Heterogenous ozone destruction within clouds
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ABSTRACT

This paper presents experimental results from the cloud measuring station on the Brocken in the Harz Mountains in Germany, showing an ozone depletion with passing clouds. We find during many cloud events that the ozone concentration is up to 50% less when compared to that before and after the cloud. Those clouds with a capacity to destroy ozone are characterized as chemically polluted clouds.

INTRODUCTION

Ozone is the key of atmospheric photooxidant. It is formed in the troposphere via NO₂ photolysis, and carbon monoxide and hydrocarbons are indirect precursors in a complex reaction cycle. The ground based ozone concentration has increased during 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 the 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 been 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, laser beam
scattering (Gerber PVM 100) instrument measures liquid water content, and in-situ analyzers measure SO$_2$, NO, and NO$_2$ (instruments from Thermoenvironmental and Ecophysics).

RESULTS AND DISCUSSION

The diurnal ozone variation on the Brocken site is small, as observed at stations above the boundary layer which are not influenced by local perturbation. On the Brocken we often observed a rapid decrease in ozone concentration with passing clouds, where the interstitial ozone concentration could be up to 50% lower than before the cloud event. When the cloud has been moved away, the ozone concentration increased again to around its former level (Fig. 1 and 2). A few events have been found where the ozone depletion coincides with SO$_2$ rich air masses from easterly directions (Fig. 2).

The fall in ozone concentration within clouds was observed to be statistically significant at cloud events between July and October in 1992 and 1993. The collected cloud water samples were subdivided according to events showing a fall in ozone concentration (class I) and samples which are not connected with any observed ozone destruction (class II). Table 1 shows the concentration of main constituents 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 an example, a strong relationship between LWC and the soluble content [7]. 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 in 1992. There are, however, significant differences in the chemical composition for the two classes, and this is surprising. In class I samples, sulphate, 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 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 sulphate production in the liquid phase during cloud transportation. From Table 2 follows that there are large differences in some cloud characteristic parameters between class I and II events.
Table 1. Mean chemical composition (in μeq/l) of different cloud water collections at Mt. Brocken (period July - October); n number of cloud events (in parenthesis number of 1-hour samples), LWC in mg/m³

<table>
<thead>
<tr>
<th>Year</th>
<th>Class</th>
<th>n</th>
<th>LWC (mg/m³)</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
<th>Na⁺</th>
<th>NH₄⁺</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>H⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>1992</td>
<td>I</td>
<td>8</td>
<td>270</td>
<td>80</td>
<td>692</td>
<td>529</td>
<td>-</td>
<td>557</td>
<td>360</td>
<td>-</td>
<td>80</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>16</td>
<td>289</td>
<td>226</td>
<td>324</td>
<td>277</td>
<td>-</td>
<td>326</td>
<td>92</td>
<td>-</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>All</td>
<td>37</td>
<td>274</td>
<td>127</td>
<td>387</td>
<td>331</td>
<td>156</td>
<td>391</td>
<td>147</td>
<td>40</td>
<td>39</td>
</tr>
<tr>
<td>1993</td>
<td>I</td>
<td>22</td>
<td>194</td>
<td>67</td>
<td>482</td>
<td>453</td>
<td>59</td>
<td>680</td>
<td>87</td>
<td>32</td>
<td>142</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>39</td>
<td>222</td>
<td>71</td>
<td>131</td>
<td>130</td>
<td>62</td>
<td>199</td>
<td>26</td>
<td>19</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>All</td>
<td>131</td>
<td>230</td>
<td>51</td>
<td>192</td>
<td>189</td>
<td>43</td>
<td>289</td>
<td>33</td>
<td>17</td>
<td>70</td>
</tr>
</tbody>
</table>

Table 2. Characteristic parameters of class I and class II events (only 1993)

<table>
<thead>
<tr>
<th>Year</th>
<th>Class</th>
<th>Mean Duration (in h)</th>
<th>Ozone Conc. (ppb)</th>
<th>Share of Precipitating Clouds (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
<td>1.4±1.0</td>
<td>45±9</td>
<td>33±8</td>
</tr>
<tr>
<td></td>
<td>II</td>
<td>20.8±15.4</td>
<td>29±3</td>
<td></td>
</tr>
</tbody>
</table>

We believe that there are different causes for the ozone depletion observed with passing clouds. There are known liquid phase reactions which consume dissolved O₃ and gas phase loss via enhanced NO₂ and NO₃ formation which subsequent scavenging into cloud droplets. On the other hand, the net formation of O₃ is reduced within clouds because of the disturbance of the ozone cycle (scavenging of HO₂ and OH into cloud droplets whereas NOₓ remains in the interstitial air). We assume that the ozone depletion observed at Mt. Brocken is not the result of processes occurring locally but a result of the different chemical processes happened in the gas-liquid interaction of the transported air mass.

