A new paradigm of quantifying ecosystem stress through chemical signatures

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Abstract. Stress-induced emissions of biogenic volatile organic compounds (VOCs) from terrestrial ecosystems may be one of the dominant sources of VOC emissions worldwide. Understanding the ecosystem stress response could reveal how ecosystems will respond and adapt to climate change and, in turn, quantify changes in the atmospheric burden of VOC oxidants and secondary organic aerosols. Here, we argue, based on preliminary evidence from several opportunistic measurement sources, that chemical signatures of stress can be identified and quantified at the ecosystem scale. We also outline future endeavors that we see as next steps toward uncovering quantitative signatures of stress, including new advances in both VOC data collection and analysis of “big data.”

Key words: chemical signatures; ecosystem; stress; volatile organic compounds.

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INTRODUCTION

Gaining understanding of how to quantify ecosystem stress is intimately tied with predicting the stress response of ecosystems and, ultimately, how ecosystems will respond and adapt to climate change. As climate change progresses, ecosystems will undergo greater amounts of environmental stress (Field et al. 2014). This will have far-reaching implications for many climate and economic sectors of the world, including natural ecosystem services, agricultural ecosystems and food production, the carbon cycle, atmospheric chemistry, and biodiversity.

The concept of stress on an ecosystem scale is difficult to measure, quantify, or even define. One major obstacle in ascertaining a definition is that the concept of stress is ambiguous at such a broad scale (Ulanowicz 1978, Ryder 1990). Kolasa and Pickett (1992) evaluate in detail the various difficulties involved in assessing stress; one of their arguments is that such assessments
depend upon recognizing changes in the ecosystem’s underlying architecture, although identifying this so-called minimum interactive structure is not without its own difficulties. Rapport (1992) argues that assessments of the health of ecosystems are necessarily subjective. Ecosystems are capable of adapting to changes in their environments, so it is difficult to argue that an adapting ecosystem is in poorer health than in a prior state. Due to these definitional challenges, attempts at quantifying ecosystem stress are scarce.

One of the first steps in quantifying stress would be to identify events that may cause stress. There are clear examples of stress events, such as severe weather, droughts, and insect infestation, but even these events have subtleties. A defoliating hail storm is a stressful event, but other forms of precipitation may not be. Droughts lack clear beginnings, ends, and thresholds, and moreover, drought severity does not necessarily correspond to well-defined changes in precipitation, temperature, or soil moisture. The impact of drought can be even farther removed from meteorology, as it depends on ecosystem-specific attributes such as plant rooting depths.

One known response of individual plants to stress events is an increase in the emissions of biogenic volatile organic compounds (VOCs; e.g., Karl et al. 2008, Kleist et al. 2012, Kaser et al. 2013). Volatile organic compound emissions are both indicators and drivers of ecological function. Plants emit VOCs in response to changes in light, temperature, and water availability (e.g., Guenther et al. 1995). Harley et al. (1999) argue that isoprene-emitting plants do so to ameliorate stresses associated with heat and high light; such responses may be more common as the threat of climate change grows more severe (Peñuelas and Llusia 2003). Plants can also emit VOCs to selectively attract different pollinating insects (Schiestl 2015, Raguso 2016), as a defense mechanism to deter infesting insects (Mentel et al. 2013), or to entice predators of herbivorous insects (Kessler and Baldwin 2001), in some cases highly selectively based on a combination of wound damage and oral secretions of the herbivore (Turlings et al. 1990, Kessler and Baldwin 2002). Higher emissions from some ecosystems can affect surrounding ecosystems (Bamberger et al. 2011), possibly as a form of chemical communication (e.g., Shulaev et al. 1997, Ton et al. 2007).

Each particular plant species, and hence each ecosystem, has a different pattern of VOC emissions that depends upon a wide variety of environmental factors. For example, Jud et al. (2016) found that postillumination bursts of acetaldehyde and green leaf volatiles from poplars had common, identifiable features. Drewniak et al. (2014) found a shift in dominant VOC emissions resulting from an expanse of red maple at the expense of oak; this serves as an example of how VOC emissions can serve as markers of climate shifts. The different factors that control VOC emissions are numerous and complex; untangling these myriad components has been a grand research challenge for well over a decade (Peñuelas and Llusia 2001).

Approximately 90% of total worldwide VOC emissions are biogenic (Guenther et al. 1995), and Bergström et al. (2014) estimate that 50–70% of all biogenic secondary organic aerosols in Central and Northern Europe forests are due to stress-induced VOC emissions. Quantifying all sources of VOC emissions, as well as how those emissions respond to biotic and abiotic factors, are crucial steps toward improving understanding of the Earth system and our role in it.

