglas-fir (*Pseudotsuga menziesii* (Mirbel) Franco) and Western hemlock (*Tsuga heterophylla*). The tallest Douglas-fir trees are between 50 and 60m, while the shade-tolerant hemlocks are typically between 20-30 m high. Maximum rooting depth is 1–2 m for the tallest, dominant Douglas-fir trees, although most of the root biomass is concentrated in the first 0.5 m (Shaw et al., 2014). The cumulative LAI is estimated to be 8-9 $m^2 m^{-2}$ (Parker et al., 2004). The soils are volcanic in origin, although most of the soil surface is covered by decaying organic matter (Shaw et al., 2004).

4.3.2   Measurements

4.3.2.1   Eddy covariance

Carbon, water and energy fluxes have been collected since 1998 using the eddy covariance (EC) technique at the Wind River AmeriFlux tower (US-wrc; Wharton and Falk 2016). The most recent EC system consists of a 3D sonic anemometer (CSAT3, Campbell Scientific, Logan, Utah) and a closed-path infrared gas analyzer (LI-7000, Li-Cor, Lincoln, Nebraska). The EC system is located approximately 10 m above the canopy top at a height of 70 m.

4.3.2.2   Transpiration from sap flow measurements

Sap flow was measured using variable length heat dissipation sap flow probes with a heated and a reference sensor, each 10 mm in length at the probe tip, at the base of tall dominant *P. menziesii* and *T. heterophylla* trees of varying sizes between June 1-September 30, 2002. The individual trees and measurements are described in detail in (Meinzer et al., 2006). Briefly, four probes were installed in each tree, at radial depths of 1cm, 3cm, 4.5cm and 6cm for *P. menziesii*, and 1.5cm, 5.5cm, 9.5cm and 15cm for *T. heterophylla*. Concurrent differential voltage measurements at each depth were recorded at 1min interval, averaged to 10min, converted to a temperature difference between the heated and the reference sensor, which were converted to sap flux using an empirical equation (Granier, 1985), and finally converted to mass flow by multiplying by the cross-sectional sap wood area. Total water use for each tree was calculated by summing up the mass flow at each sapwood depth. Finally we calculated species-specific transpiration rates for each species. For *P. menziesii*, stand-scale transpiration was estimated by calculating a mean water use for trees measured combined with the number of individuals per hectare (Shaw et al., 2004). Since *T. heterophylla* trees occupied a more diverse size and age distribution (Fig. S1b), we scaled the transpiration additionally based on the proportion of trees in different size classes. This approach allowed us to directly estimate stand-scale transpiration without relying on assumptions regarding the ratio of sapwood: ground area, which can be challenging to acquire in a forest with multiple species and age

classes. Numerous *T. heterophylla* trees were also experiencing chronic, long-term dwarf

mistletoe infection (Shaw et al., 2005), which considerably impedes plant function by lowering

branch hydraulic conductivity and whole-tree water use (Meinzer et al., 2004). Sap flow

measurements of both infected and uninfected trees (Meinzer et al., 2004), along with

information about the size distribution of both infected and uninfected individuals (Shaw et al.,

2005), allowed us to incorporate the effect of Mistletoe in our estimates of transpiration (Fig.

S.1c).

4.3.2.3   Carbonyl Sulfide

A commercially available off-axis integrated cavity output spectroscopy analyzer

manufactured by Los Gatos Research Inc., (LGR; model 914-0028) was deployed at the base of

the tower in an insulated and temperature-controlled shed between April 19-Dec 1, 2015.

Details regarding instrumentation and calibration can be found in Rastogi et al., (i*n revision*),

and the calculation of OCS flux from mixing ratios measured at the canopy top can found in

Rastogi et al., (in review). Briefly, mixing ratios of OCS, CO_2, H_2O were measured simultaneously

at a maximal scan rate of 5Hz. The system uses a 4.87 μm cascade laser coupled to a high

finesse 800 cm^3 optical cavity and light transmitted through the cavity is focused into a cooled

and amplified HgCdTe detector. OCS is detected at $\sim$2050.40 cm^{-1}, CO_2 at 2050.56 cm^{-1}, CO at

$\sim$2050.86 cm^{-1}, and H_2O at $\sim$2050.66 cm^{-1}. Pressure broadening associated with changes in

the concentration of water vapor in the samples is corrected for in the analysis routine. Air was

sampled through 0.25'' diameter Teflon PFA tubing using a diaphragm pump at a flow rate of 2L

min^{-1}, from inlets located at 70m (at the height of the eddy flux instrumentation), 60m (canopy

top), 20m, 10m, and 1m (near the ground surface). Gas calibration was performed using

ambient air stored in insulated tanks as a secondary reference. Air was sampled into the

analyzer daily, and tank pressure was routinely monitored to check for leaks. Glass flasks were

randomly sampled from calibration tanks and measured against a NOAA GMD reference

standard. Cross-referencing revealed that the accuracy of the OCS measurement from our

analyzer was within the reported minimum uncertainty of the instrument (of 12.6 pmol mol^{-1}; Berkelhammer et al., 2016).

4.3.3 Estimates of GPP:

4.3.3.1 Flux Partitioning

NEE was measured using the EC system and partitioned into ecosystem respiration (ER) and GPP by identifying a turbulence (friction velocity) threshold, fitting an exponential temperature response curve to the nighttime NEE, and extrapolating the relationship to calculate daytime ER. GPP is calculated as the residual of NEE and ER. (Reichstein et al., 2005). For full data processing protocols, including gap filling, readers are referred to Falk et al. (2008) and Wharton et al. (2012). Additionally, we used a daytime light response curve approach (Lasslop et al., 2010) to partition data. Data were gap filled and partitioned using the online tool REddyProc. For the rest of this study, the Reichstein *et al.*, (2005) method is referred to as the 'nighttime' approach, or GPP$_{EC-NT}$, while the Lasslop *et al.*, (2010) method is referred to as the 'daytime' approach, or GPP$_{EC-DT}$.

4.3.3.2 GPP from sap flow and Isotopes

We estimated GPP (distinguished from other GPP estimates as GPP$_{SF}$) using an independent estimate of transpiration determined from measurements of sap flow, and leaf δ^{13}C data collected at Wind River. This approach was recently demonstrated in a young semi-arid pine forest in Israel (Klein et al., 2016), and is based on the established relationship between intrinsic water use efficiency (WUE$_i$) and the stable isotopic composition of leaf δ^{13}C (Farquhar & Richards, 1984; Ulli Seibt et al., 2008):

$$GPP_{SF} = T.\frac{VPD}{1.6P}.C_a.\left(1 - \frac{C_i}{C_a}\right)$$

(2)

$$\frac{C_i}{C_a} = \frac{\Delta_p - a}{b - a}$$

(3)

$$\Delta_p = (\delta^{13}C_a - \delta^{13}C_p)/(1 + \delta^{13}C_p/1000) \tag{4}$$

Where GPP is estimated in $\mu mol\,m^{-2}\,s^{-1}$, T is transpiration [mmol m^{-2} s^{-1}], VPD is atmospheric vapor pressure deficit and P is atmospheric pressure [both in kPa], C_i is the CO_2 concentration in leaf intercellular spaces and C_a is the ambient CO_2 concentration [both in ppm], Δ_p is $^{13}CO_2/^{12}CO_2$ discrimination during photosynthesis [‰], a and b are fractionations due to molecular diffusion and carboxylation by the enzyme Rubisco (4.4 ‰ and -27.5 ‰ respectively), and $\delta^{13}C_p$ and $\delta^{13}C_a$ are measured isotope ratios of C in photosynthesizing leaves and atmospheric CO_2. $\delta^{13}C_p$ and $\delta^{13}C_a$ were measured for *T. heterophylla* needles at different heights for three growing seasons (1998-2000; Fessenden & Ehleringer, 2003). As we show in section 2.4.2.1, *T. heterophylla* contributes to most of the transpired water at this site; it is therefore reasonable to use its leaf $\delta^{13}C$ to estimate a canopy-scale C_i (required in eq. 1). Based on site climatology (Wharton & Falk, 2016), 2000 and 2002 were determined to be 'normal years', and we therefore used Δ_p estimates in 2000 from Fessenden & Ehleringer, (2003). Since, most of the leaf area at the site is concentrated in the mid-canopy (Parker, 1997), leaf Δ_p values from this region of the canopy were used (assumed to be constant at 20.8 ‰).

4.3.3.3   GPP from carbonyl sulfide fluxes

Fluxes of carbonyl sulfide were obtained using a simple empirical model of OCS uptake requiring water vapor fluxes and vapor pressure deficit (Rastogi et al. 2018):

$$F_{OCS} = -P.\frac{F_{H_2O}}{VPD}.[OCS] \tag{5}$$

F_{OCS} is the canopy OCS flux, [OCS] is the mixing ratio of OCS measured at the canopy top (60m), F_{H2O} is the water vapor flux measured using eddy covariance, and P and VPD are atmospheric pressure and leaf-specific vapor pressure deficit [kPa], estimating using measured leaf temperature and relative humidity.

Finally, GPP (distinguished from other GPP estimates as GPP$_{OCS}$) from this approach is estimated as:

$$GPP_{OCS} = -F_{OCS} \cdot \frac{[CO_2]}{[OCS]} \cdot \frac{1}{LRU} \tag{6}$$

Where LRU is defined as the leaf relative uptake of OCS:CO$_2$. Following Maseyk *et al.*, 2014), we modeled LRU as a non-linear function of incoming PAR, such that light-saturated LRU (i.e., when IPAR > 1200 umol/m2/s) was within 5% of the theoretical LRU obtained from estimated C$_i$/C$_a$ in section 2.3.2. The relationship between LRU and C$_i$/C$_a$ was defined by Seibt *et al.*, (2010),

as $LRU = 0.75 \cdot \left(1 - \frac{c_i}{c_a}\right)^{-1}$. GPP using Eq (6) was calculated under conditions when PAR was > 100 Wm^{-2}.

4.3.4 GPP predicted from a process model

The soil canopy observation, photochemistry, and energy fluxes (SCOPE) model is a vertical 1-D mechanistic model consisting of a radiative transfer model and an energy balance model (van der Tol et al., 2009). Scope uses the established leaf-level equations of photosynthesis and stomatal conductance to scale these quantities across a canopy. Parameters and input data for SCOPE are provided in Table 7-1.

4.4 Results

4.4.1 Flux Partitioning

Both nighttime (GPP$_{EC-NT}$; Reichstein et al., 2005) and daytime (GPP$_{EC-DT}$; Lasslop et al., 2010) flux partitioning approaches showed similar mean annual (Fig. 1a) and mean diurnal cycles (Fig. 1b) for the year 2015. GPP$_{EC}$ from both approaches peaked in the spring (highest uptake rates observed in April), when the ecosystem was not water limited, and productivity was not constrained by low light levels, declining steadily thereafter, in response to depleting soil moisture (right axis in Fig 1a). This response was better captured in the daytime approach, including a transient recovery in response to rainfall events in September that replenished soil moisture. GPP$_{EC-DT}$ was consistently lower than that from the nighttime-based approach, and this difference was least pronounced during the period of peak CO$_2$ assimilation (diel cycles for each month are shown in Fig. S2). This is readily explained by the structure of the two models.

The nighttime approach uses an exponential fit to determine the response of respiration (measured nighttime NEE) to nighttime temperature (Lloyd & Taylor, 1994), and uses these coefficients to determine respiration during the daytime. GPP is then inferred as the residual of observed NEE and modeled respiration. The daytime approach additionally models GPP as a function of incoming PAR and VPD. While the nighttime approach makes fewer assumptions, it is prone to overestimation of both respiration and GPP at high temperatures. This can be seen in the ratio of GPP:(-NEE), which increases non-linearly and artificially at high temperatures in the nighttime approach (Fig. 1c), but shows a slow decline in the daytime approach, reflecting stomatal closure at high VPD.
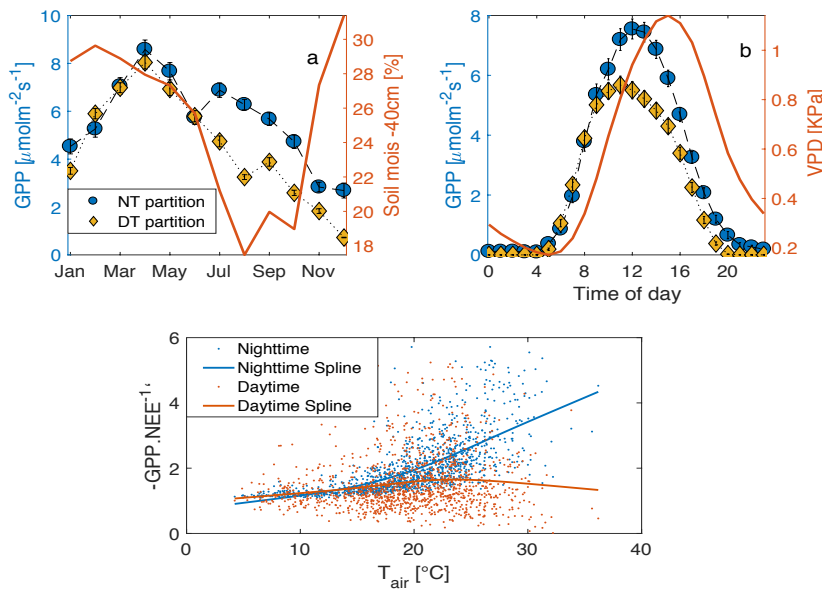
Figure 4-1. Seasonal (a), and Diurnal cycles of GPP from flux partitioning of NEE using the 'nighttime approach' or NT and the 'daytime approach' or DT. Plotted on the right axis is soil moisture at 40cm depth in (a), and mean VPD in (b). Error bars indicate one standard error. Ratio of- GPP:NEE is plotted against air temperatures in (c), showing a non-linear and artificial increase at high temperatures.

4.4.2 Sapflow-based GPP

We quantified daily GPP for the summer of 2002, by estimating transpiration using sapflow measurements, and combining it with measured leaf δ^{13}C.

4.4.2.1   Transpiration from Sap flow

Transpiration scaled from sap flow (T_{SF}) at the site was dominated by *T. heterophylla*, even as maximum sap flux from individual trees was slightly higher in *P. menziesii*, due to the much greater number of *T. heterophylla* individual trees, compared to *P. menziesii* trees (224 ha^{-1} compared to 35 ha^{-1}; Shaw *et al.*, 2004). The mean daily ratio of ecosystem-scale water transpired by the two species (i.e., T_{DF}:T_{WH}) was 0.13, with highest values observed at lower VPD and high soil moisture (Fig. 2a). This ratio declined sharply as VPD increased and stayed constant at ~ 0.1 as soil moisture continued to decreased, indicating that the more shade tolerant *T. heterophylla* trees were able to maintain sap flow throughout the summer, even as the sap flow in *P. menziesii* declined in response to high atmospheric demand (VPD) and soil drought. Diel cycles of sap flow-scaled transpiration for the two species, and the overall sum, are shown in Fig. S3. *T. heterophylla* transpiration showed a time lag of ~ 1 hour compared to *P. menziesii*, as stomatal conductance in shorter *T. heterophylla* trees is limited by light in the early mornings. Overall, transpiration from sap flow lagged eddy covariance-based estimates of evapotranspiration (ET_{EC}). This is understandable, since sap flow is measured in the lower trunk of trees and spatially separated (in this case, by up to 50-60m) from the site of water loss, i.e. the leaf (Meinzer *et al.*, 1997; Phillips *et al.*, 2002; Meinzer *et al.*, 2004; Čermák *et al.*, 2007). At daily timescales, however, transpiration and sap flow reach steady state. This enabled us to estimate mean daily water use (transpiration) using the cumulative sap flow each day normalized by the number of hours when sap flow was above zero. Transpiration estimates from sap flow were generally lower than evapotranspiration estimates from eddy covariance flux measurements (from latent heat fluxes). The median ratio of T_{SF} to ET_{EC} was ~ 0.88, declining with increasing VPD. High T:ET ratios are expected at this dense forest site, since evaporation from the soil surface is minimal (Lai *et al.*, 2006). A few outliers above 1.5 were associated with calm and cloudy days, indicated by lower turbulence (u* < 0.3) and decreased

mean daily shortwave radiation (Fig. 2b), indicating that eddy flux data may underestimate transpiration during these conditions.
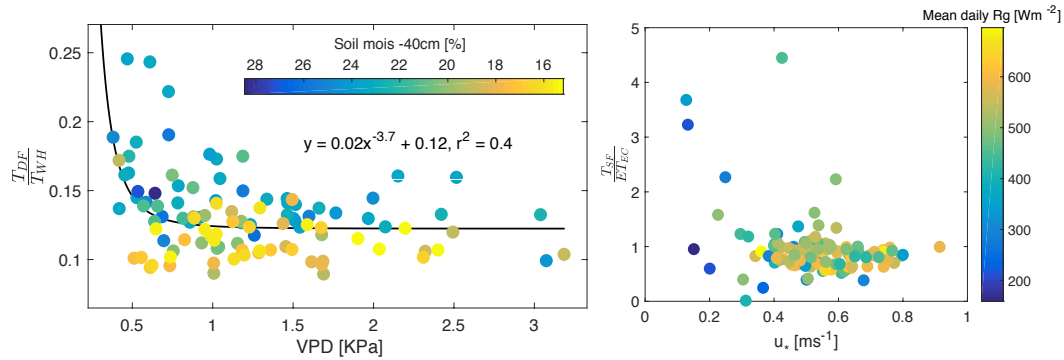
Figure 4-0-2. Ratios of cumulative daily transpiration of P. Menziesii (douglas fir or DF) individuals to T. heterophylla (western hemlock or WH) individuals are high at low VPD, and remain constant beyond ~ 1KPa. The ratio is additionally dependent on available soil moisture (color bar in a), showing that as soil drought progresses, the contribution of T. Hetrophylla to ecosystem-scale transpiration increases, and (b) the ratio of transpiration scaled using sap flow data to evapotranspiration estimates from latent heat fluxes estimated from eddy flux data is constrained, but shows values greater than 1 during times of low turbulence (low u*).

4.4.2.2 GPP from sap flow scaled transpiration

Transpiration was combined with reported leaf ^{13}C data to infer a canopy scale C_i/C_a ratio to estimate mid-day mean CO_2 assimilation for each day that sap flow was measured (equation 2). The daily mean VPD over this period was 1.2 kPa, ranging from 0.1 kPa on cloudy days to 3.2 kPa in mid-summer (Fig. 3a). Daily patterns of cumulative water use measured by eddy covariance and the sap flow technique are presented in Fig 3b and respond to fluctuations in VPD. This is reflected in the daily mean canopy conductance, calculated by re-arranging the Penman Monteith equation (presented in Chapter 2). Mean daily GPP derived from this approach (GPP$_{SF,}$ Fig 3d) was 11.2 μmolm^{-2}s^{-1} over the entire range of measurements, compared to 8.9 μmolm^{-2}s^{1} obtained from eddy flux measurements (GPP$_{EC}$; partitioned using the 'nighttime' approach reported in section 3.1).
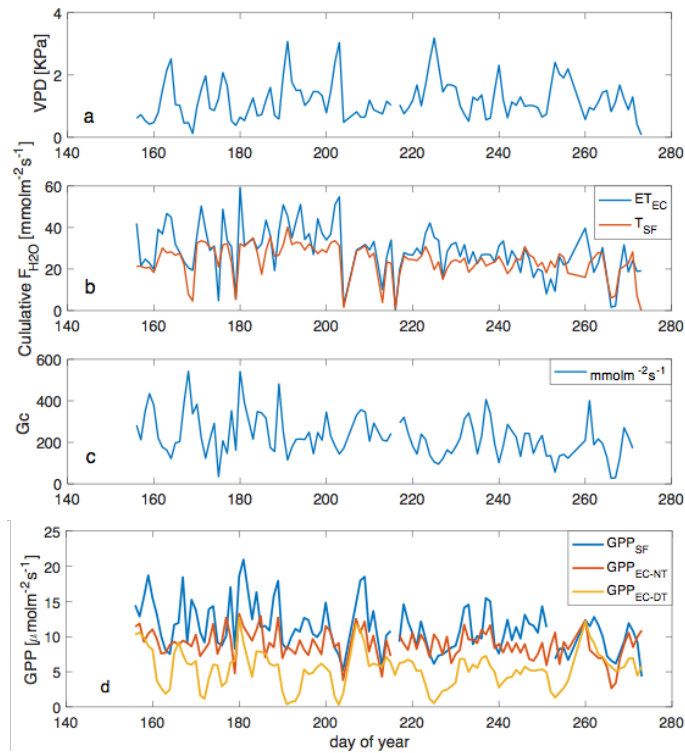
Figure 4-0-3. Daily mean VPD (a), cumulative water use from sap flow and eddy flux data (b), canopy conductance estimated from an inversion of the Penman-Monteith equation (c), and GPP estimated from sap flow and eddy flux (d).

Overall, GPP_{SF} was higher than GPP_{EC} and both estimates were positively correlated (Fig. 4a). Generally, daily (sum or mean?) GPP from both approaches was highest in the early summer, declining as the soil dried. Residuals from a linear regression showed a non-linear decline with increasing daily mean VPD for both approaches (Fig 4b). GPP_{EC-NT} exceeded GPP_{SF} towards the late summer on days with high VPD. As we showed in the previous section, the nighttime based approach leads to an overestimation of GPP at the half hourly timescale in response to high temperatures. This likely caused GPP_{EC} to remain high even as GPP_{SF} declined due to lower stomatal conductance under high VPD.
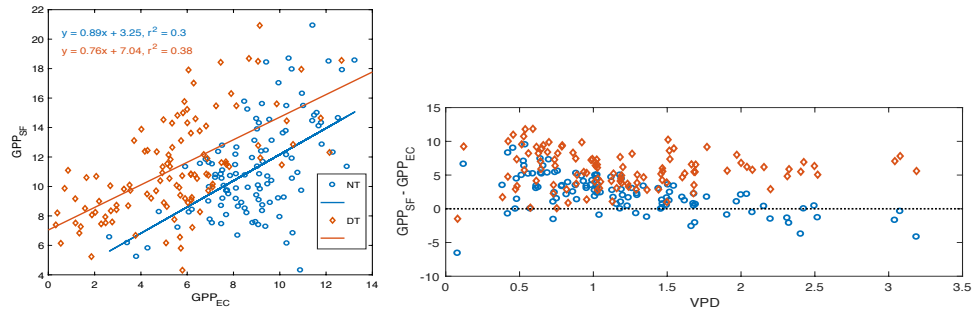
Figure 0-4-4. A linear relationship is observed between GPP estimated from the sap flow and eddy covariance flux data, partitioned using both 'nighttime' and 'daytime' (orange symbols and line) approaches' (panel a). Residuals in panel b are mostly above zero, except for the 'nighttime' approach, when GPP_{EC} exceeds GPP_{SF} at high VPD (the nighttime approach does not capture a VPD feedback on GPP as does the daytime approach).

