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Limited influence of dry deposition of semivolatile organic vapors on secondary organic aerosol formation in the urban plume

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[1] The dry deposition of volatile organic compounds (VOCs) and its impact on secondary organic aerosols (SOA) are investigated in the Mexico City plume. Gas-phase chemistry and gas-particle partitioning of oxygenated VOCs are modeled with the Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere (GECKO-A) from C₃ to C₂₅ alkanes, alkenes, and light aromatics. Results show that dry deposition of oxidized gases is not an efficient sink for SOA, as it removes <5% of SOA within the city's boundary layer and ~15% downwind. Dry deposition competes with the gas-particle uptake, and only gases with fewer than ~12 carbons dry deposit while longer species partition to SOA. Because dry deposition of submicron aerosols is slow, condensation onto particles protects organic gases from deposition, thus increasing their atmospheric burden and lifetime. In the absence of this condensation, ~50% of the regionally produced mass would have been dry deposited. **Citation:** Hodzic, A., S. Madronich, B. Aumont, J. Lee-Taylor, T. Karl, M. Camredon, and C. Mouchel-Vallon (2013), Limited influence of dry deposition of semivolatile organic vapors on secondary organic aerosol formation in the urban plume, *Geophys. Res. Lett.*, 40, 3302–3307, doi:10.1002/grl.50611.

1. Introduction

[2] Urban areas emit large amounts of pollutants that are toxic to humans and contribute to the radiative forcing of climate. Volatile organic compounds (VOCs) and the partly oxidized intermediates of their atmospheric degradation (OVOCs) are of particular concern. Given their wide volatility range, OVOCs can partition rapidly into the particle phase to form secondary organic aerosols (SOA) after only one oxidation step or remain in the gas phase for several days in the city outflow plume and undergo multigenerational oxidation to create highly functionalized products that will eventually condense.

Additional supporting information may be found in the online version of this article.

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[3] The global SOA budget is highly uncertain, and current production estimates based on top-down VOC emissions or bottom-up modeling studies range from 12 to 1820 Tg yr⁻¹ [e.g., Goldstein and Galbally, 2007]. This wide range reflects substantial uncertainties in the characterization of SOA sources, formation pathways, and removal processes. While significant work has been done over the past decade to identify new SOA formation processes and precursor emissions [e.g., Robinson *et al.*, 2007] and to model them at regional and global scales [e.g., Pye and Seinfeld, 2010; Tsimpidi *et al.*, 2010], dry removal of organic compounds from the atmosphere and its effect on the organic aerosol budget is relatively unexplored and poorly represented in current chemistry-climate models [Hallquist *et al.*, 2009].

[4] Dry deposition affects both organic aerosol particles and organic gaseous vapors. For aerosols, deposition velocities depend mainly on particle size. Dry deposition is very slow for particles of intermediate size like SOA (0.05–2 μm), as Brownian diffusion is only efficient for ultrafine particles that behave similar to gaseous molecules, and impaction or sedimentation is only efficient for diameters >2 μm [Seinfeld and Pandis, 2006]. Typical dry deposition velocities for submicron particles over water are below 0.05 cm/s [Seinfeld and Pandis, 2006], about 50 times lower than for nitric acid which deposits efficiently. Dry deposition velocities derived from flux measurements [Zalakeviciute *et al.*, 2012] in Mexico City range from 0.05 to 0.1 cm/s for both SOA and sulfate, and those reported over a pine forest for submicron aerosols are ~0.1 cm/s [Farmer *et al.*, 2011].

