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Bi-directional Exchange of Volatile Organic Compounds

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Introduction

Volatile organic compounds (VOC) are a relatively minor component of the atmosphere and yet are widely recognized to have important roles in air quality and climate. With the exception of methane, an important greenhouse gas, atmospheric VOC are primarily of interest because of their impact on other atmospheric constituents, including oxidants and aerosol. Most of the global annual VOC emission is from biogenic sources but biomass burning, fossil fuel combustion and industrial activities dominate in some regions. Each of these major sources can be further categorized, e.g., biogenic sources include plant chloroplasts, plant specialized tissues, microbes, and animals. The processes for removing VOC from the

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atmosphere include VOC surface deposition, VOC deposition to particles, and surface deposition of their oxidation products including oxidized VOC, CO and CO_2. Regional to global atmospheric chemistry and transport models (CTMs) routinely include at least some VOC emission and removal processes but in a highly simplified form. Climate models have previously included just methane but as they evolve into more comprehensive earth system models, other VOC are being included although the sources and sinks may be prescribed or highly simplified.

A comprehensive characterization of atmospheric VOC is challenging due to the overwhelming number of compounds. Tens of thousands of VOC have been measured in the atmosphere and there may be hundreds of thousands more that have not been measured (Goldstein and Galbally 2007). Treatment of these compounds could be simplified however by categorizing them with respect to their surface-atmosphere exchange characteristics: reduced VOC (RVOC), atmospheric oxidation products (AOVOC) and bi-directional VOC (BDVOC).

Reduced VOC (RVOC)

Reduced VOC are produced at or near the earth surface and emitted into the atmosphere but are not produced in the atmosphere. RVOC include hydrocarbons such as alkanes (e.g., methane), alkenes (e.g., isoprene) and arenes (e.g., benzene). VOC containing sulfur or nitrogen could be included in this category. Oxygenated VOC that are emitted from vegetation, e.g., the hemiterpene, methyl-butenol, and the monoterpene, linalool, but are not produced in the atmosphere would be considered RVOC; but any oxygenated VOC that are produced in the atmosphere would not be included.

Soils and litter are sources of several VOC (furfural, butanoic acid, methanol, …) but these sources have not yet been well quantified (Insam and Seewald 2010; Leff and Fierer 2008). Similarly composts and slurry applications may be sources

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of nitrogen containing VOC like trimethylamine (TMA) (Seewald et al. 2010; Twigg et al. 2011).

Since RVOC are not produced in the atmosphere, any RVOC deposition flux is due to molecules that were at one time emitted into the atmosphere and are now returning to the surface, although most likely to a different location. Methane and isoprene are the dominant VOC emissions and are both emitted into the atmosphere at rates of ~550 Tg per year (Guenther et al. 2006; Neef et al. 2010). These two RVOC are widely recognized as two of the most important VOC in the earth system and VOC surface exchange research has focused on these two compounds. This has primarily been investigations of emissions resulting in the development of relatively sophisticated models describing the processes controlling emissions of these two compounds. However, it has also been noted that surface sinks of these two compounds are not negligible and may account for about 5 % of the methane and isoprene emitted into the atmosphere (Cleveland and Yavitt 1997; Neef et al. 2010).

Atmospheric Oxidation (AOVOC) Products

The chemical degradation of RVOC in the atmosphere produces a large variety of oxidized VOC. For example, the oxidation of a single compound, the five carbon isoprene, produces a diverse array of AOVOC starting with four carbon first generation products, including methyl vinyl ketone (MVK) and methacrolein (MAC), that can react to form second generation products and so on until the carbon has been oxidized to CO_2. CTMs do not use explicit schemes to represent all of these AOVOC, due to the complexity and computational resources required, but most at least consider the first generation products MVK and MAC, which account for about 80 % of the carbon in the initial stage of isoprene oxidation. Some models represent them as specific species while others represent them as a lumped isoprene product. In either case, these molecules or their lumped sum are typically included in the dry deposition schemes of CTMs but this has been accomplished by assigning a dry deposition velocity that is based on measurements of other compound such as SO_2 and ozone. Karl et al. (2010) used above canopy flux measurements to demonstrate that the assumed canopy resistance for MVK and MAC used in CTMs is overestimated by about a factor of 5. They proposed that this high deposition rate was the result of active removal by leaves in order to eliminate these toxic compounds. The incorporation of a more accurate canopy resistance in a CTM results in substantial changes in simulated AOVOC deposition rates and atmospheric concentration distributions.