Modeling of VOC emissions is a fruitful approach to understanding and disentangling some of these environmental factors, particularly on an ecosystem scale. The Model of Emissions of Gases and Aerosols from Nature (MEGAN; Guenther et al. 2012) was developed for exactly this purpose: to capture the behavior of biogenic VOC emissions as a function of a wide variety of meteorological and environmental changes. As an example, in unstressed conditions, MEGAN can predict isoprene emission patterns on an ecosystem scale to within the uncertainties of observations (Potosnak et al. 2014). However, MEGAN has low skill in capturing changes in VOC emissions due to stress; MEGAN and other biogenic VOC emission models may underpredict VOC emissions during acute abiotic ecosystem stress events (e.g., storms) and overpredict emissions during chronic stress (e.g., droughts; Seco et al. 2015).

This difficulty in representing the “stress term” gives an indication of one of the key gaps in linkages between atmospheric chemistry and ecosystem studies: the connection between organism-level stress responses and a broader
atmosphere-scale perspective of the chemical signatures and effects of ecosystem stress. Specifically, although plant responses to stress have been quantified on the scale of individual plants (e.g., Niinemets et al. 2013), there has been little work to date in robustly quantifying the stress response of ecosystems, especially heterogeneous ecosystems, on the ecosystem scale. This shortage of previous work is because, until this point, there was both a lack of measurements and of techniques that can identify complex signatures in the collected data. In the past few years, there has been substantial progress made, allowing quantification of ecosystem-scale stress to proceed in new, promising directions. In this article, we identify a potential new paradigm in quantifying stress signatures in ecosystem-scale measurements of VOC emissions. We also outline the types of measurements and techniques that would be needed to build these signatures.

**Ecosystem-Scale Studies of VOC Emissions**

In this section, we discuss several sources of evidence that VOC emissions can be a sensitive indicator of stress events. Most of the examples presented here are associated with abiotic stresses, as the relationships between VOC emissions and these types of stresses are far better known than the relationships with biotic stresses. Nevertheless, there are relevant examples related to biotic stressors that we touch upon.

One example of ecosystem-scale stress-induced VOC emissions involves measurements taken at the Manitou Forest Observatory, an experimental forest near Colorado Springs, Colorado, primarily consisting of Ponderosa pine. Ortega et al. (2014) describe the site and summarize measurements taken during the BEACHON-ROCS campaign, which was designed to study the influence of forest canopies on chemical exchange and boundary layer turbulence. The campaign lasted for approximately 1 month during August 2010. On 4 August, during the campaign, there was a severe hailstorm (140 mm of hail) that physically damaged needles and branches of the trees (Kaser et al. 2013). Wound stresses are known to cause increased VOC emissions in a variety of plants, including pines (e.g., Juuti et al. 1990, Crespo et al. 2013). Monoterpene fluxes at this site were elevated to approximately four times background levels for 2 d after the event; MEGAN underpredicted monoterpene emissions over this two-day period by approximately a factor of 20, and the monthly total was underestimated by approximately 30% (Kaser et al. 2013). One compounding difficulty with measurements at this site is that repetitions of similar stresses could conceivably cause different responses. For example, there was another storm on 27 July, prior to the measured storm on 4 August (Kaser et al. 2013). Monoterpenes can be stored as well as emitted immediately after production (Peñuelas and Llusia 2001), so the storm on 4 August could have induced lower associated monoterpene emissions than the 27 July storm due to depletion of the storage pool. Alternately, after the first storm event, the plants had to repair any damage caused and could have exhausted their carbohydrate reserves; thus, after the second event, monoterpene emissions could have been substrate limited.

Another ecosystem-scale example was observed during the Canopy Horizontal Array Turbulence Study (CHATS) campaign, which was performed for 12 weeks in the spring of 2007 at a walnut plantation near Davis, California (Patton et al. 2011). The campaign was designed as a turbulent exchange study to see how forest canopies modify the exchange of gases between the boundary layer and the free troposphere. One of the VOCs measured during this campaign was methyl salicylate, which is a known plant-signaling compound and is the volatile form of compounds that are known to activate defense genes in plants (Karl et al. 2008). The campaign began on 15 March, which had relatively cold night time temperatures, and irrigation stopped for a period during the campaign (Patton et al. 2011). Methyl salicylate emissions were substantially increased over most of the campaign in response to these temperature and drought stresses, but once the site was irrigated, nearly all of the measured emissions were monoterpenes.