4.4.3   GPP from OCS

OCS fluxes had a pronounced diel cycle, indicating large uptake peaking at mid-day (Fig 5a). Modelled LRU is shown in Fig 5b. Since the relationship between 2015 flux partitioning approaches has already been explored in section 3.1, here we compare GPP_{OCS} with GPP_{EC-DT}. GPP_{OCS} was found to have a diurnal cycle that was very similar to GPP_{EC} (asymmetric diel cycle, peaking shortly before mid-day), but the magnitude of hourly GPP_{OCS} was about twice that of GPP_{EC-DT} (Fig 5c). Across the season, both fluxes showed similar variations in response to declining soil moisture (Fig 5d). High light, mid-day values (1100 – 1300 h) of GPP_{OCS} showed a linear relationship with GPP_{EC-DT} (slope ~1.31; Fig. 5e).
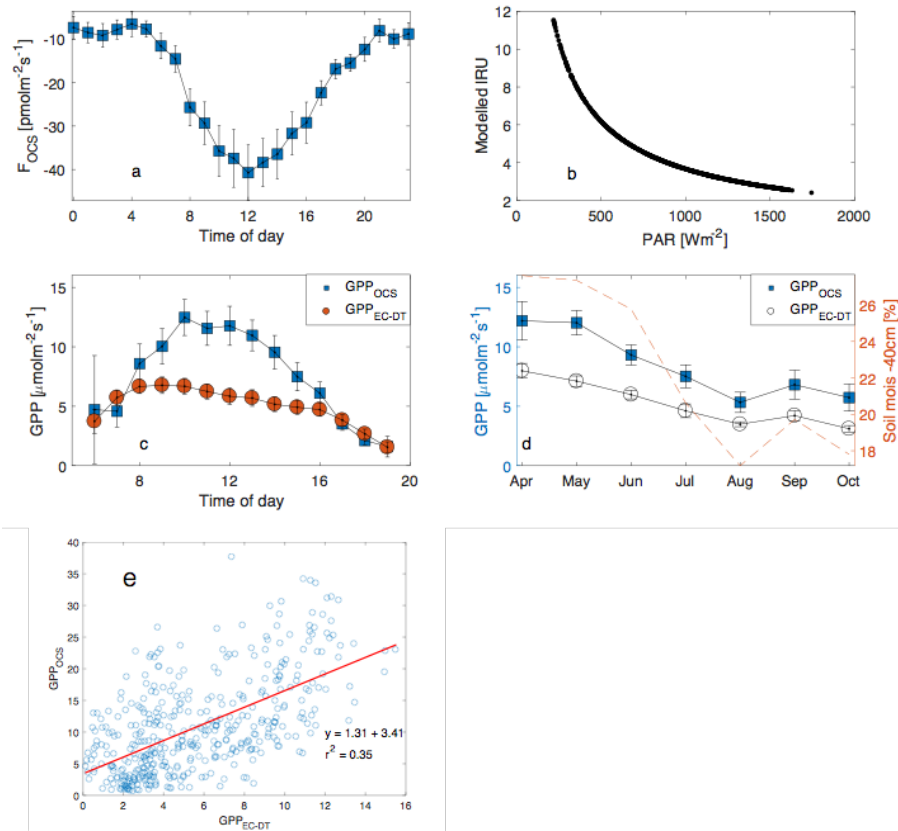
Figure 4-0-5. Diel cycle of OCS flux estimated across the measurement campaign (April 19, 2015-November 1, 2015) (a), modelled LRU (b), diel cycle of GPP estimated using eq (6) from F_{OCS} (blue squares) and partitioned from NEE using the 'daytime approach' (c), Seasonal trends of these fluxes (daily mean for periods when PAR > 100 $\mu molm^{-2} s^{-1}$; (d), and finally, linear regression between GPP from flux partitioning and GPP from OCS flux during mid- day (high light, and stable LRU values; (e).

4.5   Discussion

4.5.1   Sap flow scaling uncertainties

We scaled sap flow measured in a few individual trees to scale transpiration at the stand scale, assuming that the individuals measured were representative of the average tree. We tried to account for some of the variation in sap flow by species, size, and age distribution by sampling trees of different ages and also accounting for reduced sap flow in *T. heterophylla* individuals affected by dwarf mistletoe.

4.5.2 Uncertainties in C_i/C_a

We used a constant Ci/Ca ratio based leaf $^{13}CO_2$ reported by Fessenden and Ehleringer (2003), measured in the mid canopy of three *T. heterophylla* trees. A constant Ci/Ca is consistent with the stomatal optimality hypothesis, according to which stomata strictly maintain a constant Ci/Ca by regulating stomatal conductance. Moreover, at this extremely moist site, despite a strong summer drought imposed by an extended period of rain-free days and high mid-day VPD, trees are able to extract moisture from deeper soil layers (Warren et al., 2005), thereby maintaining carbon fixation. Estimates of $\delta^{13}C$ were consistent with other reported measurements of leaf $\delta^{13}C$ (Winner et al., 2004). While Winner et al. report a variation of Ci/Ca with height in the canopy, we did not account for this using our simple approach.

4.5.3 Uncertainties in LRU

Much of the uncertainty in modeled LRU directly results in uncertainties in Ci/Ca ratios discussed in the preceding section. In addition to canopy heterogeneity, the site contains abundant understory vegetation, including high amounts and coverage of epiphytes (McCune et al., 1997). Epiphytes contain carbonic anhydrase, the enzyme responsible for OCS hydrolysis within the leaf (Protoschill-Krebs, G Wilhelm, C Kesselmeier, 1996). Using a chamber-based study we found that epiphytes absorbed OCS both during the day and night, and uptake was highly influenced by the moisture status of the epiphyte (results are reported in Chapter 1). Thus, the presence of epiphytes and a heterogeneous canopy likely caused deviations from the LRU- light relationship (Fig 5b). To test this, we inferred LRU (LRU_{inf}) inverting eq (6) using GPP_{EC-DT}, F_{OCS}, and measured CO_2 and OCS mixing ratios. 95% of the resulting values were between 6-8 pmol.μmol^{-1} (mean = 7.4 ± 1.7), and insensitive to PAR. When PAR was held constant, a temperature dependence of LRU_{inf} emerged. These values are at the high extreme for observed (Whelan et al., 2017) and theoretical (Wohlfahrt et al., 2012) values for LRU. Inferred Ci/Ca (Ci/Ca inf) from this approach showed a linear but slow decline with increasing PAR (mean =

0.89, range 0.93 at PAR = 200 100 μmolm^{-2} s^{-1} and 0.84 at PAR > 1200 100 μmolm^{-2} s^{-1}). Such high Ci/Ca ratios for evergreen trees in a productive forest seem unreasonable, providing more evidence that GPP$_{EC-DT}$ is indeed underestimated.

4.6   Overall Synthesis and Conclusions

We tested four different and independent estimates of GPP at a single site. These included testing two widely used flux-partitioning estimates, an estimate of GPP using sap flow data, and one using carbonyl sulfide fluxes. The differences in these estimates and associated uncertainties were discussed and illustrate in part, the need to better pin down biophysical constraints on GPP estimates, as well as the role of canopy heterogeneity. At half hourly timescales, the nighttime-based flux partitioning approach was found to overestimate GPP at higher temperatures. The daytime-based approach better constrains photosynthesis at higher temperatures,). GPP estimated by scaling up transpiration from sap flow data was correlated to but higher than either eddy covariance-based estimate. The same was true of GPP calculated from carbonyl sulfide, as fluxes showed very similar diurnal and seasonal variability to EC-based estimates, but the magnitude of GPP was significantly higher at sub-daily and seasonal timescales for the OCS-based approach. Mean monthly estimates of GPP estimated from these different approaches showed that both 'proxies', i.e. OCS and sap flow, showed higher and comparable magnitude of ecosystem-scale photosynthesis, as opposed to GPP estimated from flux partitioning of NEE. Finally, these were compared with SCOPE model outputs of GPP (purple line in Fig. 6), which also showed higher mean monthly GPP estimates. SCOPE lacks a plant hydraulics and available soil water components, and is therefore prone to overestimation of GPP. Nevertheless, it is able to capture well the seasonal patterns of ecosystem photosynthesis. Moreover, light-saturated values of inferred Ci/Ca from SCOPE (~ 0.66) were comparable with those inferred from leaf-level measurements (~0.69). Differences in seasonal patterns of GPP$_{OCS}$ and GPP$_{SF}$ are partly due to these data being collected in different years

(estimates of GPP_{EC} for these two years, as well soil moisture for 2002 and 2015, show slightly different seasonal patterns – see Fig. S4).
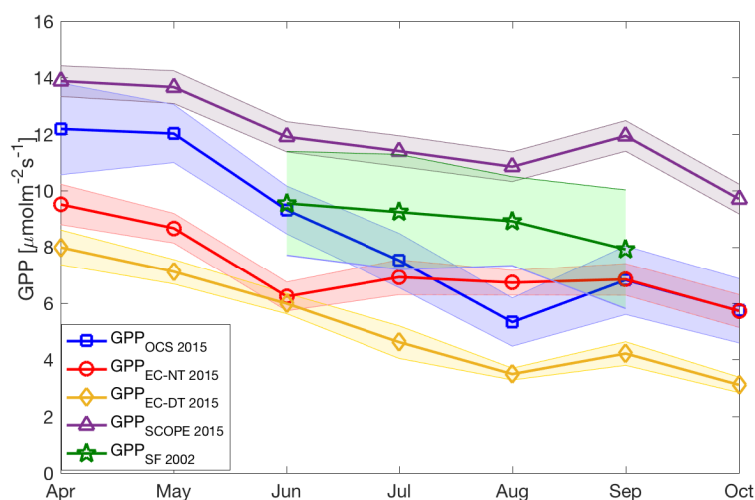
Figure 4-0-6. Mean monthly estimates of GPP from different approaches used in this study.

We conclude that eddy flux underestimates GPP at this site, in accordance with earlier comparisons with aboveground biomass estimates (Harmon et al., 2004). This can be due to either an underestimation of nighttime respiration, an underestimation of daytime NEE, or a combination of both. In tall forests, large parts of the canopy can often be decoupled from the canopy top and the overlying atmosphere, where measurements are made, and therefore the eddy flux may only represent carbon and water cycling for the uppermost canopy. This is particularly problematic at night, when wind speeds are low, and a temperature inversion typically occurs close to the canopy top. During the daytime, however, high rugosity (or the roughness of the heterogeneous canopy) and high u_* likely ensure that canopy coupling is quite high. Therefore, if daytime NEE is assumed to be representative of canopy CO_2 exchange, an underestimation of GPP can only occur if respiration is underestimated. Respiration estimates from in situ, chamber-based measurements also show systematic and significantly higher fluxes than those measured using the eddy covariance method (Fig. S5). While, chamber-based estimates from one sampling location cannot be taken to represent ecosystem-scale dynamics, together with our other independent estimates, they bolster our hypothesis of an

underestimation of respiration that propagates to underestimation of photosynthesis by the eddy covariance method.

This study highlights the value of employing multiple approaches at the same site to estimate GPP. We combined newly available datasets (OCS) and more traditional measurements (sap flow) to constrain ecosystem-scale photosynthesis. Ecosystem-scale measurements of $^{13}CO_2$ isofluxes (Wehr *et al.*, 2016; Oikawa *et al.*, 2017) and solar-induced chlorophyll fluorescence (e.g., Miao *et al.*, 2018) would also help constrain both respiration and photosynthesis in a systematic manner. Such measurements are critical, since they serve as validation for satellite-based products (e.g., Heinsch *et al.*, 2006; Sjöström *et al.*, 2013; Guanter *et al.*, 2014), regional-scale inversion modeling of CO_2 source-sink distributions (e.g., Schuh *et al.*, 2010; Alden *et al.*, 2016), and parameterizing land surface models (e.g., Wang *et al.*, 2007).

4.7   References

Alden, C. B., Miller, J. B., Gatti, L. V., Gloor, M. M., Guan, K., Michalak, A. M., … Diffenbaugh, N. S. (2016). Regional atmospheric CO2 inversion reveals seasonal and geographic differences in Amazon net biome exchange. *Global Change Biology*, *22*(10), 3427–3443. https://doi.org/10.1111/gcb.13305

Asaf, D., Rotenberg, E., Tatarinov, F., Dicken, U., Montzka, S. A., & Yakir, D. (2013). Ecosystem photosynthesis inferred from measurements of carbonyl sulphide flux. *Nature Geoscience*, *6*(3), 186–190. https://doi.org/10.1038/ngeo1730

Bala, G., Devaraju, N., Chaturvedi, R. K., Caldeira, K., & Nemani, R. (2013). Nitrogen deposition: How important is it for global terrestrial carbon uptake. *Biogeosciences*, *10*(11), 7147–7160. https://doi.org/10.5194/bg-10-7147-2013

Baldocchi, D. (2014). Measuring fluxes of trace gases and energy between ecosystems and the atmosphere - the state and future of the eddy covariance method. *Global Change Biology*, *20*(12), 3600–3609. https://doi.org/10.1111/gcb.12649

Baldocchi, D., Chu, H., & Reichstein, M. (2018). Inter-annual variability of net and gross ecosystem carbon fluxes: A review. *Agricultural and Forest Meteorology*, *249*(May 2017), 520–533. https://doi.org/10.1016/j.agrformet.2017.05.015

Ballantyne, A. P., Alden, C. B., Miller, J. B., Trans, P. P., & White, J. W. C. (2012). Increase in

observed net carbon dioxide uptake by land and oceans during the pst 50 years. *Nature*, *488*(7409), 70–73. https://doi.org/10.1038/nature11299

Belviso, S., Reiter, I. M., Loubet, B., Gros, V., Lathière, J., Montagne, D., … Genty, B. (2016). A top-down approach of surface carbonyl sulfide exchange by a Mediterranean oak forest ecosystem in Southern France. *Atmospheric Chemistry and Physics Discussions*, (June 2012), 1–25. https://doi.org/10.5194/acp-2016-525

Berkelhammer, M., Steen-Larsen, H. C., Cosgrove, A., Peters, A. J., Johnson, R., Hayden, M., & Montzka, S. A. (2016). Radiation and atmospheric circulation controls on carbonyl sulfide concentrations in themarine boundary layer. *Journal of Geophysical Research*, *121*(21), 13,113-13,128. https://doi.org/10.1002/2016JD025437

Berkelhammer, M., Asaf, D., Still, C., Montzka, S., Noone, D., Gupta, M., … Yakir, D. (2014). Constraining surface carbon fluxes using in situ measurements of carbonyl sulfide and carbon dioxide. *Global Biogeochemical Cycles*, *28*(2), 161–179. https://doi.org/10.1002/2013GB004644

Billesbach, D. P., Berry, J. A., Seibt, U., Maseyk, K., Torn, M. S., Fischer, M. L., … Campbell, J. E. (2014). Growing season eddy covariance measurements of carbonyl sulfide and CO2 fluxes: COS and CO2 relationships in Southern Great Plains winter wheat. *Agricultural and Forest Meteorology*, *184*, 48–55. https://doi.org/10.1016/j.agrformet.2013.06.007

Blonquist, J. M., Montzka, S. A., Munger, J. W., Yakir, D., Desai, A. R., Dragoni, D., … Bowling, D. R. (2011). The potential of carbonyl sulfide as a proxy for gross primary production at flux tower sites. *Journal of Geophysical Research: Biogeosciences*, *116*(4), 1–18. https://doi.org/10.1029/2011JG001723

Campbell, J. E., Berry, J., Seibt, U., Smith, S., Nature, S. M.-, & 2017, U. (2017). Large historical growth in global terrestrial gross primary production. *Nature.com*, *544*(7468), 84. Retrieved from https://www.nature.com/articles/nature22030

Campbell, J. E., Carmichael, G. R., Chai, T., Mena-Carrasco, M., Tang, Y., Blake, D. R., … Stanier, C. O. (2008). Photosynthetic control of atmospheric carbonyl sulfide during the growing season. *Science*, *322*(5904), 1085–1088. https://doi.org/10.1126/science.1164015

Čermák, J., Kucera, J., Bauerle, W. L., Phillips, N., & Hinckley, T. M. (2007). Tree water storage and its diurnal dynamics related to sap flow and changes in stem volume in old-growth Douglas-fir trees. *Tree Physiology*, *27*(2), 181–198. https://doi.org/10.1093/treephys/27.2.181

Ciais, P., Sabine, C., Bala, G., Bopp, L., Brovkin, V., Canadell, J., … Thornton, P. (2013). Carbon and Other Biogeochemical Cycles Chapter 6. *Climate Change 2013: The Physical Science Basis. Contribution of Working Group` I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, 465–570. https://doi.org/10.1017/CBO9781107415324.014

Commane, R., Meredith, L. K., Baker, I. T., Berry, J. A., Munger, J. W., Montzka, S. A., … Wofsy, S. C. (2015). Seasonal fluxes of carbonyl sulfide in a midlatitude forest. *Proceedings of the National Academy of Sciences*, *112*(46), 14162–14167. https://doi.org/10.1073/pnas.1504131112

Falk, M., Wharton, S., Schroeder, M., Ustin, S. L., & Paw U, K. T. (2008). Flux partitioning in an old-growth forest: seasonal and interannual dynamics. *Tree Physiology*, *28*(4), 509–520. https://doi.org/10.1093/treephys/28.4.509

Farquhar, G. D., & Richards, R. A. (1984). Isotopic composition of plant carbon correlates water-use efficiency of wheat genotypes. *Australian Journal of Plant Physiology*, *11*(539–552).

Fessenden, J. E., & Ehleringer, J. R. (2003). Temporal variation in δ13C of ecosystem respiration in the Pacific Northwest: Links to moisture stress. *Oecologia*, *136*(1), 129–136. https://doi.org/10.1007/s00442-003-1260-1

Forkel, M., Carvalhais, N., Rödenbeck, C., Keeling, R., Heimann, M., Thonicke, K., … Reichstein, M. (2016). Enhanced seasonal CO2 exchange caused by amplified plant productivity in northern ecosystems. *Science*, *351*(6274), 696 LP-699. Retrieved from http://science.sciencemag.org/content/351/6274/696.abstract

Granier, A. (1985). A new method to measure the raw sap flux in the trunk of trees. *Ann. For. Sci*, *42*, 193–200.

Gries, C., Nash, T. H., & Kesselmeier, J. (1994). Exchange of reduced sulfur gases between lichens and the atmosphere. *Biogeochemistry*, *26*(1), 25–39.

Guanter, L., Zhang, Y., Jung, M., Joiner, J., Voigt, M., Berry, J. A., … Griffis, T. J. (2014). Global and time-resolved monitoring of crop photosynthesis with chlorophyll fluorescence. *Proceedings of the National Academy of Sciences*, *111*(14), E1327–E1333. https://doi.org/10.1073/pnas.1320008111

Harmon, M., Bible, K., Ryan, M., Shaw, D., Chen, H., Klopatek, J., & Li, X. (2004). Production, Respiration, and Overall Carbon Balance in an Old-growth Pseudotsuga-Tsuga Forest

Ecosystem. *Ecosystems*, 498–512. https://doi.org/10.1007/s10021-004-0140-9

HEIMANN, M., & Reichstein, M. (2008). Terrestrial ecosystem carbon dynamics and climate feedbacks. *Agriculture*, *451*(7176), 289–292. Retrieved from http://www.nature.com/nature/journal/v451/n7176/full/nature06591.html

Heinsch, F. A., Zhao, M., Running, S. W., Kimball, J. S., Nemani, R. R., Davis, K. J., … Flanagan, L. B. (2006). Evaluation of remote sensing based terrestrial productivity from MODIS using regional tower eddy flux network observations. *IEEE Transactions on Geoscience and Remote Sensing*, *44*(7), 1908–1923. https://doi.org/10.1109/TGRS.2005.853936

Hilton, T., Whelan, M., Zumkehr, A., … S. K.-N. C., & 2017, U. (2017). Peak growing season gross uptake of carbon in North America is largest in the Midwest USA. *Nature.com*, *7*(6), 450. Retrieved from https://www.nature.com/articles/nclimate3272

Huntzinger, D. N., Michalak, A. M., Schwalm, C., Ciais, P., King, A. W., Fang, Y., … Zhao, F. (2017). Uncertainty in the response of terrestrial carbon sink to environmental drivers undermines carbon-climate feedback predictions. *Scientific Reports*, *7*(1), 1–8. https://doi.org/10.1038/s41598-017-03818-2

IPCC. (2014). *Climate Change 2013. the Fifth Assessment Report* (Vol. 5).

Keeling, R. F., Graven, H. D., Welp, L. R., Resplandy, L., Bi, J., Piper, S. C., … Meijer, H. A. J. (2017). Atmospheric evidence for a global secular increase in carbon isotopic discrimination of land photosynthesis. *Proceedings of the National Academy of Sciences*, 201619240. https://doi.org/10.1073/pnas.1619240114

Keenan, T. F., Hollinger, D. Y., Bohrer, G., Dragoni, D., Munger, J. W., Schmid, H. P., & Richardson, A. D. (2013). Increase in forest water-use efficiency as atmospheric carbon dioxide concentrations rise. *Nature*, *499*(7458), 324–327. https://doi.org/10.1038/nature12291

Keenan, T. F., Gray, J., Friedl, M. A., Toomey, M., Bohrer, G., Hollinger, D. Y., … Richardson, A. D. (2014). Net carbon uptake has increased through warming-induced changes in temperate forest phenology. *Nature Climate Change*, *4*(7), 598–604. https://doi.org/10.1038/nclimate2253

Kettle, A. J., Kuhn, U., Von Hobe, M., Kesselmeier, J., & Andreae, M. O. (2002). Global budget of atmospheric carbonyl sulfide: Temporal and spatial variations of the dominant sources and sinks. *Journal of Geophysical Research: Atmospheres*, *107*(D22).

Klein, T., Rotenberg, E., Tatarinov, F., & Yakir, D. (2016). Association between sap flow-derived and eddy covariance-derived measurements of forest canopy CO2 uptake. *New Phytologist*, *209*(1), 436–446. https://doi.org/10.1111/nph.13597

Knox, S. H., Dronova, I., Sturtevant, C., Oikawa, P. Y., Matthes, J. H., Verfaillie, J., & Baldocchi, D. (2017). Using digital camera and Landsat imagery with eddy covariance data to model gross primary production in restored wetlands. *Agricultural and Forest Meteorology*, *237–238*, 233–245. https://doi.org/10.1016/j.agrformet.2017.02.020

Kooijmans, L. M. J. J., Maseyk, K., Seibt, U., Sun, W., Vesala, T., Mammarella, I., … Chen, H. (2017). Canopy uptake dominates nighttime carbonyl sulfide fluxes in a boreal forest. *Atmospheric Chemistry and Physics*, *17*(18), 11453–11465. https://doi.org/10.5194/acp-17-11453-2017

Kuhn, U., & Kesselmeier, J. (2000). Environmental variables controlling the uptake of carbonyl sulfide by lichens. *Journal of Geophysical Research: Atmospheres*, *105*(D22), 26783–26792.

Kuhn, U., Wolf, A., Gries, C., Nash III, T. H., & Kesselmeier, J. (2000). Field measurements on the exchange of carbonyl sulfide between lichens and the atmosphere. *Atmospheric Environment*, *34*(28), 4867–4878.

LAI, C., Ehleringer, J. R., & Bond, B. J. (2006). Contributions of evaporation, isotopic non-steady state transpiration and atmospheric mixing on the δ18O of water vapour in Pacific Northwest coniferous forests. *Plant, Cell & Environment*, *29*(1), 77–94.

