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Organic Aerosols in the Earth's Atmosphere

JOOST DE GOUW*

Earth System Research Laboratory, National Oceanic and Atmospheric Administration, Boulder, Colorado and Cooperative Institute For Research in Environmental Sciences, University of Colorado at Boulder

JOSE L. JIMENEZ

Department of Chemistry and Biochemistry, University of Colorado at Boulder and Cooperative Institute For Research in Environmental Sciences, University of Colorado at Boulder

Organic particles are abundant in the troposphere and important for air quality and climate, but what are their sources?

Aerosols, microscopically small particles suspended in air, are an important species in the Earth's atmosphere and influence both air quality and climate. Aerosols are small enough to penetrate deep into the lungs of people and have been linked to severe short- and long-term health effects such as asthma, cardio-respiratory disease, and lung cancer. Aerosols impact the Earth's climate directly through the scattering and absorption of solar radiation, and indirectly through their role as cloud-condensation nuclei. A large

fraction (~50%) of the submicron aerosol mass in the troposphere consists of organic material (*1, 2*). Direct emissions of organic aerosol (primary organic aerosol or POA) are distinguished from secondary organic aerosol (SOA) formed in the atmosphere from gas-phase precursors. Both POA and the precursors of SOA can be from urban, biogenic, and biomass burning sources. Our understanding of each of these sources is limited at present (*3, 4*), which hinders the efforts to mitigate the adverse effects. In this feature article, we briefly review the latest insights from field studies into the sources of organic aerosol (OA). Many results were obtained using two relatively new methods for quantifying OA on time scales of minutes: particle-into-liquid sampling combined with total organic carbon analysis for measurements of water-soluble organic carbon (*5*) and aerosol mass spectrometry (AMS) (*6*); both have been evaluated in detail against other reported methods, both in terms of the mass loading (*7–10*) as well as the source apportionment (*11–13*) of organic aerosol.

Urban Sources

Global models predict that urban sources of OA are small compared with biomass burning emissions and biogenic SOA formation (*4*). Nevertheless, several recent studies found that OA was well correlated with tracers of urban pollution such as CO, acetylene (C_2H_2), iso-propylnitrate, and odd oxygen ($O_3 + NO_2$) (*8, 14–17*), suggesting that the influence of urban emissions may be larger than previously recognized. These studies showed that the good correlation is not due to emissions of POA, but to a rapid growth of SOA in urban air that overwhelms the direct POA emissions within a few hours of photochemical processing (*8, 18–20*).

The atmospheric variability in OA is due to the spatial distribution of emissions, transport, chemical transformation, and removal by deposition. By normalizing OA to an inert combustion tracer such as CO or acetylene, the variability due to emissions and transport can be accounted for to a certain extent (*8*). Enhancement ratios of OA versus CO are denoted as $\Delta OA/\Delta CO$, where Δ indicates the excess amount over the background concentration. Accounting for backgrounds is important particularly when using a long-lived species such as CO. In practice, enhancement ratios are often calculated from correlation slopes between OA and CO (*7*). CO can also be formed from biogenic volatile organic compounds (VOCs) such as isoprene (*21*); however, the good correlation between CO and acetylene in urban plumes has shown that biogenic CO does not significantly affect $\Delta OA/\Delta CO$ ratios in polluted air (*7, 14*).

Figure 1A summarizes observed $\Delta OA/\Delta CO$ enhancement ratios from different studies that were influenced by urban emissions. Red lines are estimates of emission ratios (POA) (*7, 12, 13, 22–25*); blue lines were obtained in aged air (POA + SOA) (*7, 9, 17–19, 22*). These results were determined from field studies on three continents and indicate that the $\Delta OA/\Delta CO$ ratios in aged urban air are systematically higher.