[5] For gases, deposition velocities depend on the solubility and reactivity of the depositing molecules. Multifunctional organic compounds are often water soluble [e.g., Raventos-Duran *et al.*, 2010] and are likely to undergo dry deposition similar to other soluble gases, or to partition to the aqueous phase (not treated here). The main reason why dry deposition of these species is omitted in current models is that simplified SOA treatments are based on mechanisms which lump precursors and their products by volatility, but neglect other important molecular properties [Robinson *et al.*, 2007; Lane *et al.*, 2008]. For example, first-generation oxidation products are typically grouped into one low- and one high-volatility species regardless of their solubility and functional groups. Bessagnet *et al.* [2010] estimated dry deposition over Europe with a 3-D model by assigning a solubility parameter to lumped oxidation products of aromatics and biogenic precursors, finding that dry deposition removes on average 25–30% of the SOA mass, and up to 50% in some forested regions. However, estimation of deposition velocities for lumped species is inherently uncertain, and the resulting bias to SOA budgets remains mostly unquantified.

[6] To perform such an assessment for anthropogenic precursors, we apply an explicit chemistry model GECKO-A

Table 1. GECKO-A Simulations

Name	Dry Deposition (Surface Type)	Precursors
<i>Eulerian Simulations</i>		
TRADITIONAL	No	Short $C_{<13}$ alkanes, alkenes, and light aromatics that are typically considered in 3D models (referred as traditional VOCs)
TRADITIONAL_DEP	Yes (urban)	Only traditional VOCs
ALL_VOC	No	All available VOCs
ALL_VOC_DEP	Yes (urban)	All available VOCs
<i>Lagrangian Simulations^a</i>		
W/O_DEP	No	All available VOCs
FST_DEP	Yes (20% agricultural, 40% deciduous and 40% conifer)	All available VOCs
URB_DEP	Yes (urban)	All available VOCs
FST+MOL	Yes (similar to FST_DEP) + dry deposition of organics that are in the aerosol phase using dry deposition velocities of their gaseous equivalents	All available VOCs
FST+AER	Yes (similar to FST_DEP) + dry deposition of aerosols with $V_d = 0.1$ cm/s	All available VOCs
TRAD_FST	Yes (similar to FST_DEP)	Only traditional VOCs

^aLagrangian runs are initialized from the corresponding Eulerian ones without dry deposition.

(Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere [Aumont *et al.*, 2005]) with the following goals: (i) to quantify the importance of dry deposition removal of organic vapors for SOA production within Mexico City's boundary layer as well as for the regionally exported SOA mass and (ii) to describe the properties of species undergoing dry deposition and characterize their evolution as the plume ages.

2. Modeling Approach

[7] The explicit chemical mechanism generator GECKO-A is used to create the chemical scheme for anthropogenic C_{3-25} alkanes, alkenes, and light aromatic precursors, and the generated mechanism is applied within a 0-D model over Mexico City for March 2006 MILAGRO (Megacity Initiative: Local And Global Research Observations) conditions similar to the study done by Lee-Taylor *et al.* [2011]. Here we only provide a brief description of the main characteristics of the model and the treatment of dry deposition of gases. More details can be found in Aumont *et al.* [2005] and Lee-Taylor *et al.* [2011].

2.1. GECKO-A

[8] The chemical mechanism for the oxidation of the VOCs is generated by GECKO-A, based on laboratory kinetic and mechanistic data extended by use of structure-activity relationships, thus providing a detailed and explicit representation of the partly oxidized reaction intermediates [Aumont *et al.*, 2005]. To reduce the size of the generated mechanism, only five generations of chemistry are allowed for $C_{19-C_{22}}$, and three generations for $C_{22-C_{25}}$ alkanes, whereas species with vapor pressures $< 10^{-13}$ atm are irreversibly partitioned to the aerosol [Lee-Taylor *et al.*, 2011]. Heterogeneous or aqueous phase reactions are not considered. Instantaneous gas-particle equilibrium is assumed [Pankow, 1994], and the partitioning into the bulk well-mixed organic aerosol phase is computed using Raoult's law.

