Simple, stable, and affordable: Towards long-term ecosystem scale flux measurements of VOCs

CrossMark

Biogenic volatile organic compounds (BVOC) are key players in atmospheric chemistry and climate, yet our understanding of their emission dynamics is very limited. They dominate global emissions of volatile organic compounds (VOC) with estimated rates that are an order of magnitude higher than the anthropogenic VOC emissions. Since the publication of the first global BVOC emission inventories there have been efforts to develop more realistic and process-based models of BVOC emissions. However, there are only a few ecosystem-scale BVOC flux data for evaluation and improvement of these models. Thus a reliable network of observations is urgently needed. Surface layer flux measurements by micrometeorological methods provide the most suitable data for this purpose but there are some hindrances preventing the implementation of a long-term flux measurement network.

Prior to this millennium, micrometeorological VOC flux measurements were usually conducted by indirect techniques, such as surface layer gradient and relaxed eddy accumulation, requiring parameterizations. The air samples were typically analyzed off-line with labor-intensive laboratory methods resulting in relatively small datasets. While these efforts have been useful for a broad evaluation of the diurnal performance of emission algorithms, they are insufficient for characterizing extreme events or seasonal to interannual variations.

Since the beginning of this millennium, the commercialization of fast response on-line VOC measurement instruments, such as Fast Isoprene Sensor (FIS) Proton Transfer Reaction — Quadrupole Mass Spectrometer (PTR-QMS) and Proton Transfer Reaction — Time of Flight Mass Spectrometer (PTR-ToFMS), has enabled several longer-term flux measurement data sets. These instruments have also enabled the use of the eddy covariance technique, which is the direct method to measure turbulent fluxes in the surface layer.

Thus, there now exist a few tens of ecosystem scale BVOC flux data sets covering periods from ten days to a growing season but data sets covering several growing seasons are still very rare. The above canopy VOC flux data sets are typically limited to measurements sites with good infrastructure, and thus represent only a limited set of ecosystems. In comparison, the global network of carbon dioxide, water and energy flux measurements covers an adequate number of ecosystems and the recently expanded methane flux measurement network is moving towards this level. Achieving a similar advancement of BVOC flux measurements in a wide set of ecosystems requires overcoming several challenges.

One challenge is associated with the rich diversity of BVOC compounds. The development of fast on-line VOC analyzers has focused on relatively complex instruments capable of measuring an ever-wider range of compounds. The FIS enabled measurements of the flux of one component, isoprene. PTR-QMS with the disjunct eddy covariance technique extended this to measuring fluxes of about ten species. PTR-ToFMS with the conventional eddy covariance approach has been used to measure fluxes of hundreds of compounds. This has improved our understanding of the range of BVOC fluxes but has also led to heavy, expensive instruments, requiring frequent and complex calibration and concentration calculation procedures, and that have a high power requirement and are relatively difficult to maintain for long-term measurements.

PTR-ToFMS measurements demonstrate that there are hundreds of BVOC but also show that the majority of the VOC emission is comprised of only a few compounds (Park et al., 2013; Schallhart et al., 2015). Also on the global scale, there are only a few compounds that are known to contribute to the majority of the BVOC emissions (Guenther et al., 2012). Thus we suggest that for long-term VOC flux measurements it is reasonable to concentrate on a few key species and to develop an analyzer(s) for those compounds that are robust and require minimal attendance, power and cost. The key compounds we suggest are the ones with highest global emission, isoprene, the sum of monoterpenes, and methanol in this order of priority, and as justified below.

It has been estimated that global isoprene emission is 500—600 Tg yr^{-1}, thus contributing 50—60% to the global BVOC emission (Guenther et al., 2012; Sindelarova et al., 2014). Due to isoprene's high emission and its reactivity with a typical atmospheric lifetime of about 1 h, it is the most important BVOC affecting the boundary layer atmospheric chemistry in many areas around the world. It contributes to tropospheric ozone formation thus affecting photochemical pollution, and affects the atmospheric oxidative capacity via OH. It is the most studied compound of all biogenic VOCs.

Monoterpenes are a group of compounds that mostly have a similar reactivity as isoprene, but with significantly lower global emission of 100—160 Tg yr^{-1} contributing 10—16% to the global total BVOC emission (Guenther et al., 2012; Sindelarova et al., 2014). However, in some ecosystems, such as many coniferous forests, they are the major compound group emitted. These compounds are known to take part in the secondary organic aerosol formation and growth (Tunved et al., 2006) and therefore have an important climatic role.

