Atmospheric production of oxalic acid/oxalate and nitric acid/nitrate in the Tampa Bay airshed: Parallel pathways

P. Kalyani Martinelango, Purnendu K. Dasgupta*, Rida S. Al-Horr

Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409-1061, USA

Received 9 February 2006; received in revised form 1 May 2006; accepted 2 May 2006

Abstract

Oxalic acid is the dominant dicarboxylic acid (DCA), and it constitutes up to 50% of total atmospheric DCAs, especially in non-urban and marine atmospheres. A significant amount of particulate H$_2$Ox/oxalate (Ox) occurred in the coarse particle fraction of a dichotomous sampler, the ratio of oxalate concentrations in the PM$_{10}$ to PM$_{2.5}$ fractions ranged from 1 to 2, with mean ± sd being 1.4 ± 0.2. These results suggest that oxalate does not solely originate in the gas phase and condense into particles. Gaseous H$_2$Ox concentrations are much lower than particulate Ox concentrations and are well correlated with HNO$_3$, HCHO, and O$_3$, supporting a photochemical origin. Of special relevance to the Bay Region Atmospheric Chemistry Experiment (BRACE) is the extent of nitrogen deposition in the Tampa Bay estuary. Hydroxyl radical is primarily responsible for the conversion of NO$_2$ to HNO$_3$, the latter being much more easily deposited. Hydroxyl radical is also responsible for the aqueous phase formation of oxalic acid from alkenes. Hence, we propose that an estimate of *OH can be obtained from H$_2$Ox/Ox production rate and we accordingly show that the product of total oxalate concentration and NO$_2$ concentration approximately predicts the total nitrate concentration during the same period.

Keywords: Oxalate; Oxalic acid; BRACE; Nitrogen deposition; Photochemical production

1. Introduction

The occurrence of oxalic acid (H$_2$Ox) and/or oxalate (Ox) in snow, rain, particulate matter and possibly in the gas phase was first demonstrated by Norton et al. (1983). Aside from direct analysis of rain and snow by ion chromatography (IC), this early work used serial filters to demonstrate the presence of up to 3.5 μM Ox in precipitation and 2 nmol m$^{-3}$ H$_2$Ox/Ox in air, mostly present as particulate Ox. Nylon backup filters did contain measurable oxalate indicating the presence of gaseous H$_2$Ox but it was not possible to establish its presence unequivocally as Ox was shown to evaporate from the sampled filters. This early seminal work was remarkably thorough; because of the relatively low resolution of IC analysis at that time, the authors conclusively proved the presence of Ox in their samples by showing the disappearance of the putative chromatographic peak upon prior treatment of the sample with Oxalate decarboxylase. Earlier, in a characterization of dicarboxylic acids...
(DCAs) in Los Angeles aerosol, Grosjean et al. (1978) did not report the presence of Ox. If Norton et al. can be faulted at all, it is perhaps that they placed undue importance on this earlier finding and suggested that H2Ox/Ox might only constitute a very small fraction of DCAs.

There is a large body of work that has since accumulated which unequivocally shows that not only H2Ox/Ox is the dominant DCA, it frequently constitutes ~50% of total atmospheric DCAs in mid-ocean rainwater (Sempere and Kawamura, 1996). In non-urban rainwater in southern California, Ox routinely exceeded formate and sometimes acetate (Kawamura et al., 1996); in Schenectady aerosol, Ox was reported to frequently exceed the sum of formate and acetate (Khwaja, 1995). Oxalate was reported to constitute up to 86% of DCAs in urban (Nanjing, China) PM10 and up to 65% of the PM2.5 fraction (Wang et al., 2002). Oxalate may well be the most important aerosol species in its role as cloud condensation nuclei (Yu, 2000).