Lasslop, G., Reichstein, M., Papale, D., Richardson, A., Arneth, A., Barr, A., … Wohlfahrt, G. (2010). Separation of net ecosystem exchange into assimilation and respiration using a light response curve approach: Critical issues and global evaluation. *Global Change Biology*, *16*(1), 187–208. https://doi.org/10.1111/j.1365-2486.2009.02041.x

Launois, T., Peylin, P., Belviso, S., & Poulter, B. (2015). A new model of the global biogeochemical cycle of carbonyl sulfide - Part 2: Use of carbonyl sulfide to constrain gross primary productivity in current vegetation models. *Atmospheric Chemistry and Physics*, *15*(16), 9285–9312. https://doi.org/10.5194/acp-15-9285-2015

Li, W., Ciais, P., Wang, Y., Yin, Y., Peng, S., Zhu, Z., … Piao, S. (2018). Recent Changes in Global Photosynthesis and Terrestrial Ecosystem Respiration Constrained From Multiple Observations. *Geophysical Research Letters*, 1058–1068. https://doi.org/10.1002/2017GL076622

Lloyd, J., & Taylor, J. A. (1994). On the Temperature Dependence of Soil Respiration. *Functional Ecology*, *8*(3), 315–323.

Luyssaert, S., Schulze, E.-D., Börner, A., Knohl, A., Hessenmöller, D., Law, B. E., … Grace, J. (2008). Old-growth forests as global carbon sinks. *Nature*, *455*(7210), 213.

Maseyk, K., Berry, J. A., Billesbach, D., Campbell, J. E., Torn, M. S., Zahniser, M., & Seibt, U. (2014). Sources and sinks of carbonyl sulfide in an agricultural field in the Southern Great Plains. *Proceedings of the National Academy of Sciences*, *111*(25), 9064–9069. https://doi.org/10.1073/pnas.1319132111

McCune, B., Amsberry, K. A., Camacho, F. J., Clery, S., Cole, C., Emerson, C., … Widmer, M. (1997). Vertical profile of epiphytes in a Pacific Northwest old-growth forest. *Northwest Science*, *71*(2), 145–152. Retrieved from d:%5CArtiklar%5CMcCune et al 1997.pdf

MEINZER, F. C., ANDRADE, J. L., GOLDSTEIN, G., HOLBROOK, N. M., CAVELIER, J., & JACKSON, P. (1997). Control of transpiration from the upper canopy of a tropical forest: the role of stomatal, boundary layer and hydraulic architecture components. *Plant, Cell and Environment*, *20*(10), 1242–1252. https://doi.org/10.1046/j.1365-3040.1997.d01-26.x

Meinzer, F. C., Brooks, J. R., Domec, J., Gartner, B. L., Warren, J. M., Woodruff, D. R., … Sarg, R. (2006). Dynamics of water transport and storage in conifers studied, 105–114.

Meinzer, F. C., Woodruff, D. R., & Shaw, D. C. (2004). Integrated responses of hydraulic architecture, water and carbon relations of western hemlock to dwarf mistletoe infection. *Plant, Cell and Environment*, *27*(7), 937–946. https://doi.org/10.1111/j.1365-3040.2004.01199.x

Miao, G., Guan, K., Yang, X., Bernacchi, C. J., Berry, J. A., DeLucia, E. H., … Masters, M. D. (2018a). Sun-Induced Chlorophyll Fluorescence, Photosynthesis, and Light Use Efficiency of a Soybean Field. *Journal of Geophysical Research: Biogeosciences*. https://doi.org/10.1002/2017JG004180

Miao, G., Guan, K., Yang, X., Bernacchi, C. J., Berry, J. A., DeLucia, E. H., … Masters, M. D. (2018b). Sun-Induced Chlorophyll Fluorescence, Photosynthesis, and Light Use Efficiency of a Soybean Field. *Journal of Geophysical Research: Biogeosciences*, 610–623. https://doi.org/10.1002/2017JG004180

Montzka, S. A., Calvert, P., Hall, B. D., Elkins, J. W., Conway, T. J., Tans, P. P., & Sweeney, C. S. (2007). On the global distribution, seasonality, and budget of atmospheric carbonyl sulfide (COS) and some similarities to CO_2. *Journal of Geophysical Research*

Atmospheres, *112*(9), 1–15. https://doi.org/10.1029/2006JD007665

Novick, K. A., Ficklin, D. L., Stoy, P. C., Williams, C. A., Bohrer, G., Oishi, A. C., … Phillips, R. P. (2016). The increasing importance of atmospheric demand for ecosystem water and carbon fluxes. *Nature Climate Change*, *6*(11), 1023–1027. https://doi.org/10.1038/nclimate3114

Novick, K. A., Biederman, J. A., Desai, A. R., Litvak, M. E., Moore, D. J. P., Scott, R. L., & Torn, M. S. (2018). The AmeriFlux network: A coalition of the willing. *Agricultural and Forest Meteorology*, *249*(May), 444–456. https://doi.org/10.1016/j.agrformet.2017.10.009

Oikawa, P. Y., Sturtevant, C., Knox, S. H., Verfaillie, J., Huang, Y. W., & Baldocchi, D. D. (2017a). Revisiting the partitioning of net ecosystem exchange of CO2 into photosynthesis and respiration with simultaneous flux measurements of 13CO2 and CO2, soil respiration and a biophysical model, CANVEG. *Agricultural and Forest Meteorology*, *234–235*, 149–163. https://doi.org/10.1016/j.agrformet.2016.12.016

Oikawa, P. Y., Sturtevant, C., Knox, S. H., Verfaillie, J., Huang, Y. W., & Baldocchi, D. D. (2017b). Revisiting the partitioning of net ecosystem exchange of CO2into photosynthesis and respiration with simultaneous flux measurements of13CO2and CO2, soil respiration and a biophysical model, CANVEG. *Agricultural and Forest Meteorology*, *234–235*, 149–163. https://doi.org/10.1016/j.agrformet.2016.12.016

Parker, G. G. (1997). Canopy structure and light environment of an old growth Douglas-fir/Western hemlock forest. *Northwest Science*, *71*(4), 261–271.

Parker, G. G., Harmon, M. E., Lefsky, M. A., Chen, J., Pelt, R. Van, Weis, S. B., … Frankling, J. F. (2004). Three-dimensional Structure of an Old-growth Pseudotsuga-Tsuga Canopy and Its Implications for Radiation Balance, Microclimate, and Gas Exchange. *Ecosystems*, *7*(5), 440–453. https://doi.org/10.1007/s10021-004-0136-5

Paw U, K. T., Falk, M., Suchanek, T. H., Ustin, S. L., Chen, J., Park, Y.-S., … Matista, A. A. (2004). Carbon Dioxide Exchange between an Old-Growth Forest and the Atmosphere. *Ecosystems*, *7*(5), 513–524. https://doi.org/10.1007/s10021-004-0141-8

Phillips, N., Bond, B. J., McDowell, N. G., & Ryan, M. G. (2002). Canopy and hydraulic conductance in young, mature and old Douglas-fir trees. *Tree Physiology*, *22*(2–3), 205–211. https://doi.org/10.1093/treephys/22.2-3.205

Protoschill-Krebs, G Wilhelm, C Kesselmeier, J. (1996). Consumption of carbonyl sulphide (COS) by higher plant carbonic anhydrase (CA). *Atmospheric Environment*, *30*(18), 3151–

3156. Retrieved from
https://www.sciencedirect.com/science/article/pii/135223109600026X

Le Quéré, C., Raupach, M. R., Canadell, J. G., Marland, G., Bopp, L., Ciais, P., … Woodward, F. I. (2009). Trends in the sources and sinks of carbon dioxide. *Nature Geoscience*, *2*(12), 831–836. https://doi.org/10.1038/ngeo689

Le Quéré, C., Andrew, R. M., Friedlingstein, P., Sitch, S., Pongratz, J., Manning, A. C., … Zhu, D. (2018). Global Carbon Budget 2017. *Earth Syst. Sci. Data Etsushi Kato Markus Kautz Ralph F. Keeling Kees Klein Goldewijk Nathalie Lefèvre Andrew Lenton Danica Lombardozzi Nicolas Metzl Yukihiro Nojiri Antonio Padin Janet Reimer*, *1010333739*(10), 405–448. https://doi.org/10.5194/essd-10-405-2018

Reichstein, M., Falge, E., Baldocchi, D., Papale, D., Aubinet, M., Berbigier, P., … Granier, A. (2005). On the separation of net ecosystem exchange into assimilation and ecosystem respiration: review and improved algorithm. *Global Change Biology*, *11*(9), 1424–1439.

Rossini, M., Meroni, M., Migliavacca, M., Manca, G., Cogliati, S., Busetto, L., … Colombo, R. (2010). High resolution field spectroscopy measurements for estimating gross ecosystem production in a rice field. *Agricultural and Forest Meteorology*, *150*(9), 1283–1296. https://doi.org/10.1016/j.agrformet.2010.05.011

Schimel, D., Stephens, B. B., & Fisher, J. B. (2015). Effect of increasing CO_2 on the terrestrial carbon cycle. *Proceedings of the National Academy of Sciences*, *112*(2), 436–441. https://doi.org/10.1073/pnas.1407302112

Schuh, A. E., Denning, A. S., Corbin, K. D., Baker, I. T., Uliasz, M., Parazoo, N., … Worthy, D. E. J. (2010). A regional high-resolution carbon flux inversion of North America for 2004. *Biogeosciences*, *7*(5), 1625–1644. https://doi.org/10.5194/bg-7-1625-2010

Seibt, U., Rajabi, A., Griffiths, H., & Berry, J. A. (2008). Carbon isotopes and water use efficiency: Sense and sensitivity. *Oecologia*, *155*(3), 441–454. https://doi.org/10.1007/s00442-007-0932-7

Seibt, U., Kesselmeier, J., Sandoval-Soto, L., Kuhn, U., & Berry, J. A. (2010). A kinetic analysis of leaf uptake of COS and its relation to transpiration, photosynthesis and carbon isotope fractionation. *Biogeosciences*, *7*(1), 333–341. https://doi.org/10.5194/bg-7-333-2010

Shaw, D. C., Chen, J., Freeman, E. a, & Braun, D. M. (2005). Spatial and population characteristics of dwarf mistletoe infected trees in an old-growth Douglas-fir western hemlock forest. *Canadian Journal of Forest Research*, *35*(4), 990–1001.

https://doi.org/10.1139/x05-022

Shaw, D., Franklin, J., Bible, K., Klopatek, J., Freeman, E., Greene, S., & Parker, G. (2004). Ecological Setting of the Wind River Old-growth Forest. *Ecosystems*, *7*(5), 427–439. https://doi.org/10.1007/s10021-004-0135-6

Sjöström, M., Zhao, M., Archibald, S., Arneth, A., Cappelaere, B., Falk, U., … Kutsch, W. (2013). Evaluation of MODIS gross primary productivity for Africa using eddy covariance data. *Remote Sensing of Environment*, *131*, 275–286.

Stimler, K., Nelson, D., & Yakir, D. (2010). High precision measurements of atmospheric concentrations and plant exchange rates of carbonyl sulfide using mid-IR quantum cascade laser. *Global Change Biology*, *16*(9), 2496–2503. https://doi.org/10.1111/j.1365-2486.2009.02088.x

Stimler, K., Montzka, S. A., Berry, J. A., Rudich, Y., & Yakir, D. (2010). Relationships between carbonyl sulfide (COS) and CO2 during leaf gas exchange. *New Phytologist*, *186*(4), 869–878. https://doi.org/10.1111/j.1469-8137.2010.03218.x

Thum, T., Zaehle, S., Köhler, P., Aalto, T., Aurela, M., Guanter, L., … Markkanen, T. (2017). Modelling sun-induced fluorescence and photosynthesis with a land surface model at local and regional scales in northern Europe. *Biogeosciences*, *14*(7), 1969–1984. https://doi.org/10.5194/bg-14-1969-2017

van der Tol, C., Verhoef, W., Timmermans, J., Verhoef, A., & Su, Z. (2009). An integrated model of soil-canopy spectral radiances, photosynthesis, fluorescene, temperature and energy balance. *Biogeosciences*, *6*, 3109–3129.

Toomey, M., Friedl, M. A., Frolking, S., Hufkens, K., Klosterman, S., Sonnentag, O., … Richardson, A. D. (2015). Greenness indices from digital cameras predict the timing and seasonal dynamics of canopy-scale photosynthesis. *Ecological Applications*, *25*(1), 99–115. https://doi.org/10.1890/14-0005.1

UNFCC. (2015). United nations framework convention on climate change. *Paris, France*.

Wang, Y. P., Baldocchi, D., Leuning, R., Falge, E., & Vesala, T. (2007). Estimating parameters in a land-surface model by applying nonlinear inversion to eddy covariance flux measurements from eight FLUXNET sites. *Global Change Biology*, *13*(3), 652–670. https://doi.org/10.1111/j.1365-2486.2006.01225.x

Warren, J., Meinzer, F., Brooks, J., & Domec, J. (2005). Vertical stratification of soil water storage and release dynamics in Pacific Northwest coniferous forests. *Agricultural and*

Forest Meteorology, *130*(1–2), 39–58. https://doi.org/10.1016/j.agrformet.2005.01.004

Wehr, R., & Saleska, S. R. (2015). An improved isotopic method for partitioning net ecosystem-atmosphere CO2exchange. *Agricultural and Forest Meteorology*, *214–215*, 515–531. https://doi.org/10.1016/j.agrformet.2015.09.009

Wehr, R., Munger, J. W., McManus, J. B., Nelson, D. D., Zahniser, M. S., Davidson, E. A., … Saleska, S. R. (2016). Seasonality of temperate forest photosynthesis and daytime respiration. *Nature*, *534*(7609), 680.

Wehr, R., Commane, R., Munger, J. W., Barry Mcmanus, J., Nelson, D. D., Zahniser, M. S., … Wofsy, S. C. (2017). Dynamics of canopy stomatal conductance, transpiration, and evaporation in a temperate deciduous forest, validated by carbonyl sulfide uptake. *Biogeosciences*, *14*(2), 389–401. https://doi.org/10.5194/bg-14-389-2017

Wharton, S., & Falk, M. (2016). Climate indices strongly influence old-growth forest carbon exchange. *Environmental Research Letters*, *11*(4), 1–11. https://doi.org/10.1088/1748-9326/11/4/044016

Whelan, M. E., Lennartz, S. T., Gimeno, T. E., Wehr, R., Wohlfahrt, G., Wang, Y., … Campbell, J. E. (2017). Reviews and Syntheses: Carbonyl Sulfide as a Multi-scale Tracer for Carbon and Water Cycles. *Biogeosciences Discussions*, (October), 1–97. https://doi.org/10.5194/bg-2017-427

Williams, A. P., Allen, C. D., Macalady, A. K., Griffin, D., Woodhouse, C. A., Meko, D. M., … Grissino-Mayer, H. D. (2013). Temperature as a potent driver of regional forest drought stress and tree mortality. *Nature Climate Change*, *3*(3), 292.

Winner, W., Thomas, S., Berry, J., Bond, B., Cooper, C., Hinckley, T., … Williams, M. (2004). Canopy Carbon Gain and Water Use: Analysis of Old-growth Conifers in the Pacific Northwest. *Ecosystems*, *7*(5), 482–497. https://doi.org/10.1007/s10021-004-0139-2

Wohlfahrt, G., Brilli, F., Hörtnagl, L., Xu, X., Bingemer, H., Hansel, A., & Loreto, F. (2012). Carbonyl sulfide (COS) as a tracer for canopy photosynthesis, transpiration and stomatal conductance: Potential and limitations. *Plant, Cell and Environment*, *35*(4), 657–667. https://doi.org/10.1111/j.1365-3040.2011.02451.x

Alden, C. B., Miller, J. B., Gatti, L. V., Gloor, M. M., Guan, K., Michalak, A. M., … Diffenbaugh, N. S. (2016). Regional atmospheric CO2 inversion reveals seasonal and geographic differences in Amazon net biome exchange. *Global Change Biology*, *22*(10), 3427–3443. https://doi.org/10.1111/gcb.13305

Asaf, D., Rotenberg, E., Tatarinov, F., Dicken, U., Montzka, S. A., & Yakir, D. (2013). Ecosystem photosynthesis inferred from measurements of carbonyl sulphide flux. *Nature Geoscience*, *6*(3), 186–190. https://doi.org/10.1038/ngeo1730

Bala, G., Devaraju, N., Chaturvedi, R. K., Caldeira, K., & Nemani, R. (2013). Nitrogen deposition: How important is it for global terrestrial carbon uptake. *Biogeosciences*, *10*(11), 7147–7160. https://doi.org/10.5194/bg-10-7147-2013

Baldocchi, D. (2014). Measuring fluxes of trace gases and energy between ecosystems and the atmosphere - the state and future of the eddy covariance method. *Global Change Biology*, *20*(12), 3600–3609. https://doi.org/10.1111/gcb.12649

Baldocchi, D., Chu, H., & Reichstein, M. (2018). Inter-annual variability of net and gross ecosystem carbon fluxes: A review. *Agricultural and Forest Meteorology*, *249*(May 2017), 520–533. https://doi.org/10.1016/j.agrformet.2017.05.015

Ballantyne, A. P., Alden, C. B., Miller, J. B., Trans, P. P., & White, J. W. C. (2012). Increase in observed net carbon dioxide uptake by land and oceans during the pst 50 years. *Nature*, *488*(7409), 70–73. https://doi.org/10.1038/nature11299

Belviso, S., Reiter, I. M., Loubet, B., Gros, V., Lathière, J., Montagne, D., … Genty, B. (2016). A top-down approach of surface carbonyl sulfide exchange by a Mediterranean oak forest ecosystem in Southern France. *Atmospheric Chemistry and Physics Discussions*, (June 2012), 1–25. https://doi.org/10.5194/acp-2016-525

Berkelhammer, M., Steen-Larsen, H. C., Cosgrove, A., Peters, A. J., Johnson, R., Hayden, M., & Montzka, S. A. (2016). Radiation and atmospheric circulation controls on carbonyl sulfide concentrations in themarine boundary layer. *Journal of Geophysical Research*, *121*(21), 13,113-13,128. https://doi.org/10.1002/2016JD025437

Berkelhammer, M., Asaf, D., Still, C., Montzka, S., Noone, D., Gupta, M., … Yakir, D. (2014). Constraining surface carbon fluxes using in situ measurements of carbonyl sulfide and carbon dioxide. *Global Biogeochemical Cycles*, *28*(2), 161–179. https://doi.org/10.1002/2013GB004644

Billesbach, D. P., Berry, J. A., Seibt, U., Maseyk, K., Torn, M. S., Fischer, M. L., … Campbell, J. E. (2014). Growing season eddy covariance measurements of carbonyl sulfide and CO2 fluxes: COS and CO2 relationships in Southern Great Plains winter wheat. *Agricultural and Forest Meteorology*, *184*, 48–55. https://doi.org/10.1016/j.agrformet.2013.06.007

Blonquist, J. M., Montzka, S. A., Munger, J. W., Yakir, D., Desai, A. R., Dragoni, D., …

109

Bowling, D. R. (2011). The potential of carbonyl sulfide as a proxy for gross primary production at flux tower sites. *Journal of Geophysical Research: Biogeosciences*, *116*(4), 1–18. https://doi.org/10.1029/2011JG001723

Campbell, J. E., Berry, J., Seibt, U., Smith, S., Nature, S. M.-, & 2017, U. (2017). Large historical growth in global terrestrial gross primary production. *Nature.com*, *544*(7468), 84. Retrieved from https://www.nature.com/articles/nature22030

Campbell, J. E., Carmichael, G. R., Chai, T., Mena-Carrasco, M., Tang, Y., Blake, D. R., … Stanier, C. O. (2008). Photosynthetic control of atmospheric carbonyl sulfide during the growing season. *Science*, *322*(5904), 1085–1088. https://doi.org/10.1126/science.1164015

Čermák, J., Kucera, J., Bauerle, W. L., Phillips, N., & Hinckley, T. M. (2007). Tree water storage and its diurnal dynamics related to sap flow and changes in stem volume in old-growth Douglas-fir trees. *Tree Physiology*, *27*(2), 181–198. https://doi.org/10.1093/treephys/27.2.181

Ciais, P., Sabine, C., Bala, G., Bopp, L., Brovkin, V., Canadell, J., … Thornton, P. (2013). Carbon and Other Biogeochemical Cycles Chapter 6. *Climate Change 2013: The Physical Science Basis. Contribution of Working Group` I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, 465–570. https://doi.org/10.1017/CBO9781107415324.014

Commane, R., Meredith, L. K., Baker, I. T., Berry, J. A., Munger, J. W., Montzka, S. A., … Wofsy, S. C. (2015). Seasonal fluxes of carbonyl sulfide in a midlatitude forest. *Proceedings of the National Academy of Sciences*, *112*(46), 14162–14167. https://doi.org/10.1073/pnas.1504131112

Falk, M., Wharton, S., Schroeder, M., Ustin, S. L., & Paw U, K. T. (2008). Flux partitioning in an old-growth forest: seasonal and interannual dynamics. *Tree Physiology*, *28*(4), 509–520. https://doi.org/10.1093/treephys/28.4.509

Farquhar, G. D., & Richards, R. A. (1984). Isotopic composition of plant carbon correlates water-use efficiency of wheat genotypes. *Australian Journal of Plant Physiology*, *11*(539–552).

Fessenden, J. E., & Ehleringer, J. R. (2003). Temporal variation in δ13C of ecosystem respiration in the Pacific Northwest: Links to moisture stress. *Oecologia*, *136*(1), 129–136. https://doi.org/10.1007/s00442-003-1260-1

Forkel, M., Carvalhais, N., Rödenbeck, C., Keeling, R., Heimann, M., Thonicke, K., …

Reichstein, M. (2016). Enhanced seasonal CO2 exchange caused by amplified plant productivity in northern ecosystems. *Science*, *351*(6274), 696 LP-699. Retrieved from http://science.sciencemag.org/content/351/6274/696.abstract

Granier, A. (1985). A new method to measure the raw sap flux in the trunk of trees. *Ann. For. Sci*, *42*, 193–200.

Gries, C., Nash, T. H., & Kesselmeier, J. (1994). Exchange of reduced sulfur gases between lichens and the atmosphere. *Biogeochemistry*, *26*(1), 25–39.

Guanter, L., Zhang, Y., Jung, M., Joiner, J., Voigt, M., Berry, J. A., … Griffis, T. J. (2014). Global and time-resolved monitoring of crop photosynthesis with chlorophyll fluorescence. *Proceedings of the National Academy of Sciences*, *111*(14), E1327–E1333. https://doi.org/10.1073/pnas.1320008111

Harmon, M., Bible, K., Ryan, M., Shaw, D., Chen, H., Klopatek, J., & Li, X. (2004). Production, Respiration, and Overall Carbon Balance in an Old-growth Pseudotsuga-Tsuga Forest Ecosystem. *Ecosystems*, 498–512. https://doi.org/10.1007/s10021-004-0140-9

HEIMANN, M., & Reichstein, M. (2008). Terrestrial ecosystem carbon dynamics and climate feedbacks. *Agriculture*, *451*(7176), 289–292. Retrieved from http://www.nature.com/nature/journal/v451/n7176/full/nature06591.html

Heinsch, F. A., Zhao, M., Running, S. W., Kimball, J. S., Nemani, R. R., Davis, K. J., … Flanagan, L. B. (2006). Evaluation of remote sensing based terrestrial productivity from MODIS using regional tower eddy flux network observations. *IEEE Transactions on Geoscience and Remote Sensing*, *44*(7), 1908–1923. https://doi.org/10.1109/TGRS.2005.853936

Hilton, T., Whelan, M., Zumkehr, A., … S. K.-N. C., & 2017, U. (2017). Peak growing season gross uptake of carbon in North America is largest in the Midwest USA. *Nature.com*, *7*(6), 450. Retrieved from https://www.nature.com/articles/nclimate3272

Huntzinger, D. N., Michalak, A. M., Schwalm, C., Ciais, P., King, A. W., Fang, Y., … Zhao, F. (2017). Uncertainty in the response of terrestrial carbon sink to environmental drivers undermines carbon-climate feedback predictions. *Scientific Reports*, *7*(1), 1–8. https://doi.org/10.1038/s41598-017-03818-2

IPCC. (2014). *Climate Change 2013. the Fifth Assessment Report* (Vol. 5).

