Efficient Atmospheric Cleansing of Oxidized Organic Trace Gases by Vegetation

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The biosphere is the major source and sink of non-methane volatile organic compounds (VOC) in the atmosphere. Gas phase chemical reactions initiate the removal of these compounds from the atmosphere, which ultimately proceeds via deposition at the surface or direct oxidation to CO or CO2. We performed ecosystem scale flux measurements that show the removal of oxygenated VOC via dry deposition is substantially larger than currently assumed for deciduous ecosystems. Laboratory experiments indicate efficient enzymatic conversion and potential upregulation of various stress related genes leading to enhanced uptake rates as a response to ozone and methyl vinyl ketone exposure or mechanical wounding. A revised scheme for the uptake of oxygenated VOCs, incorporated into a global chemistry-transport model, predicts appreciable regional changes in annual dry deposition fluxes.

Large quantities of non-methane volatile organic compounds (NMVOC) enter the atmosphere via biogenic, pyrogenic and anthropogenic sources. The annual production of NMVOC (~1200-1350 TgC/a) likely exceeds that of methane and CO (~500 TgC/a each) (1,2). Together these gases fuel tropospheric chemistry. Oxidation of NMVOC leads to the formation of aerosols (3–5) and modulates the oxidation capacity of the atmosphere (6) creating important climate feedbacks (7). One large uncertainty in constraining budgets of NMVOC is the amount of deposition to vegetation, which acts as a major source and sink for organic trace gases on a global scale. This has consequences for constraining secondary species produced in the gas phase, which will either oxidize to CO and CO2, condense onto or form organic aerosol (OA) and be rained out, or directly deposit to the surface via dry and wet deposition. Two recent bottom-up assessments of the tropospheric organic aerosol budget (1,3), based on different assumptions for wet and dry deposition of organic vapors resulted in different predictions of global production rates for secondary organic aerosol (SOA).

Dry deposition schemes parameterize the deposition flux according to

\[ F = v_d \cdot C \] (Eq. 1)

where \( F \) represents the deposition flux, \( C \) the ambient concentration and \( v_d \) the deposition velocity. Deposition velocities are usually treated in analogy to Ohm’s Law, where \( v_d \) can be expressed as three resistances in series:

\[ v_d = \frac{1}{R_a + R_b + R_c} \] (Eq. 2)

\( R_a \) represents the aerodynamic resistance above the surface and has the same value for all constituents. The term \( R_b \) is the quasi-laminar resistance to transport through the thin layer of air in contact with surface elements and varies with the diffusivity of a substance. Standard micrometeorological methods and modeling approaches are available to calculate \( R_a \) and \( R_b \) (8). \( R_c \) represents the resistance to uptake by surface elements and has been extensively parameterized for ozone (O3) and SO2 (9). Because O3 immediately decomposes inside plants by reduction, a relative measure of reactivity (\( f_0 = 0 - 1 \)) accounts for its loss (9). Stomatal resistance (\( R_s \)) primarily controls the deposition of highly reactive compounds (10). Due to the lack of observational constraints accounting for the uptake of organic gases occurs in analogy to O3 and SO3, solely based on their physio-chemical properties (solubility and reactivity) in the mesophyll. As a consequence all models treat NMVOCs as non-reactive or only slightly reactive species (i.e. \( f_0=0-0.1 \)) leading to large estimates of \( R_c \) (10).

In this report we combine field observations with laboratory experiments and transport modeling to investigate the influence of vegetation on the deposition of oxygenated VOCs (oVOCs). oVOCs represent the most abundant class of organic carbon and profoundly affect the chemical composition in the Earth’s oxidizing atmosphere. In six field experiments across a range of ecosystems (fig. S1), oVOCs deposited at high rates. The sum of methyl vinyl ketone (MVK) and methacrolein (MAC), which account for about 80% of the carbon in the initial stage of isoprene oxidation, exhibit the fastest deposition rates. \( R_c \) for deciduous ecosystems is much smaller than predicted and falls along a
trend that would be expected for O₃ (fₒ=1) (Fig. 1). This suggests that oVOCs, like O₃, are immediately lost once they enter a leaf through stomata. Tropical ecosystems exhibit the fastest deposition rates (Rc’s are 2.6-3.5 times smaller than predicted) and the observed deposition velocities for MVK+MAC are as large as for O₃ (up to 2.4 cm/s). We measured similarly high deposition fluxes for other oVOCs, including acetaldehyde, MVK+MAC, hydroxyacetone, glycolaldehyde, C₅-carbonyls, and nopinone (Fig. 2). All oVOCs deposited on the vegetation except acetaldehyde, which exhibited net emissions during a hot period at the beginning of the study because it is also produced by vegetation (11). Due to the bi-directional exchange of acetaldehyde vₒ should be regarded as a net deposition velocity. All oVOCs investigated here form during the photochemical oxidation of isoprene and certain monoterpenes. The vertical profiles suggest that deposition mainly occurs via uptake by vegetation elements, with the upper 70% of the canopy (Fig. 2) accounting for more than ~97% of the total deposition flux for all measured oVOCs. After correction for different molecular diffusivities in air, the corresponding Rc’s of oVOCs (except acetaldehyde) fall within 25% of O₃. Due to the bi-directional exchange, Rc for acetaldehyde is 60% higher than O₃ (Fig. 2). Large deposition fluxes imply that the internal concentration (Cᵢ) of these oVOCs is small compared to the ambient concentration (Cₐ).