Main sources of oxalic acid are thought to be photochemical oxidation of anthropogenic, biogenic and oceanic emissions and/or primary traffic emissions (Kawamura and Kaplan, 1987; Kawamura et al., 1996). Very high concentrations of oxalic acid were detected in the biomass burning plumes, suggesting that either oxalic acid is directly emitted or formed in the plume from a biogenic precursor (Jaffrezo et al., 1998). Isoprene is the major organic compound emitted by plants. It has been shown that pyruvic acid and methylglyoxal formed by the oxidation of isoprene act as intermediates in the in-cloud formation of oxalic acid (Ervens et al., 2004; Lim et al., 2005). Oxalic acid is a likely end product of the photochemical oxidation reactions and can accumulate in the atmosphere (Chebbi and Carlier, 1996; Kawamura and Ikushima, 1993). Once formed, it is expected to be very stable and to exist as fine particles. Hence, the major removal mechanism is expected to be wet deposition.

In most studies conducted thus far, oxalic acid has not been observed in the gas phase in measurable quantities (Saxena and Hildemann, 1996). This could largely be due to inadequate sensitivity/methods. Limbeck et al. (2001) used a dual filter sampling strategy to determine the gas/aerosol distribution of oxalic acid and other polar organic compounds. They reported a gas phase concentration of 23±15 ng m⁻³ and aerosol concentration of 68±40 ng m⁻³. However, the uncertainty of these values was high.

Boring et al. (2002) recently presented a new fully automated instrument for the measurement of acid gases using a parallel plate wet denuder (PPWD) with an on-line particle collector and analyzer following it. At a highly industrialized site close to the shipping channel in Houston, TX, H2Ox concentrations ranged from 0.6 to 762 ng m⁻³ and the particulate Ox was 1.3–749 ng m⁻³.

In the present work, the gas–aerosol partitioning of H2Ox–Ox, the equilibrium relationship between ammonia, H2Ox and particulate ammonium oxalate and the influence of different parameters like temperature, ozone, concentration of other gas and aerosol species on the concentrations of H2Ox and Ox are discussed.

A central concern in the Bay Region Atmospheric Chemistry Experiment (BRACE) studies was the extent of nitrogen deposition in the Tampa Bay estuary. The hydroxyl radical (•OH) is primarily responsible for the conversion of NO2 (a gas with a low deposition velocity) to HNO3 (a gas with a high deposition velocity). The primary agent responsible for the formation of oxalic acid is also believed to be •OH. We are fortunate to have a wealth of near-real time data from continuous measurement of atmospheric gases and particles over a 5-week period in 2002 at the Tampa Bay airshed. Here, we intend to show that the production of HNO3/nitrates and H2Ox/Ox often follow such parallel pathways, that the production rate of one is well correlated with that of the other.

2. Experimental section

2.1. Field data

Data were obtained from 27/4/2002 to 31/5/2002 at the BRACE supersite at Sydney, FL (27° 58' N, 82° 13' W). This site is located at a suburban–rural interface, ~22 km ENE of downtown Tampa. The exact location of this site on a map appears in a published paper (Fig. 3b, Dasgupta et al., 2005). Gas and aerosol samples were collected using a PPWD (Boring et al., 2002) coupled to a mist chamber–hydrophobic filter reflux particle collector, PC (Al-Horr et al., 2003) with the sample inlet ~1 m above shelter rooftop and ~4.5 m from the ground level. The particle collection system had an effective cutoff at ~12.5 µm.

Soluble gases, including oxalic acid, were collected using a PPWD. H2O2 of 0.5 mM serves as the denuder liquid which captures the gases.
The denuder liquid containing the soluble gases was aspirated by a peristaltic pump at a flow rate of 1 ml min$^{-1}$ and sent into the IC.