[9] The explicit chemical mechanism is used within a box model framework over Mexico City and is constrained with the measured surface daily profiles of meteorological variables, anthropogenic emissions, and initial chemical conditions for the March 2006 MILAGRO field project, as previously described by Lee-Taylor *et al.* [2011]. The background SOA are fixed to $2 \mu\text{g}/\text{m}^3$ [Hodzic *et al.*, 2009]. Two types of simulations are performed. First, the Eulerian simulation representative of the chemistry occurring in the source region within the Mexico City boundary layer (BL) is performed over a

4 day period. The simulation is forced with the daily repeating emissions and meteorological conditions. The height of the model box varies according to the BL height. Second, a Lagrangian simulation is performed to study the chemical evolution of the Mexico City plume once it has detached from the city and is transported at the regional scale. The plume is detached at 2 P.M. using the output of the Eulerian simulation and advected downwind of the city for 5 days at a height of 1.5 km above ground level. The emissions are no longer injected into the model, and a horizontal dilution with characteristic time of 1 day is assumed. An overview of the different simulations performed in this study is given in Table 1.

2.2. Dry Deposition Velocities for Gaseous Species

[10] The rate of dry deposition of species i is given by $dC_i/dt = -V_{d,i} \times C_i/h$, where C_i is the species concentration, h is the boundary layer height, and $V_{d,i}$ is the dry deposition velocity of species i . Deposition velocities depend on atmospheric stability, surface conditions, and gas properties and are calculated for each individual gas species following the Wesely [1989] resistance approach ($V_d = [R_a + R_b + R_c]^{-1}$) that opposes three resistances to the uptake of gas species including the aerodynamic resistance (R_a) determined by turbulent exchange, the resistance associated with transport through the quasi-laminar layer (R_b) in contact with the canopy and influenced by molecular diffusivity, and the canopy resistance (R_c). Four canopy types are considered, i.e., urban, agricultural, conifer forest, and deciduous forest [Wesely, 1989].

[11] R_c is the most complex term as it combines the resistances to uptake by vegetation, the lower canopy, and the ground. For vegetation, the stomatal resistance describes the uptake of species through the leaf pores, followed by transfer through the mesophyll, which is described by the mesophyll resistance. A second path of uptake is transport through the cuticle of the plant, the waxy leaf skin. R_c depends on the ratio of molecular diffusivity of water to that of the gas, as well as the solubility and reactivity of the depositing molecule. Molecular diffusivity and reactivity vary by 1 order of magnitude, whereas solubility is proportional to the Henry's law coefficient (H) and varies over more than 15 orders of magnitude. Here H refers by default to the effective Henry's law constant, which includes the hydration process. It depends mainly on the type and number of functional groups that are attached to the carbon chain. It typically increases from 10^{-4} to 10^{-1} M atm⁻¹ for parent hydrocarbon

