Evidence of Ozone Destruction in Clouds

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Ozone is a key atmospheric photooxidant. It is formed in the troposphere via NOx photolysis, and carbon monoxide and hydrocarbons are indirect precursors in a complex reaction cycle. The ground-based ozone concentration has increased over the last three or four decades by up to 2–3% per year due to an increased production of its precursors [1]. The residence time of ozone in the atmosphere is determined by sink processes, including dry deposition on surfaces, gas-phase reactions, and heterogeneous losses. Recently, it has been established [2, 3] that ozone is also removed by liquid-phase chemical reactions in clouds. In Europe, cloud chemistry studies have focused on field campaigns [4, 5], whereas long-term observations are carried out in North America [6]. An air chemistry station on the Brocken (1142 m a.s.l.) has been running since 1991 [7, 8]. Cloud water is collected using passive string collectors and analyzed by ion chromatography; ozone is measured continuously by UV absorption using a Dasibi instrument; a laser beam scattering instrument (Gerber FVM 100) measures liquid water content (LWC); and in-situ analyzers measure SO2, NO, and NO2 (instruments from Thermoelectronic and Biophysics).

The diurnal ozone variation on the Brocken site is small, as observed at stations above the boundary layer which are not influenced by local perturbations. On the lowland measuring station Werrigrodek (12 km as the crow flies, 350 m a.s.l.), provided by the Environmental Protection Board of Saxony-Anhalt, a diurnal ozone variation is observed (typical for photochemical ozone production) which shows clearly the anti-correlation between ozone and NO2 (Fig. 1a). The diurnal ozone variation at Werrigrodek is smoothed when the weather is cloudy (Fig. 1b), which is most likely a result of reduced photochemical activity. On the Brocken we often observed a rapid decrease in ozone concentration with passing clouds, where the residual ozone concentration could be up to 50% lower.

![Fig. 1: Diurnal variation of concentrations of ozone, NO, and NO2. a) for cloud-free conditions (mean cloud cover <2/8), b) for cloudy weather (mean cloud cover >4/8) at Werrigrodek (60 min averages) and ozone (10 min averages, LWC at 10 min averages) on Brocken](image-url)
than before the cloud event. When the cloud has moved away, the ozone concentration increased again to around its former level (Fig. 2). A few events have been found where the ozone depletion coincides with SO₂-rich air masses from southerly directions (Fig. 3). The fall in ozone concentrations within clouds was observed to be statistically significant during cloud events between July and October 1992. Figure 4 shows the relationship between cloud and ozone. A minimum in the day-to-day variation often coincides with a maximum in the liquid water content, i.e., the appearance of clouds. Between July and October 1992, during measuring campaigns, cloud water samples were collected for chemical analysis. We selected 24 samples with a complete data set: ozone concentration, LWC, and chemical composition. Eight of them were taken during events showing a fall in ozone concentration (class II); the other 16 samples were not connected with any observed ozone depletion (class I). Table 1 shows the concentration of some mean components (Na, K, and Mg are not listed, but counted the ionic balance) of the collected water samples. There are large variations in cloud water composition from event to event, and we believe that this is mainly due to microphysical causes. We have found, for example, a strong relationship between LWC and the soluble content [3]. Because of this large variation, it seems that many observations would be needed to smooth out the effects of microphysical changes, but it can be seen in Table 1 that there is good agreement in the average of LWC despite the small number of samples. There are, however, significant differences in the chemical composition for the two classes, and this is surprising. In class I samples, sulfate, nitrate, and calcium are significantly higher than in the class II samples, suggesting that the destruction of ozone seen within these class I events takes place because of the polluted cloud water. The much higher chloride concentration seen in the class II samples shows a maritime influence, and a few typical remote background cases with very low chloride concentrations are responsible for the large standard deviation. The high values for calcium ion in class I samples suggest that the cloud water is alkaline during the initial cloud formation period, and the somewhat more acid character for class I could be a result of sulfate precipitation in the liquid phase during cloud transportation. Our model calculations [1, 13] have shown that clouds could be effective ozone sinks. Two reactions consume ozone in the liquid phase:

\[ \text{O}_3 + \text{SO}_2^{(IV)} \rightarrow \text{O}_2 + \text{SO}_2^{(VI)} \]  

(1)

\[ \text{O}_3 + \text{O}_2^+ (\text{H}^+) \rightarrow \text{OH} + 2\text{O}_2 \]  

(2)
O₂ is formed from HNO₂, the equilibrium is pH-dependent:

$$\text{HNO}_2 \rightleftharpoons \text{H}^+ + \text{NO}_2^- \quad (pK = 4.5) \quad (3)$$