The collection efficiency of oxalic acid by the PPWD was tested in our laboratory (680 mm Hg, 22 °C) by generating oxalic acid gas by soaking a 47 mm Whatman GF/B glass fiber filter in 0.1 M oxalic acid solution, drying it and drawing air though it at 8 standard liters per minute (SLPM). This was found to generate oxalic acid at a concentration of 768 ± 6 μg m$^{-3}$. This stream was sampled at 5 SLPM through two serial PPWDs. The collection efficiency for oxalic acid gas under these conditions was measured to be 97.6 ± 0.2%. Considering that this concentration is much higher than ambient concentrations and the fact that at Tampa atmospheric pressure is sea-level pressure such that sampling at 5 SLPM actually represents a significantly lower flow velocity, we believe that the denuder capture of H$_2$Ox was essentially quantitative.

For particle collection and analysis, ambient air was first passed through a PPWD to remove the gases. Disodium hydrogen phosphate Na$_2$HPO$_4$ (10 mM, adjusted to pH 6) containing 0.5 mM H$_2$O$_2$ was used as denuder liquid to remove both acidic and basic gases. The effluent stream containing the particles entered the hydrophobic filter-based particle collection system. Water was pumped into the PC through a capillary and the air was drawn through a small aperture surrounding it. The liquid generated a fine mist. The flow was ultimately drawn through a 0.5 μm pore size PTFE filter. Water droplets coalesced on the filter forming a film in which the aerosols were captured. The droplets fell below and were collected at the bottom of the PC. The liquid was then aspirated by a peristaltic pump and sent to the IC for analysis.

The IC analysis system consisted of alternating TAC-LP1 anion preconcentrator columns, AG11HC guard and AS11HC separation columns and an electrodialytically regenerated suppressor (ASRS, operated at 100 mA). The chromatographic system itself consisted of an IS-25 chromatographic pump coupled to an EG-40 electrodialytic eluent generator (15.5 mM KOH, 1.5 mL min$^{-1}$, LC-30 oven at 29 °C), and a conductivity detector (CD, model ED40). Chromatography was conducted either on a 10- or a 15-min cycle. All chromatographic equipment and columns were from Dionex Corp.

The dichotomous filter sampler was a Partisol$^\text{®}$ Plus Model 2025 (Rupprecht and Patashnik, East Greenbush, NY) that separated the samples into PM$_{2.5}$ and PM$_{10-2.5}$ components. More details are given in Poor et al. (2002).

3. Results and discussion

3.1. Gas–particle partitioning of oxalic acid

Over the period of the study, gaseous oxalic acid concentrations ranged from 0.014 to 0.81 μg m$^{-3}$ with mean and median values of 0.074 and 0.059 μg m$^{-3}$. Particulate Ox was present typically at ~4 × greater concentration, ranging from 0.025 to 5.8 μg m$^{-3}$ with mean and median values of 0.29 and 0.21 μg m$^{-3}$. In supplementary information, detailed frequency distribution data are presented (Figure S1). This is consistent with what has been observed elsewhere: in Hong Kong, another coastal city, only ~6–12% of the total oxalate (Ox$_T$) was H$_2$Ox (Yao et al., 2002). Clegg et al. (1996) reported that Ox$_T$ in the atmosphere partitions almost completely into aqueous aerosols, except under conditions of combined low relative humidity, low aerosol pH, and temperatures greater than about 15 °C.