Jardine et al. (2010) observed emissions of oxidized VOC, including MVK and MAC, from vegetation enclosures and suggested that leaves could be a significant source of atmospheric MVK and MAC. The relative importance of foliar MVK and MAC emissions is not yet understood but the Karl et al. (2010) observations of higher than expected net deposition of MVK and MAC contradict the suggestion that vegetation is a major direct source of MVK and MAC. However, we should consider that these compounds could be emitted at substantial rates under certain conditions, such as high temperatures and other stresses. The potential importance of AOVOC emission, and thus bi-directional exchange, should be recognized and a better understanding of the rates and controlling processes is needed.

Bi-directional VOC (BDVOC)

The final category of VOC have substantial source and sink terms at both the earth surface and in the atmosphere. Emission and deposition processes are of similar importance for these BDVOC and so the accurate estimation of the net flux requires consideration of both. Kesselmeier (2001) identified four low molecular weight oxygenated VOC (acetaldehyde, formaldehyde, acetic acid, and formic acid) as compounds that are both emitted and taken up by plants in substantial quantities. These compounds can also be of anthropogenic origin and are produced in the atmosphere from the oxidation of RVOC. Kesselmeier (2001) recognized that the surface-atmosphere exchange of these compounds is bi-directional and their fluxes should be incorporated into models using an approach that includes a compensation point where emission occurs when ambient concentrations are below a certain level and deposition occurs with higher ambient concentrations. The compensation points reported by Kesselmeier (2001) indicate that plants are likely to be a source of these compounds in a clean remote environment and a sink in a polluted environment.

Of the four BDVOC identified by Kesselmeier (2001), acetaldehyde tended to have the highest leaf level emissions and this has also been observed for net ecosystem fluxes (Schade and Goldstein 2002). Acetaldehyde emission sources in terrestrial ecosystems include soil and leaf litter in addition to plant canopies (Warneke et al. 1999). Jardine et al. (2009) used a stable carbon isotope as a tracer for characterizing multiple pathways for producing acetaldehyde in plants and also report that emissions were elevated following both leaf anoxia and mechanical stress. These findings highlight the complexity associated with accurately simulating the processes controlling just the emissions component of acetaldehyde emissions. Above canopy acetaldehyde fluxes from three forests were compared by Jardine et al. (2008). Acetaldehyde was emitted from a forest canopy with an LAI of 3 but there was a net deposition observed for canopies with LAI of 4.6 and 5.3. Vertical profiles of acetaldehyde gradients within and above these canopies showed that acetaldehyde was emitted by the upper canopy and taken up by the lower canopy. This is in agreement with previous observations by Kesselmeier (2001) showing that acetaldehyde and other BDVOC can be emitted from sunlit leaves and taken up by shaded leaves.

The above canopy atmosphere is not the only location where RVOC can be oxidized. The canopy air space contains oxidants that can react with RVOC to produce oxidized VOC but it is a relatively small volume in comparison to the atmospheric boundary layer and so has previously been thought to be a relatively small source of oxidized VOC. DiGangi et al. (2011) recently measured a surprisingly large flux of formaldehyde from a forest canopy into the atmosphere. Branch and soil enclosure measurements indicated that these direct emission sources could only account for ~15 % of the observed ecosystem flux. They concluded that the remainder was due to the oxidation of biogenic VOC within the canopy airspace. The canopy they studied was an open woodland with a relatively short residence time which would minimize the production of formaldehyde. On the other hand, the open canopy has more light penetration which would stimulate photochemistry and VOC oxidation.