Methanol is a ubiquitous compound that is emitted by all ecosystems resulting in a global emission of same magnitude with monoterpenes (100—130 Tg yr^{-1}, 10—13% of the total BVOC emission; Guenther et al., 2012; Sindelarova et al., 2014). Due to its relatively low reactivity its atmospheric lifetime is several days and it can be transported into the free troposphere where it affects oxidant concentrations especially in the upper troposphere (Tie et al., 2003). Methanol also can show significant deposition into ecosystems (e.g. Laffineur et al., 2012).

The chamber technique was previously the most used method to measure BVOC emissions. However, it does not directly provide ecosystem scale emission. Furthermore, the chamber typically disturbs the measured branch. Thus a method measuring ecosystem scale emission directly is preferred. Micrometeorological surface layer flux measurement techniques fill this requirement.

There are a variety of micrometeorological techniques to measure ecosystem-atmosphere gas exchange. Techniques such as eddy covariance (EC), relaxed eddy accumulation (REA), and surface layer gradient (SLG) have been used to measure BVOC emissions. EC and SLG techniques have been used for long-term BVOC flux measurements (e.g. Pressley, 2005; Hörtnagl et al., 2011; Rantala et al., 2015). As eddy covariance is the most direct of these methods, and thus least dependent on empirical parameterizations, we should aim for long-term measurements with this technique. This method also has the advantage of requiring a less complicated air-sampling inlet.

In order to be applicable for eddy covariance measurements, a trace gas analyzer must meet two basic requirements. *I*: It needs to measure trace gas concentration variations at relevant atmospheric levels, and *II*: the instrument needs to have a short enough response time to be able to resolve the short-term variations at time-scales relevant for turbulent transport. These requirements need to be critically assessed in order to identify a feasible but theoretically sound measurement system.

The accuracy needed for requirement *I* depends on the acceptable lower limit of fluxes and level of uncertainty, and the measurement setup, e.g. measurement height. In order to be able to resolve the diurnal cycle of the fluxes of our target compounds, we should aim at a flux detection limit of 20% of the typical daytime flux. The magnitudes of fluxes of the target compounds vary widely across ecosystems. Some ecosystems emit isoprene during daytime with rates exceeding 10 nmol m^{-2} s^{-1} (e.g. Pressley, 2005; Schallhart et al., 2015), but there are ecosystems with considerably lower emissions. In many ecosystems that are considered isoprene emitters, the daytime emission range is around 1–2 nmol m^{-2} s^{-1} (e.g. Holst et al., 2010; Laffineur et al., 2011; Copeland et al., 2014). The monoterpene emissions are often lower than the highest isoprene emissions. Typical daytime emissions in many monoterpene emitting ecosystems range between 0.4 and 1 nmol m^{-2} s^{-1} (e.g. Rinne et al., 2009; Laffineur et al., 2011). The lower range of methanol emission is according to recent review (Wohlfahrt et al., 2015) around 3 nmol m^{-2} s^{-1}. Thus, we should aim at flux detection limits of 0.2 nmol m^{-2} s^{-1} for isoprene, 0.08 nmol m^{-2} s^{-1} for sum of monoterpenes, and 0.6 nmol m^{-2} s^{-1} for methanol.

The requirement *II* for fast response is usually taken to mean a response time of 0.1 s (10 Hz measurement frequency). However for measuring fluxes relatively high above the canopy, as is the case with measurements at forested locations, even a response time as slow as 1 s causes a relatively small flux underestimation. Furthermore, this underestimation can be corrected for, as the spectral behavior of turbulent fluxes at high frequencies can be measured and is well known. A quantitative analysis of the required accuracies and response times for different conditions is thus the first step in order to arrive at the most feasible VOC analyzer for long-term flux measurements.

In addition to meeting the abovementioned basic requirements for eddy covariance, a suitable system must also be feasible for measurements covering timescales over several growing seasons. Especially this requires long-term stability to reduce the frequency of site visits for calibration. Remote control capability and automatic calibration systems can also be used to reduce the need for site visits. Also the need for e.g. special gases or liquid nitrogen could hinder the operation of an instrument at more remote locations, and should be avoided.

Finally, affordability of the VOC analyzer is a key hurdle for its wider utilization in a measurement network. This includes both purchasing costs and the annual operating cost. The existing global CO_2 and H_2O eddy covariance flux network utilizes analyzer that cost about 20 000 € and has very low annual operating costs. The expanding CH_4 network uses analyzers with costs ranging from 40 000 € to 80 000 €. The current fast response VOC analyzers have either a too limited range of compounds and are difficult to maintain (FIS) or have purchase costs that considerably exceed that of CO_2 or CH_4 detectors (PTR-QMS, PTR-ToFMS). The development of a fast response BVOC analyzer suitable for a global BVOC flux network, likely using mass spectrometry or a spectroscopy approach, is needed.