Although these two campaigns give a strong indication that VOC emissions are affected by stress, it is difficult to quantify stress in a way that would allow for robust assessment of ecosystem health. During the BEACHON-ROCS campaign, the stress event was clearly defined, but the campaign was too short to determine baseline VOC emission patterns, and there may
be complications in measurements due to repetition of the stress event. During the CHATS campaign, the site was quite homogeneous, but VOC emissions were in response to multiple sources of stress, so individual stress signatures could not be determined easily.

The Missouri Flux Site (MOFlux) is a long-term observation station that is part of the AmeriFlux Network. The site is primarily broad-leaf deciduous trees (dominated by isoprene-emitting oaks), located in the Ozarks near Columbia, Missouri. In 2011, the site experienced a drought, concurrent with the highest isoprene fluxes ever measured to that point (Potosnak et al. 2014). In 2012, the drought was more severe and widespread (Seco et al. 2015). Although drought stress is more difficult to quantify than wound stress, the advantage of this site is that VOC emissions were recorded for multiple years, and meteorological data have been collected at the site for nearly a decade.

There are currently multiple methods of quantifying drought. The North American Drought Monitor (Svoboda et al. 2002, NCDC 2014) indicated drought at the MOFlux site during the summers of 2011 and 2012 (Figs. 1–3), although the footprint of this index as calculated by NCDC (2014) is substantially larger than the MOFlux site. Fig. 4 shows different measurements taken at the MOFlux site in 2011 and 2012 that are also indicators of drought. Values from 2011 are the same as were reported by Potosnak et al. (2014), and values from 2012 are the same as those reported by Seco et al. (2015). All of the indicators (net ecosystem exchange, soil moisture, air vapor pressure deficit, and predawn leaf water potential) replicate the broad features of the results in Figs. 1–3, in that the 2012 drought was more severe and had an earlier onset than the 2011 drought. However, it is difficult to obtain a more quantitative picture of drought from this figure, as some of the indicators are noisy. Moreover, there is no clear indication of a threshold beyond which there is ecosystem damage, yet Fig. 5 shows that there are clear visible signals of stress in the canopy; leaf necrosis was widespread by the end of summer in 2012.

As an additional metric, we tested use of the Keetch–Byram Drought Index (KBDI), which was originally developed for determining the amount of biomass available to burn in forest fires (Keetch and Byram 1968, Alexander 1990). This index can be easily calculated using daily meteorological data collected at the site, thus necessarily giving a more local representation of drought level than the North American Drought Monitor, which is often calculated at mesoscales or synoptic scales. It can also provide fine temporal resolution using relatively robust measurements. Use of this index requires a long enough time record such that KBDI = 0 when the tabulation is initiated (i.e., the index is initiated in conditions that are clearly non-drought). Fig. 6 shows a drought index calculated from the KBDI for the MOFlux site from 2004 to 2013. By this index, the drought in 2012 was the most severe in this record period, indicating that for our purposes, the KBDI reproduces known occurrences of drought at the MOFlux site and can thus serve as a coarse indicator of drought stress. The KBDI also gives a similar quantitative picture to the results in Fig. 4, in that it indicates that the drought in 2012 was more severe and had an earlier onset than the drought in 2011.

One possible hypothesis describing the physiological response of this ecosystem is that severe drought stress can cause early senescence, or the point at which deciduous trees begin to shed their leaves in preparation for winter (Fig. 5 provides strong anecdotal evidence for this hypothesis). Fig. 7 shows that for the years 2008–2010, which had comparatively low maximum KBDI values over the course of the year (<300), senescence began after Julian Day 240–260, which is roughly the month of September. The onset of senescence here is defined as the point at which leaf area index begins to decline. For other years, the onset of senescence is anticorrelated with the maximum KBDI value calculated for that year ($R^2 = 0.73$).