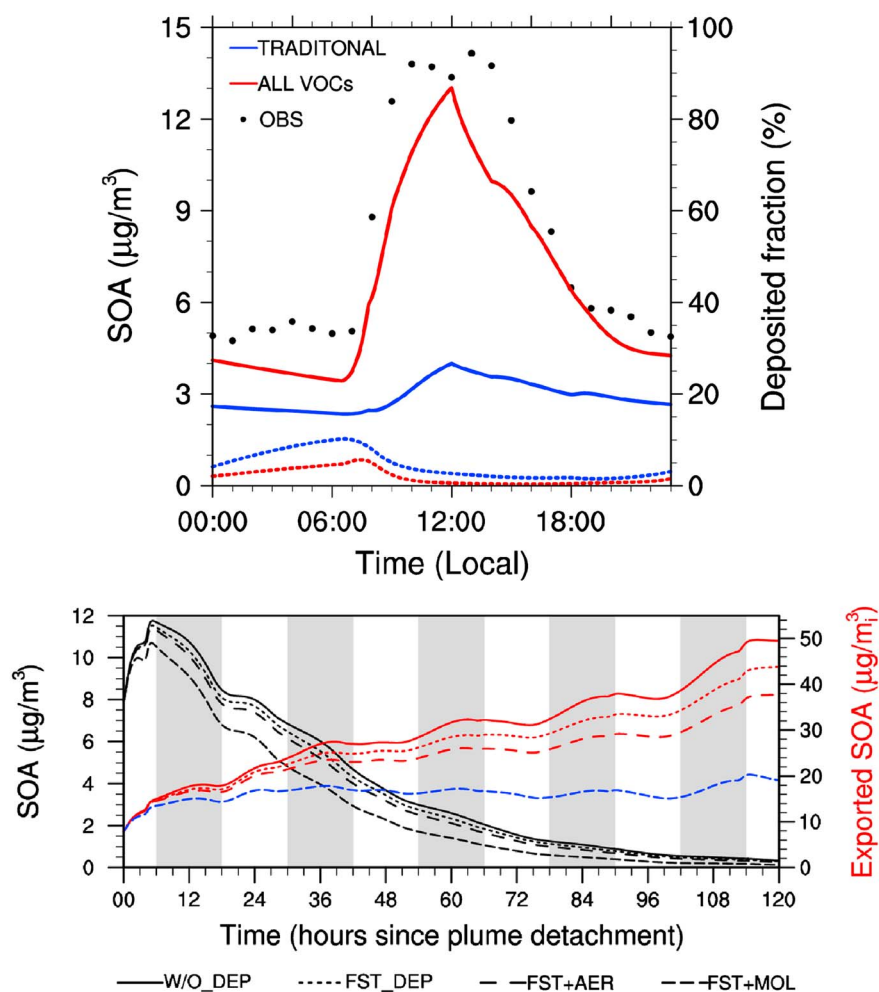


Figure 1. (a) Diurnal evolution of observed (dots) and predicted surface SOA from the chemistry of all C_3 – C_{25} (red line) or only TRADITIONAL $\text{C}_{<13}$ (blue) precursors in Mexico City during March 2006. Dotted lines represent the percent decrease in formed SOA mass due to dry deposition of organic vapors. (b) Five day evolution of SOA concentrations (black lines) and exported total mass (red lines, except for FST + MOL which is blue) in the Mexico City outflow region for Lagrangian runs (Table 1). Here $2 \mu\text{g}/\text{m}^3$ of background organics is not included. The mass integrated over the initial volume is represented by $\mu\text{g}/\text{m}_i^3$. Nighttime (6 P.M.–6 A.M.) is indicated in gray.

species, from 10^{-1} to 10^5 M atm^{-1} for chains with one functional group, and from 10^3 to 10^9 M atm^{-1} for chains with two functional groups. Compounds with $H > 10^3 \text{ M atm}^{-1}$ are typically sufficiently soluble to partition to an aqueous phase depending on the liquid water content that is available [Seinfeld and Pandis, 2006].

[12] Values of H for organic compounds are estimated at 298 K using the group contribution method for Henry's law estimate [Raventos-Duran et al. 2010] based on data for 488 organic compounds (393 aliphatic and 95 aromatic) with a wide range of functional groups. A multiple linear regression based on functional groups and the number of carbon and hydrogen atoms is applied to derive H for species that were not measured.

3. Results and Discussion

3.1. Impact on the SOA Production Within the City

[13] GECKO-A reproduces reasonably well the observed levels and diurnal evolution of SOA in Mexico City during March 2006 (Figure 1a). At night, within a shallow BL of 0.25 km, the model produces $2 \mu\text{g}/\text{m}^3$ of SOA in addition to

the fixed background of $2 \mu\text{g}/\text{m}^3$. During the morning hours, photochemical production leads to a strong increase in SOA concentrations (up to $13 \mu\text{g}/\text{m}^3$) despite dilution with background air, as the BL grows to ~ 3.2 km by early afternoon. Most of this first-day SOA mass ($>90\%$) is derived from the longer C_{13-25} alkanes, as shown (Figure 1a) by the drastically reduced SOA if only light hydrocarbons ($\text{C}_{<13}$) are included.

