O$_3$-NO$_x$-VOC sensitivity and NO$_x$-VOC indicators in Paris: Results from models and Atmospheric Pollution Over the Paris Area (ESQUIF) measurements

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[1] A three-dimensional photochemical model has been used to interpret aircraft measurements from the Atmospheric Pollution Over the Paris Area campaign near Paris, with special attention to measurements that are related to predicted O$_3$-NO$_x$-volatile organic compound (VOC) sensitivity. The model (CHIMERE) includes a representation of ozone formation over Europe and a more detailed spatial representation of the region around Paris. A series of model scenarios were developed with varying wind speeds and emission rates. Comparisons are shown with measured O$_3$, total reactive nitrogen (NO$_x$), summed VOCs, and isoprene. Results show that model NO$_x$-VOC sensitivity predictions are correlated with the ratio O$_3$/NO$_x$ but not with O$_3$-peroxycetyl nitrate. Measured O$_3$ and NO$_x$ in high-ozone days tends to agree with model values when models predict NO$_x$-sensitive or transitional chemistry but not when models predict VOC-sensitive chemistry. Model values for O$_3$/NO$_x$ and the O$_3$-NO$_x$ slope are lower than measured values, suggesting the possibility of missing, unmeasured VOCs in the Paris plume. Standard performance tests for ozone models, such as normalized bias, show good agreement between models and measurements, even in cases where significant differences appear in the O$_3$-NO$_x$ correlation. Model predictions shift slightly toward NO$_x$-sensitive chemistry when model wind speeds are increased. Isoprene represents 20% of total VOC reactivity—weighted carbon in the center of the Paris plume and 50% in the surrounding rural area during high-ozone events.

INDEX TERMS: 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; KEYWORDS: ozone, nitrogen oxides, VOCs, isoprene, photochemical models


1. Introduction

[2] It is generally thought that in the densely populated regions of northern Europe, ozone is more likely to be sensitive to emissions of volatile organic compounds (VOCs) than to NO$_x$. Previous model-based studies of pollution events in northern Europe have found that ozone chemistry is limited by the availability of VOC and that biogenics have a minor impact, although there is considerable uncertainty [Simpson, 1995]. The situation in northern Europe stands in contrast with results from southern Europe and parts of the eastern U.S., where ozone is often sensitive to NO$_x$ rather than to VOC and where biogenics have a significant impact [e.g., Chameides et al., 1988; Sillman et al., 1995; Staffelbach et al., 1997a, 1997b].

[3] The recent Atmospheric Pollution Over the Paris Area (ESQUIF) field measurements provide an opportunity to examine predicted O$_3$-NO$_x$-VOC sensitivity in comparison with measurements. The ESQUIF project, described elsewhere [Menut et al., 2000b; Vautard et al., this issue], includes aircraft measurements of O$_3$, speciated VOCs, and total reactive nitrogen (NO$_x$). NO$_x$ is especially important because previous investigations have suggested that measured NO$_x$ can be used as an “indicator” for O$_3$-NO$_x$-VOC sensitivity. Results from both models and measurements suggest that the ratio O$_3$/NO$_x$ has a relatively low value during VOC-sensitive conditions and a high value during NO$_x$-sensitive conditions [Sillman, 1995; Sillman et al., 1998; Sillman and He, 2002]. Measured values of this ratio provide an indirect way of evaluating model predictions for NO$_x$-VOC sensitivity. This type of correlation is also
subject to large uncertainties and is not necessarily applicable to all locations [Lu and Chang, 1998].

[4] Here we show results from model calculations and ESQUIF measurements that relate to the NO$_x$-VOC sensitivity in the Paris urban plume. We will use a three-dimensional (3D) photochemical transport model (CHIMERE) to represent ozone formation and transport over continental Europe, with finer resolution for the Paris area. A series of model scenarios will be developed based on uncertainties that might affect NO$_x$-VOC predictions. Correlations between model species concentrations and NO$_x$-VOC sensitivity predictions will be examined to see whether the previously identified indicators can be correlated with NO$_x$-VOC sensitivity in this case. Comparison with measured reactive nitrogen and VOCs will be used to identify model biases and to address the issue of uncertainties associated with NO$_x$-VOC chemistry.

[5] The model and measurements are described in section 2. Section 3 presents correlations between O$_3$ and reactive nitrogen from various model scenarios and results concerning the abilities of these species to act as indicators for NO$_x$-VOC sensitivity. Section 4 shows measured correlations between O$_3$ and NO$_x$ in comparison with model results, along with other model-measurement comparisons. Section 5 discusses other issues and uncertainties, including the impacts of isoprene and of wind speed on ozone chemistry.

2. Methods

[6] The photochemical model (CHIMERE) and ESQUIF measurements are both described in detail elsewhere [Vautard et al., 2001; Menut et al., 2000b; Vautard et al., this issue]. A brief description is given here.

2.1. ESQUIF Project

[7] About a fifth of the French population lives in the vicinity of Paris, over an area of ~12,000 km$^2$. As in many urbanized areas, the Paris area frequently has elevated pollutant levels, including high ozone in summer. One of the purposes of the ESQUIF project is to quantify the rate of production of ozone within the region and also to identify transport from distant emission sources. During the summers of 1998, 1999, and 2000, 12 intensive observation periods (IOPs) were carried out to document the dynamical and chemical processes in the region. These IOPs included both a network of surface measurements and numerous aircraft-based measurements. As the Paris area presents a circular form (from the most important surface emissions at the center to rural areas at its boundaries), and as it is far from other major cities or emission sources, the aircraft measurements were made along flight paths that looped around the Paris urban center. The aircraft range and altitude varied from day to day based on aircraft capabilities, local meteorology, and the predicted pollution event.

2.2. Model

[8] A 3D Eulerian model (CHIMERE) [Vautard et al., 2001; Schmidt et al., 2001; Vautard et al., this issue] is used to simulate photochemistry and transport of pollutants within the boundary layer. We only briefly describe the model characteristics here, referring the reader to the previous papers for further details.

[9] The model domain is designed with two subsections. The first, a continental-scale subsection, is used to model chemistry and transport over western and central Europe, with a horizontal resolution of 0.5°. The second, an urban/suburban subsection, is used to model the behavior of pollutants over the Paris area. It represents a 150 × 150 km region centered on Paris, with a horizontal resolution of 6 × 6 km. Pollutant concentrations from the continental-scale subsection are used as boundary conditions for the regional-scale subsection (one-way nesting).