Keeling, R. F., Graven, H. D., Welp, L. R., Resplandy, L., Bi, J., Piper, S. C., … Meijer, H. A. J. (2017). Atmospheric evidence for a global secular increase in carbon isotopic

discrimination of land photosynthesis. *Proceedings of the National Academy of Sciences*, 201619240. https://doi.org/10.1073/pnas.1619240114

Keenan, T. F., Hollinger, D. Y., Bohrer, G., Dragoni, D., Munger, J. W., Schmid, H. P., & Richardson, A. D. (2013). Increase in forest water-use efficiency as atmospheric carbon dioxide concentrations rise. *Nature*, *499*(7458), 324–327. https://doi.org/10.1038/nature12291

Keenan, T. F., Gray, J., Friedl, M. A., Toomey, M., Bohrer, G., Hollinger, D. Y., … Richardson, A. D. (2014). Net carbon uptake has increased through warming-induced changes in temperate forest phenology. *Nature Climate Change*, *4*(7), 598–604. https://doi.org/10.1038/nclimate2253

Kettle, A. J., Kuhn, U., Von Hobe, M., Kesselmeier, J., & Andreae, M. O. (2002). Global budget of atmospheric carbonyl sulfide: Temporal and spatial variations of the dominant sources and sinks. *Journal of Geophysical Research: Atmospheres*, *107*(D22).

Klein, T., Rotenberg, E., Tatarinov, F., & Yakir, D. (2016). Association between sap flow-derived and eddy covariance-derived measurements of forest canopy CO2 uptake. *New Phytologist*, *209*(1), 436–446. https://doi.org/10.1111/nph.13597

Knox, S. H., Dronova, I., Sturtevant, C., Oikawa, P. Y., Matthes, J. H., Verfaillie, J., & Baldocchi, D. (2017). Using digital camera and Landsat imagery with eddy covariance data to model gross primary production in restored wetlands. *Agricultural and Forest Meteorology*, *237–238*, 233–245. https://doi.org/10.1016/j.agrformet.2017.02.020

Kooijmans, L. M. J. J., Maseyk, K., Seibt, U., Sun, W., Vesala, T., Mammarella, I., … Chen, H. (2017). Canopy uptake dominates nighttime carbonyl sulfide fluxes in a boreal forest. *Atmospheric Chemistry and Physics*, *17*(18), 11453–11465. https://doi.org/10.5194/acp-17-11453-2017

Kuhn, U., & Kesselmeier, J. (2000). Environmental variables controlling the uptake of carbonyl sulfide by lichens. *Journal of Geophysical Research: Atmospheres*, *105*(D22), 26783–26792.

Kuhn, U., Wolf, A., Gries, C., Nash III, T. H., & Kesselmeier, J. (2000). Field measurements on the exchange of carbonyl sulfide between lichens and the atmosphere. *Atmospheric Environment*, *34*(28), 4867–4878.

LAI, C., Ehleringer, J. R., & Bond, B. J. (2006). Contributions of evaporation, isotopic non-steady state transpiration and atmospheric mixing on the δ18O of water vapour in Pacific

Northwest coniferous forests. *Plant, Cell & Environment*, *29*(1), 77–94.

Lasslop, G., Reichstein, M., Papale, D., Richardson, A., Arneth, A., Barr, A., … Wohlfahrt, G. (2010). Separation of net ecosystem exchange into assimilation and respiration using a light response curve approach: Critical issues and global evaluation. *Global Change Biology*, *16*(1), 187–208. https://doi.org/10.1111/j.1365-2486.2009.02041.x

Launois, T., Peylin, P., Belviso, S., & Poulter, B. (2015). A new model of the global biogeochemical cycle of carbonyl sulfide - Part 2: Use of carbonyl sulfide to constrain gross primary productivity in current vegetation models. *Atmospheric Chemistry and Physics*, *15*(16), 9285–9312. https://doi.org/10.5194/acp-15-9285-2015

Li, W., Ciais, P., Wang, Y., Yin, Y., Peng, S., Zhu, Z., … Piao, S. (2018). Recent Changes in Global Photosynthesis and Terrestrial Ecosystem Respiration Constrained From Multiple Observations. *Geophysical Research Letters*, 1058–1068. https://doi.org/10.1002/2017GL076622

Lloyd, J., & Taylor, J. A. (1994). On the Temperature Dependence of Soil Respiration. *Functional Ecology*, *8*(3), 315–323.

Luyssaert, S., Schulze, E.-D., Börner, A., Knohl, A., Hessenmöller, D., Law, B. E., … Grace, J. (2008). Old-growth forests as global carbon sinks. *Nature*, *455*(7210), 213.

Maseyk, K., Berry, J. A., Billesbach, D., Campbell, J. E., Torn, M. S., Zahniser, M., & Seibt, U. (2014). Sources and sinks of carbonyl sulfide in an agricultural field in the Southern Great Plains. *Proceedings of the National Academy of Sciences*, *111*(25), 9064–9069. https://doi.org/10.1073/pnas.1319132111

McCune, B., Amsberry, K. A., Camacho, F. J., Clery, S., Cole, C., Emerson, C., … Widmer, M. (1997). Vertical profile of epiphytes in a Pacific Northwest old-growth forest. *Northwest Science*, *71*(2), 145–152. Retrieved from d:%5CArtiklar%5CMcCune et al 1997.pdf

MEINZER, F. C., ANDRADE, J. L., GOLDSTEIN, G., HOLBROOK, N. M., CAVELIER, J., & JACKSON, P. (1997). Control of transpiration from the upper canopy of a tropical forest: the role of stomatal, boundary layer and hydraulic architecture components. *Plant, Cell and Environment*, *20*(10), 1242–1252. https://doi.org/10.1046/j.1365-3040.1997.d01-26.x

Meinzer, F. C., Brooks, J. R., Domec, J., Gartner, B. L., Warren, J. M., Woodruff, D. R., … Sarg, R. (2006). Dynamics of water transport and storage in conifers studied, 105–114.

Meinzer, F. C., Woodruff, D. R., & Shaw, D. C. (2004). Integrated responses of hydraulic architecture, water and carbon relations of western hemlock to dwarf mistletoe infection.

Plant, Cell and Environment, *27*(7), 937–946. https://doi.org/10.1111/j.1365-3040.2004.01199.x

Miao, G., Guan, K., Yang, X., Bernacchi, C. J., Berry, J. A., DeLucia, E. H., … Masters, M. D. (2018a). Sun-Induced Chlorophyll Fluorescence, Photosynthesis, and Light Use Efficiency of a Soybean Field. *Journal of Geophysical Research: Biogeosciences*. https://doi.org/10.1002/2017JG004180

Miao, G., Guan, K., Yang, X., Bernacchi, C. J., Berry, J. A., DeLucia, E. H., … Masters, M. D. (2018b). Sun-Induced Chlorophyll Fluorescence, Photosynthesis, and Light Use Efficiency of a Soybean Field. *Journal of Geophysical Research: Biogeosciences*, 610–623. https://doi.org/10.1002/2017JG004180

Montzka, S. A., Calvert, P., Hall, B. D., Elkins, J. W., Conway, T. J., Tans, P. P., & Sweeney, C. S. (2007). On the global distribution, seasonality, and budget of atmospheric carbonyl sulfide (COS) and some similarities to CO_2. *Journal of Geophysical Research Atmospheres*, *112*(9), 1–15. https://doi.org/10.1029/2006JD007665

Novick, K. A., Ficklin, D. L., Stoy, P. C., Williams, C. A., Bohrer, G., Oishi, A. C., … Phillips, R. P. (2016). The increasing importance of atmospheric demand for ecosystem water and carbon fluxes. *Nature Climate Change*, *6*(11), 1023–1027. https://doi.org/10.1038/nclimate3114

Novick, K. A., Biederman, J. A., Desai, A. R., Litvak, M. E., Moore, D. J. P., Scott, R. L., & Torn, M. S. (2018). The AmeriFlux network: A coalition of the willing. *Agricultural and Forest Meteorology*, *249*(May), 444–456. https://doi.org/10.1016/j.agrformet.2017.10.009

Oikawa, P. Y., Sturtevant, C., Knox, S. H., Verfaillie, J., Huang, Y. W., & Baldocchi, D. D. (2017a). Revisiting the partitioning of net ecosystem exchange of CO2 into photosynthesis and respiration with simultaneous flux measurements of 13CO2 and CO2, soil respiration and a biophysical model, CANVEG. *Agricultural and Forest Meteorology*, *234–235*, 149–163. https://doi.org/10.1016/j.agrformet.2016.12.016

Oikawa, P. Y., Sturtevant, C., Knox, S. H., Verfaillie, J., Huang, Y. W., & Baldocchi, D. D. (2017b). Revisiting the partitioning of net ecosystem exchange of CO2into photosynthesis and respiration with simultaneous flux measurements ofl3CO2and CO2, soil respiration and a biophysical model, CANVEG. *Agricultural and Forest Meteorology*, *234–235*, 149–163. https://doi.org/10.1016/j.agrformet.2016.12.016

Parker, G. G. (1997). Canopy structure and light environment of an old growth Douglas-fir/Western hemlock forest. *Northwest Science*, *71*(4), 261–271.

Parker, G. G., Harmon, M. E., Lefsky, M. A., Chen, J., Pelt, R. Van, Weis, S. B., … Frankling, J. F. (2004). Three-dimensional Structure of an Old-growth Pseudotsuga-Tsuga Canopy and Its Implications for Radiation Balance, Microclimate, and Gas Exchange. *Ecosystems*, *7*(5), 440–453. https://doi.org/10.1007/s10021-004-0136-5

Paw U, K. T., Falk, M., Suchanek, T. H., Ustin, S. L., Chen, J., Park, Y.-S., … Matista, A. A. (2004). Carbon Dioxide Exchange between an Old-Growth Forest and the Atmosphere. *Ecosystems*, *7*(5), 513–524. https://doi.org/10.1007/s10021-004-0141-8

Phillips, N., Bond, B. J., McDowell, N. G., & Ryan, M. G. (2002). Canopy and hydraulic conductance in young, mature and old Douglas-fir trees. *Tree Physiology*, *22*(2–3), 205–211. https://doi.org/10.1093/treephys/22.2-3.205

Protoschill-Krebs, G Wilhelm, C Kesselmeier, J. (1996). Consumption of carbonyl sulphide (COS) by higher plant carbonic anhydrase (CA). *Atmospheric Environment*, *30*(18), 3151–3156. Retrieved from https://www.sciencedirect.com/science/article/pii/135223109600026X

Le Quéré, C., Raupach, M. R., Canadell, J. G., Marland, G., Bopp, L., Ciais, P., … Woodward, F. I. (2009). Trends in the sources and sinks of carbon dioxide. *Nature Geoscience*, *2*(12), 831–836. https://doi.org/10.1038/ngeo689

Le Quéré, C., Andrew, R. M., Friedlingstein, P., Sitch, S., Pongratz, J., Manning, A. C., … Zhu, D. (2018). Global Carbon Budget 2017. *Earth Syst. Sci. Data Etsushi Kato Markus Kautz Ralph F. Keeling Kees Klein Goldewijk Nathalie Lefèvre Andrew Lenton Danica Lombardozzi Nicolas Metzl Yukihiro Nojiri Antonio Padin Janet Reimer*, *1010333739*(10), 405–448. https://doi.org/10.5194/essd-10-405-2018

Reichstein, M., Falge, E., Baldocchi, D., Papale, D., Aubinet, M., Berbigier, P., … Granier, A. (2005). On the separation of net ecosystem exchange into assimilation and ecosystem respiration: review and improved algorithm. *Global Change Biology*, *11*(9), 1424–1439.

Rossini, M., Meroni, M., Migliavacca, M., Manca, G., Cogliati, S., Busetto, L., … Colombo, R. (2010). High resolution field spectroscopy measurements for estimating gross ecosystem production in a rice field. *Agricultural and Forest Meteorology*, *150*(9), 1283–1296. https://doi.org/10.1016/j.agrformet.2010.05.011

Schimel, D., Stephens, B. B., & Fisher, J. B. (2015). Effect of increasing CO_2 on the terrestrial carbon cycle. *Proceedings of the National Academy of Sciences*, *112*(2), 436–441. https://doi.org/10.1073/pnas.1407302112

Schuh, A. E., Denning, A. S., Corbin, K. D., Baker, I. T., Uliasz, M., Parazoo, N., … Worthy, D. E. J. (2010). A regional high-resolution carbon flux inversion of North America for 2004. *Biogeosciences*, *7*(5), 1625–1644. https://doi.org/10.5194/bg-7-1625-2010

Seibt, U., Rajabi, A., Griffiths, H., & Berry, J. A. (2008). Carbon isotopes and water use efficiency: Sense and sensitivity. *Oecologia*, *155*(3), 441–454. https://doi.org/10.1007/s00442-007-0932-7

Seibt, U., Kesselmeier, J., Sandoval-Soto, L., Kuhn, U., & Berry, J. A. (2010). A kinetic analysis of leaf uptake of COS and its relation to transpiration, photosynthesis and carbon isotope fractionation. *Biogeosciences*, *7*(1), 333–341. https://doi.org/10.5194/bg-7-333-2010

Shaw, D. C., Chen, J., Freeman, E. a, & Braun, D. M. (2005). Spatial and population characteristics of dwarf mistletoe infected trees in an old-growth Douglas-fir western hemlock forest. *Canadian Journal of Forest Research*, *35*(4), 990–1001. https://doi.org/10.1139/x05-022

Shaw, D., Franklin, J., Bible, K., Klopatek, J., Freeman, E., Greene, S., & Parker, G. (2004). Ecological Setting of the Wind River Old-growth Forest. *Ecosystems*, *7*(5), 427–439. https://doi.org/10.1007/s10021-004-0135-6

Sjöström, M., Zhao, M., Archibald, S., Arneth, A., Cappelaere, B., Falk, U., … Kutsch, W. (2013). Evaluation of MODIS gross primary productivity for Africa using eddy covariance data. *Remote Sensing of Environment*, *131*, 275–286.

Stimler, K., Nelson, D., & Yakir, D. (2010). High precision measurements of atmospheric concentrations and plant exchange rates of carbonyl sulfide using mid-IR quantum cascade laser. *Global Change Biology*, *16*(9), 2496–2503. https://doi.org/10.1111/j.1365-2486.2009.02088.x

Stimler, K., Montzka, S. A., Berry, J. A., Rudich, Y., & Yakir, D. (2010). Relationships between carbonyl sulfide (COS) and CO2 during leaf gas exchange. *New Phytologist*, *186*(4), 869–878. https://doi.org/10.1111/j.1469-8137.2010.03218.x

Thum, T., Zaehle, S., Köhler, P., Aalto, T., Aurela, M., Guanter, L., … Markkanen, T. (2017). Modelling sun-induced fluorescence and photosynthesis with a land surface model at local and regional scales in northern Europe. *Biogeosciences*, *14*(7), 1969–1984. https://doi.org/10.5194/bg-14-1969-2017

van der Tol, C., Verhoef, W., Timmermans, J., Verhoef, A., & Su, Z. (2009). An integrated model of soil-canopy spectral radiances, photosynthesis, fluorescene, temperature and

energy balance. *Biogeosciences*, *6*, 3109–3129.

Toomey, M., Friedl, M. A., Frolking, S., Hufkens, K., Klosterman, S., Sonnentag, O., … Richardson, A. D. (2015). Greenness indices from digital cameras predict the timing and seasonal dynamics of canopy-scale photosynthesis. *Ecological Applications*, *25*(1), 99–115. https://doi.org/10.1890/14-0005.1

UNFCC. (2015). United nations framework convention on climate change. *Paris, France*.

Wang, Y. P., Baldocchi, D., Leuning, R., Falge, E., & Vesala, T. (2007). Estimating parameters in a land-surface model by applying nonlinear inversion to eddy covariance flux measurements from eight FLUXNET sites. *Global Change Biology*, *13*(3), 652–670. https://doi.org/10.1111/j.1365-2486.2006.01225.x

Warren, J., Meinzer, F., Brooks, J., & Domec, J. (2005). Vertical stratification of soil water storage and release dynamics in Pacific Northwest coniferous forests. *Agricultural and Forest Meteorology*, *130*(1–2), 39–58. https://doi.org/10.1016/j.agrformet.2005.01.004

Wehr, R., & Saleska, S. R. (2015). An improved isotopic method for partitioning net ecosystem-atmosphere CO2exchange. *Agricultural and Forest Meteorology*, *214–215*, 515–531. https://doi.org/10.1016/j.agrformet.2015.09.009

Wehr, R., Munger, J. W., McManus, J. B., Nelson, D. D., Zahniser, M. S., Davidson, E. A., … Saleska, S. R. (2016). Seasonality of temperate forest photosynthesis and daytime respiration. *Nature*, *534*(7609), 680.

Wehr, R., Commane, R., Munger, J. W., Barry Mcmanus, J., Nelson, D. D., Zahniser, M. S., … Wofsy, S. C. (2017). Dynamics of canopy stomatal conductance, transpiration, and evaporation in a temperate deciduous forest, validated by carbonyl sulfide uptake. *Biogeosciences*, *14*(2), 389–401. https://doi.org/10.5194/bg-14-389-2017

Wharton, S., & Falk, M. (2016). Climate indices strongly influence old-growth forest carbon exchange. *Environmental Research Letters*, *11*(4), 1–11. https://doi.org/10.1088/1748-9326/11/4/044016

Whelan, M. E., Lennartz, S. T., Gimeno, T. E., Wehr, R., Wohlfahrt, G., Wang, Y., … Campbell, J. E. (2017). Reviews and Syntheses: Carbonyl Sulfide as a Multi-scale Tracer for Carbon and Water Cycles. *Biogeosciences Discussions*, (October), 1–97. https://doi.org/10.5194/bg-2017-427

Williams, A. P., Allen, C. D., Macalady, A. K., Griffin, D., Woodhouse, C. A., Meko, D. M., … Grissino-Mayer, H. D. (2013). Temperature as a potent driver of regional forest drought

stress and tree mortality. *Nature Climate Change*, *3*(3), 292.

Winner, W., Thomas, S., Berry, J., Bond, B., Cooper, C., Hinckley, T., … Williams, M. (2004). Canopy Carbon Gain and Water Use: Analysis of Old-growth Conifers in the Pacific Northwest. *Ecosystems*, *7*(5), 482–497. https://doi.org/10.1007/s10021-004-0139-2

Wohlfahrt, G., Brilli, F., Hörtnagl, L., Xu, X., Bingemer, H., Hansel, A., & Loreto, F. (2012). Carbonyl sulfide (COS) as a tracer for canopy photosynthesis, transpiration and stomatal conductance: Potential and limitations. *Plant, Cell and Environment*, *35*(4), 657–667. https://doi.org/10.1111/j.1365-3040.2011.02451.x

Alden, C. B., Miller, J. B., Gatti, L. V., Gloor, M. M., Guan, K., Michalak, A. M., … Diffenbaugh, N. S. (2016). Regional atmospheric CO2 inversion reveals seasonal and geographic differences in Amazon net biome exchange. *Global Change Biology*, *22*(10), 3427–3443. https://doi.org/10.1111/gcb.13305

Asaf, D., Rotenberg, E., Tatarinov, F., Dicken, U., Montzka, S. A., & Yakir, D. (2013). Ecosystem photosynthesis inferred from measurements of carbonyl sulphide flux. *Nature Geoscience*, *6*(3), 186–190. https://doi.org/10.1038/ngeo1730

Bala, G., Devaraju, N., Chaturvedi, R. K., Caldeira, K., & Nemani, R. (2013). Nitrogen deposition: How important is it for global terrestrial carbon uptake. *Biogeosciences*, *10*(11), 7147–7160. https://doi.org/10.5194/bg-10-7147-2013

Baldocchi, D. (2014). Measuring fluxes of trace gases and energy between ecosystems and the atmosphere - the state and future of the eddy covariance method. *Global Change Biology*, *20*(12), 3600–3609. https://doi.org/10.1111/gcb.12649

Baldocchi, D., Chu, H., & Reichstein, M. (2018). Inter-annual variability of net and gross ecosystem carbon fluxes: A review. *Agricultural and Forest Meteorology*, *249*(May 2017), 520–533. https://doi.org/10.1016/j.agrformet.2017.05.015

Ballantyne, A. P., Alden, C. B., Miller, J. B., Trans, P. P., & White, J. W. C. (2012). Increase in observed net carbon dioxide uptake by land and oceans during the pst 50 years. *Nature*, *488*(7409), 70–73. https://doi.org/10.1038/nature11299

Belviso, S., Reiter, I. M., Loubet, B., Gros, V., Lathière, J., Montagne, D., … Genty, B. (2016). A top-down approach of surface carbonyl sulfide exchange by a Mediterranean oak forest ecosystem in Southern France. *Atmospheric Chemistry and Physics Discussions*, (June 2012), 1–25. https://doi.org/10.5194/acp-2016-525

Berkelhammer, M., Steen-Larsen, H. C., Cosgrove, A., Peters, A. J., Johnson, R., Hayden, M., &

Montzka, S. A. (2016). Radiation and atmospheric circulation controls on carbonyl sulfide concentrations in themarine boundary layer. *Journal of Geophysical Research*, *121*(21), 13,113-13,128. https://doi.org/10.1002/2016JD025437

Berkelhammer, M., Asaf, D., Still, C., Montzka, S., Noone, D., Gupta, M., … Yakir, D. (2014). Constraining surface carbon fluxes using in situ measurements of carbonyl sulfide and carbon dioxide. *Global Biogeochemical Cycles*, *28*(2), 161–179. https://doi.org/10.1002/2013GB004644

Billesbach, D. P., Berry, J. A., Seibt, U., Maseyk, K., Torn, M. S., Fischer, M. L., … Campbell, J. E. (2014). Growing season eddy covariance measurements of carbonyl sulfide and CO2 fluxes: COS and CO2 relationships in Southern Great Plains winter wheat. *Agricultural and Forest Meteorology*, *184*, 48–55. https://doi.org/10.1016/j.agrformet.2013.06.007

Blonquist, J. M., Montzka, S. A., Munger, J. W., Yakir, D., Desai, A. R., Dragoni, D., … Bowling, D. R. (2011). The potential of carbonyl sulfide as a proxy for gross primary production at flux tower sites. *Journal of Geophysical Research: Biogeosciences*, *116*(4), 1–18. https://doi.org/10.1029/2011JG001723

Campbell, J. E., Berry, J., Seibt, U., Smith, S., Nature, S. M.-, & 2017, U. (2017). Large historical growth in global terrestrial gross primary production. *Nature.com*, *544*(7468), 84. Retrieved from https://www.nature.com/articles/nature22030

Campbell, J. E., Carmichael, G. R., Chai, T., Mena-Carrasco, M., Tang, Y., Blake, D. R., … Stanier, C. O. (2008). Photosynthetic control of atmospheric carbonyl sulfide during the growing season. *Science*, *322*(5904), 1085–1088. https://doi.org/10.1126/science.1164015

Čermák, J., Kucera, J., Bauerle, W. L., Phillips, N., & Hinckley, T. M. (2007). Tree water storage and its diurnal dynamics related to sap flow and changes in stem volume in old-growth Douglas-fir trees. *Tree Physiology*, *27*(2), 181–198. https://doi.org/10.1093/treephys/27.2.181

Ciais, P., Sabine, C., Bala, G., Bopp, L., Brovkin, V., Canadell, J., … Thornton, P. (2013). Carbon and Other Biogeochemical Cycles Chapter 6. *Climate Change 2013: The Physical Science Basis. Contribution of Working Group`I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, 465–570. https://doi.org/10.1017/CBO9781107415324.014

Commane, R., Meredith, L. K., Baker, I. T., Berry, J. A., Munger, J. W., Montzka, S. A., … Wofsy, S. C. (2015). Seasonal fluxes of carbonyl sulfide in a midlatitude forest. *Proceedings of the National Academy of Sciences*, *112*(46), 14162–14167.

https://doi.org/10.1073/pnas.1504131112

Falk, M., Wharton, S., Schroeder, M., Ustin, S. L., & Paw U, K. T. (2008). Flux partitioning in an old-growth forest: seasonal and interannual dynamics. *Tree Physiology*, *28*(4), 509–520. https://doi.org/10.1093/treephys/28.4.509

Farquhar, G. D., & Richards, R. A. (1984). Isotopic composition of plant carbon correlates water-use efficiency of wheat genotypes. *Australian Journal of Plant Physiology*, *11*(539–552).