[14] Removal of gas species by dry deposition does not significantly affect SOA mass within the Mexico City BL (Figure 1a, dashed red lines). SOA mass is reduced by $<2\%$ during the day and by $<5\%$ in the shallower nighttime BL. The light hydrocarbons ($\text{C}_{<13}$, dashed blue lines) give higher fractional deposition, reflecting the generally higher solubility of their products compared to those derived from long-chain alkanes.

3.2. Impact on the Regional SOA Mass

[15] Figure 1b shows the 5 day evolution of SOA concentrations in the Mexico City plume during its regional transport, as well as the corresponding total exported regional SOA mass. Changes in SOA concentration are driven by chemical

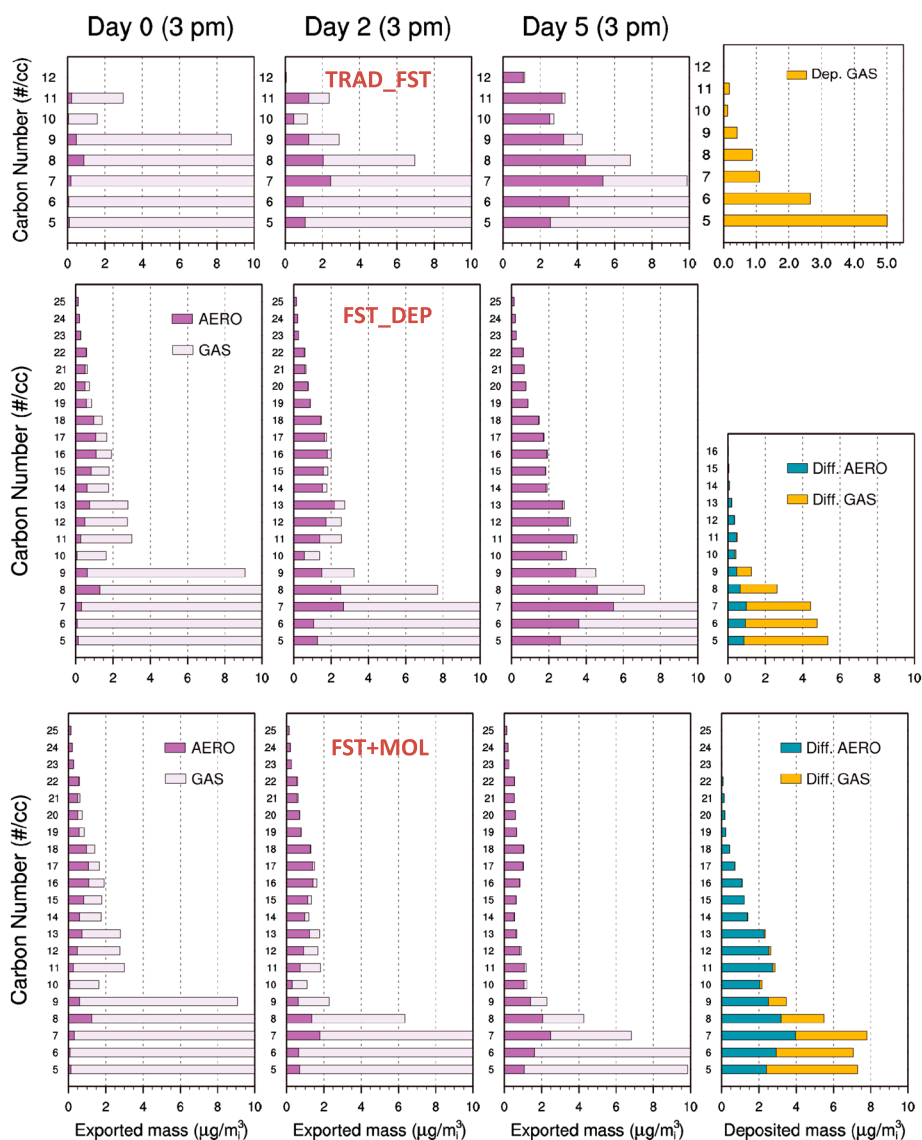


Figure 2. Five day evolution of gas-particle partitioning of the organic mass as a function of carbon number as simulated by TRAD_FST (first row), FST_DEP (second row), and FST+MOL (third row). Also shown are the deposited mass for TRAD_FST and the differences between FST_DEP and W/O_DEP runs, and between FST+MOL and W/O_DEP runs computed over 5 days.