To investigate mechanisms that can potentially influence the uptake of oVOCs in particular MVK and MAC we performed a series of leaf cuvette experiments with *Populus trichocarpa x deltoides*. We observed a linear flux-concentration relationship between the uptake (i.e. flux) of oVOCs by a leaf as a function of oVOC concentration (figs. S3 and S5), which is indicative of enzymatic reactions metabolizing oVOCs. The compensation point (Cₚ) of a compound, defined as the concentration where the net uptake is zero, typically followed an exponential increase with leaf temperature (fig. S6). When oVOCs form or decompose inside a leaf, the Cₚ is typically greater than zero, resulting in emission below and uptake above the Cₚ. The mesophyll resistance (Rₘ) expressed as a deposition velocity (vₘ = 1/Rₘ) was highest between 15 °C and 20 °C, dropping significantly above a narrow temperature range between 25 °C and 28 °C (fig. S6). The light response curves of vₘ exhibited a functional form similar to electron transport.

Plants possess the ability to detoxify through various mechanisms [i.e. via oxidative stress or conversion by the aldehyde dehydrogenase (ALDH) family]. As an example, ALDHs are a protein superfamily of NAD(P+)-dependent enzymes known to oxidize a wide range of carbonyls. ALDH enzymes play an important role in the detoxification of aldehydes by oxidizing these to their corresponding carboxylic acids (12). Stress induced upregulation of these and potentially other (e.g. various peroxidase) enzymes could help reduce concentrations of aldehydes and other oVOCs that would otherwise build up to toxic levels.

Based on exposure experiments with *P. trichocarpa x deltoides*, we suggest that chemical and mechanical stress impact uptake rates of acetaldehyde and MVK (Fig. 3). For both plants, vₘ for acetaldehyde dropped during fumigation with MVK, but changed little for MVK. The corresponding Cₚ for acetaldehyde increased during the fumigation period, suggesting increased internal production occurring as a response to oxidative / metabolic stress. During MVK fumigation conversion rates of aldehydes may have also decreased by enzyme saturation or depletion of reactive oxygen species (ROS), which would explain the relatively small change of vₘ for MVK during fumigation as opposed to a large increase immediately after fumigation. For the MVK experiment the post-exposure vₘ drastically increased for acetaldehyde (~2 fold) and MVK (~20 fold) suggesting short-term upregulation of metabolic activity in response to MVK exposure during the previous days; however vₘ decreased after one day in both cases. Because vₘ for MVK increased direct or indirect enzymatic reactions rather than purely non-enzymatic reactions (e.g. Michael addition) likely regulated the metabolic consumption. MVK fumigation also resulted in physiological changes. After a certain exposure period, stomatal conductance (Gₛ) and photosynthesis dropped by 30-50% and 20-50% respectively each day. Gₛ and photosynthesis however recovered every morning. This corroborates the finding that MVK actively goes through stomata inducing a biological response in the mesophyll.

We did not observe any physiological changes (Gₛ and photosynthesis) for plant B during the course of the O₃ fumigation experiment. Vₘ for MVK increased by ~70% immediately after we exposed plant B to O₃ and gradually increased by another ~25% during the course of the fumigation where it remained after we turned the O₃ supply off (Fig. 3). We observed similar behavior for acetaldehyde. For both compounds vₘ remained high for 2 days after stopping the fumigation. A set of experiments inducing mechanical wounding resulted in increased uptake of MVK, qualitatively similar to the chemical exposure experiments. The uptake of acetaldehyde decreased and occurred in parallel with an increasing Cₚ. This is consistent with the idea that mechanical wounding increases the internal production of acetaldehyde (11). Upon recovery the uptake rates (vₘ) for acetaldehyde increased subsequently and at times exceeded the pre-wounding values.

The increase of vₘ for acetaldehyde and MVK after (plant A and B) and during fumigation (plant B) imply that these plants responded to acute chemical exposure by upregulating the activity of processes responsible for detoxification.
Quantitative polymerase chain reaction (qPCR) identified changes in several characteristic genes indicative of enhanced metabolic activity as a response to chemical and mechanical stress (Table S3). All chemical treatments (MVK, O₃) showed elevated gene expression patterns related to ROS (superoxide dismutase, ascorbate peroxidase). Mechanical wounding and chemical exposure experiments (MVK and O₃) resulted in upregulation of aldehyde oxidase (AAO2) and aldehyde dehydrogenase (ALDH2). We observed elevated levels of p450 cytochrome, typically associated with the oxidation of organic substances, for all chemical treatments along with increases in WRKY transcription factors, encoding proteins involved in plant responses to biotic and abiotic stresses. These changes in gene expression patterns support the gas exchange measurements showing that plants can adjust their metabolism (i.e. vₐ) and increase oVOC decomposition as a response to environmental factors.