Methanol is the predominant oxidized VOC in the global atmosphere with an annual global emission rate that is thought to be the third largest of any VOC, after methane and isoprene (Guenther et al.). High rates of biogenic methanol emission were first reported by MacDonald and Fall (1993) who noted that emissions were especially high from young expanding leaves. Heikes et al. (2002) compiled methanol sources and sinks into a global budget and estimated that about a fourth of the emitted methanol is dry deposited to terrestrial surfaces and another fourth is dry deposited to the ocean. Millet et al. (2008) developed a global budget using additional observations and estimated that dry deposition is responsible for about half of the methanol sink but that the ocean sink is 2.5 times greater than for land. These analyses indicate that methanol uptake by terrestrial ecosystems is important and should be considered as a BDVOC in surface exchange models.

After methanol, acetone is thought to be the next most dominant oxygenated VOC in the atmosphere. An analysis of the global acetone budget by Jacob (Jacob 2002) concluded that surface deposition was responsible for only 12 % of the total acetone sinks. However, this deposition is ~20 % of the emission from a terrestrial ecosystem since nearly half of the acetone is produced by atmospheric oxidation of RVOC. This indicates the complexity of acetone sources and sinks and argues for classifying it as a BDVOC that should be represented in CTM with a unified emissions and deposition model.

As can be seen from the above consideration of the best-studied VOCs, even such an apparently simple categorization approach would present many challenges. The approaches currently used in numerical models are described in Section "Current Parameterizations in CTMs for Reduced VOC and Atmospheric Oxidation Products" and the major deficiencies associated with these approaches are described in Section "Gaps and Disadvantages of Current Parameterizations". A brief description of key features of an ideal model is given in Section "The Ideal Model" and the conclusions are presented in Section Conclusion.

Current Parameterizations in CTMs for Reduced VOC and Atmospheric Oxidation Products

Reduced VOC (e.g., isoprene, α-pinene) emissions are estimated with approaches based on simple mechanistic (semi empirical) approaches that include algorithms describing emission response to variations in environmental conditions (Guenther et al. 1993; Niinemets et al. 1999) and the calculation of landscape average emission factors. The models consider the major processes driving variations in emissions. For isoprene emissions, this includes a light response that is based on electron transport, a temperature response based on enzymatic activity, and a CO_2 response based on changes in metabolite pools, enzyme activity and gene expression. The emission activity factors can account for emission response to light, temperature, leaf age, soil moisture, leaf area index and CO_2 inhibition (Guenther et al. 2012).

The surface sinks of methane and isoprene, which may account for about 5 % of the amounts emitted into the atmosphere, is either neglected or incorporated into CTMs using an emission model and a deposition model that are independent of each other even though they have similar driving variables. The deposition models are driven by land cover and weather variables along with atmospheric concentrations (2012). Although a 5 % uptake is small compared to the uncertainties in the net fluxes of methane, isoprene and other RVOC, an accurate representation of the deposition of these compounds may be important, particularly on a regional or local level as the heterogeneity of source and sink processes can result in significant net transport of these compounds. Megonigal and Guenther (2008) note that the upland ecosystems, that are primarily sinks of methane, cover a far greater area than the wetland areas that are a source of methane. The potential shift of these upland landscapes between source and sink regions could significantly impact the global methane budget and should be considered in earth system models.

The fraction of isoprene and other reactive RVOC emitted by a forest canopy that is taken up before it can escape to the above canopy atmosphere is highly dependent on the oxidizing capacity of the canopy airspace and the canopy residence time. Surface exchange models currently do not simulate these processes although in some cases a net flux and a variable sink term is used to account for these losses (2006). An accurate representation of these processes is necessary especially for highly reactive RVOC, such as the sesquiterpene β-caryophyllene, that have a large and variable fraction of emission that is removed in the canopy before reaching the above canopy atmosphere. The presence of these highly reactive VOCs in the canopy is also essential to quantify as they may play a significant role in yet unexplained non-stomatal removal of O_3 (Wolfe et al. 2011).