[10] For both subsections the CHIMERE model consists of five vertical layers, including a surface layer (0–50 m) and upper layers with 500–1000 m thicknesses. Vertical diffusion is estimated as eddy diffusion, based on a Richardson-number-profiles methodology and linearly depending on the boundary layer depth.

[11] These dynamical parameters, wind components, temperature, specific humidity, cloudiness, and pressure, are all derived from the European Centre for Medium-Range Weather Forecasts (ECMWF) model (10 vertical hybrid levels from ground to 700 hPa with a 3 h time resolution). Photochemistry is represented by the MELCHIOR mechanism [Laureau, 1997; Schmidt et al., 2001] and includes gas-phase reactions only. The equations of chemistry and transport are solved using the TWOSTEP solver [Ferwer and Simpson, 1995], where all processes are solved all together to avoid well-known splitting-operators problems.

[12] Anthropogenic emissions were derived from several databases [Menut et al., 2000a; Vautard et al., 2001]. An updated speciation of VOCs was used for this study [R. Friedrich, IER, University of Stuttgart, private communication, 2001; see also Vautard et al., this issue]. Emissions were also modified to reflect differences between weekdays, Saturdays, and Sundays using urban diurnal profiles deduced from measurements from the AIRPARIF network [Vautard et al., this issue]. In addition, studies of traffic patterns in Paris suggest that substantially lower traffic occurs during Saturdays in August than at other times. This August traffic pattern has not been used in the standard model scenario, but a separate scenario has been created that includes the August traffic pattern as a basis for emissions on Saturdays. Emissions of isoprene and α-pinene were included based on the work of Derognat et al. [this issue]. Nitric oxide biogenic emissions due to biological processing of fertilizers in the soils are also considered, following the methodology of Stohl et al. [1996]. The model was exercised for a 3 week period in July 1999. Results will be shown here for 16, 17, and 18 July in comparison with measurements.

2.3. Model Scenarios

[13] A series of scenarios with alternate base case emissions will be developed, including the following: (1) the initial scenario, based on emissions and meteorology described above; (2) scenarios with anthropogenic VOC increased by 40% and with NO$_x$ reduced by 30% relative to the inventory values; (3) scenarios with isoprene emission rates doubled relative to the inventory values; (4) scenarios with wind speeds increased by 25% and 75% relative to the original meteorology; and (5) scenarios with the height of the afternoon mixed layer increased by 25% relative to the original meteorology. The scenarios with increased VOC and reduced NO$_x$ were developed based on the uncertainty of...
VOC and NO\textsubscript{x} emissions, estimated as ±40% [Beekmann and Derognat, this issue; Vautard et al., this issue]. Vautard et al. [this issue] also provide cases with different NO\textsubscript{x}-VOC sensitivity from the initial scenario. As in previous studies of this type [Sillman et al., 1995, 1998], scenarios with different predicted NO\textsubscript{x}-VOC sensitivities will be used to evaluate uncertainty in model predictions and to identify whether comparisons with measurements can reduce this uncertainty.

The scenarios with higher wind speeds reflect uncertainties in winds during the event. Because winds are generally light during the period (2 m s\textsuperscript{-1} or less), a 25% change is likely within the range of uncertainty associated with wind measurement and interpolation. A scenario with 75% higher wind speeds was added in order to identify the impact of wind speed on NO\textsubscript{x}-VOC sensitivity. The scenarios with higher daytime mixed layers are based on lidar measurements reported by Vautard et al. [2003], which suggest that the height of the afternoon mixed layer may be higher than originally estimated. A scenario with emissions on 17 July modified based on the changes observed in traffic patterns [Vautard et al., 2001] has been added, as described above.

Along with each scenario, control strategy simulations will be performed with 30% reductions in either anthropogenic VOC or NO\textsubscript{x} emissions relative to the base case. These control scenarios will be used to identify the NO\textsubscript{x}-VOC sensitivity of each case.

### 2.4. Measurements

Measured reactive nitrogen and VOCs are shown from the flights of the DIMONA aircraft [see Konrad and Volz-Thomas, 2000]. The aircraft flew a perimeter around Paris at a distance ~30 km from the city center and at an altitude of ~600 m above ground level. Measurements from three flights are studied in this paper: (1) 16 July 1999 at 1135–1536 local standard time (LST); (2) 17 July 1999 at 1416–1824 LST; and (3) 18 July 1999 at 1216–1615 LST. Flight trajectories are shown in Figure 1.

NO\textsubscript{y} and peroxyacetyl nitrate (PAN) were measured by the “NO\textsubscript{x},TO\textsubscript{y}” instrument [Kanter et al., 2001], which was also used and validated during the BERLIOZ campaign. Speciated VOCs (C\textsubscript{4}–C\textsubscript{10}) were measured by the Airmotec HC-1010 gas-phase chromatograph [Konrad and Volz-Thomas, 2000]. The VOC measurements represent average ambient values over 10 min intervals. O\textsubscript{3} and reactive nitrogen represent instantaneous measurements at 10 s intervals.

### 3. Model NO\textsubscript{x}-VOC Sensitivity and Indicator Ratios

The relation between total reactive nitrogen and O\textsubscript{3}-NO\textsubscript{x}-VOC sensitivity in Paris is shown in Figure 2. Figure 2 shows a composite plot of O\textsubscript{3} versus NO\textsubscript{x} from several model scenarios, including both predominantly VOC-sensitive and NO\textsubscript{x}-sensitive cases. Results are shown for several days at afternoon hours corresponding with measurements. Figure 2 also shows each location categorized as VOC-sensitive, NO\textsubscript{x}-sensitive, or mixed based on the predicted response of model O\textsubscript{3} to a 30% reduction in emissions of anthropogenic VOCs or NO\textsubscript{x}. The categorization of model...
locations is based on definitions similar to those used in previous studies of this type [Sillman, 1995; Sillman et al., 1998]. Simulated O₃ at a specific time and location are compared for a model base case, for a scenario with 30% reduced anthropogenic VOC emissions, and for a scenario with 30% reduced NOₓ. Locations are classified as NOₓ-sensitive (green circles), VOC-sensitive (crosses), and mixed or with near-zero sensitivity (pink points) based on the predicted impact of reduced NOₓ and VOCs at that location and hour. The line represents an O₃/NOₓ ratio of 6.5.