These results clearly indicate physiological responses that correlate with our chosen index of drought stress. However, this coarse comparison can only indicate threshold events. That is, identification of sufficient stress to cause early senescence is only determined after senescence has begun. Ideally, signatures could be identified that serve as early warnings when ecosystems are undergoing stress or could indicate more subtle changes in ecosystem health that may not appear in standard assessments of drought. Measurements of changes in biogenic VOC emissions show promise in revealing those signatures.
Fig. 1. Monthly averages of the North American Drought Index (Svoboda et al. 2002, NCDC 2014) for June 2011 and 2012. At the Missouri Flux site (indicated by a green star), June 2011 shows no drought.
Fig. 2. Monthly averages of the North American Drought Index (Svoboda et al. 2002, NCDC 2014) for July 2011 and 2012. At the Missouri Flux site (indicated by a green star), July 2011 shows abnormally dry (D0) conditions. In contrast, the drought in 2012 is extreme (D3).
Fig. 3. Monthly averages of the North American Drought Index (Svoboda et al. 2002, NCDC 2014) for August 2011 and 2012. At the Missouri Flux site (indicated by a green star), August 2011 shows abnormally dry (D0) conditions. In contrast, the drought in 2012 is severe (D2) to exceptional (D4).
Fig. 8 shows daytime average VOC measurements from the MOFlux site during the summers of 2011 and 2012. Isoprene measurements from 2011 were taken using a chemiluminescence analyzer (Potosnak et al. 2014), and isoprene, methanol, and monoterpene measurements in 2012 were taken with a Proton Transfer Reaction Mass Spectrometer (PTR-MS) (Seco et al. 2015). Isoprene and monoterpene emissions clearly show threshold behavior at KBDI ≈ 500. Before this point, the VOC fluxes increase with KBDI as expected; isoprene and monoterpene emissions correlate with temperature, and temperature increases are one of the primary contributors to increased values of KBDI. However, for KBDI values >500, isoprene and monoterpene emissions decrease with further increases in KBDI, suggesting the ecosystems are undergoing sufficiently high levels of stress to modify their physiological responses to their environment. Analyses of Fig. 7 would not reveal this threshold behavior, especially in terms of predictive capability. Methanol shows no strong response to changes in KBDI, although methanol emissions are known to respond to other types of stress (Peñuelas et al. 2005, Wohlfahrt et al. 2015).

Fig. 9 shows that when forced with the meteorological data collected at the MOFlux site, MEGAN clearly underrepresents isoprene and monoterpene emissions before the drought and overrepresents these emissions during and after the drought. Moreover, this underrepresentation does not necessarily correlate with increases or decreases in the KBDI. The MEGAN results shown in this figure may differ depending upon...
the emission factor used (which has uncertainties), but this cannot explain why, at certain times, predictions from MEGAN do not match observed values of VOC fluxes. More succinctly, the “stress term” is currently poorly represented in MEGAN. Discovering biogenic VOC signatures of stress will enable the research community to better represent environmental influences on VOC emissions in models.

**Quantifying Ecosystem Stress Through Biogenic VOC Signatures**

Using measurements of biogenic VOCs, indications of stress on the ecosystem scale can be targeted and quantified to a finer degree than, for example, using estimates of carbon uptake and transpiration to quantify stress (e.g., Fig. 4). Moreover, they have the potential to be predictive, providing an “early warning” before stress causes serious damage to the ecosystem.

Developments in several main areas that represent recent advances in measurement technology have the potential to push this field toward a new paradigm in which robust signatures of ecosystem stress can be identified and quantified. The first step in quantifying ecosystem stress is collecting sufficient data of VOC emissions. The campaigns discussed in the previous section were not designed to collect data for identification of stress signatures, so all of the measurements discussed were serendipitous. Targeted measurement campaigns would involve long-term, multiyear deployment of VOC measurement instruments in all seasons so a baseline of emissions could be established and longitudinal data surrounding stress events could be collected. Similar measurements have repeatedly been justified for CO$_2$ flux data collection (e.g., Boden et al. 2013); such efforts could differentiate “normal” emissions from stress-induced emissions and also identify shifts in seasonal patterns.

![Fig. 6. Daily values of the Keetch-Byram Drought Index (KBDI) for 2004–2013 as calculated from meteorological data collected at the Missouri Flux site. Colored shading shows the drought level; increases in drought level correspond to a 100-point increase in KBDI, where the maximum possible value is 800. Dashed vertical lines indicate 1 January of a particular year.](image-url)
of emissions, such as changes in leafout and senescence timing.

A useful instrument for conducting these studies is a Proton Transfer Reaction Time-of-Flight Mass Spectrometer (PTR-TOF-MS), a device that has become available only in the past few years (Graus et al. 2010). Previously, instruments used to measure VOC emissions could only measure a small number of compounds. The PTR-TOF-MS can differentiate a multitude of compounds with fewer sources of interference in near-real time; such an instrument is crucial for characterizing the atmospheric VOC budget (Park et al. 2013). Further advances in ease of maintenance of this instrument may be necessary for long-term (multiple seasons) deployment. In the meantime, using simpler instrumentation that avoids the price and complexity of the PTR-TOF-MS could be useful in providing long-term measurements of isoprene, monoterpenes, and methanol (Rinne et al. 2016).