Oxalate has been reported to be distributed over the whole particle size spectrum, having a dominant accumulation mode (0.1–2 μm), an Aitken mode (<0.1 μm) and a coarse particle mode (>2 μm) (Fridlind et al., 2000). This suggests that multiple pathways may exist for the formation of oxalate: while some of the H$_2$Ox is formed as gaseous H$_2$Ox and condenses to fine particles, another portion of oxalate may be formed in the aqueous phase and H$_2$Ox may even degas from it given appropriate conditions of droplet acidity, temperature and RH. In Tampa, NaCl aerosol concentration is large and it is present with a mode around 4 μm. This can provide a significant surface area for condensation/dissolution of H$_2$Ox leading to a prominent coarse particle mode for Ox. Previously, we had measured H$_2$Ox and PM$_{2.5}$ Ox in Houston and Philadelphia. In Tampa, a coastal city, the overall mode of ambient aerosol size is shifted up due to the major presence of sea-salt particles, this is not the case in the other two cities and a comparison of PM$_{12.5}$ Ox in Tampa with PM$_{2.5}$ Ox in Houston and Philadelphia is not inappropriate. Median concentrations of Ox (H, P, T: 41, 369 and 214 ng m$^{-3}$) and especially H$_2$Ox (H, P, T: 66, 67, 59 ng m$^{-3}$) are not dramatically different in the three cities but the highest concentration of Ox is significantly higher in
Tampa (5.9 μg m⁻³), compared to those in Houston (0.75 μg m⁻³) or Philadelphia (1.9 μg m⁻³). We believe this may be related to actual production of Ox in the solution phase associated with sea-salt aerosol from isoprene and/or ethene and acetylene (Lim et al., 2005; Warneck, 2003). Warneck (2003) has previously suggested that ethene and acetylene may serve as precursors for the intermediates glyoxal, glyoxylic acid, glycolic acid that are oxidized to form oxalic acid in the aqueous phase and Crahan et al. (2004) have observed evidence of in-cloud production of oxalate. Very recently Yu et al. (2005) have also argued that cloud processing must be involved in the formation of Ox and Warneck (2005) have explored in detail the conversion of ethene and acetylene in the marine atmosphere in a box model.

Other evidence also indicates that oxalate in the Tampa Bay airshed does not solely form in the gas phase and then condense to fine particles. We analyzed 19 randomly selected PM₁₀–₂.₅ and PM₂.₅ filter pairs from a dichotomous sampler from the period spanning June 2002–May 2003. The data were reconstituted to PM₁₀ and PM₂.₅. The ratio of PM₁₀/PM₂.₅ for sulfate which forms dominantly in the fine particles was 1.1 ± 0.1 while nitrate which forms nearly exclusively in coarse particles was 14.1 ± 17.0. This ratio for oxalate was 1.4 ± 0.2. Moreover, for individual filter samples, the PM₁₀/PM₂.₅ ratio for nitrate and oxalate was reasonably well correlated ($r^2 = 0.49$).

The large concentration of NaCl present in Tampa can result in a substantial liquid water content associated with the aerosol phase at high RH values. The sampling period, however, was mostly an exceptionally dry period for the region that year; only 4 days had any rainfall during these 5 weeks. With respect to in-cloud formation of oxalate, it is interesting to note that Ox was the highest on 18th and 19th May, the 2 days on which the rainfall was the highest (1.5 and 0.9 cm, respectively).

### 3.2 Diurnal variation

As has been previously observed in many other locations, in Tampa, daytime concentrations of both Ox and H₂Ox were almost always higher than the corresponding nighttime concentrations. Only on occasion, when the daytime concentrations were very low for reasons that are presently unclear to us, did the nighttime concentrations exceed those during the day.

We have recently measured the gaseous H₂Ox concentrations in equilibrium with solid oxalic acid as a function of temperature. These results will be published elsewhere. It is sufficient to note here that $p_{H₂Ox}$ is 3–5 orders of magnitude lower than predicted by the equilibrium above. Limbeck and Puxbaum (2000) have shown that the atmospheric phase distribution of DCAs is not necessarily directly related to the vapor pressure; rather, other physical and chemical processes such as adsorption onto available particle surfaces, absorption into a liquid phase, etc. greatly modify the observed results. Indeed, some gas to particle conversion occurs even when $p_{H₂Ox}$ is significantly below the predicted equilibrium pressure at that temperature.

The concentration maxima for H₂Ox occur during the time of the day when the temperature and light intensity are at their maximum (Fig. 1). This is consistent with a photochemically mediated path for the formation of oxalate, whether via homogeneous gas phase or heterogeneous solution phase pathways. Oxalate peaks after gaseous H₂Ox when the temperature starts to decrease; as condensation is favored as the temperature decreases.