[18] As shown in Figure 2, NOₓ-sensitive and VOC-sensitive locations are associated with a different range of values of O₃ and NOₓ. NOₓ-sensitive locations have higher O₃/NOₓ ratios and tend to occupy a relatively narrow range of O₃ and NOₓ values, with O₃ increasing with increasing NOₓ. VOC-sensitive locations have lower O₃/NOₓ ratios and occur over a wider range of O₃ and NOₓ. There is also less correlation between O₃ and NOₓ among VOC-sensitive locations in this composite plot, but individual VOC-sensitive events may still show a positive correlation between O₃ and NOₓ.

[19] Previouly, Sillman [1995] expressed the above relationship in terms of the ratio O₃/NOₓ. NOₓ-sensitive locations were identified with O₃/NOₓ above a certain transition value (6.5 in this case), and VOC-sensitive locations were identified with O₃/NOₓ below the transition value. A line representing the transition value has been superimposed in Figure 2. It is apparent that the O₃/NOₓ ratio and the transition value is an imperfect representation of the relation between model O₃, NOₓ, and NOₓ-VOC sensitivities. At low O₃ and NOₓ, VOC-sensitive conditions persist for O₃/NOₓ somewhat higher than the transition value, while at higher O₃ and NOₓ, NOₓ-sensitive conditions persist for somewhat lower O₃/NOₓ. A similar pattern of variation was found in model results from the U.S. [Sillman and He, 2002]. The transition value is also sensitive to the level of background O₃ and NOₓ [see Sillman and He, 2002]. Though imperfect, the ratio provides a concise way for summarizing the relation between reactive nitrogen and NOₓ-VOC sensitivity in models.

[20] Sillman et al. [1998] identified the NOₓ-VOC transition value for O₃/NOₓ and other indicator ratios by examining the percentile distribution of O₃/NOₓ among model NOₓ-sensitive and VOC-sensitive locations. The 95th percentile value for VOC-sensitive locations and the 5th percentile value for NOₓ-sensitive locations were interpreted to show the value associated with the transition from VOC-sensitive to NOₓ-sensitive chemistry. Table 1 shows the results for the Paris simulation in comparison with previous results for simulations in the U.S. (Nashville, Tennessee). Results show that O₃/NOₓ and the other indicator ratios behave similarly in the Paris simulations as in the previously reported cases discussed by Sillman et al. [1998]. The transition values for indicators in the Paris simulations are similar to the values reported for Nashville simulations with similar dry deposition for HNO₃ (2.5 cm s⁻¹). Slightly higher transition values were found for Nashville in simulations with higher dry deposition (see Table 1).

[21] A similar pattern to Figure 2 is also found for O₃ versus NOₓ (defined as NOₓ-NOX) and for O₃ versus HNO₃. These are summarized in transition value statistics shown in Table 1. However, the correlation between O₃ and PAN behaves differently. As shown in Figure 3, O₃ versus PAN is not correlated with model NOₓ-VOC sensitivity. O₃ is positively correlated with PAN in models, and the correlation varies from day to day (due to changes in temperature). The same values of O₃ and PAN appear for both NOₓ-sensitive and VOC-sensitive locations. The correlation between NOₓ-VOC sensitivity and O₃/NOₓ, illustrated in Figure 2, is driven specifically by HNO₃ (and, to a lesser extent, by NOₓ) rather than by PAN and other organic nitrates. This is consistent with the radical chemistry associated with NOₓ-VOC sensitivity (see the summary by Sillman [1999]) and with results from the work of Tonnesen and Dennis [2000].

4. Model-Measurement Comparisons

4.1. O₃ and NOₓ

[22] Figure 4 shows comparisons between model and measured O₃ and NOₓ on 17 July (1600 LST) for three model scenarios: the standard scenario (VOC-sensitive), the scenario with higher VOC and lower NOₓ emissions (NOₓ-sensitive), and the scenario with higher VOC emissions and with the daytime mixed layer increased by 25% (mixed sensitivity). As in the previous figures, model values have been categorized as NOₓ-sensitive, VOC-sensitive, or mixed...
based on the predicted sensitivity at each location for the given hour. Results associated with peak O₃ for each scenario are also shown in Table 2.

[23] Results show that predicted NOₓ-VOC sensitivity varies considerably among the three model scenarios. The initial scenario predicts VOC-sensitive chemistry throughout the Paris urban plume. NOₓ-sensitive chemistry is associated with lower O₃ and NOₓ along the plume outskirts or in the surrounding rural region. The scenario with increased VOC and decreased NOₓ emissions predicts NOₓ-sensitive chemistry almost everywhere, even for locations near the city center. The scenario with higher VOC emissions and increased wind speeds predicts mixed sensitivity, with VOC-sensitive conditions near the city center, NOₓ-sensitive conditions at downwind and rural locations, and equal sensitivity to NOₓ and VOC in the plume locations with highest O₃. These varying NOₓ-VOC predictions occur despite the fact that O₃ is similar in all three scenarios.

[24] Comparison between models and measurements show good agreement only when the model predicts mixed or NOₓ-sensitive chemistry. A strong correlation between O₃ and NOₓ is predicted for the NOₓ-sensitive subregion in all three model scenarios, and this correlation matches visually with measurements. By contrast, the VOC-sensitive locations in the standard scenario differ substantially from measured values. Peak O₃ in the standard scenario is slightly lower than measured peak O₃ (131 ppb modeled, 142 ppb measured); NOₓ concurrent with peak O₃ is significantly higher (33 ppb modeled, 21 ppb measured), and O₃/NOₓ is much lower (4.0 ppb modeled, 6.8 ppb measured) (see Table 2). The NOₓ-sensitive and mixed scenarios have similar peak O₃ to the standard scenario but with lower NOₓ. These agree more closely with measured peak O₃ and NOₓ, though O₃/NOₓ (4.7–5.0) is still underestimated. Correlation statistics (Table 3) show that the rate of increase of O₃ with NOₓ is underestimated in all model scenarios. The underestimate is smaller in the NOₓ-sensitive scenario but even here, the model O₃-NOₓ slope is 25% lower than the measured slope.