processing of its precursors, gas-aerosol partitioning, and horizontal dilution of the plume by the clean background. Concentrations of SOA in a nondepositing plume (W/O_DEP) slowly decrease from 10–12 $\mu\text{g}/\text{m}^3$ on the first day to less than 1 $\mu\text{g}/\text{m}^3$ on the fourth day due to dilution. However, the regionally exported mass (corrected for the effects of dilution) continues to increase from initial 10 to 50 $\mu\text{g}/\text{m}^3$ on the fifth day, because despite the plume dilution and subsequent evaporation of organic material from the particle phase, chemical processing in the gas phase continues for several days, forming highly functionalized and less volatile organic products that are preferentially partitioned to the particle. These findings are consistent with the results of Lee-Taylor *et al.* [2011].

[16] Comparison with the FST_DEP simulation that includes deposition of organic vapors over a forest canopy suggests that gas phase precursor removal does not significantly influence SOA concentrations, or overall SOA regional mass.

The predicted decrease due to dry deposition (FST_DEP versus W/O_DEP) is less than 15% of the outflow mass. Dry deposition of organic aerosols (FST+AER) is of the same order ($\sim 10\%$ of SOA mass) as that of organic vapors if a V_d of 0.1 cm/s is assumed for particles.

[17] The land cover and the assumed BL height in which the plume is transported can affect the calculated dry deposition efficiency (section 2.2). Forested canopies typically have a greater surface area and tend to collect more efficiently species by dry deposition. The use of other land types (e.g., urban) would thus give even smaller deposition fluxes. This explains why the simulated removal over a mixed forest surface (FST_DEP) is almost two times larger than over urban surfaces (URB_DEP, see Text S1 in the supporting information). We have assumed here that the species are exported within a BL layer of 1.5 km thickness in contact with the surface, but in a shallower layer, the effect of dry deposition would be proportionately larger. For Mexico City, the chosen