Fessenden, J. E., & Ehleringer, J. R. (2003). Temporal variation in δ13C of ecosystem respiration in the Pacific Northwest: Links to moisture stress. *Oecologia, 136*(1), 129–136. https://doi.org/10.1007/s00442-003-1260-1

Forkel, M., Carvalhais, N., Rödenbeck, C., Keeling, R., Heimann, M., Thonicke, K., … Reichstein, M. (2016). Enhanced seasonal CO2 exchange caused by amplified plant productivity in northern ecosystems. *Science*, *351*(6274), 696 LP-699. Retrieved from http://science.sciencemag.org/content/351/6274/696.abstract

Granier, A. (1985). A new method to measure the raw sap flux in the trunk of trees. *Ann. For. Sci*, *42*, 193–200.

Gries, C., Nash, T. H., & Kesselmeier, J. (1994). Exchange of reduced sulfur gases between lichens and the atmosphere. *Biogeochemistry*, *26*(1), 25–39.

Guanter, L., Zhang, Y., Jung, M., Joiner, J., Voigt, M., Berry, J. A., … Griffis, T. J. (2014). Global and time-resolved monitoring of crop photosynthesis with chlorophyll fluorescence. *Proceedings of the National Academy of Sciences*, *111*(14), E1327–E1333. https://doi.org/10.1073/pnas.1320008111

Harmon, M., Bible, K., Ryan, M., Shaw, D., Chen, H., Klopatek, J., & Li, X. (2004). Production, Respiration, and Overall Carbon Balance in an Old-growth Pseudotsuga-Tsuga Forest Ecosystem. *Ecosystems*, 498–512. https://doi.org/10.1007/s10021-004-0140-9

HEIMANN, M., & Reichstein, M. (2008). Terrestrial ecosystem carbon dynamics and climate feedbacks. *Agriculture*, *451*(7176), 289–292. Retrieved from http://www.nature.com/nature/journal/v451/n7176/full/nature06591.html

Heinsch, F. A., Zhao, M., Running, S. W., Kimball, J. S., Nemani, R. R., Davis, K. J., … Flanagan, L. B. (2006). Evaluation of remote sensing based terrestrial productivity from MODIS using regional tower eddy flux network observations. *IEEE Transactions on Geoscience and Remote Sensing*, *44*(7), 1908–1923.

https://doi.org/10.1109/TGRS.2005.853936

Hilton, T., Whelan, M., Zumkehr, A., … S. K.-N. C., & 2017, U. (2017). Peak growing season gross uptake of carbon in North America is largest in the Midwest USA. *Nature.com*, *7*(6), 450. Retrieved from https://www.nature.com/articles/nclimate3272

Huntzinger, D. N., Michalak, A. M., Schwalm, C., Ciais, P., King, A. W., Fang, Y., … Zhao, F. (2017). Uncertainty in the response of terrestrial carbon sink to environmental drivers undermines carbon-climate feedback predictions. *Scientific Reports*, *7*(1), 1–8. https://doi.org/10.1038/s41598-017-03818-2

IPCC. (2014). *Climate Change 2013. the Fifth Assessment Report* (Vol. 5).

Keeling, R. F., Graven, H. D., Welp, L. R., Resplandy, L., Bi, J., Piper, S. C., … Meijer, H. A. J. (2017). Atmospheric evidence for a global secular increase in carbon isotopic discrimination of land photosynthesis. *Proceedings of the National Academy of Sciences*, 201619240. https://doi.org/10.1073/pnas.1619240114

Keenan, T. F., Hollinger, D. Y., Bohrer, G., Dragoni, D., Munger, J. W., Schmid, H. P., & Richardson, A. D. (2013). Increase in forest water-use efficiency as atmospheric carbon dioxide concentrations rise. *Nature*, *499*(7458), 324–327. https://doi.org/10.1038/nature12291

Keenan, T. F., Gray, J., Friedl, M. A., Toomey, M., Bohrer, G., Hollinger, D. Y., … Richardson, A. D. (2014). Net carbon uptake has increased through warming-induced changes in temperate forest phenology. *Nature Climate Change*, *4*(7), 598–604. https://doi.org/10.1038/nclimate2253

Kettle, A. J., Kuhn, U., Von Hobe, M., Kesselmeier, J., & Andreae, M. O. (2002). Global budget of atmospheric carbonyl sulfide: Temporal and spatial variations of the dominant sources and sinks. *Journal of Geophysical Research: Atmospheres*, *107*(D22).

Klein, T., Rotenberg, E., Tatarinov, F., & Yakir, D. (2016). Association between sap flow-derived and eddy covariance-derived measurements of forest canopy CO2 uptake. *New Phytologist*, *209*(1), 436–446. https://doi.org/10.1111/nph.13597

Knox, S. H., Dronova, I., Sturtevant, C., Oikawa, P. Y., Matthes, J. H., Verfaillie, J., & Baldocchi, D. (2017). Using digital camera and Landsat imagery with eddy covariance data to model gross primary production in restored wetlands. *Agricultural and Forest Meteorology*, *237–238*, 233–245. https://doi.org/10.1016/j.agrformet.2017.02.020

Kooijmans, L. M. J. J., Maseyk, K., Seibt, U., Sun, W., Vesala, T., Mammarella, I., … Chen, H.

(2017). Canopy uptake dominates nighttime carbonyl sulfide fluxes in a boreal forest. *Atmospheric Chemistry and Physics*, *17*(18), 11453–11465. https://doi.org/10.5194/acp-17-11453-2017

Kuhn, U., & Kesselmeier, J. (2000). Environmental variables controlling the uptake of carbonyl sulfide by lichens. *Journal of Geophysical Research: Atmospheres*, *105*(D22), 26783–26792.

Kuhn, U., Wolf, A., Gries, C., Nash III, T. H., & Kesselmeier, J. (2000). Field measurements on the exchange of carbonyl sulfide between lichens and the atmosphere. *Atmospheric Environment*, *34*(28), 4867–4878.

LAI, C., Ehleringer, J. R., & Bond, B. J. (2006). Contributions of evaporation, isotopic non-steady state transpiration and atmospheric mixing on the δ18O of water vapour in Pacific Northwest coniferous forests. *Plant, Cell & Environment*, *29*(1), 77–94.

Lasslop, G., Reichstein, M., Papale, D., Richardson, A., Arneth, A., Barr, A., … Wohlfahrt, G. (2010). Separation of net ecosystem exchange into assimilation and respiration using a light response curve approach: Critical issues and global evaluation. *Global Change Biology*, *16*(1), 187–208. https://doi.org/10.1111/j.1365-2486.2009.02041.x

Launois, T., Peylin, P., Belviso, S., & Poulter, B. (2015). A new model of the global biogeochemical cycle of carbonyl sulfide - Part 2: Use of carbonyl sulfide to constrain gross primary productivity in current vegetation models. *Atmospheric Chemistry and Physics*, *15*(16), 9285–9312. https://doi.org/10.5194/acp-15-9285-2015

Li, W., Ciais, P., Wang, Y., Yin, Y., Peng, S., Zhu, Z., … Piao, S. (2018). Recent Changes in Global Photosynthesis and Terrestrial Ecosystem Respiration Constrained From Multiple Observations. *Geophysical Research Letters*, 1058–1068. https://doi.org/10.1002/2017GL076622

Lloyd, J., & Taylor, J. A. (1994). On the Temperature Dependence of Soil Respiration. *Functional Ecology*, *8*(3), 315–323.

Luyssaert, S., Schulze, E.-D., Börner, A., Knohl, A., Hessenmöller, D., Law, B. E., … Grace, J. (2008). Old-growth forests as global carbon sinks. *Nature*, *455*(7210), 213.

Maseyk, K., Berry, J. A., Billesbach, D., Campbell, J. E., Torn, M. S., Zahniser, M., & Seibt, U. (2014). Sources and sinks of carbonyl sulfide in an agricultural field in the Southern Great Plains. *Proceedings of the National Academy of Sciences*, *111*(25), 9064–9069. https://doi.org/10.1073/pnas.1319132111

McCune, B., Amsberry, K. A., Camacho, F. J., Clery, S., Cole, C., Emerson, C., … Widmer, M. (1997). Vertical profile of epiphytes in a Pacific Northwest old-growth forest. *Northwest Science*, *71*(2), 145–152. Retrieved from d:%5CArtiklar%5CMcCune et al 1997.pdf

MEINZER, F. C., ANDRADE, J. L., GOLDSTEIN, G., HOLBROOK, N. M., CAVELIER, J., & JACKSON, P. (1997). Control of transpiration from the upper canopy of a tropical forest: the role of stomatal, boundary layer and hydraulic architecture components. *Plant, Cell and Environment*, *20*(10), 1242–1252. https://doi.org/10.1046/j.1365-3040.1997.d01-26.x

Meinzer, F. C., Brooks, J. R., Domec, J., Gartner, B. L., Warren, J. M., Woodruff, D. R., … Sarg, R. (2006). Dynamics of water transport and storage in conifers studied, 105–114.

Meinzer, F. C., Woodruff, D. R., & Shaw, D. C. (2004). Integrated responses of hydraulic architecture, water and carbon relations of western hemlock to dwarf mistletoe infection. *Plant, Cell and Environment*, *27*(7), 937–946. https://doi.org/10.1111/j.1365-3040.2004.01199.x

Miao, G., Guan, K., Yang, X., Bernacchi, C. J., Berry, J. A., DeLucia, E. H., … Masters, M. D. (2018a). Sun-Induced Chlorophyll Fluorescence, Photosynthesis, and Light Use Efficiency of a Soybean Field. *Journal of Geophysical Research: Biogeosciences*. https://doi.org/10.1002/2017JG004180

Miao, G., Guan, K., Yang, X., Bernacchi, C. J., Berry, J. A., DeLucia, E. H., … Masters, M. D. (2018b). Sun-Induced Chlorophyll Fluorescence, Photosynthesis, and Light Use Efficiency of a Soybean Field. *Journal of Geophysical Research: Biogeosciences*, 610–623. https://doi.org/10.1002/2017JG004180

Montzka, S. A., Calvert, P., Hall, B. D., Elkins, J. W., Conway, T. J., Tans, P. P., & Sweeney, C. S. (2007). On the global distribution, seasonality, and budget of atmospheric carbonyl sulfide (COS) and some similarities to CO_2. *Journal of Geophysical Research Atmospheres*, *112*(9), 1–15. https://doi.org/10.1029/2006JD007665

Novick, K. A., Ficklin, D. L., Stoy, P. C., Williams, C. A., Bohrer, G., Oishi, A. C., … Phillips, R. P. (2016). The increasing importance of atmospheric demand for ecosystem water and carbon fluxes. *Nature Climate Change*, *6*(11), 1023–1027. https://doi.org/10.1038/nclimate3114

Novick, K. A., Biederman, J. A., Desai, A. R., Litvak, M. E., Moore, D. J. P., Scott, R. L., & Torn, M. S. (2018). The AmeriFlux network: A coalition of the willing. *Agricultural and Forest Meteorology*, *249*(May), 444–456. https://doi.org/10.1016/j.agrformet.2017.10.009

Oikawa, P. Y., Sturtevant, C., Knox, S. H., Verfaillie, J., Huang, Y. W., & Baldocchi, D. D. (2017a). Revisiting the partitioning of net ecosystem exchange of CO2 into photosynthesis and respiration with simultaneous flux measurements of 13CO2 and CO2, soil respiration and a biophysical model, CANVEG. *Agricultural and Forest Meteorology, 234–235*, 149–163. https://doi.org/10.1016/j.agrformet.2016.12.016

Oikawa, P. Y., Sturtevant, C., Knox, S. H., Verfaillie, J., Huang, Y. W., & Baldocchi, D. D. (2017b). Revisiting the partitioning of net ecosystem exchange of CO2into photosynthesis and respiration with simultaneous flux measurements of13CO2and CO2, soil respiration and a biophysical model, CANVEG. *Agricultural and Forest Meteorology, 234–235*, 149–163. https://doi.org/10.1016/j.agrformet.2016.12.016

Parker, G. G. (1997). Canopy structure and light environment of an old growth Douglas-fir/Western hemlock forest. *Northwest Science, 71*(4), 261–271.

Parker, G. G., Harmon, M. E., Lefsky, M. A., Chen, J., Pelt, R. Van, Weis, S. B., … Frankling, J. F. (2004). Three-dimensional Structure of an Old-growth Pseudotsuga-Tsuga Canopy and Its Implications for Radiation Balance, Microclimate, and Gas Exchange. *Ecosystems, 7*(5), 440–453. https://doi.org/10.1007/s10021-004-0136-5

Paw U, K. T., Falk, M., Suchanek, T. H., Ustin, S. L., Chen, J., Park, Y.-S., … Matista, A. A. (2004). Carbon Dioxide Exchange between an Old-Growth Forest and the Atmosphere. *Ecosystems, 7*(5), 513–524. https://doi.org/10.1007/s10021-004-0141-8

Phillips, N., Bond, B. J., McDowell, N. G., & Ryan, M. G. (2002). Canopy and hydraulic conductance in young, mature and old Douglas-fir trees. *Tree Physiology, 22*(2–3), 205–211. https://doi.org/10.1093/treephys/22.2-3.205

Protoschill-Krebs, G Wilhelm, C Kesselmeier, J. (1996). Consumption of carbonyl sulphide (COS) by higher plant carbonic anhydrase (CA). *Atmospheric Environment, 30*(18), 3151–3156. Retrieved from https://www.sciencedirect.com/science/article/pii/135223109600026X

Le Quéré, C., Raupach, M. R., Canadell, J. G., Marland, G., Bopp, L., Ciais, P., … Woodward, F. I. (2009). Trends in the sources and sinks of carbon dioxide. *Nature Geoscience, 2*(12), 831–836. https://doi.org/10.1038/ngeo689

Le Quéré, C., Andrew, R. M., Friedlingstein, P., Sitch, S., Pongratz, J., Manning, A. C., … Zhu, D. (2018). Global Carbon Budget 2017. *Earth Syst. Sci. Data Etsushi Kato Markus Kautz Ralph F. Keeling Kees Klein Goldewijk Nathalie Lefèvre Andrew Lenton Danica Lombardozzi Nicolas Metzl Yukihiro Nojiri Antonio Padin Janet Reimer, 1010333739*(10),

405–448. https://doi.org/10.5194/essd-10-405-2018

Reichstein, M., Falge, E., Baldocchi, D., Papale, D., Aubinet, M., Berbigier, P., … Granier, A. (2005). On the separation of net ecosystem exchange into assimilation and ecosystem respiration: review and improved algorithm. *Global Change Biology*, *11*(9), 1424–1439.

Rossini, M., Meroni, M., Migliavacca, M., Manca, G., Cogliati, S., Busetto, L., … Colombo, R. (2010). High resolution field spectroscopy measurements for estimating gross ecosystem production in a rice field. *Agricultural and Forest Meteorology*, *150*(9), 1283–1296. https://doi.org/10.1016/j.agrformet.2010.05.011

Schimel, D., Stephens, B. B., & Fisher, J. B. (2015). Effect of increasing CO_2 on the terrestrial carbon cycle. *Proceedings of the National Academy of Sciences*, *112*(2), 436–441. https://doi.org/10.1073/pnas.1407302112

Schuh, A. E., Denning, A. S., Corbin, K. D., Baker, I. T., Uliasz, M., Parazoo, N., … Worthy, D. E. J. (2010). A regional high-resolution carbon flux inversion of North America for 2004. *Biogeosciences*, *7*(5), 1625–1644. https://doi.org/10.5194/bg-7-1625-2010

Seibt, U., Rajabi, A., Griffiths, H., & Berry, J. A. (2008). Carbon isotopes and water use efficiency: Sense and sensitivity. *Oecologia*, *155*(3), 441–454. https://doi.org/10.1007/s00442-007-0932-7

Seibt, U., Kesselmeier, J., Sandoval-Soto, L., Kuhn, U., & Berry, J. A. (2010). A kinetic analysis of leaf uptake of COS and its relation to transpiration, photosynthesis and carbon isotope fractionation. *Biogeosciences*, *7*(1), 333–341. https://doi.org/10.5194/bg-7-333-2010

Shaw, D. C., Chen, J., Freeman, E. a, & Braun, D. M. (2005). Spatial and population characteristics of dwarf mistletoe infected trees in an old-growth Douglas-fir western hemlock forest. *Canadian Journal of Forest Research*, *35*(4), 990–1001. https://doi.org/10.1139/x05-022

Shaw, D., Franklin, J., Bible, K., Klopatek, J., Freeman, E., Greene, S., & Parker, G. (2004). Ecological Setting of the Wind River Old-growth Forest. *Ecosystems*, *7*(5), 427–439. https://doi.org/10.1007/s10021-004-0135-6

Sjöström, M., Zhao, M., Archibald, S., Arneth, A., Cappelaere, B., Falk, U., … Kutsch, W. (2013). Evaluation of MODIS gross primary productivity for Africa using eddy covariance data. *Remote Sensing of Environment*, *131*, 275–286.

Stimler, K., Nelson, D., & Yakir, D. (2010). High precision measurements of atmospheric concentrations and plant exchange rates of carbonyl sulfide using mid-IR quantum cascade

laser. *Global Change Biology*, *16*(9), 2496–2503. https://doi.org/10.1111/j.1365-2486.2009.02088.x

Stimler, K., Montzka, S. A., Berry, J. A., Rudich, Y., & Yakir, D. (2010). Relationships between carbonyl sulfide (COS) and CO2 during leaf gas exchange. *New Phytologist*, *186*(4), 869–878. https://doi.org/10.1111/j.1469-8137.2010.03218.x

Thum, T., Zaehle, S., Köhler, P., Aalto, T., Aurela, M., Guanter, L., … Markkanen, T. (2017). Modelling sun-induced fluorescence and photosynthesis with a land surface model at local and regional scales in northern Europe. *Biogeosciences*, *14*(7), 1969–1984. https://doi.org/10.5194/bg-14-1969-2017

van der Tol, C., Verhoef, W., Timmermans, J., Verhoef, A., & Su, Z. (2009). An integrated model of soil-canopy spectral radiances, photosynthesis, fluorescene, temperature and energy balance. *Biogeosciences*, *6*, 3109–3129.

Toomey, M., Friedl, M. A., Frolking, S., Hufkens, K., Klosterman, S., Sonnentag, O., … Richardson, A. D. (2015). Greenness indices from digital cameras predict the timing and seasonal dynamics of canopy-scale photosynthesis. *Ecological Applications*, *25*(1), 99–115. https://doi.org/10.1890/14-0005.1

UNFCC. (2015). United nations framework convention on climate change. *Paris, France*.

Wang, Y. P., Baldocchi, D., Leuning, R., Falge, E., & Vesala, T. (2007). Estimating parameters in a land-surface model by applying nonlinear inversion to eddy covariance flux measurements from eight FLUXNET sites. *Global Change Biology*, *13*(3), 652–670. https://doi.org/10.1111/j.1365-2486.2006.01225.x

Warren, J., Meinzer, F., Brooks, J., & Domec, J. (2005). Vertical stratification of soil water storage and release dynamics in Pacific Northwest coniferous forests. *Agricultural and Forest Meteorology*, *130*(1–2), 39–58. https://doi.org/10.1016/j.agrformet.2005.01.004

Wehr, R., & Saleska, S. R. (2015). An improved isotopic method for partitioning net ecosystem-atmosphere CO2exchange. *Agricultural and Forest Meteorology*, *214–215*, 515–531. https://doi.org/10.1016/j.agrformet.2015.09.009

Wehr, R., Munger, J. W., McManus, J. B., Nelson, D. D., Zahniser, M. S., Davidson, E. A., … Saleska, S. R. (2016). Seasonality of temperate forest photosynthesis and daytime respiration. *Nature*, *534*(7609), 680.

Wehr, R., Commane, R., Munger, J. W., Barry Mcmanus, J., Nelson, D. D., Zahniser, M. S., … Wofsy, S. C. (2017). Dynamics of canopy stomatal conductance, transpiration, and

evaporation in a temperate deciduous forest, validated by carbonyl sulfide uptake. *Biogeosciences*, *14*(2), 389–401. https://doi.org/10.5194/bg-14-389-2017

Wharton, S., & Falk, M. (2016). Climate indices strongly influence old-growth forest carbon exchange. *Environmental Research Letters*, *11*(4), 1–11. https://doi.org/10.1088/1748-9326/11/4/044016

Whelan, M. E., Lennartz, S. T., Gimeno, T. E., Wehr, R., Wohlfahrt, G., Wang, Y., … Campbell, J. E. (2017). Reviews and Syntheses: Carbonyl Sulfide as a Multi-scale Tracer for Carbon and Water Cycles. *Biogeosciences Discussions*, (October), 1–97. https://doi.org/10.5194/bg-2017-427

Williams, A. P., Allen, C. D., Macalady, A. K., Griffin, D., Woodhouse, C. A., Meko, D. M., … Grissino-Mayer, H. D. (2013). Temperature as a potent driver of regional forest drought stress and tree mortality. *Nature Climate Change*, *3*(3), 292.

Winner, W., Thomas, S., Berry, J., Bond, B., Cooper, C., Hinckley, T., … Williams, M. (2004). Canopy Carbon Gain and Water Use: Analysis of Old-growth Conifers in the Pacific Northwest. *Ecosystems*, *7*(5), 482–497. https://doi.org/10.1007/s10021-004-0139-2

Wohlfahrt, G., Brilli, F., Hörtnagl, L., Xu, X., Bingemer, H., Hansel, A., & Loreto, F. (2012). Carbonyl sulfide (COS) as a tracer for canopy photosynthesis, transpiration and stomatal conductance: Potential and limitations. *Plant, Cell and Environment*, *35*(4), 657–667. https://doi.org/10.1111/j.1365-3040.2011.02451.x

Alden CB, Miller JB, Gatti L V., Gloor MM, Guan K, Michalak AM, van der Laan-Luijkx IT, Touma D, Andrews A, Basso LS, *et al.* 2016. Regional atmospheric CO2 inversion reveals seasonal and geographic differences in Amazon net biome exchange. *Global change biology* 22: 3427–3443.