[25] Measurements on 18 July (Figure 4d) also show a strong correlation between O₃ and NOₓ, with slightly higher O₃ for equivalent NOₓ compared to 17 July. The standard model scenario predicts NOₓ-sensitive conditions in most of the Paris plume (though with mixed NOₓ-VOC sensitivity in the plume center with highest O₃) and a strong correlation between O₃ and NOₓ. In contrast with 17 July the model tends to underestimate O₃ relative to NOₓ throughout the entire region, not just in the Paris plume. The model also underestimates the rate of increase of O₃, with NOₓ somewhat relative to measured values (see Table 3). Measurements on 16 July (Figure 4e) show a different pattern, with

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**Table 1.** Percentile Distribution of Indicator Values in NOₓ-Sensitive and VOC-Sensitive Locations

<table>
<thead>
<tr>
<th>Indicator</th>
<th>VOC-Sensitive Locations</th>
<th>NOₓ-Sensitive Locations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5th Percentile</td>
<td>50th Percentile</td>
</tr>
<tr>
<td>O₃/NOₓ</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paris</td>
<td>3.0</td>
<td>4.7</td>
</tr>
<tr>
<td>Nashville, low deposition</td>
<td>2.2</td>
<td>3.6</td>
</tr>
<tr>
<td>Nashville, high deposition</td>
<td>2.6</td>
<td>5.3</td>
</tr>
<tr>
<td>O₃/HNO₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paris</td>
<td>5.2</td>
<td>6.1</td>
</tr>
<tr>
<td>Nashville, low deposition</td>
<td>5.3</td>
<td>6.3</td>
</tr>
<tr>
<td>Nashville, high deposition</td>
<td>7.0</td>
<td>8.8</td>
</tr>
<tr>
<td>H₂O₂/HNO₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paris</td>
<td>11.0</td>
<td>12.0</td>
</tr>
<tr>
<td>Nashville, low deposition</td>
<td>6.0</td>
<td>8.0</td>
</tr>
<tr>
<td>Nashville, high deposition</td>
<td>8.0</td>
<td>11.0</td>
</tr>
</tbody>
</table>

*aShown are 5th percentile, 50th percentile, and 95th percentile indicator values (with percentile ordering by indicator value) for VOC-sensitive locations and for NOₓ-sensitive locations as defined in the text. Results from the Paris standard scenario (at 1600 LST, 17 July) are compared with results from Nashville scenarios with low deposition (2.5 cm s⁻¹ for H₂O₂ and HNO₃) and with high deposition (5 cm s⁻¹) [Sillman et al., 1998].

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**Figure 3.** Same as in Figure 2, but for composite O₃ versus peroxyacetyl nitrate (PAN) (ppb).
much lower O₃, higher NOₓ, a low O₃-NOₓ slope, and likely VOC-sensitive chemistry. The model standard scenario predicts VOC-sensitive chemistry throughout the domain and shows good agreement with O₃ versus NOₓ.

Figure 5 shows a comparison between O₃ and NOₓ in Paris on 17 and 18 July with previously measured O₃ and NOₓ in urban plumes in Atlanta, Georgia, and in Nashville [Sillman et al., 1995, 1998]. As shown in Figure 5, the observed pattern of O₃ and NOₓ in Paris on 18 July is similar to the previous observations in Nashville in terms of both magnitude and the O₃-NOₓ slope (see also Figure 2). The O₃-NOₓ slope in Paris on 17 July is similar to the O₃-NOₓ slope on 18 July but with higher NOₓ for equivalent O₃. The O₃/NOₓ ratio concurrent with peak O₃ in Paris (6.8 on 17 July, 7.9 on 18 July) is somewhat lower than peak O₃/NOₓ in Nashville (8.4). The O₃/NOₓ ratio in Paris is much lower than the equivalent O₃/NOₓ in Atlanta (11–16) and is much higher than in Los Angeles, California (3.6 [Sillman et al., 1997]). Measured O₃/NOₓ in Atlanta and in Los Angeles represent the likely extreme values associated with NOₓ-sensitive and VOC-sensitive chemistry, respectively, while the intermediate value at Nashville was associated with intermediate NOₓ-VOC chemistry. O₃/NOₓ concurrent with peak O₃ in Paris on 16 July was also very low (1.9).

4.2. Spatial Distribution and Other Species

Ozone in the region forms in a coherent plume extending downwind from the Paris urban center. This spatial pattern appears in both the model and in the measurements (see Vautard et al. [this issue] for more details). The location of the downwind plume in the model is generally consistent with aircraft measurements. This is illustrated in Figure 6, which shows model and measured species along the aircraft flight path on 17 July. Elevated O₃, NOₓ, and anthropogenic VOCs appear when the aircraft flight path intersects with the Paris urban plume. The location and structure of these plumes is generally consistent between model and measurements. The underestimate of NOₓ in the urban plume in the model base case is also evident in Figure 6.

Figure 7 and Table 4 show the correlation between summed anthropogenic VOCs and NOₓ from measurements and from the standard model scenario along the aircraft trajectory for 17 July. Summed VOCs have been expressed as propene-equivalent carbon [Chameides et al., 1992], a sum in which each primary VOC species is weighted by its

Figure 4. (opposite) Measured O₃ versus NOₓ (ppb) (blue diamonds) compared with model results. Model values are classified as NOₓ-sensitive (green circles), VOC-sensitive (crosses), and mixed or with near-zero sensitivity (pink points) based on the predicted impact of reduced NOₓ and VOCs at that location and hour. The results are for (a) 17 July 1999 (1600 LST) with a standard model scenario, (b) 17 July 1999 with a scenario with increased VOCs and lowered NOₓ, (c) 17 July 1999 with wind speeds increased by 25%, (d) 18 July 1999 (1600 LST) with a standard scenario, and (e) 16 July 1999 (1400 LST) with a standard scenario. Linear least squares coefficients are shown in Table 3.
rate of reactivity with OH (normalized relative to propene) and by the number of carbon atoms. Results for individual VOCs are shown in Vautard et al. [this issue]. As shown in Figure 7, anthropogenic VOCs and NO\textsubscript{x} are generally correlated both in models and in measurements. Peak measured VOC levels are significantly lower than the model maximum values, but this may be the result of the relatively long averaging time (10 min) for the individual measurements. Measured VOCs are higher than model VOCs for equivalent NO\textsubscript{x}, but the slope between VOCs and NO\textsubscript{x} is just +12% despite the apparent overestimate of NO\textsubscript{x} in Figures 4 and 6. The statistics for summed VOCs are generally comparable in magnitude with measured values. However, there is considerable uncertainty over the impact of vertical mixing on isoprene concentrations, as discussed in section 5.