As outlined above, CTMs do not use explicit schemes to represent all AOVOC, due to the complexity and computational resources required. Those molecules or their lumped sum that are represented are typically included in the dry deposition schemes of CTMs by assigning a dry deposition velocity that is based on measurements of other compound such as SO_2 and ozone. As outlined previously, Karl et al. (2010) showed that the incorporation of a more accurate canopy resistance in a CTM results in substantial changes in simulated AOVOC deposition rates and atmospheric concentration distributions.

The flux of atmospheric oxidation products is estimated with parameterizations that assume the flux is equal to the product of the ambient concentration and a deposition velocity. The deposition velocity is usually treated with an approach, developed by Weseley (1989), analogous to Ohm's Law where it is expressed as the product of three resistances in series: aerodynamic resistance above the surface, quasi-laminar resistance to transport through the thin layer of air in contact with surface elements, and resistance to uptake by surface elements.

While some simple approaches have been used to integrate emission and uptake into a unified model to account for BDVOC fluxes (Millet et al. 2010; Stavrakou et al. 2011) these fluxes are typically represented in CTMs as separate emission and deposition models and one or the other may be completely neglected. A uniform approach for modeling BDVOC exchange between terrestrial ecosystems and the atmosphere is needed.

Jardine et al. (2009) proposed a modeling approach based on ambient acetaldehyde concentration, a compensation point that is a function of light and temperature, and stomatal resistance to acetaldehyde but this technique was not implemented in a CTM. A simpler approach described by Millet et al. (2010) was used in a CTM to estimate global distributions of acetaldehyde as a function of LAI, light and temperature. The model simulated maximum acetaldehyde emissions for an LAI of 2 with decreasing emissions for lower or higher LAI. Stavrakou et al. (2011) proposed and implemented a simple CTM algorithm that included both emission and deposition of methanol. However, these algorithms are not used in most CTMs.

Currently, regional scale models do not include detailed in-canopy chemistry and turbulence. In-canopy loss reactions and product formation is usually not considered explicitly. Multilayer simulations indicate that the in-canopy oxidation of the major RVOC usually results in 5–10 % reduction in emission fluxes. In-canopy reactions within CTMs are either handled with the same approach used by the CTM for outside the canopy or parameterized (Guenther et al. 2006).

Gaps and Disadvantages of Current Parameterizations

Surface-atmosphere exchange behavior is typically not considered when categorizing VOC for surface exchange models and yet this could facilitate the development of effective VOC modeling approaches. This is especially important for compounds such as acetaldehyde which have strong bi-directional exchange. The current approach of having one model for emissions of acetaldehyde and a second model for deposition of acetaldehyde is not likely to be able to adequately represent fluxes of acetaldehyde and other compounds with bi-directional exchange. The use of a single model for both emission and deposition may be especially important for accurate representations of feedbacks.

Processes that will need an improved description within most regional models, or that are missing completely, are the effect of humidity and reactions on wet surfaces on deposition or the effect of toxic compounds on BVOC emission and stomatal aperture. However, most of these effects just need to be incorporated into the available deposition schemes rather than requiring a new scheme.

The land cover classification schemes (land use, plant functional type) used in regional and global models are generally inadequate for characterizing VOC fluxes. The schemes suitable for many other processes are not sufficient, especially for characterizing biogenic VOC emission capacities. For example, broad-leaf forests include both low and high isoprene emitting trees.

The Ideal Model

One-Dimensional (1-D) Approach

Ideally, VOC emissions and deposition could be described by simulating the concentration inside the stomata that drives a gradient (Niinemets and Reichstein, 2003), with the in-stomata concentration based on a physiological model of the BVOC formation process within the plant cells. Given a model for the production of these compounds, this model would ideally reproduce the bi-directional behavior observed for some oxidized VOCs and could be easily adapted to reproduce the fluxes of RVOCs and AOVOCs.