These requirements become somewhat more difficult and nuanced for biotic stressors. Such stress events occur at outbreak sites that are not necessarily ideally located for flux tower measurements. A more suitable approach in this case might involve drones or tethered balloons (e.g., Greenberg et al. 2014), either to support lightweight samples directly or to lift tubing that serves as an inlet for larger in situ samplers; these are easily movable and rapidly deployable when stress episodes are located. In addition, aircraft PTR-MS measurements have been demonstrated (Karl et al. 2013) and could be valuable tools for targeting and characterizing short-term stress events. As a starting point, it may be easier to observe more stationary biotic stresses, such as plant disease; Jansen et al. (2011) found that VOCs can provide indications of disease, and the emission signatures may be distinct for different diseases. Biotic stressors that can move rapidly (such as insect infestations) may prove to be more logistically challenging.

In addition to field-based measurements, there are promising new techniques in remote sensing that could be used to quantify VOC emissions on a global scale. Unique high-spectral-resolution measurements have been used to isolate signals of chlorophyll fluorescence and reflectance (e.g., Gamon et al. 1992, Peñuelas et al. 1995), providing real-time estimates of vegetation status (Joiner et al. 2011). A decline in photosynthetic activity, which is directly related to chlorophyll fluorescence, has been tied to long-term drought stress in tropical forests, serving as an early warning of loss of greenness (Zhou et al. 2014). Not only can these measurements be used to give accurate estimates of gross primary productivity on a global scale (Guanter et al. 2014), but they can also be used as an indirect estimator of isoprene emissions at the ecosystem level (Peñuelas et al. 2013). As such, satellite measurements could improve ecosystem-scale measurements of VOC emissions on a global scale, complementing the higher spatial and temporal resolution of in situ VOC emission measurements. In turn, in situ measurements can be used to interpret and validate satellite measurements.

Another promising source of data for quantifying ecosystem stress concerns a relatively new idea called ecometabolomics (Peñuelas and Sardans 2009, Sardans et al. 2011, Rivas-Ubach et al. 2013). This concept takes the approach that environmental conditions trigger reactions along specific metabolic pathways. Then, as a physiological response, plants will produce volatile emissions.

Fig. 7. Yearly peak leaf area index (LAI) timing (Julian Day) vs. yearly maximum Keetch-Byram Drought Index (KBDI) for years 2006–2012. Peak LAI is defined as the last day of measurements before LAI values begin to decrease for the winter season. The maximum KBDI is the largest value of KBDI during spring, summer, or fall of that year (winter is excluded to avoid counting drought carryover from previous years). Black line indicates ordinary least-squares regression through the plotted points.
metabolites (i.e., VOCs). This approach has the potential to capture dynamical changes in ecosystem metabolomes, revealing ecophysiological mechanisms that are activated to produce VOC emissions (Peñuelas and Sardans 2009). One of the major challenges is that the plant kingdom has on the order of 10^5 metabolites, and individual metabolomes in a living population may vary (Sardans et al. 2011). As such, explorations of ecometabolomics have thus far been limited to narrow, controlled cases. Nevertheless, if these difficulties can be overcome, ecometabolomics could be used in conjunction with targeted field measurements in revealing not only the missing “stress term,” but also how stress-induced VOC emissions may change with climate change.

In addition to direct measurements, proxy measurements may be useful in locating and providing qualitative indicators of stress. For example, large insect outbreaks in boreal forests have been tracked through observations of secondary organic aerosol formation and consequent changes in cloud cover via aerosol–cloud interactions (Berg et al. 2013, Joutensaari et al. 2015).

The amount of VOC emission data that would be required to identify signatures is sufficiently large that advanced “big data” techniques may become necessary to robustly identify signatures of stress. In particular, these techniques must be able to reconstruct signatures that depend upon multiple sources of variability and are convolved with other signatures, all in the presence of noise and potential missing data. As an example, plant emissions of isoprene are affected by the interactive effects of CO_2 concentration and leaf temperature (Fotosnak 2014); sophisticated analysis tools are required to untangle these complex relationships.