Asaf D, Rotenberg E, Tatarinov F, Dicken U, Montzka SA, Yakir D. 2013. Ecosystem photosynthesis inferred from measurements of carbonyl sulphide flux. *Nature Geoscience* 6: 186–190.

Baldocchi D. 2014. Measuring fluxes of trace gases and energy between ecosystems and the atmosphere - the state and future of the eddy covariance method. *Global Change Biology* 20: 3600–3609.

Baldocchi D, Chu H, Reichstein M. 2018. Inter-annual variability of net and gross ecosystem carbon fluxes: A review. *Agricultural and Forest Meteorology* 249: 520–533.

Berkelhammer M, Steen-Larsen HC, Cosgrove A, Peters AJ, Johnson R, Hayden M, Montzka SA. 2016. Radiation and atmospheric circulation controls on carbonyl sulfide concentrations in themarine boundary layer. *Journal of Geophysical Research* 121: 13,113-13,128.

Čermák J, Kucera J, Bauerle WL, Phillips N, Hinckley TM. 2007. Tree water storage and its diurnal dynamics related to sap flow and changes in stem volume in old-growth Douglas-fir trees. *Tree Physiology* 27: 181–198.

Commane R, Meredith LK, Baker IT, Berry JA, Munger JW, Montzka SA, Templer PH, Juice SM, Zahniser MS, Wofsy SC. 2015. Seasonal fluxes of carbonyl sulfide in a midlatitude forest. *Proceedings of the National Academy of Sciences* 112: 14162–14167.

Falk M, Wharton S, Schroeder M, Ustin SL, Paw U KT. 2008. Flux partitioning in an old-growth forest: seasonal and interannual dynamics. *Tree physiology* 28: 509–520.

Farquhar GD, Richards RA. 1984. Isotopic composition of plant carbon correlates water-use efficiency of wheat genotypes. *Australian Journal of Plant Physiology* 11.

Fessenden JE, Ehleringer JR. 2003. Temporal variation in δ13C of ecosystem respiration in the Pacific Northwest: Links to moisture stress. *Oecologia* 136: 129–136.

Forkel M, Carvalhais N, Rödenbeck C, Keeling R, Heimann M, Thonicke K, Zaehle S, Reichstein M. 2016. Enhanced seasonal CO2 exchange caused by amplified plant productivity in northern ecosystems. *Science* 351: 696 LP-699.

Granier A. 1985. A new method to measure the raw sap flux in the trunk of trees. *Ann. For. Sci* 42: 193–200.

Guanter L, Zhang Y, Jung M, Joiner J, Voigt M, Berry JA, Frankenberg C, Huete AR, Zarco-Tejada P, Lee J-E, *et al.* 2014. Global and time-resolved monitoring of crop photosynthesis with chlorophyll fluorescence. *Proceedings of the National Academy of Sciences* 111: E1327–E1333.

Harmon M, Bible K, Ryan M, Shaw D, Chen H, Klopatek J, Li X. 2004. Production, Respiration, and Overall Carbon Balance in an Old-growth Pseudotsuga-Tsuga Forest Ecosystem. *Ecosystems*: 498–512.

Heimann M, Reichstein M. 2008. Terrestrial ecosystem carbon dynamics and climate feedbacks. *Agriculture* 451: 289–292.

Heinsch FA, Zhao M, Running SW, Kimball JS, Nemani RR, Davis KJ, Bolstad P V., Cook BD, Desai AR, Ricciuto DM, *et al.* 2006. Evaluation of remote sensing based terrestrial productivity from MODIS using regional tower eddy flux network observations. *IEEE Transactions on Geoscience and Remote Sensing* 44: 1908–1923.

Huntzinger DN, Michalak AM, Schwalm C, Ciais P, King AW, Fang Y, Schaefer K, Wei Y, Cook RB, Fisher JB, *et al.* 2017. Uncertainty in the response of terrestrial carbon sink to environmental drivers undermines carbon-climate feedback predictions. *Scientific Reports* 7: 1–8.

Keenan TF, Gray J, Friedl MA, Toomey M, Bohrer G, Hollinger DY, Munger JW, O'Keefe J, Schmid HP, Wing IS, *et al.* 2014. Net carbon uptake has increased through warming-induced changes in temperate forest phenology. *Nature Climate Change* 4: 598–604.

Keenan TF, Hollinger DY, Bohrer G, Dragoni D, Munger JW, Schmid HP, Richardson AD. 2013. Increase in forest water-use efficiency as atmospheric carbon dioxide concentrations rise. *Nature* 499: 324–327.

Klein T, Rotenberg E, Tatarinov F, Yakir D. 2016. Association between sap flow-derived and eddy covariance-derived measurements of forest canopy CO2 uptake. *New Phytologist* 209: 436–446.

Knox SH, Dronova I, Sturtevant C, Oikawa PY, Matthes JH, Verfaillie J, Baldocchi D. 2017. Using digital camera and Landsat imagery with eddy covariance data to model gross primary production in restored wetlands. *Agricultural and Forest Meteorology* 237–238: 233–245.

Kooijmans LMJJ, Maseyk K, Seibt U, Sun W, Vesala T, Mammarella I, Kolari P, Aalto J, Franchin A, Vecchi R, *et al.* 2017. Canopy uptake dominates nighttime carbonyl sulfide fluxes in a boreal forest. *Atmospheric Chemistry and Physics* 17: 11453–11465.

Lai C, Ehleringer JR, Bond BJ. 2006. Contributions of evaporation, isotopic non-steady state transpiration and atmospheric mixing on the δ18O of water vapor in Pacific Northwest coniferous forests. *Plant, Cell & Environment* 29: 77–94.

Lasslop G, Reichstein M, Papale D, Richardson A, Arneth A, Barr A, Stoy P, Wohlfahrt G. 2010. Separation of net ecosystem exchange into assimilation and respiration using a light response curve approach: Critical issues and global evaluation. *Global Change Biology* 16: 187–208.

Li W, Ciais P, Wang Y, Yin Y, Peng S, Zhu Z, Bastos A, Yue C, Ballantyne AP, Broquet G, *et al.* 2018. Recent Changes in Global Photosynthesis and Terrestrial Ecosystem Respiration Constrained From Multiple Observations. *Geophysical Research Letters*: 1058–1068.

Lloyd J, Taylor JA. 1994. On the Temperature Dependence of Soil Respiration. *Functional Ecology* 8: 315–323.

Maseyk K, Berry JA, Billesbach D, Campbell JE, Torn MS, Zahniser M, Seibt U. 2014. Sources and sinks of carbonyl sulfide in an agricultural field in the Southern Great Plains. *Proceedings of the National Academy of Sciences* 111: 9064–9069.

McCune B, Amsberry KA, Camacho FJ, Clery S, Cole C, Emerson C, Felder G, French P, Greene D, Harris R, *et al.* 1997. Vertical profile of epiphytes in a Pacific Northwest old-growth forest. *Northwest Science* 71: 145–152.

Meinzer FC, Andrade JL, Goldstein G, Holbrook NM, Cavelier J, Jackson P. 1997. Control of transpiration from the upper canopy of a tropical forest: the role of stomatal, boundary layer and hydraulic architecture components. *Plant, Cell and Environment* 20: 1242–1252.

Meinzer FC, Brooks JR, Domec J, Gartner BL, Warren JM, Woodruff DR, Bible K, Shaw, DC. 2006. Dynamics of water transport and storage in conifers studied with deuterium and heat tracing techniques. *Plant, Cell and Environment* 29: 105–114.

Meinzer FC, Woodruff DR, Shaw DC. 2004. Integrated responses of hydraulic architecture, water and carbon relations of western hemlock to dwarf mistletoe infection. *Plant, Cell and Environment* 27: 937–946.

Miao G, Guan K, Yang X, Bernacchi CJ, Berry JA, DeLucia EH, Wu J, Moore CE, Meacham K, Cai Y, *et al.* 2018a. Sun-Induced Chlorophyll Fluorescence, Photosynthesis, and Light Use Efficiency of a Soybean Field. *Journal of Geophysical Research: Biogeosciences*.

Miao G, Guan K, Yang X, Bernacchi CJ, Berry JA, DeLucia EH, Wu J, Moore CE, Meacham K, Cai Y, *et al.* 2018b. Sun-Induced Chlorophyll Fluorescence, Photosynthesis, and Light Use Efficiency of a Soybean Field. *Journal of Geophysical Research: Biogeosciences*: 610–623.

Novick KA, Biederman JA, Desai AR, Litvak ME, Moore DJP, Scott RL, Torn MS. 2018. The AmeriFlux network: A coalition of the willing. *Agricultural and Forest Meteorology* 249: 444–456.

Novick KA, Ficklin DL, Stoy PC, Williams CA, Bohrer G, Oishi AC, Papuga SA, Blanken PD, Noormets A, Sulman BN, *et al.* 2016. The increasing importance of atmospheric demand for ecosystem water and carbon fluxes. *Nature Climate Change* 6: 1023–1027.

Oikawa PY, Sturtevant C, Knox SH, Verfaillie J, Huang YW, Baldocchi DD. 2017a. Revisiting the partitioning of net ecosystem exchange of CO2 into photosynthesis and respiration with simultaneous flux measurements of 13CO2 and CO2, soil respiration and a biophysical model, CANVEG. *Agricultural and Forest Meteorology* 234–235: 149–163.

Parker GG. 1997. Canopy structure and light environment of an old growth Douglas-fir/Western hemlock forest. *Northwest Science* 71: 261–271.

Parker GG, Harmon ME, Lefsky MA, Chen J, Pelt R Van, Weis SB, Thomas SC, Winner WE, Shaw DC, Frankling JF. 2004. Three-dimensional Structure of an Old-growth Pseudotsuga-Tsuga Canopy and Its Implications for Radiation Balance, Microclimate, and Gas Exchange. *Ecosystems* 7: 440–453.

Paw U KT, Falk M, Suchanek TH, Ustin SL, Chen J, Park Y-S, Winner WE, Thomas SC, Hsiao TC, Shaw RH, *et al.* 2004. Carbon Dioxide Exchange between an Old-Growth Forest and the Atmosphere. *Ecosystems* 7: 513–524.

Phillips N, Bond BJ, McDowell NG, Ryan MG. 2002. Canopy and hydraulic conductance in young, mature and old Douglas-fir trees. *Tree physiology* 22: 205–211.

Protoschill-Krebs, G Wilhelm, C Kesselmeier J. 1996. Consumption of carbonyl sulphide (COS) by higher plant carbonic anhydrase (CA). *Atmospheric Environment* 30: 3151–3156.

Reichstein M, Falge E, Baldocchi D, Papale D, Aubinet M, Berbigier P, Bernhofer C, Buchmann N, Gilmanov T, Granier A. 2005. On the separation of net ecosystem exchange into assimilation and ecosystem respiration: review and improved algorithm. *Global Change Biology* 11: 1424–1439.

Rossini M, Meroni M, Migliavacca M, Manca G, Cogliati S, Busetto L, Picchi V, Cescatti A, Seufert G, Colombo R. 2010. High resolution field spectroscopy measurements for estimating gross ecosystem production in a rice field. *Agricultural and Forest Meteorology* 150: 1283–1296.

Schuh AE, Denning AS, Corbin KD, Baker IT, Uliasz M, Parazoo N, Andrews AE, Worthy DEJ. 2010. A regional high-resolution carbon flux inversion of North America for 2004. *Biogeosciences* 7: 1625–1644.

Seibt U, Kesselmeier J, Sandoval-Soto L, Kuhn U, Berry JA. 2010. A kinetic analysis of leaf uptake of COS and its relation to transpiration, photosynthesis and carbon isotope fractionation. *Biogeosciences* 7: 333–341.

Seibt U, Rajabi A, Griffiths H, Berry JA. 2008. Carbon isotopes and water use efficiency: Sense and sensitivity. *Oecologia* 155: 441–454.

Shaw DC, Chen J, Freeman E a, Braun DM. 2005. Spatial and population characteristics of dwarf mistletoe infected trees in an old-growth Douglas-fir western hemlock forest. *Canadian Journal of Forest Research* 35: 990–1001.

Shaw D, Franklin J, Bible K, Klopatek J, Freeman E, Greene S, Parker G. 2004. Ecological Setting of the Wind River Old-growth Forest. *Ecosystems* 7: 427–439.

Sjöström M, Zhao M, Archibald S, Arneth A, Cappelaere B, Falk U, De Grandcourt A, Hanan N, Kergoat L, Kutsch W. 2013. Evaluation of MODIS gross primary productivity for Africa using eddy covariance data. *Remote sensing of environment* 131: 275–286.

van der Tol C, Verhoef W, Timmermans J, Verhoef A, Su Z. 2009. An integrated model of soil-canopy spectral radiances, photosynthesis, fluorescene, temperature and energy balance. *Biogeosciences* 6: 3109–3129.

Toomey M, Friedl MA, Frolking S, Hufkens K, Klosterman S, Sonnentag O, Baldocchi DD, Bernacchi CJ, Biraud SC, Bohrer G, *et al.* 2015. Greenness indices from digital cameras predict the timing and seasonal dynamics of canopy-scale photosynthesis. *Ecological Applications* 25: 99–115.

Wang YP, Baldocchi D, Leuning R, Falge E, Vesala T. 2007. Estimating parameters in a land-surface model by applying nonlinear inversion to eddy covariance flux measurements from eight FLUXNET sites. *Global Change Biology* 13: 652–670.

Warren JM, Meinzer FC, Brooks JR, Domec JC. 2005. Vertical stratification of soil water storage and release dynamics in Pacific Northwest coniferous forests. *Agricultural and Forest Meteorology* 130: 39–58.

Wehr R, Munger JW, McManus JB, Nelson DD, Zahniser MS, Davidson EA, Wofsy SC, Saleska SR. 2016. Seasonality of temperate forest photosynthesis and daytime respiration. *Nature* 534: 680.

Wehr R, Saleska SR. 2015. An improved isotopic method for partitioning net ecosystem-atmosphere CO2exchange. *Agricultural and Forest Meteorology* 214–215: 515–531.

Wharton S, Falk M. 2016. Climate indices strongly influence old-growth forest carbon exchange. *Environmental Research Letters* 11: 1–11.

Whelan ME, Lennartz ST, Gimeno TE, Wehr R, Wohlfahrt G, Wang Y, Kooijmans LMJ, Hilton TW, Belviso S, Peylin P, *et al.* 2017. Reviews and Syntheses: Carbonyl Sulfide as a Multi-scale Tracer for Carbon and Water Cycles. *Biogeosciences Discussions*: 1–97.

Winner W, Thomas S, Berry J, Bond B, Cooper C, Hinckley T, Ehleringer J, Fessenden J, Lamb B, McCarthy S, *et al.* 2004. Canopy Carbon Gain and Water Use: Analysis of Old-growth Conifers in the Pacific Northwest. *Ecosystems* 7: 482–497.

Wohlfahrt G, Brilli F, Hörtnagl L, Xu X, Bingemer H, Hansel A, Loreto F. 2012. Carbonyl sulfide (COS) as a tracer for canopy photosynthesis, transpiration and stomatal conductance: Potential and limitations. *Plant, Cell and Environment* 35: 657–667.

5   CONCLUSIONS

An increase in anthropogenic activities since the industrial revolution, primarily due to burning of fossil fuels and changes in land cover, has resulted in a steady increase in the global mean atmospheric CO_2 concentrations (Ciais et al., 2013).

While there is unequivocal scientific evidence on global warming and its multidimensional impacts on natural and human systems (IPCC, 2014), uncertainties on the magnitude of future warming persist, propagating from uncertainties in the response of terrestrial plants to changing climates .

The vegetated terrestrial surface plays a critical role in global carbon cycling, and annual variability in CO_2 removal from the atmosphere is highly dependent on the strength of the terrestrial carbon sink (Heimann & Reichstein, 2008). However, despite large advances in measurement and modeling techniques and increased spatio-temporal measurements of CO_2 concentrations, carbon-climate coupled model intercomparison efforts still fail to converge on even the sign of the shift in the cumulative land sink in response to recent global warming (Huntzinger et al., 2017). This is in part, due to our inability to directly measure photosynthesis beyond the leaf level.

Measurements of carbonyl sulfide OCS have recently been shown to provide an independent and direct estimate of plant productivity (Blonquist et al., 2011; Campbell et al., 2008; Whelan et al., 2017 and references therein). OCS is the most abundant reduced sulfur gas present in the atmosphere, with a mean atmospheric concentration of ~ 500 ppt (parts per trillion; (Montzka et al., 2007) and is emitted into the atmosphere from oceans via direct emissions or oxidation of CS_2 (Kettle et al., 2002), and taken up by leaves of actively photosynthesizing plants.

The overall focus of this dissertation was to further assess OCS as a proxy for ecosystem-scale stomatal conductance and photosynthesis in a temperate old-growth coniferous forest.

This dissertation was composed of three studies conducted at the Wind River Experimental forest located within the Gifford Pinchot National Forest in southwest Washington state, USA (45°49′13.76′′ N; 121°57′06.88′′ W; 371 m above sea level).

5.1 Summary of Chapter 2:

The objective of this study was to ascertain biotic and abiotic constraints on canopy-atmosphere exchange of carbonyl sulfide. We collected continuous in-situ measurements of OCS mixing ratios in ambient air at various heights in the canopy. OCS decreased with height throughout the canopy, but mixing ratios at all heights showed an increase between mid-morning and afternoon. We were unable to identify any within-canopy or surface sources of OCS, except for very small emissions from dormant epiphytes. Using a mass balance approach, we inferred a strong entrainment signal driving daytime increase in concentrations. Entrainment replenished the canopy air with OCS that was taken up by various parts of the ecosystem at nighttime (incomplete stomatal closure and uptake by epiphytes). Moreover, this approach can provide a method of disentangling biotic and abiotic fluxes of OCS that influence concentration profiles within vegetated canopies. We found that epiphytic material was a moisture dependent sink of OCS in the dark. While previous studies have characterized the role of lichen in OCS exchange, this is the first study that shows that epiphytes may be an important control on OCS exchange in a moist forested canopy. However, questions remain regarding constraints on CA-catalyzed OCS consumption by epiphytes.

5.2 Summary of chapter 3

The objective of this study was to predict OCS fluxes (F_{OCS}) from measurements of its mixing ratios, and to compare OCS fluxes with collocated and independent measurements of CO_2 fluxes. Over hourly and seasonal timescales, estimates of F_{OCS} generally tracked fluctuations in ecosystem-scale photosynthesis or GPP inferred from eddy covariance measurements, implying stomatal control of CO_2 and OCS fluxes at the site. The forest surface was found to be a

soil moisture dependent sink of OCS, with magnitudes that were roughly half of nighttime ecosystem fluxes, indicating other components of the ecosystem (epiphytes present throughout the canopy and partial stomatal closure) were also absorbing OCS during these hours. Ecosystem fluxes of OCS and CO_2 were found to be strongly sensitive to the ratio of diffuse to direct radiation reaching the top of the canopy, a phenomenon that has been widely reported for CO2 fluxes but not for OC fluxes. Uptake of both OCS and CO_2 increased as sky conditions changed from clear to partly cloudy. A much smaller increase in uptake was observed as sky conditions changed from partly cloudy to overcast, except during the early summer, when soil moisture was not limiting, and was mediated by the sensitivity of stomata to changing cloudiness and soil moisture, as estimated from canopy-scale stomatal conductance. Finally, we examined the response of OCS, CO_2 and H_2O fluxes on heat waves, and found that sequential heat waves lead to suppression in stomatal gas exchange of all three fluxes.

5.3   Summary of chapter 4

In this study we used OCS fluxes estimated in chapter 3 to predict GPP. GPP estimated from OCS flux showed similar seasonal and diurnal patterns as that obtained from flux partitioning of NEE at the site. However, we find that the magnitude of GPP obtained using this method was significantly higher. To test these, a third independent estimate was GPP was calculated using measurements of sap flow in trees of dominant species in the forest and the stable isotopic composition of C in needle tissue of actively photosynthesizing trees (i.e., leaf $\delta^{13}CO_2$). These latter GPP estimates were also higher than from flux partitioning, and comparable to estimates from OCS fluxes. GPP predictions from a well-known process based model corroborate these findings. We conclude that flux partitioning of NEE results in a systematic underestimation of both source and sink terms, likely due to an underestimation of respiratory fluxes.

5.4   Overall Synthesis

Accurate predictions of GPP are necessary to understand carbon-climate feedbacks. At the ecosystem-scale, GPP is estimated by partitioning net fluxes by the eddy covariance method. While the EC method has been adopted globally to assess ecosystem productivity and change, it still needs independent verification, particularly in different and diverse ecosystems . Novel measurements such as carbonyl sulfide can help constrain and validate GPP at the ecosystem-scale, by providing independent estimates of canopy scale stomatal conductance. This dissertation built on existing work on carbonyl sulfide and shed new light on biotic and abiotic factors that regulate the flux of this gas in a forested ecosystem.

Our results support the growing body of work that suggests ecosystem-scale OCS uptake is controlled by stomatal dynamics. Moreover, we find that GPP estimated from OCS is significantly higher than those obtained from partitioning of net fluxes measured by the eddy covariance method. These findings were corroborated using independent estimates of GPP using measurements of sap flow and ratios of stable isotopes of carbon (^{12}C/^{13}C) incorporated into leaf dry matter, and a well-known process-based model.

While moist old-growth forests in Pacific Northwestern U.S. do not represent a very large fraction of the global terrestrial surface area, results from this study are likely relevant for other old-growth forests, particularly dense and very wet forests with extensive epiphyte cover, which are widespread in the humid tropics.

ReferencesAlden, C. B., Miller, J. B., Gatti, L. V., Gloor, M. M., Guan, K., Michalak, A. M., … Diffenbaugh, N. S. (2016). Regional atmospheric CO2 inversion reveals seasonal and geographic differences in Amazon net biome exchange. *Global Change Biology*, *22*(10), 3427–3443. https://doi.org/10.1111/gcb.13305

Asaf, D., Rotenberg, E., Tatarinov, F., Dicken, U., Montzka, S. A., & Yakir, D. (2013). Ecosystem

photosynthesis inferred from measurements of carbonyl sulphide flux. *Nature Geoscience*, *6*(3), 186–190. https://doi.org/10.1038/ngeo1730

Bala, G., Devaraju, N., Chaturvedi, R. K., Caldeira, K., & Nemani, R. (2013). Nitrogen deposition: How important is it for global terrestrial carbon uptake. *Biogeosciences*, *10*(11), 7147–7160. https://doi.org/10.5194/bg-10-7147-2013

Baldocchi, D. (2014). Measuring fluxes of trace gases and energy between ecosystems and the atmosphere - the state and future of the eddy covariance method. *Global Change Biology*, *20*(12), 3600–3609. https://doi.org/10.1111/gcb.12649

Baldocchi, D., Chu, H., & Reichstein, M. (2018). Inter-annual variability of net and gross ecosystem carbon fluxes: A review. *Agricultural and Forest Meteorology*, *249*(May 2017), 520–533. https://doi.org/10.1016/j.agrformet.2017.05.015

Ballantyne, A. P., Alden, C. B., Miller, J. B., Trans, P. P., & White, J. W. C. (2012). Increase in observed net carbon dioxide uptake by land and oceans during the pst 50 years. *Nature*, *488*(7409), 70–73. https://doi.org/10.1038/nature11299

Belviso, S., Reiter, I. M., Loubet, B., Gros, V., Lathière, J., Montagne, D., … Genty, B. (2016). A top-down approach of surface carbonyl sulfide exchange by a Mediterranean oak forest ecosystem in Southern France. *Atmospheric Chemistry and Physics Discussions*, (June 2012), 1–25. https://doi.org/10.5194/acp-2016-525

Berkelhammer, M., Steen-Larsen, H. C., Cosgrove, A., Peters, A. J., Johnson, R., Hayden, M., & Montzka, S. A. (2016). Radiation and atmospheric circulation controls on carbonyl sulfide concentrations in themarine boundary layer. *Journal of Geophysical Research*, *121*(21), 13,113-13,128. https://doi.org/10.1002/2016JD025437

Berkelhammer, M., Asaf, D., Still, C., Montzka, S., Noone, D., Gupta, M., … Yakir, D. (2014). Constraining surface carbon fluxes using in situ measurements of carbonyl sulfide and carbon dioxide. *Global Biogeochemical Cycles*, *28*(2), 161–179. https://doi.org/10.1002/2013GB004644

Billesbach, D. P., Berry, J. A., Seibt, U., Maseyk, K., Torn, M. S., Fischer, M. L., … Campbell, J. E.