A high gas-phase SO₂ and a correspondingly high S(IV) in the liquid phase, should increase the ozone consumption via reaction (5), especially at higher pH due to the strong dependency of the reaction rate on pH:

$$R_{O_3} = k_{O_3}[\text{O}_3][\text{S(IV)}]$$

with $k_{O_3} = k_O$. However, reaction (6) competes with reaction (1):

$$\text{H}_2\text{O}_2 + \text{S(IV)} \rightarrow \text{products} + \text{S(VI)} \quad (4)$$

and has a reaction rate constant

$$k_{\text{H}_2\text{O}_2} = k_{\text{H}_2\text{O}_2}/[\text{H}_2\text{O}_2][\text{S(IV)}] = [\text{H}^+]k_1$$

which strongly increases with decreasing pH. On the other hand, as pH > 5 ozone is consumed via reaction (3), and the significance of this reaction for ozone destruction on a global scale has already been shown [2]. The results of our model [3] are illustrated in Fig. 5 and show the influence of SO₂ concentration on ozone consumption for both pathways (sensitization due to physical ozone dissolution is negligible; ozone transfer is controlled only by liquid-phase reactions). At low SO₂ concentrations the solution becomes more alkaline (less S(IV)) and the $\text{O}_3 = \text{O}_2$ reaction is favored. An indirect heterogeneous loss of ozone is possible via the reaction pathway:

\[ \text{NO} \rightarrow \text{NO}_2 \rightarrow \text{O}_3 \rightarrow \text{O}_2 \rightarrow \text{N}_2\text{O}_5 \]

in formation of nitrate; the NO₃ radical reacts rapidly in a liquid phase with $\text{SO}_4^{2-}$, $\text{H}_2\text{SO}_4$, and other species to form the nitrate ion.

Another process can lead to a fall in ozone concentration in clouds: scavenging of $\text{H}_2\text{O}_2$ and OH from the gas phase into cloud water reduces the rate of formation of ozone in clouds by 10–50% [16]. In this way, aqueous-phase chemistry can change the gas-phase (interstitial) concentration ratios and so reduce significantly the ozone concentration where clouds are present. Moreover, the reaction $\text{O}_3 + \text{NO} = \text{NO}_2 + \text{O}_2$ becomes more important and because the NO₂ photolysis is probably reduced in clouds, NO₂ is enriched and O₃ depleted. This effect has been shown by modeling the chemistry below clouds [11]. We should note the difficulty in distinguishing between ozone destruction (by heterogeneous processes) and a lack of ozone production due to lower light levels in the cloud UVB radiation to manufacture OH. In contrast, vertical mixing within clouds can enhance the formation of tropospheric ozone [3]. The ozone budget, therefore, depends on the air chemical situation as well as the dynamics and microphysical characteristics of the cloud.

Table 1: Mean chemical composition (in meq/l) of different cloud water solutions at Mt. Bromo from July – October 1992, a number of cloud events, LWC in mg/m²

<table>
<thead>
<tr>
<th>Class</th>
<th>n</th>
<th>LWC</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>NH₄⁺</th>
<th>Ca²⁺</th>
<th>H⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>8</td>
<td>270 ± 56</td>
<td>10 ± 33</td>
<td>60 ± 711</td>
<td>59 ± 768</td>
<td>360 ± 199</td>
<td>360 ± 199</td>
<td>30 ± 199</td>
</tr>
<tr>
<td>II</td>
<td>16</td>
<td>210 ± 95</td>
<td>210 ± 137</td>
<td>304 ± 288</td>
<td>278 ± 266</td>
<td>326 ± 318</td>
<td>95 ± 193</td>
<td>26</td>
</tr>
</tbody>
</table>

Fig. 4. Monthly variation of ozone and LWC (as 64-milligrams)

Fig. 5. Mean fluxes of ozone into the cloud water phase and its fraction as a function of the gas-phase SO₂ concentration; model results

We can summarize the possible causes of ozone destruction within clouds. At pH ≥ 5, ozone is destroyed via reaction (2), \( O_3 + O^+ \). This situation probably occurs during cloud formation where CCN determines the chemical composition (high calcium ion concentration). In this case of a SO4-rich environment, high S(IV) concentrations build up due to effective scavenging of SO2 and additional ozone destruction occurs with sulfate formation via reaction (1). Fig. 3 supports this hypothesis. Our experimental results for clouds where ozone is decreased (class I in Table I) show a cloud-water composition high in calcium ions and sulfate. Nitrate is also enriched in these clouds. Class II clouds, characterized as maritime or remote, do not show a capacity to destroy ozone; however, this does not mean that ozone was not destroyed within these clouds, but that the destruction capacity was low when they were observed over the Brocket, and the interstitial ozone was similar so that outside the cloud.

Another possible explanation for the ozone decrease with passing clouds is that ozone can be a different ozone content due to changing vertical and horizontal transport processes. We cannot totally exclude local vertical transports, but this is typically observed during the formation of orographic clouds (cap clouds). Most cloud events with ozone depletion, however, have been characterized as orographically induced. The large-scale air motion. In our opinion, the most probable explanation of the ozone depletion is the simultaneous occurrence of two effects: (a) chemical processes within the cloud and (b) changing mesoscale transport advection air with a different ozone content.

Based on the experimental results, we conclude that clouds deplete and destroy ozone and that this removal capacity increases with pollutants; the results support the different ozone removal pathways suggested by models. Our preliminary data show that a shallow ozone balance would be incomplete without consideration of chemical processes within clouds. We are continuing these investigations, as our data from 1993 show this behavior between ozone and clouds. Thus, a more detailed analysis should be possible using sufficiently analyzed events and track-trajectory calculations. For helpful discussions we would like to thank W. Meilicke. We thank the Environmental Protection Board of the Land Saxony-Anhalt for providing the data from Werrigerode. This work was funded by the German Ministry for Science and Technology within the projects EANA and EUROTRAC.

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