[56] The U.S. Environmental Protection Agency (EPA) uses two statistics to characterize the performance of air quality models: normalized bias, \((1/N)\sum_j[(C_m - C_o)/C_o]\), and normalized gross error, \((1/N)\sum_j[(C_m - C_o)/C_m]\), where \(C_m\) and \(C_o\) represent model and observed concentrations, respectively. These statistics are shown in Table 5. They show unusually good agreement for O\textsubscript{3} in most of the model scenarios, with the normalized bias <5% and a normalized gross error of 10%. The normalized bias for NO\textsubscript{x} is just +12% despite the apparent overestimate of NO\textsubscript{x} in Figures 4 and 6. The statistics for summed VOCs

### Table 2. Peak O\textsubscript{3}, NO\textsubscript{x}, and Predicted NO\textsubscript{x}-VOC Sensitivity in Paris\textsuperscript{a}

<table>
<thead>
<tr>
<th>Scenario</th>
<th>16 July 1999 (1400 LST)</th>
<th>17 July 1999 (1600 LST)</th>
<th>18 July 1999 (1600 LST)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Reduced VOCs</td>
<td>Reduced NO\textsubscript{x}</td>
<td>Reduced VOCs</td>
</tr>
<tr>
<td>Measured</td>
<td>60 34</td>
<td>143 21</td>
<td>120 15</td>
</tr>
<tr>
<td>Model scenario\textsuperscript{b}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weekend adjustment</td>
<td>59 9–18 6</td>
<td>131 33 24 9</td>
<td>109 17 6 7</td>
</tr>
<tr>
<td>Higher VOCs</td>
<td>129 30 17 11</td>
<td>105 15 4 8</td>
<td></td>
</tr>
<tr>
<td>High VOCs, low NO\textsubscript{x}</td>
<td>142 34 11 15</td>
<td>115 18 5 10</td>
<td></td>
</tr>
<tr>
<td>25% higher wind</td>
<td>119 24 15 10</td>
<td>101 14 4 6</td>
<td></td>
</tr>
<tr>
<td>25% higher wind and double isoprene</td>
<td>121 24 14 11</td>
<td>103 15 4 7</td>
<td></td>
</tr>
<tr>
<td>25% higher wind and higher VOCs</td>
<td>126 27 12 13</td>
<td>107 18 5 8</td>
<td></td>
</tr>
<tr>
<td>75% higher wind</td>
<td>108 20 11 9</td>
<td>97 15 4 5</td>
<td></td>
</tr>
<tr>
<td>25% higher mixing height</td>
<td>118 25 16 8</td>
<td>104 17 5 6</td>
<td></td>
</tr>
<tr>
<td>25% higher mixing height and higher VOCs</td>
<td>127 26 9 13</td>
<td>109 18 4 9</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Shown are the following: peak O\textsubscript{3} in the Paris urban plume; NO\textsubscript{x} concurrent with peak O\textsubscript{3}; the predicted reduction in peak O\textsubscript{3} resulting from a 30% decrease in the emission of anthropogenic VOCs in the Paris region; and the predicted reduction in peak O\textsubscript{3} resulting from a 30% decrease in NO\textsubscript{x} (Negative values represent a predicted increase in O\textsubscript{3} resulting from reduced emissions.)

\textsuperscript{b}The model scenarios are: (1) the standard scenario; (2) a scenario with emissions adjusted based on weekend estimates from the work of Vautard et al. [2001]; (3) a scenario with anthropogenic VOC emissions increased by 40% relative to scenario 1; (4) a scenario with anthropogenic emissions increased by 40% and NO\textsubscript{x} decreased by 30% relative to scenario 1; (5) a scenario with wind speeds throughout the Paris region increased by 25%; (6) scenario 5 with double isoprene emissions; and (7) scenario 5 with anthropogenic VOC emissions increased by 40%. Also shown is O\textsubscript{3} from calculations with 30% reduced anthropogenic VOC and 30% reduced NO\textsubscript{x} relative to each scenario base case.

### Table 3. Linear Least Squares Coefficients For O\textsubscript{3} Versus NO\textsubscript{x}\textsuperscript{a}

<table>
<thead>
<tr>
<th>Scenario</th>
<th>16 July 1999 (1400 LST)</th>
<th>17 July 1999 (1600 LST)</th>
<th>18 July 1999 (1600 LST)</th>
<th>Nashville, 13 July 1999 (1400 LST)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a_0)</td>
<td>(a_1)</td>
<td>(r^2)</td>
<td>(a_0)</td>
</tr>
<tr>
<td>Measured</td>
<td>44.0</td>
<td>.38</td>
<td>.28</td>
<td>40.0</td>
</tr>
<tr>
<td>Model scenario\textsuperscript{b}</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Weekend adjustment</td>
<td>41.0</td>
<td>.78</td>
<td>.49</td>
<td>53.0</td>
</tr>
<tr>
<td>Higher VOCs</td>
<td>50.0</td>
<td>2.6</td>
<td>.89</td>
<td>60.0</td>
</tr>
<tr>
<td>High VOCs, low NO\textsubscript{x}</td>
<td>50.0</td>
<td>2.7</td>
<td>.84</td>
<td>61.0</td>
</tr>
<tr>
<td>25% higher wind</td>
<td>46.0</td>
<td>3.3</td>
<td>.90</td>
<td>57.0</td>
</tr>
<tr>
<td>25% higher wind and double isoprene</td>
<td>53.0</td>
<td>2.2</td>
<td>.73</td>
<td>63.0</td>
</tr>
<tr>
<td>25% higher wind and higher VOCs</td>
<td>52.0</td>
<td>2.4</td>
<td>.79</td>
<td>64.0</td>
</tr>
<tr>
<td>75% higher wind</td>
<td>51.0</td>
<td>2.7</td>
<td>.84</td>
<td>61.0</td>
</tr>
<tr>
<td>75% higher wind</td>
<td>52.0</td>
<td>2.3</td>
<td>.69</td>
<td>63.0</td>
</tr>
<tr>
<td>25% higher mixing height</td>
<td>52.0</td>
<td>2.3</td>
<td>.70</td>
<td>60.0</td>
</tr>
<tr>
<td>25% higher mixing height and higher VOCs</td>
<td>50.0</td>
<td>2.7</td>
<td>.84</td>
<td>58.0</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Shown are the linear least squares estimators for the linear correlation \([\text{O}_3] = a_0 + a_1[\text{NO}_x]\) in ppb from Figure 4 along with the correlation coefficient \((r^2)\) from measurements and model scenarios. Results for Nashville (from measurements and models described by Sillman et al. [1998]) are shown for comparison.