Urban $\Delta POA/\Delta CO$ ratios are in the same range as observations from a tunnel study (labeled CA tunnel),
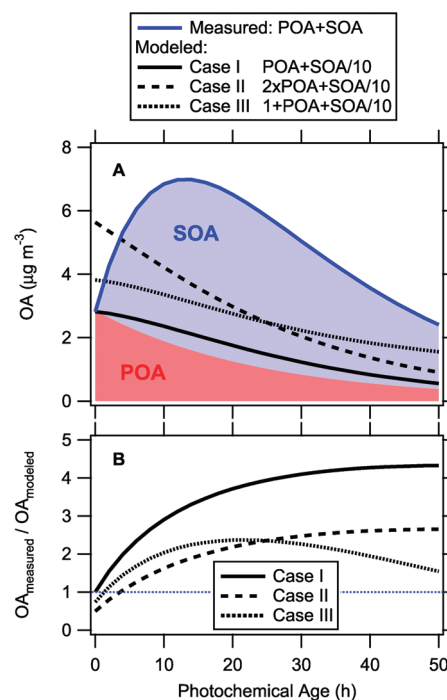
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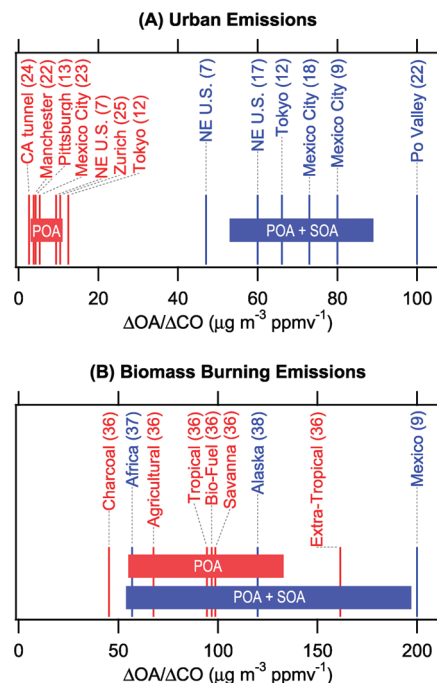
FIGURE 1. Enhancement ratios of OA relative to CO reported in the literature for fresh and aged urban and biomass burning emissions. Vertical sticks show published ratios, with the reference in parentheses. The horizontal bars represent the variability (mean $\pm$ 1σ). OA is reported in μg m^{-3} at 295 K and 1 atm here and elsewhere in the manuscript.

FIGURE 2. Estimated evolution of OA in urban plumes based on observations in the northeastern U.S. The blue curve represents the sum of POA and SOA, with the red and blue shaded areas representing the contributions from POA and SOA, respectively, as calculated using eq 5 in de Gouw et al. (7). The evolution inferred from measurements is compared with a model that underestimates SOA formation by a factor of 10 (case I). Also included are two models that, in addition, overestimate POA by a factor 2 (case II) and overestimate the background OA by 1 μg m^{-3} (case III).

consistent with the notion that vehicle emissions are an important source of POA in urban air. ΔPOA/ΔCO ratios from statistical analyses of ambient AMS data (labeled Pittsburgh) were lower than the ΔOA/ΔCO ratios under POA-dominated conditions from other field studies (7, 12, 25). We suspect that the lower values are more accurate as it is difficult to account for rapid formation of SOA or small amounts of background SOA when measuring downwind from an urban area. Robinson et al. described the partitioning of semi-volatiles from POA to the gas phase as air masses dilute (26). These effects are not evident for the data in Figure 1, i.e., there is no clear dependence of ΔPOA/ΔCO ratios on the absolute POA mass loadings. A possible reason is that the effects of partitioning are smaller than the variability in ΔPOA/ΔCO ratios between different studies and regions of the atmosphere. For reasons of simplicity, we will regard POA as nonvolatile in what follows.

The only reasonable explanation for the increase in ΔOA/ΔCO ratios with photochemical processing in Figure 1 is formation of SOA: aging of nonvolatile POA may lead to a more oxidized aerosol, but it can only lead to a modest increase in organic mass. It should also be noted that ΔOA/ΔCO ratios in aged urban air did not vary dramatically (70 $\pm$ 20 μg m^{-3} ppmv^{-1}) between different regions of the atmosphere despite differences in emissions and photochemistry.

Several studies related the increase in SOA to the gas-phase removal of measured VOC precursors and their particulate mass yields, but found that the observed growth in SOA is an order of magnitude larger than expected (7, 18, 20). The reasons for this discrepancy are unknown, although several factors may play a role. First, SOA mass yields determined in the laboratory may not be representative for the conditions in the real atmosphere and recent research has focused on this question. Mass yields were found to depend strongly on NO$_x$ levels, for example, and can be higher than previously reported (27). Second, the main anthropogenic precursors of SOA may not be measured by current

methods. Indirect evidence showed that semivolatile organic compounds repartition from the particle into the gas-phase shortly after emission and may form a pool of efficient SOA precursors (26); work has started to determine SOA yields for such species (28). Third, aqueous-phase chemistry in aerosols (29) and/or cloud droplets (30) may play a larger role than previously thought. Finally, it has been suggested that SOA formation from biogenic VOCs may be more efficient in polluted air (8, 17) as discussed below.