In recent years, a wide variety of tools that deal with complex data have become available. An example of such tools are genetic algorithms that...
robustly identify key parameters that explain features in complex data, as well as identify latent variables that are missing from explanations of signatures (e.g., Heredia-Langner et al. 2013). Another example involves machine learning techniques, such as support vector machine learning or Bayesian compressive sensing (e.g., Cacciatore et al. 2014) to distinguish unique features and identify commonalities in signatures, providing answers to two crucial questions: (1) Can signatures associated with different types of stress be distinguished from each other? and (2) Are there commonalities among signatures of the same stress type in different ecosystems with potentially different dominant plant phenotypes? Understanding complex, multidimensional relationships can be aided by recent advances in visualization techniques (Poco et al. 2014) in concert with parallel processing using, for example, divide-and-recombine data processing approaches (e.g., Hafen et al. 2013) to discover features, analyze and compare data, or potentially perform real-time analysis of data streams to adaptively target field measurements.

**FUTURE DIRECTIONS**

Establishing robust, quantifiable, predictive signatures of ecosystem stress has numerous applications to a wide variety of sectors. From an atmospheric science standpoint, the ultimate goal is to characterize the radiative and chemical impacts of changes in biogenic VOC emissions in the face of anthropogenic climate change. One major component of this goal involves improvements in representations of the “stress term” by MEGAN and other biogenic VOC models; in turn, these models are being incorporated into Earth System Models.

Fig. 9. Volatile organic compound (VOC) fluxes (y-axis) as a function of Julian Day (x-axis). Green lines indicate the maximum daily value of VOC emission. Blue lines indicate calculations of VOC emissions from Model of Emissions of Gases and Aerosols from Nature when forced with local meteorological measurements. Shading indicates the drought level; an increase in drought level corresponds to a 100-point increase in Keetch-Byram Drought Index.
such as the Community Earth System Model (CESM; Hurrell et al. 2013) to understand the interactions with and feedbacks between biogenic VOC emissions and climate change.

An additional application of these techniques is in the field of precision farming. In the cases of agricultural and bioenergy crops, the optimal growing strategy will involve maximizing production while minimizing environmental impact. By understanding early warning signatures of stress through VOC emission measurements, farmers can alter irrigation, planting timing, and even planting location to minimize plant stress and increase productivity. This would simultaneously decrease aggregate VOC emissions, thereby reducing biogenic environmental impacts. On a somewhat different note, there exists the potential to breed crops that naturally emit antifungal or herbivore-repellent VOCs to enhance resilience without having to resort to pesticides (Stenberg et al. 2015); using observations of such plants as a control case could help better identify signatures of stress.

There remains a great deal of work in seeing the ideas presented here to fruition. Measurement of ecosystem-scale chemical signatures will be the result of a confluence of new foci in research efforts with new technologies and techniques. Concerted effort and investment by the research community in this new paradigm of quantification has the potential to transform a broad range of communities that depend on understanding stress at the ecosystem level.

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Literature Cited

Alexander, M. E. 1990. Computer calculation of the Keetch-Byram Drought Index – programmers beware! Fire Management Notes 51:23–25.
Bamberger, I., et al. 2011. Deposition fluxes of terpenes over grassland. Journal of Geophysical Research 116:D14305.
Berg, A. R., C. L. Heald, K. E. Huff Hartz, A. G. Hallar, A. J. H. Meddens, J. A. Hicke, J. F. Lamarque, and S. Tilmes. 2013. The impact of bark beetle infestations on monoterpen emission and secondary organic aerosol formation in western North America. Atmospheric Chemistry and Physics 13:3149–3161.
Bergström, R., M. Hallquist, D. Simpson, J. Wildt, and T. F. Mentel. 2014. Biotic stress: A significant contributor to organic aerosol in Europe? Atmospheric Chemistry and Physics 14:13603–13647.
Boden, T. A., M. Krassovski, and B. Yang. 2013. The AmeriFlux data activity and data system: an evolving collection of data management techniques, tools, products and services. Geoscientific Instrumentation, Methods and Data Systems 2:165–176.
Cacciatore, S., C. Luchinat, and L. Tenori. 2014. Knowledge discovery by accuracy maximization. Proceedings of the National Academy of Sciences USA 111:5117–5122.
Crespo, E., M. Graus, J. B. Gilman, B. M. Lerner, R. Fall, F. J. M. Warren, and C. Warnke. 2013. Volatile organic compound emissions from elephant grass and bamboo cultivars used as potential bioethanol crop. Atmospheric Environment 65:61–68.
Drewniak, B. A., P. K. Snyder, A. L. Steiner, T. E. Twine, and D. J. Wuebbles. 2014. Simulated changes in biogenic VOC emissions and ozone formation from habitat expansion of Acer rubrum (red maple). Environmental Research Letters 9:014006.
Field, C. B., et al. 2014. Technical summary. In C. B. Field, et al., editors. Climate change 2014: impacts, adaptation, and vulnerability. Contribution of Working Group II to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, UK and New York, New York, USA.
Gamon, J. A., J. Peñuelas, and C. B. Field. 1992. A narrow-waveband spectral index that tracks diurnal changes in photosynthetic efficiency. Remote Sensing of Environment 41:35–44.
Graus, M., M. Müller, and A. Hansel. 2010. High resolution PTR-TOF: quantification and formula confirmation of VOC in real time. Journal of the American Society for Mass Spectrometry 21:1037–1044.