There has been a growing interest in the past decade in the development of miniaturized, low power mass spectrometers, for a range of applications (e.g., Bristow et al., 2014; Huang et al., 2010; Pulliam et al., 2015). While the BVOC scientific community can take advantage of the developments occurred for other purposes, it is likely that a targeted effort will be required in order to develop mass spectrometers suitable for measuring fluxes of specific BVOC.

Another area of active instrument development has been the development of fast response laser spectroscopy systems suitable for EC measurements of trace gas fluxes. Relatively affordable, robust eddy flux systems have successfully been demonstrated for the simplest hydrocarbon, methane (e.g. Jackowicz-Korczyński et al., 2010; Yuan et al., 2015). Spectroscopic techniques have also been used for fast-response detection of many VOCs (e.g., Yokelson et al., 2008) but not with the sensitivity required for BVOC flux studies. However, the use of multi-pass systems and other approaches for lowering instrument noise could overcome the obstacle and lead to potential for EC measurements of at least for some of the important BVOCs (e.g., Brauer et al., 2014; Phillips et al., 2015; Sun et al., 2015).

If the basic requirements for eddy covariance measurements together with simplicity, stability and affordability were met, the open scientific questions would drive the bottom-up generation of an ecosystem scale VOC flux measurement network. For example, the effects of extreme weather events or herbivore attacks have been mostly studied in a branch or plant scale (e.g. Maja et al., 2014; Vanzo et al., 2015). Detection of these on ecosystem scale requires longer-term measurements both to catch any of these sporadically occurring phenomena and to establish reliable baseline outside the event. This would build on the success of the existing carbon/water/energy flux network and advance our understanding of the role of BVOC emissions in the earth system and improve air quality and climate model predictions.

References

Brauer, et al., 2014. Atmos. Meas. Tech. 7, 3839–3847.
Bristow, et al., 2014. J. Am. Soc. Mass Spectrom. 25, 1794–1802.
Copeland, et al., 2014. Atmos. Environ. 94, 86–95.
Guenther, et al., 2012. Geosci. Model Dev. 5, 1471–1492.
Holst, et al., 2010. Atmos. Chem. Phys. 10, 1617–1634.
Hörtnagl, et al., 2011. J. Geophys. Res. 116, G03021. http://dx.doi.org/10.1029/2011JG001641.
Huang, et al., 2010. J. Am. Soc. Mass Spectrom. 21, 132–135.
Jackowicz-Korczyński, et al., 2010. J. Geophys. Res. G02009. http://dx.doi.org/10.1029/2008JG000913.
Laffineur, et al., 2011. Atmos. Environ. 45, 3157–3168.
Laffineur, et al., 2012. Atmos. Chem. Phys. 12, 577–590.
Maja, et al., 2014. Tree Physiol. 34, 241–252.
Park, et al., 2013. Science 9 (341), 643–647.
Phillips et al., 2015, 93700Z–93700Z-14.
Pressley, 2005. J. Geophys. Res. 110, D07301. http://dx.doi.org/10.1029/2004JD005523.
Pulliam, et al., 2015. J. Am. Soc. Mass Spectrom. 26, 224–230.

Rantala, et al., 2015. Biogeosciences 12, 5753—5770.
Rinne, et al., 2009. Boreal Environ. Res. 14, 807—826.
Schallhart, et al., 2015. Atmos. Chem. Phys. Discuss. 15, 27627—27673.
Sindelarova, et al., 2014. Atmos. Chem. Phys. 14, 9317—9341.
Sun, et al., 2015. Rev. Sci. Inst. 86 (095003).
Tie, et al., 2003. Geophys. Res. Lett. 30, 1881. http://dx.doi.org/10.1029/2003G L017167.
Tunved, et al., 2006. Science 312, 261—263.
Vanzo, et al., 2015. Plant Physiol. 169.
Wohlfahrt, et al., 2015. Atmos. Chem. Phys. 15, 7413—7427.
Yokelson, et al., 2008. Atmos. Chem. Phys. 8, 3509—3527.
Yuan, et al., 2015. J. Geophys. Res. 120, 6271—6289.

J. Rinne[*]
Department of Geosciences and Geography, University of Helsinki, Finland

Department of Physical Geography and Ecosystem Science, Lund University, Sweden

T. Karl
Institute of Atmospheric and Cryospheric Sciences, University of Innsbruck, Austria

A. Guenther
Department of Earth System Science, University of California, Irvine, CA, USA

[*] Corresponding author. Lund University, Department of Physical Geography and Ecosystem Science, Sölvegatan 12, S-22362 Lund, Sweden.
E-mail address: janne.rinne@nateko.lu.se (J. Rinne).

25 September 2015
Available online 9 February 2016