(2014). Growing season eddy covariance measurements of carbonyl sulfide and CO2 fluxes: COS and CO2 relationships in Southern Great Plains winter wheat. *Agricultural and Forest Meteorology*, *184*, 48–55. https://doi.org/10.1016/j.agrformet.2013.06.007

Blonquist, J. M., Montzka, S. A., Munger, J. W., Yakir, D., Desai, A. R., Dragoni, D., … Bowling, D. R. (2011). The potential of carbonyl sulfide as a proxy for gross primary production at flux tower sites. *Journal of Geophysical Research: Biogeosciences*, *116*(4), 1–18. https://doi.org/10.1029/2011JG001723

Campbell, J. E., Berry, J., Seibt, U., Smith, S., Nature, S. M.-, & 2017, U. (2017). Large historical growth in global terrestrial gross primary production. *Nature.com*, *544*(7468), 84. Retrieved from https://www.nature.com/articles/nature22030

Campbell, J. E., Carmichael, G. R., Chai, T., Mena-Carrasco, M., Tang, Y., Blake, D. R., … Stanier, C. O. (2008). Photosynthetic control of atmospheric carbonyl sulfide during the growing season. *Science*, *322*(5904), 1085–1088. https://doi.org/10.1126/science.1164015

Čermák, J., Kucera, J., Bauerle, W. L., Phillips, N., & Hinckley, T. M. (2007). Tree water storage and its diurnal dynamics related to sap flow and changes in stem volume in old-growth Douglas-fir trees. *Tree Physiology*, *27*(2), 181–198. https://doi.org/10.1093/treephys/27.2.181

Ciais, P., Sabine, C., Bala, G., Bopp, L., Brovkin, V., Canadell, J., … Thornton, P. (2013). Carbon and Other Biogeochemical Cycles Chapter 6. *Climate Change 2013: The Physical Science Basis. Contribution of Working Group`I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, 465–570. https://doi.org/10.1017/CBO9781107415324.014

Commane, R., Meredith, L. K., Baker, I. T., Berry, J. A., Munger, J. W., Montzka, S. A., … Wofsy, S. C. (2015). Seasonal fluxes of carbonyl sulfide in a midlatitude forest. *Proceedings of the National Academy of Sciences*, *112*(46), 14162–14167. https://doi.org/10.1073/pnas.1504131112

Falk, M., Wharton, S., Schroeder, M., Ustin, S. L., & Paw U, K. T. (2008). Flux partitioning in an

old-growth forest: seasonal and interannual dynamics. *Tree Physiology*, *28*(4), 509–520. https://doi.org/10.1093/treephys/28.4.509

Farquhar, G. D., & Richards, R. A. (1984). Isotopic composition of plant carbon correlates water-use efficiency of wheat genotypes. *Australian Journal of Plant Physiology*, *11*(539–552).

Fessenden, J. E., & Ehleringer, J. R. (2003). Temporal variation in δ13C of ecosystem respiration in the Pacific Northwest: Links to moisture stress. *Oecologia*, *136*(1), 129–136. https://doi.org/10.1007/s00442-003-1260-1

Forkel, M., Carvalhais, N., Rödenbeck, C., Keeling, R., Heimann, M., Thonicke, K., … Reichstein, M. (2016). Enhanced seasonal CO2 exchange caused by amplified plant productivity in northern ecosystems. *Science*, *351*(6274), 696 LP-699. Retrieved from http://science.sciencemag.org/content/351/6274/696.abstract

Granier, A. (1985). A new method to measure the raw sap flux in the trunk of trees. *Ann. For. Sci*, *42*, 193–200.

Gries, C., Nash, T. H., & Kesselmeier, J. (1994). Exchange of reduced sulfur gases between lichens and the atmosphere. *Biogeochemistry*, *26*(1), 25–39.

Guanter, L., Zhang, Y., Jung, M., Joiner, J., Voigt, M., Berry, J. A., … Griffis, T. J. (2014). Global and time-resolved monitoring of crop photosynthesis with chlorophyll fluorescence. *Proceedings of the National Academy of Sciences*, *111*(14), E1327–E1333. https://doi.org/10.1073/pnas.1320008111

Harmon, M., Bible, K., Ryan, M., Shaw, D., Chen, H., Klopatek, J., & Li, X. (2004). Production, Respiration, and Overall Carbon Balance in an Old-growth Pseudotsuga-Tsuga Forest Ecosystem. *Ecosystems*, 498–512. https://doi.org/10.1007/s10021-004-0140-9

HEIMANN, M., & Reichstein, M. (2008). Terrestrial ecosystem carbon dynamics and climate feedbacks. *Agriculture*, *451*(7176), 289–292. Retrieved from http://www.nature.com/nature/journal/v451/n7176/full/nature06591.html

Heinsch, F. A., Zhao, M., Running, S. W., Kimball, J. S., Nemani, R. R., Davis, K. J., … Flanagan, L.

B. (2006). Evaluation of remote sensing based terrestrial productivity from MODIS using regional tower eddy flux network observations. *IEEE Transactions on Geoscience and Remote Sensing*, *44*(7), 1908–1923. https://doi.org/10.1109/TGRS.2005.853936

Hilton, T., Whelan, M., Zumkehr, A., … S. K.-N. C., & 2017, U. (2017). Peak growing season gross uptake of carbon in North America is largest in the Midwest USA. *Nature.com*, *7*(6), 450. Retrieved from https://www.nature.com/articles/nclimate3272

Huntzinger, D. N., Michalak, A. M., Schwalm, C., Ciais, P., King, A. W., Fang, Y., … Zhao, F. (2017). Uncertainty in the response of terrestrial carbon sink to environmental drivers undermines carbon-climate feedback predictions. *Scientific Reports*, *7*(1), 1–8. https://doi.org/10.1038/s41598-017-03818-2

IPCC. (2014). *Climate Change 2013*. *the Fifth Assessment Report* (Vol. 5).

Keeling, R. F., Graven, H. D., Welp, L. R., Resplandy, L., Bi, J., Piper, S. C., … Meijer, H. A. J. (2017). Atmospheric evidence for a global secular increase in carbon isotopic discrimination of land photosynthesis. *Proceedings of the National Academy of Sciences*, 201619240. https://doi.org/10.1073/pnas.1619240114

Keenan, T. F., Hollinger, D. Y., Bohrer, G., Dragoni, D., Munger, J. W., Schmid, H. P., & Richardson, A. D. (2013). Increase in forest water-use efficiency as atmospheric carbon dioxide concentrations rise. *Nature*, *499*(7458), 324–327. https://doi.org/10.1038/nature12291

Keenan, T. F., Gray, J., Friedl, M. A., Toomey, M., Bohrer, G., Hollinger, D. Y., … Richardson, A. D. (2014). Net carbon uptake has increased through warming-induced changes in temperate forest phenology. *Nature Climate Change*, *4*(7), 598–604. https://doi.org/10.1038/nclimate2253

Kettle, A. J., Kuhn, U., Von Hobe, M., Kesselmeier, J., & Andreae, M. O. (2002). Global budget of atmospheric carbonyl sulfide: Temporal and spatial variations of the dominant sources and sinks. *Journal of Geophysical Research: Atmospheres*, *107*(D22).

Klein, T., Rotenberg, E., Tatarinov, F., & Yakir, D. (2016). Association between sap flow-derived

and eddy covariance-derived measurements of forest canopy CO2 uptake. *New Phytologist*, *209*(1), 436–446. https://doi.org/10.1111/nph.13597

Knox, S. H., Dronova, I., Sturtevant, C., Oikawa, P. Y., Matthes, J. H., Verfaillie, J., & Baldocchi, D. (2017). Using digital camera and Landsat imagery with eddy covariance data to model gross primary production in restored wetlands. *Agricultural and Forest Meteorology*, *237–238*, 233–245. https://doi.org/10.1016/j.agrformet.2017.02.020

Kooijmans, L. M. J. J., Maseyk, K., Seibt, U., Sun, W., Vesala, T., Mammarella, I., … Chen, H. (2017). Canopy uptake dominates nighttime carbonyl sulfide fluxes in a boreal forest. *Atmospheric Chemistry and Physics*, *17*(18), 11453–11465. https://doi.org/10.5194/acp-17-11453-2017

Kuhn, U., & Kesselmeier, J. (2000). Environmental variables controlling the uptake of carbonyl sulfide by lichens. *Journal of Geophysical Research: Atmospheres*, *105*(D22), 26783–26792.

Kuhn, U., Wolf, A., Gries, C., Nash III, T. H., & Kesselmeier, J. (2000). Field measurements on the exchange of carbonyl sulfide between lichens and the atmosphere. *Atmospheric Environment*, *34*(28), 4867–4878.

LAI, C., Ehleringer, J. R., & Bond, B. J. (2006). Contributions of evaporation, isotopic non-steady state transpiration and atmospheric mixing on the δ18O of water vapour in Pacific Northwest coniferous forests. *Plant, Cell & Environment*, *29*(1), 77–94.

Lasslop, G., Reichstein, M., Papale, D., Richardson, A., Arneth, A., Barr, A., … Wohlfahrt, G. (2010). Separation of net ecosystem exchange into assimilation and respiration using a light response curve approach: Critical issues and global evaluation. *Global Change Biology*, *16*(1), 187–208. https://doi.org/10.1111/j.1365-2486.2009.02041.x

Launois, T., Peylin, P., Belviso, S., & Poulter, B. (2015). A new model of the global biogeochemical cycle of carbonyl sulfide - Part 2: Use of carbonyl sulfide to constrain gross primary productivity in current vegetation models. *Atmospheric Chemistry and Physics*, *15*(16), 9285–9312. https://doi.org/10.5194/acp-15-9285-2015

Li, W., Ciais, P., Wang, Y., Yin, Y., Peng, S., Zhu, Z., … Piao, S. (2018). Recent Changes in Global

Photosynthesis and Terrestrial Ecosystem Respiration Constrained From Multiple Observations. *Geophysical Research Letters*, 1058–1068. https://doi.org/10.1002/2017GL076622

Lloyd, J., & Taylor, J. A. (1994). On the Temperature Dependence of Soil Respiration. *Functional Ecology*, *8*(3), 315–323.

Luyssaert, S., Schulze, E.-D., Börner, A., Knohl, A., Hessenmöller, D., Law, B. E., … Grace, J. (2008). Old-growth forests as global carbon sinks. *Nature*, *455*(7210), 213.

Maseyk, K., Berry, J. A., Billesbach, D., Campbell, J. E., Torn, M. S., Zahniser, M., & Seibt, U. (2014). Sources and sinks of carbonyl sulfide in an agricultural field in the Southern Great Plains. *Proceedings of the National Academy of Sciences*, *111*(25), 9064–9069. https://doi.org/10.1073/pnas.1319132111

McCune, B., Amsberry, K. A., Camacho, F. J., Clery, S., Cole, C., Emerson, C., … Widmer, M. (1997). Vertical profile of epiphytes in a Pacific Northwest old-growth forest. *Northwest Science*, *71*(2), 145–152. Retrieved from d:%5CArtiklar%5CMcCune et al 1997.pdf

MEINZER, F. C., ANDRADE, J. L., GOLDSTEIN, G., HOLBROOK, N. M., CAVELIER, J., & JACKSON, P. (1997). Control of transpiration from the upper canopy of a tropical forest: the role of stomatal, boundary layer and hydraulic architecture components. *Plant, Cell and Environment*, *20*(10), 1242–1252. https://doi.org/10.1046/j.1365-3040.1997.d01-26.x

Meinzer, F. C., Brooks, J. R., Domec, J., Gartner, B. L., Warren, J. M., Woodruff, D. R., … Sarg, R. (2006). Dynamics of water transport and storage in conifers studied, 105–114.

Meinzer, F. C., Woodruff, D. R., & Shaw, D. C. (2004). Integrated responses of hydraulic architecture, water and carbon relations of western hemlock to dwarf mistletoe infection. *Plant, Cell and Environment*, *27*(7), 937–946. https://doi.org/10.1111/j.1365-3040.2004.01199.x

Miao, G., Guan, K., Yang, X., Bernacchi, C. J., Berry, J. A., DeLucia, E. H., … Masters, M. D. (2018a). Sun-Induced Chlorophyll Fluorescence, Photosynthesis, and Light Use Efficiency of a Soybean Field. *Journal of Geophysical Research: Biogeosciences*.

https://doi.org/10.1002/2017JG004180

Miao, G., Guan, K., Yang, X., Bernacchi, C. J., Berry, J. A., DeLucia, E. H., … Masters, M. D. (2018b). Sun-Induced Chlorophyll Fluorescence, Photosynthesis, and Light Use Efficiency of a Soybean Field. *Journal of Geophysical Research: Biogeosciences*, 610–623. https://doi.org/10.1002/2017JG004180

Montzka, S. A., Calvert, P., Hall, B. D., Elkins, J. W., Conway, T. J., Tans, P. P., & Sweeney, C. S. (2007). On the global distribution, seasonality, and budget of atmospheric carbonyl sulfide (COS) and some similarities to CO_2. *Journal of Geophysical Research Atmospheres*, *112*(9), 1–15. https://doi.org/10.1029/2006JD007665

Novick, K. A., Ficklin, D. L., Stoy, P. C., Williams, C. A., Bohrer, G., Oishi, A. C., … Phillips, R. P. (2016). The increasing importance of atmospheric demand for ecosystem water and carbon fluxes. *Nature Climate Change*, *6*(11), 1023–1027. https://doi.org/10.1038/nclimate3114

Novick, K. A., Biederman, J. A., Desai, A. R., Litvak, M. E., Moore, D. J. P., Scott, R. L., & Torn, M. S. (2018). The AmeriFlux network: A coalition of the willing. *Agricultural and Forest Meteorology*, *249*(May), 444–456. https://doi.org/10.1016/j.agrformet.2017.10.009

Oikawa, P. Y., Sturtevant, C., Knox, S. H., Verfaillie, J., Huang, Y. W., & Baldocchi, D. D. (2017a). Revisiting the partitioning of net ecosystem exchange of CO2 into photosynthesis and respiration with simultaneous flux measurements of 13CO2 and CO2, soil respiration and a biophysical model, CANVEG. *Agricultural and Forest Meteorology*, *234–235*, 149–163. https://doi.org/10.1016/j.agrformet.2016.12.016

Oikawa, P. Y., Sturtevant, C., Knox, S. H., Verfaillie, J., Huang, Y. W., & Baldocchi, D. D. (2017b). Revisiting the partitioning of net ecosystem exchange of CO2into photosynthesis and respiration with simultaneous flux measurements of13CO2and CO2, soil respiration and a biophysical model, CANVEG. *Agricultural and Forest Meteorology*, *234–235*, 149–163. https://doi.org/10.1016/j.agrformet.2016.12.016

Parker, G. G. (1997). Canopy structure and light environment of an old growth Douglas-

fir/Western hemlock forest. *Northwest Science*, *71*(4), 261–271.

Parker, G. G., Harmon, M. E., Lefsky, M. A., Chen, J., Pelt, R. Van, Weis, S. B., … Frankling, J. F. (2004). Three-dimensional Structure of an Old-growth Pseudotsuga-Tsuga Canopy and Its Implications for Radiation Balance, Microclimate, and Gas Exchange. *Ecosystems*, *7*(5), 440–453. https://doi.org/10.1007/s10021-004-0136-5

Paw U, K. T., Falk, M., Suchanek, T. H., Ustin, S. L., Chen, J., Park, Y.-S., … Matista, A. A. (2004). Carbon Dioxide Exchange between an Old-Growth Forest and the Atmosphere. *Ecosystems*, *7*(5), 513–524. https://doi.org/10.1007/s10021-004-0141-8

Phillips, N., Bond, B. J., McDowell, N. G., & Ryan, M. G. (2002). Canopy and hydraulic conductance in young, mature and old Douglas-fir trees. *Tree Physiology*, *22*(2–3), 205–211. https://doi.org/10.1093/treephys/22.2-3.205

Protoschill-Krebs, G Wilhelm, C Kesselmeier, J. (1996). Consumption of carbonyl sulphide (COS) by higher plant carbonic anhydrase (CA). *Atmospheric Environment*, *30*(18), 3151–3156. Retrieved from https://www.sciencedirect.com/science/article/pii/135223109600026X

Le Quéré, C., Raupach, M. R., Canadell, J. G., Marland, G., Bopp, L., Ciais, P., … Woodward, F. I. (2009). Trends in the sources and sinks of carbon dioxide. *Nature Geoscience*, *2*(12), 831–836. https://doi.org/10.1038/ngeo689

Le Quéré, C., Andrew, R. M., Friedlingstein, P., Sitch, S., Pongratz, J., Manning, A. C., … Zhu, D. (2018). Global Carbon Budget 2017. *Earth Syst. Sci. Data Etsushi Kato Markus Kautz Ralph F. Keeling Kees Klein Goldewijk Nathalie Lefèvre Andrew Lenton Danica Lombardozzi Nicolas Metzl Yukihiro Nojiri Antonio Padin Janet Reimer*, *1010333739*(10), 405–448. https://doi.org/10.5194/essd-10-405-2018

Reichstein, M., Falge, E., Baldocchi, D., Papale, D., Aubinet, M., Berbigier, P., … Granier, A. (2005). On the separation of net ecosystem exchange into assimilation and ecosystem respiration: review and improved algorithm. *Global Change Biology*, *11*(9), 1424–1439.

Rossini, M., Meroni, M., Migliavacca, M., Manca, G., Cogliati, S., Busetto, L., … Colombo, R. (2010). High resolution field spectroscopy measurements for estimating gross ecosystem

production in a rice field. *Agricultural and Forest Meteorology*, *150*(9), 1283–1296. https://doi.org/10.1016/j.agrformet.2010.05.011

Schimel, D., Stephens, B. B., & Fisher, J. B. (2015). Effect of increasing CO_2 on the terrestrial carbon cycle. *Proceedings of the National Academy of Sciences*, *112*(2), 436–441. https://doi.org/10.1073/pnas.1407302112

Schuh, A. E., Denning, A. S., Corbin, K. D., Baker, I. T., Uliasz, M., Parazoo, N., … Worthy, D. E. J. (2010). A regional high-resolution carbon flux inversion of North America for 2004. *Biogeosciences*, *7*(5), 1625–1644. https://doi.org/10.5194/bg-7-1625-2010

Seibt, U., Rajabi, A., Griffiths, H., & Berry, J. A. (2008). Carbon isotopes and water use efficiency: Sense and sensitivity. *Oecologia*, *155*(3), 441–454. https://doi.org/10.1007/s00442-007-0932-7

Seibt, U., Kesselmeier, J., Sandoval-Soto, L., Kuhn, U., & Berry, J. A. (2010). A kinetic analysis of leaf uptake of COS and its relation to transpiration, photosynthesis and carbon isotope fractionation. *Biogeosciences*, *7*(1), 333–341. https://doi.org/10.5194/bg-7-333-2010

Shaw, D. C., Chen, J., Freeman, E. a, & Braun, D. M. (2005). Spatial and population characteristics of dwarf mistletoe infected trees in an old-growth Douglas-fir western hemlock forest. *Canadian Journal of Forest Research*, *35*(4), 990–1001. https://doi.org/10.1139/x05-022

Shaw, D., Franklin, J., Bible, K., Klopatek, J., Freeman, E., Greene, S., & Parker, G. (2004). Ecological Setting of the Wind River Old-growth Forest. *Ecosystems*, *7*(5), 427–439. https://doi.org/10.1007/s10021-004-0135-6

Sjöström, M., Zhao, M., Archibald, S., Arneth, A., Cappelaere, B., Falk, U., … Kutsch, W. (2013). Evaluation of MODIS gross primary productivity for Africa using eddy covariance data. *Remote Sensing of Environment*, *131*, 275–286.

Stimler, K., Nelson, D., & Yakir, D. (2010). High precision measurements of atmospheric concentrations and plant exchange rates of carbonyl sulfide using mid-IR quantum cascade laser. *Global Change Biology*, *16*(9), 2496–2503. https://doi.org/10.1111/j.1365-

2486.2009.02088.x

Stimler, K., Montzka, S. A., Berry, J. A., Rudich, Y., & Yakir, D. (2010). Relationships between carbonyl sulfide (COS) and CO2 during leaf gas exchange. *New Phytologist*, *186*(4), 869–878. https://doi.org/10.1111/j.1469-8137.2010.03218.x

Thum, T., Zaehle, S., Köhler, P., Aalto, T., Aurela, M., Guanter, L., … Markkanen, T. (2017). Modelling sun-induced fluorescence and photosynthesis with a land surface model at local and regional scales in northern Europe. *Biogeosciences*, *14*(7), 1969–1984. https://doi.org/10.5194/bg-14-1969-2017

van der Tol, C., Verhoef, W., Timmermans, J., Verhoef, A., & Su, Z. (2009). An integrated model of soil-canopy spectral radiances, photosynthesis, fluorescene, temperature and energy balance. *Biogeosciences*, *6*, 3109–3129.

Toomey, M., Friedl, M. A., Frolking, S., Hufkens, K., Klosterman, S., Sonnentag, O., … Richardson, A. D. (2015). Greenness indices from digital cameras predict the timing and seasonal dynamics of canopy-scale photosynthesis. *Ecological Applications*, *25*(1), 99–115. https://doi.org/10.1890/14-0005.1

UNFCC. (2015). United nations framework convention on climate change. *Paris, France*.

Wang, Y. P., Baldocchi, D., Leuning, R., Falge, E., & Vesala, T. (2007). Estimating parameters in a land-surface model by applying nonlinear inversion to eddy covariance flux measurements from eight FLUXNET sites. *Global Change Biology*, *13*(3), 652–670. https://doi.org/10.1111/j.1365-2486.2006.01225.x

Warren, J., Meinzer, F., Brooks, J., & Domec, J. (2005). Vertical stratification of soil water storage and release dynamics in Pacific Northwest coniferous forests. *Agricultural and Forest Meteorology*, *130*(1–2), 39–58. https://doi.org/10.1016/j.agrformet.2005.01.004

Wehr, R., & Saleska, S. R. (2015). An improved isotopic method for partitioning net ecosystem-atmosphere CO2exchange. *Agricultural and Forest Meteorology*, *214–215*, 515–531. https://doi.org/10.1016/j.agrformet.2015.09.009

Wehr, R., Munger, J. W., McManus, J. B., Nelson, D. D., Zahniser, M. S., Davidson, E. A., … Saleska, S. R. (2016). Seasonality of temperate forest photosynthesis and daytime respiration. *Nature*, *534*(7609), 680.