\textsuperscript{b}The model scenarios are: (1) the standard scenario; (2) a scenario with emissions adjusted based on weekend estimates from the work of Vautard et al. [2001]; (3) a scenario with anthropogenic VOC emissions increased by 40% relative to scenario 1; (4) a scenario with anthropogenic emissions increased by 40% and NO\textsubscript{x} decreased by 30% relative to scenario 1; (5) a scenario with wind speeds throughout the Paris region increased by 25%; (6) scenario 5 with double isoprene emissions; and (7) scenario 5 with anthropogenic VOC emissions increased by 40%. Also shown is O\textsubscript{3} from calculations with 30% reduced anthropogenic VOC and 30% reduced NO\textsubscript{x} relative to each scenario base case.
that the Paris plume may include regions of both NO\textsubscript{y} and VOC-sensitive chemistry in different locations and on different days. This conclusion is supported by both sensitive and VOC-sensitive chemistry in different locations.

bars also show the flight interval associated with each measurement, representing a 10 min period.

The solid line represents the model; the points represent measured values. For VOCs and isoprene, the horizontal ratio of 6.5.

Figure 5. Measured O\textsubscript{3} versus NO\textsubscript{y} (ppb) in the Paris plume on 17 July (crosses) and 18 July (blue diamonds) compared with similar measurements in Atlanta, Georgia (green circles), and in Nashville, Tennessee (pink points) [from Sillman et al., 1995, 1998]. The line represents an O\textsubscript{3}/NO\textsubscript{y} ratio of 6.5.

show a slight underestimate (\(-21\%\)) in the model standard scenario.

5. Discussion

The results shown in section 4 suggest that ozone chemistry in the Paris plume is often close to the transition between VOC-sensitive and NO\textsubscript{y}-sensitive conditions and that the Paris plume may include regions of both NO\textsubscript{y}-sensitive and VOC-sensitive chemistry in different locations and on different days. This conclusion is supported by both model and measured O\textsubscript{3} and NO\textsubscript{y}. Models predict regions of both NO\textsubscript{y}-sensitive and VOC-sensitive chemistry, and predicted NO\textsubscript{y}-VOC sensitivity in models varies from day to day. Measured O\textsubscript{3} and NO\textsubscript{y} on 17 July are close to the range of values associated with the transition from NO\textsubscript{y}-sensitive to VOC-sensitive chemistry in model calculations (e.g., compare Figures 2 and 5). Measurements on 18 July had higher O\textsubscript{3}/NO\textsubscript{y} ratios, suggesting NO\textsubscript{y}-sensitive chemistry, while measurements on 16 July had much lower O\textsubscript{3}/NO\textsubscript{y} ratios, suggesting VOC-sensitive chemistry. Here we suggest that uncertainties in model predictions may be due to the fact that conditions in Paris are close to the NO\textsubscript{y}-VOC transition.

Model measurement comparisons also suggest that the standard model scenarios underestimate the rate of ozone production per NO\textsubscript{y} in the Paris urban plume. The ratio O\textsubscript{3}/NO\textsubscript{y} associated with peak O\textsubscript{3} is underestimated by 40% on 17 July and by somewhat less (24%) on 18 July. This underestimate suggests that the ozone production chemistry may not be sufficiently reactive, possibly because of an underestimate in reactive VOCs. Better agreement between models and measurements can be obtained by using model scenarios with 25% higher wind speeds, higher mixed layer heights, and/or adjusted VOC emissions, but a tendency to underestimate O\textsubscript{3}/NO\textsubscript{y} remains. Underestimated O\textsubscript{3}/NO\textsubscript{y} also can be interpreted as evidence that model NO\textsubscript{y}-VOC predictions are biased and overestimate sensitivity to VOCs. The slope between O\textsubscript{3} and NO\textsubscript{y} (defined as \(\Delta O\textsubscript{3}/\Delta NO\textsubscript{y}\)) as opposed to the ratio O\textsubscript{3}/NO\textsubscript{y} is underestimated by 15–25% in models relative to measurements. A similar underestimate was found previously for Nashville [Sillman et al., 1998] (see Table 3). From Figure 4, it appears that the underestimated slope on 17 July is associated specifically with the region of peak O\textsubscript{3} and NO\textsubscript{y} in the Paris plume, although on 18 July the discrepancy between models and measurements appears over the entire data set.

The most likely cause of this model-measurement discrepancy is an underestimate of VOCs or of VOC reactivity in the Paris plume. However, the underestimated O\textsubscript{3}/NO\textsubscript{y} in models could also be due to errors associated with the NO\textsubscript{y} lifetime and removal. It is possible that reactive nitrogen is removed by dry deposition more rapidly than implied by the model deposition velocity. It is also possible that differences between model and measured NO\textsubscript{y} are due to a conversion of reactive nitrogen to aerosol nitrate [Martilli et al., 2002]. Conversion to aerosol nitrate has not been included in the model, and measured NO\textsubscript{y} probably does not include aerosol nitrate. It is also possible that measurements underestimate total NO\textsubscript{y} due to deposition of HNO\textsubscript{3} along the inlet tube [Parrish and Fehsenfeld, 2000; McClenney, 2000]. Previously, it was estimated that uncertain deposition rates can cause a 20% uncertainty in O\textsubscript{3}/NO\textsubscript{y} [Sillman et al., 1998]. Gao et al. [1996] also found 20% uncertainties in O\textsubscript{3} associated with uncertain photochemical reaction rates. In the current exercise the discrepancy between measured values and the model standard scenario for 17 July is \(~40\%\), somewhat larger than these uncertainty estimates.