The presented laboratory and field observations show that oVOCs can be efficiently metabolized by plants through constitutive and induced detoxification mechanisms. Because the general route of atmospheric photo-oxidation of NMVOCs goes through the formation of carbonyls and hydroxycarbonyls these findings have consequences for understanding the atmospheric evolution of these oVOCs. To place these findings on a broader scale we modified the dry deposition scheme for oVOCs in a comprehensive global model (13, 14). Fast metabolic conversion of oVOCs was incorporated according to our field observations by setting fₜ to one (9). The total dry deposition flux of organics on a carbon basis increases (by up to 110%) relative to previous estimates (Fig. 4). Large changes especially occur in tropical regions such as the Amazon, where the annual dry deposition flux increases between 65-85%. Globally, dry deposition of organics increases by about 36%. More importantly, deposition fluxes are substantially altered due to increases (50-100%) in dry deposition of relatively insoluble species [e.g. carboxyls with Henry’s Law Constant (HLC) < 50 M/atm] leading to decreases (up to 30%) in wet deposition of certain soluble species [e.g. peroxides with HLCs >300 M/atm (fig. S8)]. Higher dry deposition of relatively in-soluble species also leads to a decrease in dry deposition of certain peroxides due to lower atmospheric concentrations in the gasphase. Modeled oVOC concentrations in the surface layer change substantially (e.g. 30-60%). These results have consequences for capturing the dynamic behavior and repartitioning between NMVOC oxidation products and SOA (5, 14, 15). The modifications change OH radical concentrations by up to 15% above the land surface layer (fig. S11). Tropospheric O₃ concentrations are slightly reduced (e.g. by 1-3%) in the Northern Hemisphere and enhanced in the tropical land regions (e.g. by 0.5-1.5%) (fig. S10).

Dry deposition of organic trace gases addresses a poorly quantified process in the atmosphere (3, 10). We estimate a lower and upper bound for the annual deposition flux of gas phase oVOCs between 37-56% relative to the annual NMVOC emission flux on a carbon basis (table S4). It is conceivable that oVOC deposition fluxes to vegetation could increase as a consequence of acute or chronic exposure to high O₃ concentrations in polluted regions (16).

References and Notes
14. Materials and methods are available as supporting material on Science Online
17. The National Center for Atmospheric Research is operated by the University Corporation for Atmospheric Research under sponsorship from the National Science Foundation.

Supporting Online Material
www.sciencemag.org/cgi/content/full/science.1192534DC1
Materials and Methods
Figs. S1 to S16
Tables S1 to S4
References
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Fig. 1. Canopy resistance (Rc) for MVK+MAC plotted versus leaf area index (LAI) for six field sites. Black solid line represents dry deposition, where the reactivity factor fₜ was set to 1 (maximum deposition). The dotted line shows Rc with a dry deposition that would be conventionally used (fₜ = 0). LAI data are plotted as mean +/- SD (n=10); the SD for Rc was calculated as the sum of systematic and random errors associated with turbulent flux measurements (14) and the
errors associated with instrument precision for wind measurements using a sonic anemometer.

**Fig. 2.** Canopy integrated deposition velocity for ozone (O$_3$), C$_5$ carbonyls (C$_5$CHO), nopinone, glycolaldehyde (GLY), hydroxyacetone (HYAC), MVK+MAC and acetaldehyde (CH$_3$CHO) as function of normalized canopy height (z/h), where a z/h of one represents the top of the canopy (A). (B) depicts the leaf area index (LAI) per layer.

**Fig. 3.** Mesophyllic deposition velocity ($v_m = 1/R_m$) for acetaldehyde and MVK; $v_m$ is plotted as a function of cumulative MVK (A) and O$_3$ (B) uptake. Pre-fumigation levels of $v_m$ (open circles) are inserted at the beginning; post fumigation levels of $v_m$ (open diamonds) are inserted at the end. 95% confidence intervals ($n=6$ (O$_3$ fumigation); $n=7$ (MVK fumigation)) are shown as vertical bars for pre and post fumigation experiments; the dotted lines represent the 95% confidence interval during the fumigation experiment obtained from a polynomial regression (2$^{nd}$ order) depicted by the solid lines.

**Fig. 4.** Relative change of the total annual dry deposition flux of oVOC based on a modified dry deposition scheme in which oVOC are assumed to be rapidly metabolized within the leaf.