Greenberg, J. P., et al. 2014. A tethered-balloon PTRMS sampling approach for rapid surveying of landscape-scale biogenic VOC fluxes. Atmospheric Measurement Techniques 7:2263–2271.

Guanter, L., et al. 2014. Global and time-resolved monitoring of crop photosynthesis with chlorophyll fluorescence. Proceedings of the National Academy of Sciences USA 111:1327–1333.

Guenther, A. B., X. Jiang, C. L. Heald, T. Sakulyanontvittaya, T. Duhl, L. K. Emmons, and X. Wang. 2012. The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions. Geoscientific Model Development 5:1471–1492.

Guenther, A. B., et al. 1995. A global model of natural volatile organic compound emissions. Journal of Geophysical Research 100:8873–8892.

Hafen, R., L. Gosink, J. McDermott, K. Rodland, K. K. Van Dam, and W. S. Cleveland. 2013. Trelliscope: a system for detailed visualization in the deep analysis of complex data. IEEE Symposium on Large-Scale Data Analysis and Visualization.

Harley, P. C., R. K. Monson, and M. T. Lerdau. 1999. Ecological and evolutionary aspects of isoprene emission from plants. Oecologia 118:109.

Heredia-Langner, A., K. H. Jarman, B. G. Amidan, and J. G. Pounds. 2013. Genetic algorithms and classification trees in feature discovery: diabetes and the NHANES database. The 9th International Conference on Data Mining (DMIN13).

Hurrell, J. W., et al. 2013. The community earth system model: a framework for collaborative research. Bulletin of the American Meteorological Society 94:1339–1360.

Jansen, R. M. C., J. Wildt, I. F. Kappers, H. J. Bouwmeester, J. W. Hofstee, and E. J. van Henten. 2011. Detection of diseased plants by analysis of volatile organic compound emission. Annual Review of Phytopathology 49:157–174.

Joiner, J., Y. Yoshida, A. P. Vasilkov, Y. Yoshida, L. A. Corp, and E. M. Middleton. 2011. First observations of global and seasonal terrestrial chlorophyll fluorescence from space. Biogeosciences 8:637–651.

Joutensaari, J., et al. 2015. Biotic stress accelerates formation of climate-relevant aerosols in boreal forests. Atmospheric Chemistry and Physics 15:12139–12157.

Judd, W., E. Vanzo, Z. Li, A. Ghirardo, I. Zimmer, T. D. Sharkey, A. Hansel, and J. P. Schnitzler. 2016. Effects of heat and drought stress on post-illumination bursts of volatile organic compounds in isoprene-emitting and non-emitting poplar. Plant, Cell, and Environment 39:1204–1215.

Juuti, S., J. Arey, and R. Atkinson. 1990. Monoterpene emission rate measurements from a monterey pine. Journal of Geophysical Research 95:7515–7519.

Karl, T., A. Guenther, A. Turnipseed, E. G. Patton, and K. Jardine. 2008. Chemical sensing of plant stress at the ecosystem scale. Biogeosciences 5:1287–1294.

Karl, T., P. K. Misztal, H. H. Jonsson, S. Shertz, A. H. Goldstein, and A. B. Guenther. 2013. Airborne flux measurements of BVOCs above Californian oak forests: experimental investigation of surface and entrainment fluxes, OH densities and Dahmköhler numbers. Journal of Atmospheric Science 70:3277–3287.

Kaser, L., et al. 2013. Undisturbed and disturbed above canopy ponderosa pine emissions: PTR-TOF-MS measurements and MEGAN 2.1 model results. Atmospheric Chemistry and Physics 13:11935–11947.

Keetch, J. J., and G. M. Byram. 1968. A drought index for forest fire control. Tech. rep., U.S. Department of Agriculture – Forest Service, Washington, D.C., USA.

Kessler, A., and I. T. Baldwin. 2001. Defensive function of herbivore-induced plant volatile emissions in nature. Science 291:2141–2144.

Kessler, A., and I. T. Baldwin. 2002. Plant responses to insect herbivory: the emerging molecular analysis. Annual Review of Plant Biology 53:299–328.