Given these uncertainties, it is especially significant that O\textsubscript{3} and NO\textsubscript{y} in the standard model scenario agree with measured values in NO\textsubscript{y}-sensitive rural areas and disagree only in the center of the Paris plume, where the model predicts VOC-sensitive chemistry. Possible errors associated with NO\textsubscript{y} lifetime and removal or with measurements would cause model-measurement discrepancies over the entire region rather than just in the Paris plume. By contrast, an underestimate in either VOC emissions or reactivity would be consistent with the actual model-measurement discrepancy that appears only in the Paris plume. The discrepancy is much less in model scenarios that have higher mixing heights and more reactive VOCs. These scenarios also move the model in the direction of greater sensitivity to NO\textsubscript{y}.

Vautard et al. [this issue] found no evidence for errors in either anthropogenic VOC emissions or in the VOC/NO\textsubscript{y} ratio, but they found significant uncertainty (\(\pm 40\%\)) in the emission estimates. In contrast with measured O\textsubscript{3} and NO\textsubscript{y}, measured VOCs generally provide evidence

Figure 6. (opposite) Model versus measured species concentrations along the flight trajectory on 17 July (model standard scenario) for (a) O\textsubscript{3} (ppb), (b) NO\textsubscript{y} (ppb), (c) summed primary VOCs in propene-equivalents (ppbC), and (d) isoprene (ppb). The solid line represents the model; the points represent measured values. For VOCs and isoprene, the horizontal bars also show the flight interval associated with each measurement, representing a 10 min period.
against the NO$_x$-sensitive model scenario for 17 July. The NO$_x$-sensitive scenario requires emission inventories with a higher ratio of VOC/NO$_x$ (or more reactive VOCs) than in the standard scenario. This would cause the model to overestimate the slope between VOCs and NO$_x$ (see Table 4) and overestimate VOCs inside the Paris plume. If the model is underestimating ozone production per NO$_x$, as suggested above, the underestimate must be associated with VOC species that were not included in the ensemble of ESQUIF measurements.

Emission rates for isoprene have uncertainties of a factor of 2 or more, especially when uncertainties associated with land use and forest composition are included [Simpson et al., 1999]. As shown in Figure 8, isoprene does not correlate with NO$_x$, and the highest isoprene tends to occur in rural locations with relatively low NO$_x$. Model isoprene tends to be lower than measured values, although the comparison is inconclusive. The comparison between model and measured isoprene is also inconclusive because the model lacks adequate resolution for representing the vertical distribution of isoprene. Andronache et al. [1994] and Guenther et al. [1996a, 1996b] have shown that isoprene varies significantly with altitude, even within a convective mixed layer. The model representation of vertical mixing, based on eddy diffusion, does not properly represent mixing processes within a convective layer [e.g., Stull, 1994; Pleim and Chang, 1992; Hourdin et al., 2002]. The model isoprene in Figure 8 represents values for a vertical layer extending from 50 to $\sim$600 m altitude in comparison with measured values at 500 m. Isoprene is expected to decrease with altitude over this range, and the next higher model layer (representing $\sim$600–1200 m) has lower isoprene by a factor of 3. This suggests that the model underestimate of isoprene is somewhat larger than is shown in Figure 7. Other species ($O_3$, NO$_x$, anthropogenic VOCs) show little variation with altitude within the model convective mixed layer. Expressed as propene-equivalent carbon, measured isoprene represents 20% of total VOCs in the center of the Paris plume (1.4–3.7 ppbC isoprene, 11 ppbC anthropogenic VOCs) and 50% of total VOCs in the surrounding rural area.

As shown in Tables 2 and 3, peak $O_3$ in the Paris plume does not change significantly when the isoprene emission rate in models is doubled. Increased isoprene emissions also have no impact on NO$_x$-VOC sensitivity for peak $O_3$ in the Paris plume. However, the spatial extent of the VOC-sensitive region in the Paris plume decreases by 40% in models with doubled isoprene emissions, as the shift

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**Figure 7.** Summed anthropogenic VOCs as propene-equivalent carbon (ppbC) versus NO$_y$ (ppb) in the Paris plume on 17 July from measurements (diamonds) and from the standard model scenario (crosses). Linear least squares coefficients are shown in Table 4.

**Figure 8.** Isoprene versus NO$_y$ (ppb) in the Paris plume on 17 July from measurements (diamonds) and from the standard model scenario (crosses). One ppb isoprene is equal to 19.5 ppbC propene-equivalent carbon.

---

**Table 4.** Linear Least Squares Coefficients for VOCs Versus NO$_x$$^a$

<table>
<thead>
<tr>
<th></th>
<th>17 July 1999 (1600 LST)</th>
<th>18 July 1999 (1600 LST)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured</td>
<td>$a_0$</td>
<td>$a_1$</td>
</tr>
<tr>
<td>Standard</td>
<td>1.2</td>
<td>.51</td>
</tr>
<tr>
<td>Weekend adjustment</td>
<td>$-1.2$</td>
<td>.56</td>
</tr>
<tr>
<td>Modified VOCs</td>
<td>$-1.3$</td>
<td>.62</td>
</tr>
<tr>
<td>High VOCs, low NO$_x$</td>
<td>$-3.2$</td>
<td>1.3</td>
</tr>
</tbody>
</table>

$^a$Shown are the linear least squares estimators for the linear correlation [VOC] = $a_0 + a_1 [NO_x]$ from Figure 6 along with the correlation coefficient ($r^2$) from measurements and model scenarios. VOCs represent the sum of primary anthropogenic species as propene-equivalent carbon (ppbC).