Many chemistry-transport models underestimate the mass loadings of OA in the polluted atmosphere (16, 31). However, the discrepancy is rarely an order of magnitude as suggested in the previous paragraph. Why is that the case? First, emissions of POA and SOA precursors were constrained by measurements in the studies that reported underestimates in urban SOA (7, 18, 20), whereas emission inventories used in models may not have been consistent with actual ambient measurements. Second, the SOA model underestimation (%) is expected to be highest at a large distance from emission sources, where OA is lower due to dilution and regional models depend on assumed boundary conditions.

A simple thought experiment may help illustrate these points. Figure 2A shows the evolution of POA and SOA in urban plumes calculated from reported ΔOA/ΔCO ratios in the northeastern U.S. These curves were computed using eq 5 in de Gouw et al. (7), a ΔCO mixing ratio of 300 ppbv, and dilution represented through an exponential decrease with a 24 h e-folding time (blue curve). This calculation ignores the semivolatile nature of POA, which most chemistry-transport models do not currently take into account. OA maximizes after one day and then decreases slowly. The contribution of POA is 100% at zero age ($t = 0$) and then decreases rapidly. Imagine a model that underestimates SOA

by an order of magnitude (case I). The model discrepancy rises rapidly with time and is about a factor of 4 after two days of processing (black, solid curve). Averaged over all ages, the model discrepancy is a factor of 3.5. If in addition to the SOA underestimate, the POA emissions were overestimated by a factor of 2 (case II), then the model discrepancy is a factor of ≤3 (black, dashed curve) and 2.1 averaged over all ages. If the model had an OA background that is too high by $1 \mu g \, m^{-3}$ (case III), for example due to overestimated boundary conditions in a regional model or by underestimating deposition in a global model, then the discrepancy is a factor of ≤3 (black, dotted curve) and 2.0 averaged over all ages. It should also be noted that these model underestimates would be even smaller if the comparison were done for organic carbon, because the OA/OC ratio is much higher for SOA (see Figure S1 in the Supporting Information). In summary, even if SOA is underestimated by an order of magnitude in a chemistry-transport model, the expected discrepancy for total OA is much less than a factor of 10 and, importantly, very sensitive to modeled emissions, backgrounds, dispersion, and removal.

There are significant uncertainties in U.S. emissions estimates for urban POA and SOA precursors. Bond reported an urban POA source of 0.25 TgC year^{-1} (32), whereas a source of 0.52 TgC year^{-1} was used in the GEOS-CHEM model (33). Here, we estimate the U.S. source of urban POA to be 0.19 TgC year^{-1} from the ΔPOA/ΔCO ratio of Zhang (4.3 $\mu g \, m^{-3}$ ppmv^{-1}) (13), an OA/OC ratio of 1.25 for POA, and an estimated fossil-fuel CO source of 63.2 Tg year^{-1} (34). There is significant uncertainty in this estimate due to (i) the variability in ΔPOA/ΔCO ratios (Figure 1A) and (ii) the source estimate of CO, which may be overestimated (21). Moreover, POA emissions may need to be re-evaluated in light of their semivolatile character (26), i.e., the emissions depend on temperature and should be measured at atmospherically relevant dilutions.

Models also need accurate emissions of SOA precursors. In that regard, it should be noted that urban emissions of toluene, one of the main anthropogenic SOA precursors (7), may be overestimated by a factor of 3 in the U.S. (35). We conclude that significant uncertainties in POA and SOA precursor emission inventories exist and recommend that the evaluation of 3-D model performance for OA should be accompanied by an evaluation of the POA and SOA precursor emissions used, and of oxidant fields and other products of VOC photochemistry.

Biomass Burning Sources

Unlike urban aerosol, there is a large variability in the POA emission factors from biomass burning based on fuel type and burning conditions. Figure 1B summarizes ΔOA/ΔCO emission ratios (36), as well as enhancement ratios observed in aged biomass burning plumes (9, 37, 38). There is a large overlap between the two groups, which does not permit strong conclusions about net SOA formation in biomass burning plumes to be drawn at present. Laboratory studies have indicated that SOA can be efficiently formed from gas-phase precursors in biomass burning emissions (39). However, the results from field measurements have not been clear in all cases: for example during the African Monsoon Multidisciplinary Analysis (AMMA) campaign, physical and chemical transformation of biomass burning aerosol was observed over West Africa, while enhancement ratios with respect to CO did not increase (37). We conclude that more research is needed to characterize the net effect of SOA formation on OA mass in biomass burning plumes.