Kleist, E., et al. 2012. Irreversible impacts of heat on the emissions of monoterpenes, sesquiterpenes, phenolic BVOC and green leaf volatiles from several tree species. Biogeosciences 9:5111–5123.

Kolasa, J., and T. A. Pickett. 1992. Ecosystem stress and health: an expansion of the conceptual basis. Journal of Aquatic Ecosystem Health 1:7–13.

Mentel, T. F., et al. 2013. Secondary organic aerosol formation from stress-induced biogenic emissions and possible climate feedbacks. Atmospheric Chemistry and Physics 13:8755–8770.

NCDC. 2014. North American drought monitor. https://www.ncdc.noaa.gov/temp-and-precip/drought/nadm/.

Niinemets, Ü., A. Kannaste, and L. Copolovici. 2013. Quantitative patterns between plant volatile emissions induced by biotic stresses and the degree of damage. Frontiers in Plant Science 4:262.

Ortega, J., et al. 2014. Overview of the Manitou Experimental Forest Observatory. Atmospheric Chemistry and Physics 14:1647–1709.

Park, J. H., A. H. Goldstein, J. Timovskyy, S. Fares, R. Weber, J. Karl, and R. Holzinger. 2013. Active atmosphere-ecosystem exchange of the vast majority of detected volatile organic compounds. Science 341:643–647.
Patton, E. G., et al. 2011. The canopy horizontal array turbulence study. Bulletin of the American Meteorological Society 92:593–611.

Peñuelas, J., I. Filella, and J. A. Gamon. 1995. Assessment of photosynthetic radiation-use efficiency with spectral reflectance. New Phytologist 131:291–296.

Peñuelas, J., I. Filella, C. Stefanescu, and J. Lluísia. 2005. Caterpillars of *Euphydryas aurinia* (Lepidoptera: Nymphalidae) feeding on *Succisa pratensis* leaves induce large foliar emissions of methanol. New Phytologist 167:851–857.

Peñuelas, J., and J. Llusia. 2001. The complexity of factors driving volatile organic compound emissions by plants. Biologia Plantarum 44:481–487.

Peñuelas, J., and J. Lluísia. 2003. BVOCs: Plant defense against climate warming? Trends in Plant Science 8:105–109.

Peñuelas, J., G. Marino, J. Llusia, C. Morfopoulos, G. Farré-Armengol, and I. Filella. 2013. Photochemical reflectance index as an indirect estimator of foliar isoprenoid emissions at the ecosystem level. Nature Communications 4:2604.

Pocó, J., A. Dasgupta, Y. Wei, W. Hargrove, C. Schwalm, R. Cook, E. Bertini, and C. Silva. 2014. SimilarityExplorer, a visual inter-comparison tool for multifaceted climate data. In H. Carr, P. Rheingans, and H. Schumann, editors. Eurographics Conference on Visualization (EuroVis) 2014. Volume 33.

Potosnak, M. J. 2014. Including the interactive effect of elevated CO$_2$ concentration and leaf temperature in global models of isoprene emission. Plant, Cell, and Environment 37:1723–1726.

Potosnak, M., et al. 2014. Observed and modeled ecosystem isoprene fluxes from an oak-dominated temperate forest and the influence of drought stress. Atmospheric Environment 84:314–322.

Raguso, R. A. 2016. More lessons from linalool: insights gained from a ubiquitous oral volatile. Current Opinion in Plant Biology 32:31–36.

Rapport, D. J. 1992. Evaluating ecosystem health. Journal of Aquatic Ecosystem Health 1:15–24.

Rinne, J., T. Karl, and A. Guenther. 2007. Priming by airborne signals boosts direct and indirect resistance in maize. Plant Journal 49:16–26.

Rivad, T., J. C. Turlings, and W. J. Lewis. 1990. Exploitation of herbivore-induced plant odors by host-seeking parasitic wraps. Science 250:1251–1253.

Ulanowicz, R. E. 1978. Modeling environmental stress. Pages 1–18 in J. H. Thorp and J. W. Gibbons, editors. Energy and environmental stress in aquatic systems. Technical Information Center, U.S. Department of Energy, Washington, D.C., USA.

Wohlfahrt, G., et al. 2015. An ecosystem-scale perspective of the net land methanol flux: synthesis of micrometeorological flux measurements. Atmospheric Chemistry and Physics 15:7413–7427.

Zhou, L., et al. 2014. Widespread decline of Congo rainforest greenness in the past decade. Nature 509:86–90.