Regardless of day or night, H₂Ox concentration exhibits a good positive correlation with temperature. Fig. 2 shows hourly average data, covering 5–95% of the total concentration span sorted in 45° wind direction bins (the 315–360° bin does not contain enough data to plot) and sorted in daytime (10 AM–6 PM) and nighttime (8 PM–6 AM) values. Both the nighttime and the daytime concentrations of gaseous H₂Ox appear to be driven by temperature and there is no obvious dependence on wind direction.

As shown in Fig. 3, the maxima in oxalate concentrations always coincide with the minima in RH. Since the latter is also related to temperature, we suspect that this is more directly related to temperature than to RH; however, at this point, no definitive conclusions can be drawn, especially as temperature and RH changes are diurnal and thus also associated with change in air mass origin.

### 3.3 Is oxalate present as ammonium oxalate?

Lefer and Talbot (2001) studied the similarity of the size distributions of oxalate and ammonium and suggested that ammonium oxalate aerosol may be directly formed from the gaseous precursors: ammonia and oxalic acid. If ammonium oxalate is indeed the form in which oxalate is present in the
aerosol phase, the temperature-dependent dissociation of ammonium oxalate (rather than H₂Ox directly) may well predict the observed temperature dependence behavior of the ambient aerosol. It is not of course possible to definitively determine in what form oxalate exists in the Tampa aerosol without single particle analysis. However, we note that particulate NH₄⁺ and Ox are generally well
correlated, especially in the nighttime (the data for a 10-day period are shown in Fig. 4, \( r^2 = 0.686 \)) and less so during the daytime (\( r^2 = 0.253 \)). The overall correlation between gaseous ammonia and H\(_2\)Ox is poor and is of the same order both during day and night (\( r^2 = 0.247 \) for day and nighttime data).

Fig. 3. Maxima in oxalate concentrations always corresponded with minima in relative humidity.

Fig. 4. Relation between particulate oxalate and ammonium (4/5/2002–13/5/2002).
combined). It does not therefore appear that the data conform to ammonia and oxalic acid primarily originating from the dissociation of ammonium oxalate. Other auxiliary experiments not discussed here indicate that ammonium in the Tampa aerosol is primarily in PM$_{2.5}$ whereas as previously discussed, oxalate is dominantly in the PM$_{10-2.5}$ fraction.

3.4. Evidence of photochemical production

Formaldehyde is also a product of atmospheric photooxidation. Formaldehyde was measured at the site at the same time (Li et al., 2005; Dasgupta et al., 2005) During 6 May to 11 May the wind field was stable and referring to these data, gaseous oxalic acid concentrations were very well correlated with that of HCHO (Fig. 5a, $r^2 = 0.784$). The correlation between H$_2$Ox concentrations and O$_3$ is almost as good (Fig. 5b, $r^2 = 0.700$). Hydrogen peroxide and methyl hydroperoxide were similarly measured at the site (Li et al., 2003). It is interesting that H$_2$Ox and H$_2$O$_2$ exhibited no correlation ($r^2 < 0.0001$) whereas methyl hydroperoxide, which requires an active hydrocarbon intermediate to be formed, is reasonably well correlated with H$_2$Ox (Fig. 6, $r^2 = 0.609$). Significant production of alkyl hydroperoxides during olefin oxidation is predicted by the Warneck (2005) model. Similar photochemical origins of HNO$_3$/nitrate and H$_2$Ox/Ox are suggested by other, significant portions of the data. For the 10-day period beginning on 4/5/2002, for example, gaseous HNO$_3$ and H$_2$Ox concentrations during the daytime were well correlated (Fig. 7, $r^2 = 0.642$).