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**Table 5.** Performance Statistics For 17 July$^a$

<table>
<thead>
<tr>
<th></th>
<th>$O_3$</th>
<th>NO$_x$</th>
<th>VOCs</th>
<th>Isoprene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model Scenario$^b$</td>
<td>Bias</td>
<td>Error</td>
<td>Bias</td>
<td>Error</td>
</tr>
<tr>
<td>Standard</td>
<td>$-0.02$</td>
<td>$+.10$</td>
<td>$+.12$</td>
<td>$-.38$</td>
</tr>
<tr>
<td>High VOCs, low NO$_x$</td>
<td>$-0.04$</td>
<td>$+.10$</td>
<td>$-.09$</td>
<td>$+.23$</td>
</tr>
<tr>
<td>High mixing height</td>
<td>$-0.04$</td>
<td>$+.09$</td>
<td>$+.25$</td>
<td>$-.05$</td>
</tr>
</tbody>
</table>

$^a$The table shows normalized bias and normalized gross error between model and aircraft measurements for $O_3$, NO$_x$, summed primary VOCs (as propene-equivalent carbon), and isoprene on 17 July.

$^b$The model scenarios are: (1) the standard scenario; (2) a scenario with anthropogenic emissions increased by 40% and NO$_x$ decreased by 30% relative to scenario 1; and (3) a scenario with a 25% higher mixing height and higher VOCs.
to NO\textsubscript{x}-sensitive conditions in the downwind plume occurs more rapidly.

[38] It is noteworthy that the statistics used for model evaluations in the U.S., normalized bias and normalized gross error, do not provide a strong basis for evaluating model accuracy. The U.S. EPA requires that models have normalized biases of <15% and normalized gross errors of <35%. All model scenarios meet these criteria for O\textsubscript{3}, and all scenarios either meet or slightly exceed the criteria for NO\textsubscript{y} (see Table 5). Evaluation based on the O\textsubscript{3}-NO\textsubscript{x} and VOC-NO\textsubscript{x} correlations provides a more rigorous basis for evaluating the success of a model in representing the ozone formation process.

[39] A final issue concerns the impacts of wind speed and dilution on O\textsubscript{3}-NO\textsubscript{x}-VOC chemistry. Previously, Milford et al. [1994] and Sillman [1999] suggested that greater dilution (including higher wind speeds) should cause a shift toward greater sensitivity to NO\textsubscript{x} rather than to VOCs. However, Honore\'e et al. [2000] found that higher wind speeds would lead to increased sensitivity to VOCs in box model calculations for Paris. In the model calculations shown here (Table 2), no significant change in NO\textsubscript{x}-VOC sensitivity occurs in scenarios with wind speeds increased by 25%. When wind speeds are increased by 75%, peak O\textsubscript{3} in the Paris plume shows mixed sensitivity to NO\textsubscript{x} and VOCs, whereas in the model base case, peak O\textsubscript{3} was strongly VOC-sensitive. The spatial extent of the VOC-sensitive region in the center of Paris also becomes smaller in the scenario with wind speeds increased by 75%. This result is consistent with the discussions by Milford et al. [1994] and Sillman [1999], although the impact of wind speed on NO\textsubscript{x}-VOC sensitivity is small. The results from Honore\'e et al. [2000] may only be valid for extremely stagnant conditions in which air remains in a single metropolitan area for 2 days or longer.

6. Conclusions

[40] The above analysis of ozone, reactive nitrogen, and VOCs in the Paris urban plume has yielded a number of conclusions concerning ozone chemistry and O\textsubscript{3}-NO\textsubscript{x}-VOC sensitivity. Results from models and measurements both suggest that ozone in Paris is often close to the transition from NO\textsubscript{x}-sensitive to VOC-sensitive chemistry. NO\textsubscript{x}-VOC sensitivity in the Paris plume varies from day to day. The correlation between O\textsubscript{3} and NO\textsubscript{x} in Paris is roughly comparable to that of Nashville during high-ozone events, and the O\textsubscript{3}-NO\textsubscript{x} slope is underestimated in models. Model reactivity-weighted VOCs are generally consistent with measurements, though with significant scatter. Measured isoprene is high enough to account for a significant portion of total VOC reactivity, even in the center of the Paris urban plume, but it has relatively little impact on ozone formation. Model-measurement comparisons for isoprene are especially difficult due to the uncertain vertical distribution of isoprene.

[41] The standard model scenario underestimates NO\textsubscript{y} and the O\textsubscript{3}/NO\textsubscript{x} ratio in the center of the Paris plume and also underestimates the O\textsubscript{3}-NO\textsubscript{x} slope. This discrepancy appears in the O\textsubscript{3}-NO\textsubscript{x} correlation plots but is not obvious in the standard performance tests for ozone models, such as normalized bias. This type of discrepancy suggests that the model underestimates VOCs and/or VOC reactivity in the Paris plume possibly due to errors in emission inventories. Comparisons with measured VOCs do not support the hypothesis that VOC emissions are underestimated, but they do not rule out a possible underestimate of VOCs of up to 40%. The underestimated O\textsubscript{3}-NO\textsubscript{x} slope may be due to the presence of reactive VOCs in the Paris plume that were not included in the recent measurements. Alternately, the model-measurement discrepancy might be caused by loss of NO\textsubscript{x} within the Paris plume (or within the measurement apparatus). Because the model-measurement discrepancy occurs at the center of the Paris plume rather than in the surrounding region, any such unknown VOC or removal of NO\textsubscript{x} must be associated specifically with urban conditions.

[42] It is intriguing that on the days with high O\textsubscript{3}, measured O\textsubscript{3} versus NO\textsubscript{x} tends to agree with the model correlation only when the model predicts either NO\textsubscript{x}-sensitive or transitional chemistry. As in previous studies of this type, the correlation between O\textsubscript{3} and NO\textsubscript{x} in models is closely associated with model NO\textsubscript{x}-VOC sensitivity predictions. The fact that model O\textsubscript{3}/NO\textsubscript{x} is lower than measured values in scenarios with VOC-sensitive chemistry provides some evidence that the VOC-sensitive scenarios may be incorrect.

[43] Acknowledgments. Discussions with Yves Balkansky, Daniel Martin, Bruno Nenninger, Nadege Blond, and Hauke Schmidt were especially helpful in preparing this manuscript. Support for this research was provided by the Centre National de la Recherche Scientifique and by the National Science Foundation (grants ATM-9713567 and ATM-0207841). The results may not necessarily reflect the views of the National Science Foundation, and no official endorsement should be inferred.

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