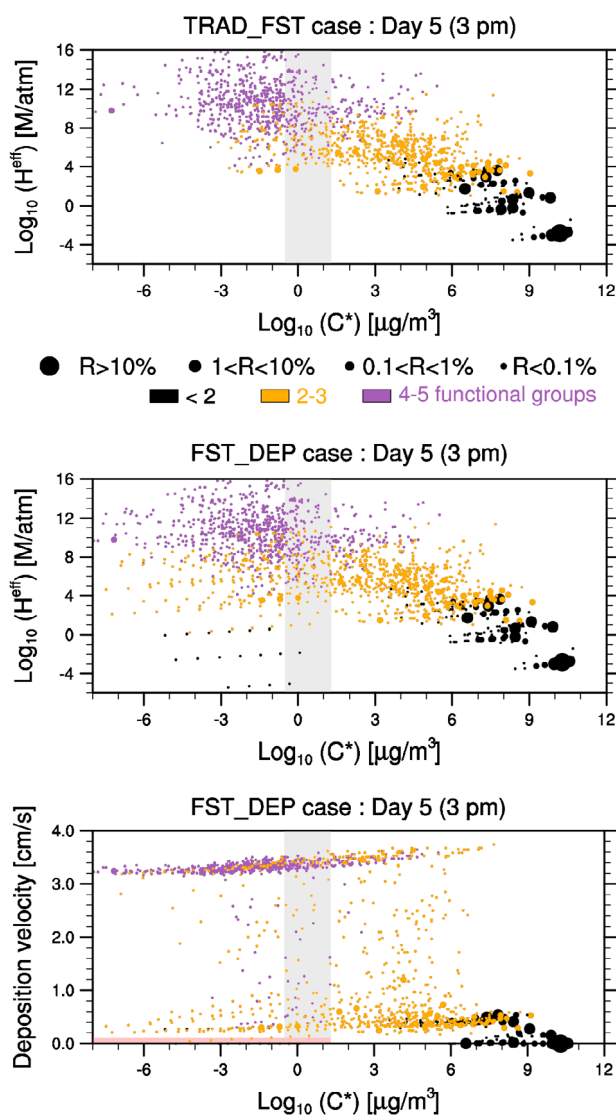


Figure 3. (a, b) Henry's law coefficients and (c) dry deposition velocities of molecules as a function of their volatility. The size of each circle indicates the relative contribution (R) of the specific compound to the total organic mass. Gray shading indicates the gas-particle partitioning zone for the current mixture: left (right) of the gray region, 90% of the mass is in the aerosol (gas). Pink shading indicates typical aerosol dry deposition velocity. Isomers with the same C^* and H are lumped together, and species with total concentrations of less than 10^3 molecules/cm³ are not considered.

outflow height seems to be a lower limit, as the outflow has been reported to occur at ~ 2 – 3 km elevation above ground level [Tie *et al.* 2009].

[18] Figure 2 shows the gas-particle partitioning and the effects of dry deposition of organic vapors during the Lagrangian transport as a function of the carbon chain length. The results indicate that at the beginning of the Lagrangian run, only a small fraction of the organic material is in the particle phase, and $\sim 90\%$ of its mass is derived from long-chain alkanes ($C_{>12}$). Two to five days into the Lagrangian run, chemical processing significantly increases the particle-phase fraction, especially for compounds derived from short-chain alkanes, alkenes, and aromatics.

[19] The removal of organic vapors by dry deposition seems to affect mainly gas compounds with fewer than nine carbons (Figure 2, first row, in yellow). Species with 9 to 12 carbons deposit only a minor fraction of their overall mass. The difference between the FST_DEP and W/O_DEP simulations illustrates the resulting limited effect on the aerosol mass (Figure 2, second row, in green), which seems to nearly equally affect aerosol species with 5 to 12 carbons (through gas-aerosol partitioning).

3.3. Visualization on a 2-D Volatility-Solubility Grid

[20] Here the Mexico City organic mixture at the end of the Lagrangian run is represented in a 2-D volatility-solubility grid space, where volatility is represented by effective saturation mass concentrations, C^* ($\mu\text{g}/\text{m}^3$), derived from the saturation vapor pressures of all nonradical species in GECKO-A, and solubility is represented by the effective Henry's law coefficient. The advantage of using the volatility-solubility grid is that it allows determination of H associated with various volatility bins that are commonly used to describe the SOA formation in 3-D models (VBS or volatility basis set [Lane *et al.*, 2008]). The VBS-type parameterizations do not provide other properties of lumped organic products besides their volatility, although some of them, such as oxygen to carbon ratio, number of functional groups, or solubility, are key for determining the dry and wet removal of organics or their ability to activate as clouds condensation nuclei.

[21] Figures 3a and 3b describe the Mexico City organic mixture 5 days into the Lagrangian simulation as predicted by the TRAD_FST and FST_DEP runs. The results show that solubility is increasing with the increasing number of functional groups and is inversely associated with volatility. Most highly functionalized compounds (four to five functional groups, purple) are also very soluble but are partitioned to the aerosol phase and cannot undergo dry deposition in the gas phase. Figure 3c suggests that their dry deposition velocities generally exceed 3 cm/s, which is 10 times larger than those for aerosols (pink shading).

[22] Compounds with zero or one functional group are generally very volatile and remain in the gas phase, except for long-chain alkanes that condense directly onto particles (Figure 3b). They are not influenced by dry deposition as their low solubility ($H < 10^3 \text{ M atm}^{-1}$) gives dry deposition velocities typically below 0.5 cm/s. Compounds with two to three functional groups span the entire volatility space and have the largest variability in H (10^2 – 10^9 M atm^{-1}) as well as in the dry deposition velocity (0.2–3.5 cm/s).