In the liquid phase, oxalate is dominantly ionized and remains as such irrespective of the change in other parameters such as light intensity, oxidant concentration, etc. Thus, the correlations between particulate oxalate and HCHO, O$_3$, or MHP are significantly weaker ($r^2 = 0.310, 0.361, and 0.404$, respectively) during these periods. For particulate nitrate and Ox, we sorted the hourly averaged data into night and day bins and also calculated the wind direction (and standard deviation) during this period. These data are plotted in Fig. 8. In all cases, when the windfield is stable (this is more typical in the nighttime than during the day), there is superb correlation between the two species. Moreover, on all but one of the nighttime data sets, the airmass flows out to sea, originating in a 90–120° direction. The sampling site is 30 km due west of Old Tampa Bay and ~60 km west from the Gulf of Mexico. On the west of the sampling site,

Fig. 7. Relation between gaseous oxalic and nitric acids (4/5/2002–13/5/2002).
the Atlantic ocean is more than 200 km distant, across the width of the peninsula. The recent history of the sampled air mass is thus of inland origin. The nitrate–oxalate relationship has a slope \(7.0 \pm 1.0\) on all five data sets and on the one occasion that the daytime wind direction falls within these bounds, it has a slope of 7.3. Remarkably, on the one night (4–5 May) that the wind direction was very variable and significantly originated from the direction of the bay where the power plants are located, nitrate was proportionally much greater than oxalate.

All of these observations suggest a photochemical origin for oxalic acid and further support the contention that the formation of oxalate is linked with that of nitrate.

### 3.5. Is automotive emission a significant source of oxalic acid?

The bulk of the extant literature proposes that the primary source of oxalic acid is homogeneous gas phase oxidation of aromatic hydrocarbons, most notably toluene, originating from automotive exhaust (Kawamura and Kaplan, 1987; Kawamura et al., 2001). The senior author of this manuscript was responsible for deploying the first airborne IC for trace gas measurements in the summer of 1988 (Kok et al., 1990). He observed at the time that gaseous H₂Ox concentration was always higher above forest canopies and have had reservations about auto exhaust being the dominant source of oxalic acid since that time. Only very recently have alternative mechanisms and precursors been proposed for oxalic acid (Warneck, 2003, 2005; Crahan et al., 2004; Lim et al., 2005; Yu et al., 2005). In a major urban area such as Tampa, automotive exhaust emission could conceivably be the dominant source for OxT. However, the correlation of H₂Ox with potential traffic markers such as NO, NO₂, NOₓ, and especially CO were extremely poor (\(r^2\) values, 0.0025, 0.0189, 0.0183, and 0.0308, respectively). The correlation with toluene (data courtesy of R. Zika, University of Miami) was investigated and also found to be poor (\(r^2 = 0.0037\)). Analysis of the oxalic acid/oxalate data as a function of wind direction did not indicate that high oxalate concentrations are correlated with incoming airmass from downtown Tampa. These
results do not support the contention that automotive exhaust emissions are a major source of H$_2$Ox or precursors thereof. The corresponding correlations with Ox with any of the above parameters were also very poor.

3.6. Oxalic acid formation and its implications in nitrogen processing

A central concern in the BRACE studies is the extent of nitrogen deposition in the Tampa Bay estuary. The location of N deposition can be dependent on the efficiency with which primary emissions of NOx, gases with relatively low deposition velocity, are converted to HNO$_3$, a gas with very high deposition velocity (Pryor et al., 2002), or to particulate nitrate. The conversion of NO$_2$ to HNO$_3$ is brought about by •OH and the aqueous phase formation of oxalic acid from alkenes is also thought to be brought about by •OH (Lim et al., 2005; Crahan et al., 2004). Indeed, one end product of oxidation of some of these alkenes is formaldehyde, with which the excellent correlation of H$_2$Ox has already been mentioned. We make the following assumptions:

(a) the production of oxalic acid is limited by the availability of •OH (since we do not have data on reactive hydrocarbons, we cannot take into account any dependence on potential hydrocarbon precursors), and
(b) the loss of Ox$_T$ and NO$_{3T}$ (particulate nitrate and gaseous HNO$_3$) from our system in a box occur at comparable rates.