Wehr, R., Commane, R., Munger, J. W., Barry Mcmanus, J., Nelson, D. D., Zahniser, M. S., … Wofsy, S. C. (2017). Dynamics of canopy stomatal conductance, transpiration, and evaporation in a temperate deciduous forest, validated by carbonyl sulfide uptake. *Biogeosciences*, *14*(2), 389–401. https://doi.org/10.5194/bg-14-389-2017

Wharton, S., & Falk, M. (2016). Climate indices strongly influence old-growth forest carbon exchange. *Environmental Research Letters*, *11*(4), 1–11. https://doi.org/10.1088/1748-9326/11/4/044016

Whelan, M. E., Lennartz, S. T., Gimeno, T. E., Wehr, R., Wohlfahrt, G., Wang, Y., … Campbell, J. E. (2017). Reviews and Syntheses: Carbonyl Sulfide as a Multi-scale Tracer for Carbon and Water Cycles. *Biogeosciences Discussions*, (October), 1–97. https://doi.org/10.5194/bg-2017-427

Williams, A. P., Allen, C. D., Macalady, A. K., Griffin, D., Woodhouse, C. A., Meko, D. M., … Grissino-Mayer, H. D. (2013). Temperature as a potent driver of regional forest drought stress and tree mortality. *Nature Climate Change*, *3*(3), 292.

Winner, W., Thomas, S., Berry, J., Bond, B., Cooper, C., Hinckley, T., … Williams, M. (2004). Canopy Carbon Gain and Water Use: Analysis of Old-growth Conifers in the Pacific Northwest. *Ecosystems*, *7*(5), 482–497. https://doi.org/10.1007/s10021-004-0139-2

Wohlfahrt, G., Brilli, F., Hörtnagl, L., Xu, X., Bingemer, H., Hansel, A., & Loreto, F. (2012). Carbonyl sulfide (COS) as a tracer for canopy photosynthesis, transpiration and stomatal conductance: Potential and limitations. *Plant, Cell and Environment*, *35*(4), 657–667. https://doi.org/10.1111/j.1365-3040.2011.02451.x
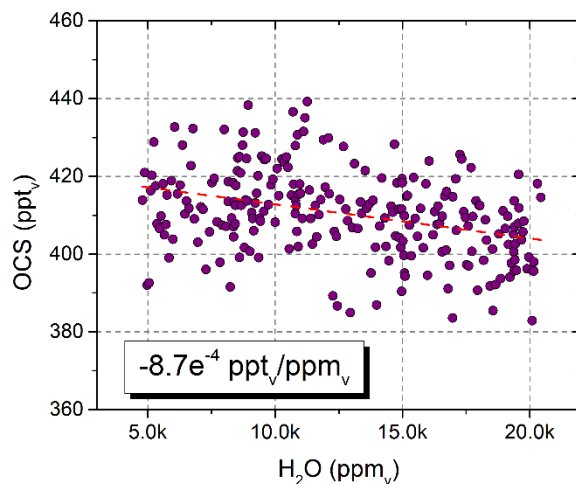
Figure 6-1. OCS water vapor cross-interference tested in the lab. The magnitude of this cross interference is negligible compared to observed canopy- atmosphere ecosystem exchange in this study.
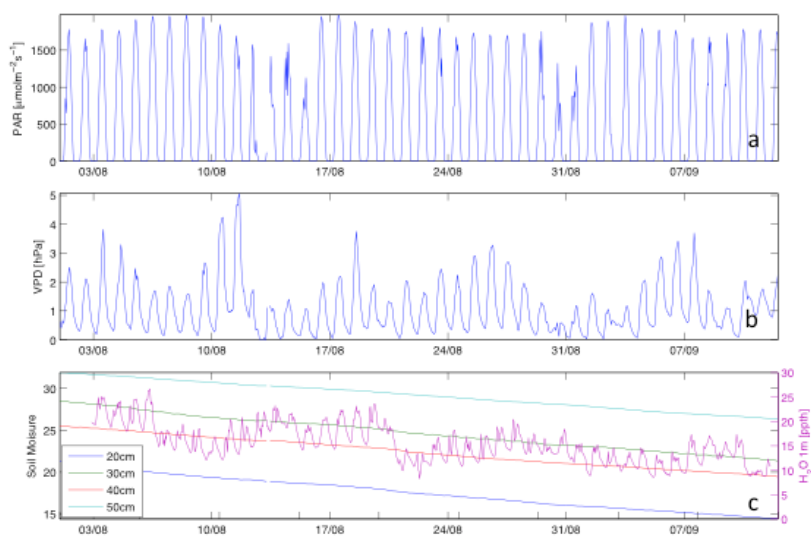

Figure 6-2. Complete time series of Photosynthetically Active Radiation measured at 70m (a), Vapor Pressure Deficit calculated from air temperature and relative humidity measured at 70m (b), and soil moisture at 20cm, 30cm, 40cm and 50cm below the soil surface alongside water vapor mixing ratios at 1m above the canopy surface (c).
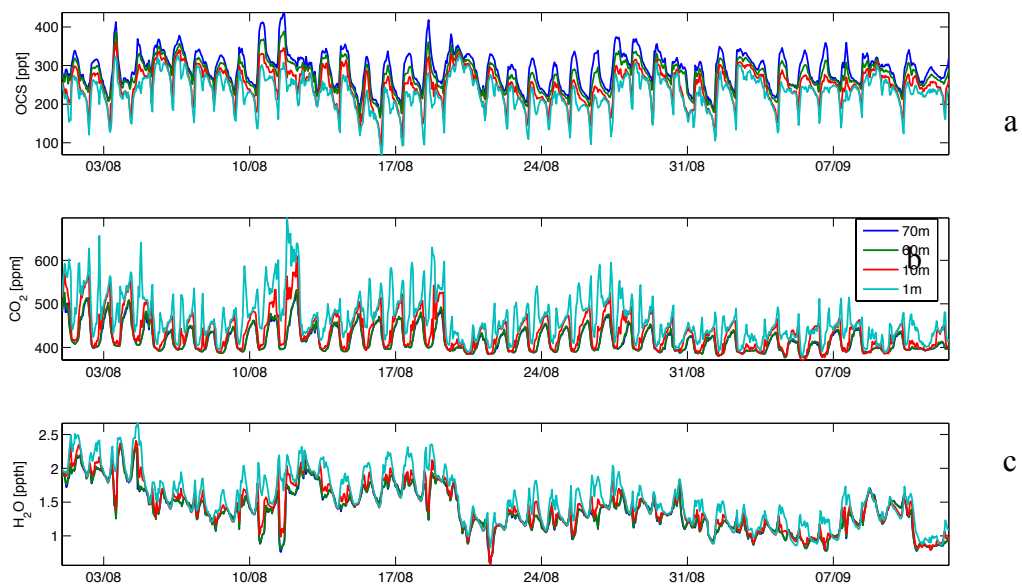
Figure 6-3. Time series of all hourly data, measured using the LGR instrument: OCS (a), CO₂ (b), and H₂O (c).
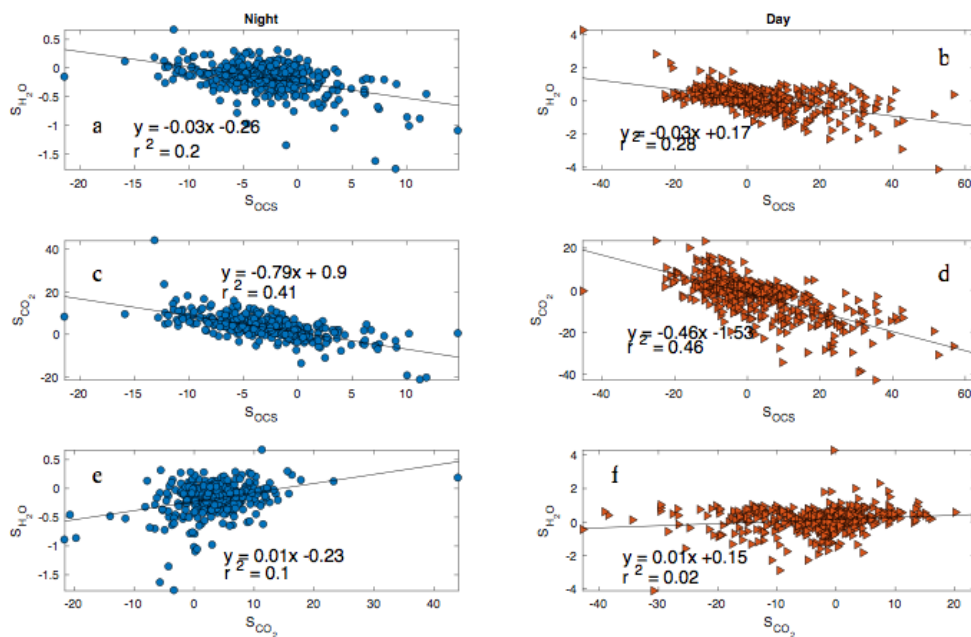
Figure 6-4. Relationship between SOCS and SCO2 and SOCS and SH2O, SH2O and SCO2 during nighttime (a,c,e) and daylight hours (b,d,f). Units for SOCS and SCO2 and SH2O are [pmolm-2s-1], [umolm-2s-1] and [mmolm-2s-1] respectively.
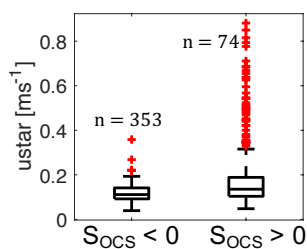

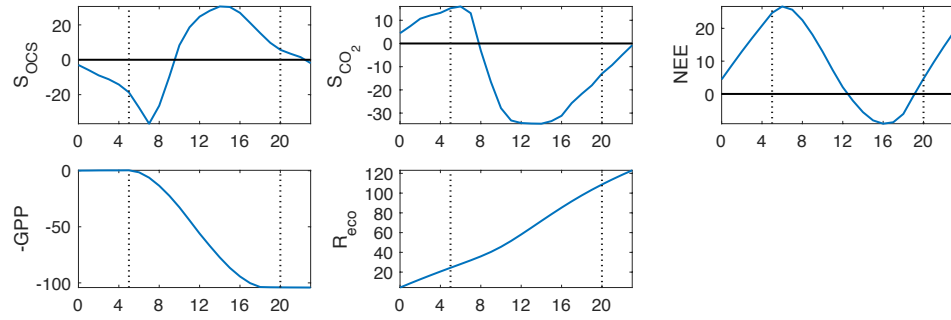*Figure 6-5. Boxplots of nighttime friction velocity (u*) for hours when SOCS is negative and positive (right)*

Figure 6-6. Boxplots showing the mean diurnal cycle of cumulative storage fluxes of OCS and CO2 (a-b), as well NEE, GPP and ecosystem respiration fluxes (c-e). Dotted lines indicate sunrise and sunset times. Units for OCS and CO2 fluxes are pmolm-2s-1 and umolm-2s-1 respectively.
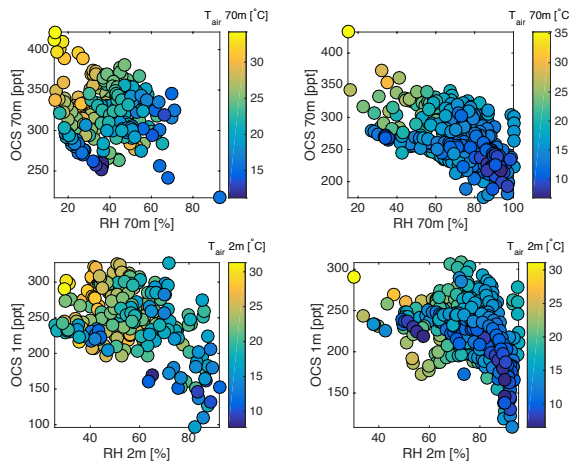

Figure 6-7. a-d Relationship between mean diurnal cycle of OCS with and relative humidity at the canopy top (a-b) and above the forest floor (c-d). Data are partitioned according to aerodynamic conductance (Ga) thresholds corresponding to well mixed i.e. high Ga (a,c) and stratified(b-d). The colors represent air temperature.
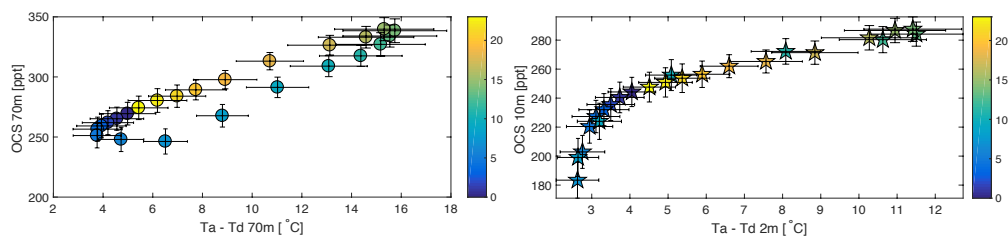
Figure 6-8. OCS mixing ratios plotted against dew point depression (DPD) above the canopy (a), and near the forest floor (b). While OCS mixing ratios decline in response to decreasing DPD at both heights, the decline is precipitous in the understory, especially when DPD falls below 4°C.

Table 6-1. Table with ancillary measurements

| Variable	Measurement height [meters above ground]
Temperature	70, 2
Relative Humidity	70, 2
Horizontal Wind speed	70, 2
Vertical wind speed	70
Pressure	70
Photosynthetically Active Radiation	70, 2
Net Radiation (Shortwave and Longwave upwelling and downwelling)	70
Net Ecosystem Exchange	70
Soil temperature and Moisture	10cm, 20cm, 30cm, 40cm, 50cm, 60m below ground
Latent heat Flux	70
Sensible Heat Flux	70
Precipitation	1000 m away from tower
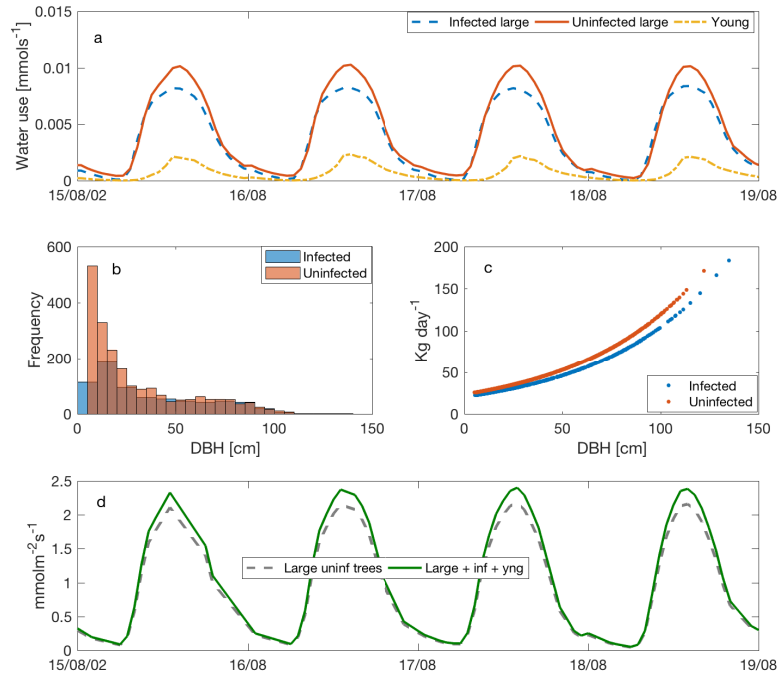
Figure 7-1.Time courses showing transpiration calculated from sap flow in hemlock trees (mean for all large infected, large uninfected and young trees (a), diameter at breast height (DBH) distributions for infected and uninfected hemlocks (b), daily water use plotted as function of DBH for hemlock trees, and diurnal cycles for stand scale transpiration using only large uninfected trees and considering large, young, infected, and uninfected hemlocks.
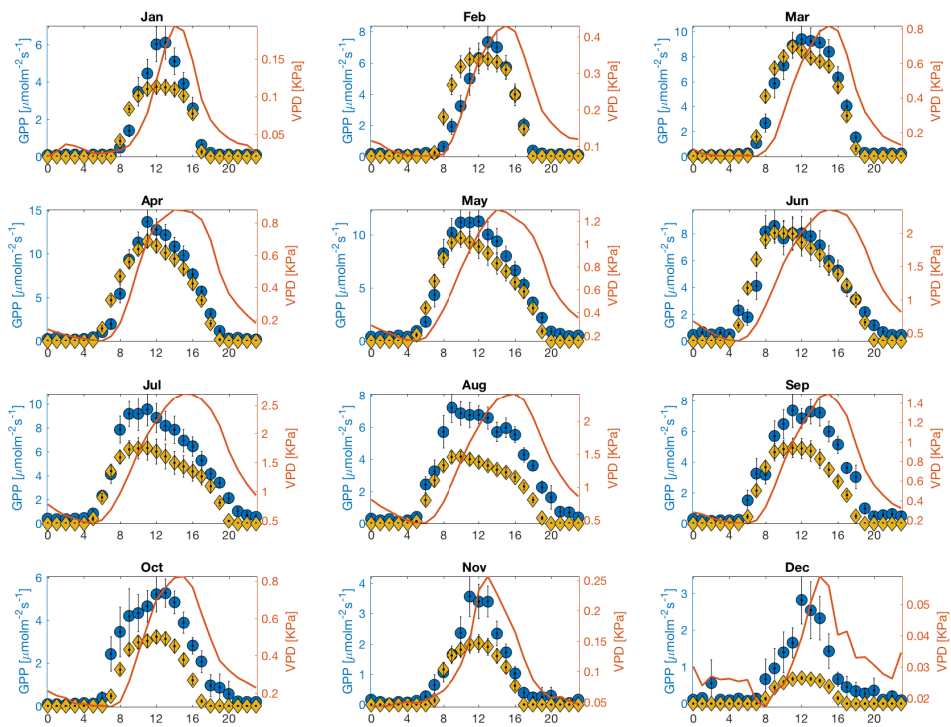
Figure 7-2. Diel cycles for daytime and nighttime flux partitioning of NEE estimated from the eddy covariance method.
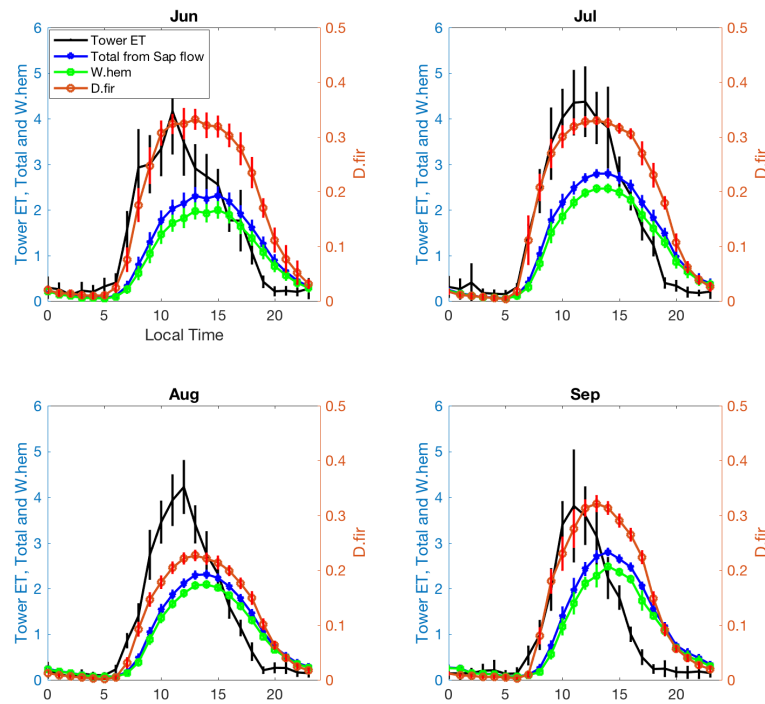
Figure 7-3.Mean diel cycle of transpiration rates for douglas fir (red; right y axis), western hemlock and total transpiration , and total evapotranspiration estimated from eddy covariance based latent heat flux (black) at the canopy top (left y axis).

Table 7-1. Parameters and input data for SCOPE

Parameters	Description	Value/units	Source
	Leaf biochemistry		
Vcmo	Maximum carboxylation capacity at 25 °C	90 µmol m^{-2} s^{-1}	Woodruff et al., (2007)
m	Ball-berry stomatal conductance parameter	8	
Rdparam	Parameter for dark respiration ($R_d = R_d$param $\times$ Vcmo)	0.5	0
Leaf optical			
Cab	Chlorophyll content density	30 µg cm^{-2}	
Cw	Leaf equivalent water thickness	cm	Measured
Cdm	Dry matter content	g cm^{-2}	Measured
N	Leaf thickness parameters	1.4	
	Canopy		

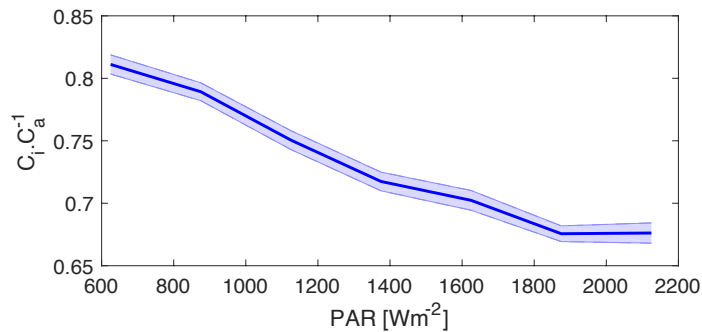|			
LAI	Leaf area index	6 m^{2}m^{-2} (max allowed)	Actual LAI~ 8 (Parker et al., 2004)
LIDFa	LIDF parameter a, which controls the average leaf scope	—	Inversion
LIDFb	LIDF parameter b, which controls the distribution's bimodality	—	−0.15
Fluorescence			
fqe2	Fluorescence efficiency for PSII in dark-adapted condition	—	0.01
fqe1/fqe2	Ratio of fqe1 to fqe2	—	0.2
Meteorology (input data)			
Rin	Broadband incoming shortwave radiation (0.4–2.5 µm)	Wm^{-2}	Measured
Ta	Air temperature	T	Measured
p	Air pressure	hPa	Measured
ea	Atmospheric vapor pressure	hPa	Measured
u	Wind speed at measurement height	m s^{-1}	Measured
Ca	Atmospheric CO_2 concentration	mg m^{-3}	Measured
Geometry			
LAT	Latitude	°	Measured
LON	Longitude	°	Measured
VZA	Observation zenith angle	°	0

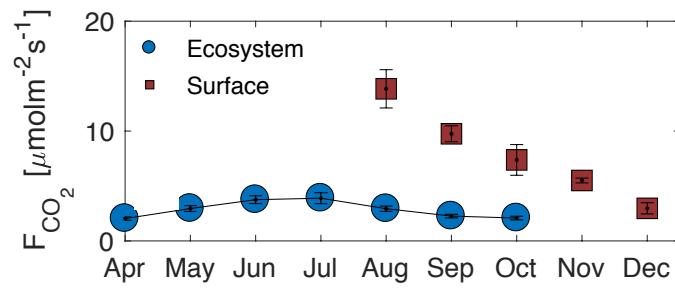*Figure 7-4.Modeled Ci/Ca from SCOPE plotted as a function of incoming PAR.*

Figure 7-5.Respiration estimates from chamber measurements at the forest floor are significantly higher than those from above canopy eddy flux measurements.