Biogenic Sources

Biogenic VOCs have been shown to form SOA in smog chambers and have much larger global emissions than urban VOCs. Therefore, global models attribute a large fraction of OA to biogenic SOA (4, 40). Measurements also show good evidence for this. For example, analyses of molecular tracers in aerosol have shown the presence of oxidation products from biogenic VOCs (41, 42) and radiocarbon dating of OA typically shows a dominant contribution from modern carbon (43−45). Of course, the latter observation does not rule out a biomass-burning source and urban sources of POA and SOA precursors, such as food cooking and fireplaces, can also lead to a 10−30% modern carbon fraction for OA in urban air (46). Finally, recent studies have provided initial estimates of emissions of primary biological aerosol particles (47), but these are largely in the super-micron size range, as opposed to other sources discussed here, and will not be considered further in this paper.

In contrast with the above, OA in the northeastern U.S. was found to correlate with anthropogenic tracers in the presence of significant biogenic VOC emissions (8, 14, 17). Two studies argued that all these findings can be reconciled if biogenic SOA formation is more efficient in polluted air (8, 17). In that scenario, the organic carbon is biogenic, but the OA correlates with anthropogenic tracers. If this were the case, one would expect to see higher OA relative to anthropogenic tracers in the presence of biogenic VOCs, but evidence from field measurements is not convincing (14, 17). It is also unclear which pollutant can promote the formation of biogenic SOA, although pre-existing particles (48) and the formation of organosulfates (49) might play a role. If biogenic SOA formation were enhanced by anthropogenic emissions, it should be noted that the presence of biogenic carbon does not imply that the aerosol is natural, i.e., also present in the absence of anthropogenic emissions.

Biogenic emissions are highest in the tropics and several recent field studies have focused on biogenic SOA formation in this region of the atmosphere. During the AMMA study over East Africa, high levels of isoprene and its gas-phase photoproducts were observed from the BAE-146 aircraft in relatively pristine conditions (50). The concentration of OA was ~1 $\mu g \, m^{-3}$. During the Amazonian Aerosol Characterization Experiment (AMAZE), measured OA at a ground site was <1 $\mu g \, m^{-3}$ except when the site was impacted by long-range transport of biomass burning and urban emissions (51). Such relatively low mass loadings of OA are consistent with global models that predict concentrations of biogenic SOA of <3 $\mu g \, m^{-3}$ in most regions of the atmosphere (4, 40). While the analysis of data from AMAZE and other missions is ongoing, one general conclusion emerging is that global models do not appear to underestimate the formation of biogenic SOA in pristine conditions by anywhere near an order of magnitude, conversely to urban SOA.

Zonal Distribution of Organic Aerosol Sources

While biomass burning and biogenic SOA formation may be the largest sources of organic aerosol globally, it should be recognized that these sources are predominantly located in the tropics, whereas anthropogenic emissions are mostly located at northern midlatitudes. To illustrate this point, we estimate the zonal distribution of different sources of organic aerosol (Figure 3).

POA from urban, biofuel, and open biomass burning (wildfires and agricultural burning) sources are taken from Bond (32). The total source of biogenic SOA from isoprene and monoterpenes is taken from global-model calculations by Henze and Seinfeld (40), with the zonal distribution according to Guenther (52). We also added biogenic SOA from other reactive VOCs (sesquiterpenes, etc.) according to Kanakidou (4). Compared to total biogenic VOC emissions of 1150 Tg yr^{-1} (52), the biogenic SOA source of 31.4 Tg yr^{-1} represents a mass yield of about 2.7%. Also included is an
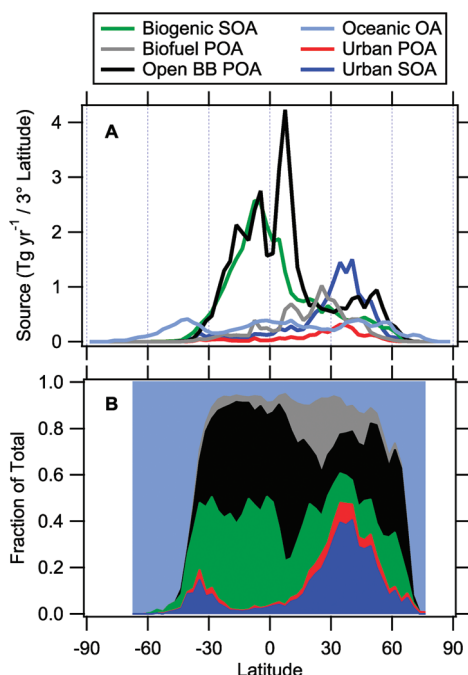
FIGURE 3. Estimated mean zonal distribution of organic aerosol sources. Biogenic SOA (*4, 40, 52*), oceanic OA (*53*), and POA (*32*) are taken from the literature. Urban SOA is calculated here. Note that the zonal distribution of concentrations may deviate from that of sources due to transport.