With these assumptions, if we confine ourselves to the daytime data when the Ox$_T$ and NO$_{3T}$ are both increasing, the incremental increase in Ox$_T$ between two successive 15 min periods, D Ox$_T$, should be related directly to the •OH concentration during that period. Considering that NO$_{3T}$ originates from the reaction:

$$\text{NO}_2 + \cdot \text{OH} \rightarrow \text{HNO}_3 \rightarrow \text{NO}_3^-.$$

If D Ox$_T$ is multiplied by the prevalent NO$_2$ concentration, this should approximately predict D NO$_{3T}$ during the same period, D NO$_{3T}$ being defined the same way as D Ox$_T$. Although data meeting both criteria were no plentiful, such a plot is shown for hourly averaged data in Fig. 9 for a 12-day period. Particulate oxalate alone is also reasonably correlated with the $f(\cdot \text{OH})$, the •OH concentration parameter being defined as $f(\cdot \text{OH}) = \Delta \text{NO}_{3T}/\text{NO}_2$ ($r^2 = 0.514$).

4. Conclusions

Gas and aerosol phase data of several atmospheric species collected from a 5 week study in Tampa, FL has been used to study the gas–aerosol partitioning behavior of H$_2$Ox/Ox and to shed light into the parameters influencing the formation of oxalic acid. The median Ox concentration is nearly an order of magnitude greater than H$_2$Ox concentration which is consistent with what others have observed elsewhere. Significant amounts of oxalate occurred in an aerosol size larger than 2.5 μm. This is consistent with appreciable amounts of oxalate being formed in liquid water associated with coarse particles.

The concentration maxima for H$_2$Ox coincide with the maxima in temperature and insolation intensity. Gaseous H$_2$Ox concentrations are often well correlated with levels of HCHO, HNO$_3$, and O$_3$ ($r^2 = 0.784$, 0.642, and 0.704, respectively), all consistent with a photochemically mediated path for the formation of oxalate. The concentrations of particulate NH$_4^+$ and Ox are also often well correlated, especially in the nighttime ($r^2 = 0.686$) which suggests that as temperature decreases, H$_2$Ox may be condensing as ammonium oxalate.
Much of the extant literature suggests that the primary source of oxalic acid is homogeneous gas phase oxidation of aromatic hydrocarbons originating from automotive exhaust followed by condensed phase reaction of the intermediates. We did not find any correlation between H₂Oₓ and/or Ox and traffic phase reaction of the intermediates. We did not find primary source of oxalic acid is homogeneous gas source of H₂Oₓ is photochemical reactions in the estuary, we examined the lessons the formation of H₂Oₓ/Ox provides regarding nitrogen processing. 

The production of H₂Oₓ/Ox from alkenes and HNO₃/NO₃ from NO₂ are parallel reactions mediated by •OH. Assuming the production of oxalic acid is limited by the availability of •OH and that the depositional loss processes of oxalate and nitrate species occur at comparable rates, we were able to show that the incremental increase in nitrate species during any given period is typically well correlated to the incremental increase in oxalate species during the same period multiplied by the NO₂ concentration. This suggests that the availability of •OH for the conversion of NO₂ to HNO₃ is also being limited by the production of oxallic acid.

An attempt was made to model the concentration of H₂Oₓ from a box model where the primary source of H₂Oₓ is photochemical reactions in aqueous droplets. Over at least a portion of the study period, the predicted profile was similar to what was observed.

Acknowledgments

The BRACE measurements by the Texas Tech University group were supported in part by the Florida Department of Environmental Protection with the assistance of the Environmental Protection Commission of Hillsborough County. The preparation of this manuscript was partly supported by the US EPA Science To Achieve Results (STAR) Program Grant RD-83107401-0. We thank SM Rahmat Ullah for the collection efficiency measurements. This manuscript would not have been possible without data and other material help from Dr. Noreen D. Poor, University of South Florida.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.atmosenv.2006.05.085.

References