An additional consideration is the need to compute within canopy chemistry. The fraction of isoprene and other reactive RVOC emitted by a forest canopy that is taken up before it can escape to the above canopy atmosphere is highly dependent on the oxidizing capacity of the canopy airspace and the canopy residence time. A multi-layer model is needed but this may not require a large number of layers. Model evaluations with canopy vertical profile observations are needed to determine the number of layers required. So far, process based BVOC emission models of different complexity (Monson et al. 2012) within physiologically based plant models are only available for isoprenoid emissions. Despite the value of these models for investigating the processes involved in isoprenoid synthesis, their ability to account for different stress factors and to explicitly simulate the composition of emitted monoterpenes and sesquiterpenes, together with the large number of parameters required for this type of model limits their usefulness, particularly for regional models. In addition to a process based description of the formation of oxidized VOC, which is not yet available, a description of the non-stomatal uptake is necessary for a complete representation of deposition. Finally, it has to be taken into account, that process based descriptions are generally based on leaf or branch level and must be up-scaled to canopy level by a multi-layer model for use in CTMs and climate models.

Given the number and complexity of the processes involved in surface exchange, the development of the "ideal" model, that also includes in-canopy transport and chemistry, could only be considered for sensitivity studies to investigate which degree of detail will significantly improve model estimates of surface-atmosphere exchange of BVOC. For practical applications within CTMs a simple unified emission-deposition model with a variable compensation point for bi-directional VOCs seems to be more appropriate.

Regional/Global Scale Approach

Since observations (Karl and Guenther 2004; Karl et al. 2010) and modeling (Forkel and Knoche 2006) indicate that deposition is underestimated for oxygenated VOCs, improved parameterizations are required. Efforts should also be made to include improved descriptions of non-stomatal uptake (effect of humidity/water films) or feedbacks with gas phase toxic compounds such as MVK.

Up-scaling of sub-grid scale processes is a general key problem for three-dimensional CTMs. A minimum constraint, which is not always fulfilled in existing CTMs, is the application of consistent land use or land cover for meteorology, soil model, emission, and deposition. Deposition could be calculated for sub-grid tiles, similar to the way how emissions are calculated. If bi-directional VOC are to be described by a unified model, this seems necessary anyway.

It is common practice to account for the extinction of solar radiation within the canopy also in single layer BVOC emission models. However, for deposition, this is rarely the case. This issue might need further investigation.

Computed chemical loss rates of between 5 and 10 % within the canopy for the major emitted isoprenoids suggest that explicit in-canopy chemistry is not required in a CTM or climate model. Whether this is required for highly reactive VOC should be a subject of further investigations.

Highly desirable is an improved consideration of emissions resulting from land management. In parallel, a better representation of plant functional types is also urgently required.

Conclusion

The working group concluded that the VOC flux parameterizations used in current models are insufficient. The lack of an integrated approach for characterizing bi-directional exchange, for selected compounds such as acetaldehyde, is a key deficiency. In addition, the lack of parameterizations to account for within canopy transformations (production and loss) is likely to limit current model capabilities to characterize fluxes of at least some VOC. The "ideal" model would use the same framework for all categories of VOC seek to parameterize all of them as bi-directional with parameters set to zero where appropriate for RVOC and AOVOC.

A detailed description of emission, deposition, and in canopy chemistry and turbulence seems premature for every dawy CTMs applications but it should be the subject of specific process models. Such one-dimensional models should then be used to conduct a series of sensitivity studies to determine the conditions under which explicit representations of the individual processes involved in the surface exchange of VOCs are necessary in three-dimensional models and can direct the development of suitable parameterizations.

There was general agreement that the observational database is insufficient for making significant progress on improving model parameterizations of the bi-directional exchange of VOC. However, the development of a community model framework would be useful for driving efforts to improve observational data that could be used for a model test bed, thereby bridging the current gap between models and measurements.

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