oceanic source of OC of 8 TgC yr^{-1} from Spracklen (*53*) that we multiplied here with an OA/OC ratio of 1.6.

The distribution for urban SOA in Figure 3 is calculated here. We used an average ΔSOA/ΔCO ratio of 64 μg m^{-3} ppmv^{-1} (Figure 1A) and multiplied this ratio with fossil fuel CO emissions according to the global inventory EDGAR (*34*). Obviously, this estimate has a large uncertainty (-50% to $+100\%$) because of the variability in observed ΔSOA/ΔCO ratios and inaccuracies in CO emission inventories (*21*). Compared to total anthropogenic VOC emissions of 105 Tg yr^{-1} (fossil fuel related sources and industrial processes) (*34*), the urban SOA source of 13.5 Tg yr^{-1} represents a mass yield of ~13%, i.e., a global yield approximately five times higher than that for biogenic SOA. We call this source urban SOA, as it correlates with urban tracers and is calculated from observations in urban plumes, but a fraction of the SOA could be formed from biogenic VOCs as discussed above.

While all source estimates in Figure 3 are very uncertain (by a factor of 2 or more) this analysis indicates that biomass burning and biogenic SOA are the largest sources of OA globally, but suggests that anthropogenic sources could be 50% at northern midlatitudes. This fraction may be even higher in densely populated areas of the U.S., Western Europe, and Eastern Asia. These findings are not inconsistent with source apportionment in polluted regions of the U.S. (*8*). Finally, the contribution from oceanic OA, though relatively small on an absolute scale, could be ~100% over the Southern Ocean.

Conclusions and Future Research

We have briefly reviewed the latest results from field studies of the sources of organic aerosol. Urban SOA formation, though poorly understood, could be a much larger source of aerosol at northern midlatitudes than previously recognized. Biomass burning is possibly the largest source of OA globally, but determining the net effect of SOA formation in biomass burning plumes needs further research. Early indications are that biogenic SOA is reasonably well represented by models.

There are many uncertainties regarding the sources of OA that should be addressed in future studies. The conclusions in the previous paragraph should be put to the test with new instruments and in unexplored or under-sampled regions of the atmosphere. In addition, there is some conflicting evidence in the literature that should be critically reviewed. First, the evidence that urban SOA is important but largely underestimated conflicts with chemistry-transport model calculations that agree reasonably well with observations. We argue here that model evaluations should not just focus on comparison with OA observations, but also include detailed evaluations of the emissions of POA and SOA precursors. Second, multiple radiocarbon dating studies have indicated that OA in rural atmospheres contains mostly modern carbon, which conflicts with our suggestion that ~50% of the OA at northern midlatitudes is associated with urban emissions. This conundrum should be addressed in future studies by using radiocarbon dating measurements in parallel with other methods of source attribution, with as high a time resolution as possible, and in regions of the atmosphere where biogenic and biomass burning emissions are expected to have different degrees of importance.

Joost de Gouw is a senior scientist with the Earth System Research Laboratory of the National Oceanic and Atmospheric Administration (NOAA) and a fellow of the Cooperative Institute for Research in Environmental Sciences (CIRES) of the University of Colorado. Jose-Luis Jimenez is an associate professor in the Department of Chemistry and Biochemistry at the University of Colorado, Boulder, and also a fellow of CIRES. Please address correspondence regarding this Feature to Joost.deGouw@noaa.gov.

Supporting Information Available
This material is available free of charge via the Internet at http://pubs.acs.org.

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