[23] Removal by dry deposition is expected to be important for gas species with relatively high H ($> 10^5 \text{ M atm}^{-1}$) and that are still too volatile to partition to the aerosol phase ($C^* > 1 \mu\text{g}/\text{m}^3$ here). Dry deposition velocities exceeded 2 cm/s for species with $H > 10^7 \text{ M atm}^{-1}$. According to Figures 3a and 3b, a relatively small fraction of the organic mass falls into that category, which explains why dry deposition has a limited effect of SOA formation for this anthropogenic mixture.

3.4. Competition Between Gas Dry Deposition Removal and Aerosol Formation

[24] While dry deposition removal of anthropogenic organic vapors does not seem to greatly affect SOA mass and can reasonably be neglected in 3-D models, modeling of SOA formation could have a much larger impact on the atmospheric budgets of organic vapors. Figure 1b shows

the results of the FST+MOL run (blue) in which organic compounds continue to dry deposit according to their molecular H regardless of whether they are in the particle or the gas phase. Comparison with W/O_DEP suggests a 60% decrease in regional SOA due to in-aerosol deposition. This is not meant to be a realistic case as aerosol particles deposit at a unique and relatively low deposition velocity based on their size. This sensitivity simulation illustrates that organic compounds partitioned to the slower-depositing particle phase are protected from dry removal. Figure 3c also shows that the dry deposition velocities calculated in the aerosol phase for individual compounds are larger by an order of magnitude than the average aerosol dry deposition velocities. This dry removal affects compounds with 5 to 17 carbons (Figure 2c). This result suggests that neglecting or underestimating the SOA formation in 3-D chemistry-climate models will lead to an overestimation of dry deposition rates and underestimation of the organic residence time and burden in the atmosphere.

4. Conclusions

[25] In this study, we have applied the explicit chemistry model GECKO-A to evaluate the importance of the dry deposition removal of anthropogenic VOCs on SOA regional mass exported downwind of a megacity. Our main conclusions are as follows:

[26] 1. In Mexico City, ~90% of SOA may be explained by long-chain ($C_{>12}$) alkanes, while ~10% is from the light hydrocarbons ($C_{<13}$) typically used in 3-D models. However, the contribution of the light hydrocarbons to the SOA budget approaches that of the long-chain alkanes at the regional scale after several days of chemical processing. This result suggests that considering only first generation products from anthropogenic precursors, as often done in 3-D models, is insufficient to predict the anthropogenic contribution to regional and global SOA.

[27] 2. Dry deposition removal of anthropogenic organic vapors was found to be a small loss term for SOA and can reasonably be neglected in 3-D models, as it removes less than 5% of the SOA mass produced within Mexico City and less than 15% from the outflow. Gas species with fewer than 12 carbons were found to dry deposit more efficiently, whereas longer carbon chain compounds were partitioned preferentially to the aerosol phase. Dry deposition velocities below 1 cm/s (above 2 cm/s) were reported for species with $H < 10^5 \text{ M atm}^{-1}$ ($> 10^7 \text{ M atm}^{-1}$). Our results show a much smaller effect of dry deposition compared to the 25–50% removal suggested by Bessagnet *et al.* [2010] over Europe. Given the fact that their SOA were ~95% biogenic produced mainly from isoprene (70%) and only 5% anthropogenic, our results cannot be directly compared (see supporting information for more details).

[28] 3. Dry deposition was found to compete with uptake of gases to the organic particle phase. Once organic gases are condensed to the particle, they are protected from dry deposition removal and can stay longer in the atmosphere. Without that gas-to-particle partitioning, more than 50% of the regionally produced mass would have been removed through dry deposition.

[29] 4. When the results are seen in a 2-D volatility-solubility grid space, they suggest a strong relationship between aerosol

volatility, functionalization, and solubility. Future work will focus on using those relationships to develop a 3-D modeling framework providing additional characteristics including solubility for the VBS-lumped products of major VOC precursors.

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