The ozone budget, therefore, depends on the air chemical situation as well as the dynamics and microphysical characteristics of the cloud.
In following we discuss the possible loss processes in more detail; Fig. 3 summarized schematically the chemical processes in the interaction between gaseous and liquid phase. Our model calculations [3,10] have shown that clouds could be effective ozone sinks. Two reactions consume ozone in the liquid phase;

\[ \text{O}_3 + \text{S(IV)} \rightarrow \text{O}_2 + \text{S(VI)}; \] (1)

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

\( \text{O}_2^- \) is formed from \( \text{HO}_2 \), the equilibrium is pH dependent;

\[ \text{HO}_2 \rightleftharpoons \text{H}^+ + \text{O}_2^- \quad (\text{pK} = 4.5). \] (3)

A high gas phase \( \text{SO}_2 \), and a correspondingly high \( \text{S(IV)} \) in the liquid phase, should increase the ozone consumption via reaction (1), especially at higher pH due to the strong dependency of the reaction rate on pH:

\[ R_{\text{O}_3} = k_{\text{O}_3}[\text{O}_3][\text{S(IV)}] = [\text{O}_3](k_1[\text{HSO}_3^-] + k_2[\text{SO}_3^{2-}]) \]

with \( k_2 > k_1 \). However, reaction (4) is in competition to reaction (1)

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

and has a reaction rate constant

\[ k_{\text{H}_2\text{O}_2} = R_{\text{H}_2\text{O}_2}/([\text{H}_2\text{O}_2][\text{S(IV)}]) = [\text{H}^+]k_3 \]

which strongly increases with decreasing pH. On the other hand, at pH > 5 ozone is consumed via reaction (2), and the significance of this reaction for ozone destruction on a global scale has already been demonstrated [2]. At low \( \text{SO}_2 \) concentrations the solution is more alkaline (less \( \text{S(IV)} \)) and the \( \text{O}_3 + \text{O}_2^- \) reaction is favouredized.

Another process can lead to a fall in ozone concentration in clouds. Scavenging of \( \text{HO}_2 \) and \( \text{OH} \) from the gas phase into cloud water reduces the rate of formation of ozone in clouds by 10-50% [9]. 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 $O_3 + NO \rightarrow O_2 + NO_2$ becomes more important and because the $NO_2$ photolysis is probably reduced in clouds, $NO_2$ enriches and $O_3$ depletes. This effect have been shown by modelling the chemistry below clouds [11]. An indirect heterogeneous loss of ozone is possible via the reaction pathway

$$\text{NO} \xrightarrow{O_3} \text{NO}_2 \xrightarrow{O_3} \text{NO}_3 \xrightarrow{\text{scavenging}} \text{NO}_3^- \xrightarrow{\text{scavenging}} \text{N}_2\text{O}_5$$

in formation of nitrate; the $NO_3^-$ radical reacts rapidly in liquid phase with $\text{Cl}^-$, $\text{HSO}_4^-$, and other species to form the nitrate ion.

In contrast, vertical mixing within clouds can enhance the formation of tropospheric ozone [9]. The ozone budget, therefore, depends on the air chemical situation as well as the dynamics and microphysical characteristics of the cloud.

We can summarize the possible causes for ozone destruction within clouds. At $pH > 5$ ozone is destroyed via reaction (2), $O_3 + O_2^-$; this situation probably occurs during cloud formation where CCN determines the chemical composition (high calcium ion concentration). In the case of $SO_2$ rich environment, high S(IV) concentrations build up due to effective scavenging of $SO_2$, and additional ozone destruction occurs with sulphate formation via reaction (1); Fig. 2 supports this hypothesis. Our experimental results for clouds where ozone is destroyed (class I in Table 1) show a cloud water composition high in calcium ions and sulphate. Nitrate is also enriched in these clouds. Class II clouds, characterised 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 nil when they were observed over the Brocken, and the interstitial ozone was similar to that outside the cloud.

Another possible explanation for the ozone decrease with passing clouds, however, could 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 formation of orographic clouds (cap clouds). The very most cloud events with ozone depletion, however, have been characterized as non-orographic clouds within large-scale air motion. In our mind the most probable explanation of the ozone depletion is
the simultaneous occurrence of two effects: (a) chemical processes within the cloud on its pathway as suggested by the different chemical compositions of cloud water classes I and II and (b) changing mesoscale transport advecting air with a different ozone content.

CONCLUSIONS

Based on the experimental results we conclude that (a) clouds depletes and destroy ozone and (b) that this removal capacity increases with pollution, the results support the different ozone removal pathways suggested by models. Our preliminary data show that an understanding of tropospheric ozone balance would be incomplete without consideration chemical processes within clouds. We continue these investigations; our data from 1993 show a similar behaviour between ozone and clouds. Thus a more detailed analysis should be possible using enough analyzed events and back trajectory calculations.

REFERENCES

7. Möller, D., Acker, K. and Wieprecht, W. ´Cloud Chemistry at the Brocken in the Harz Mountains, Germany´ EUROTRAC Newsletters, Vol. 12, pp. 24-29,
1993


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Fig. 1 Diurnal variation of concentrations of ozone, SO$_2$, NO and NO$_2$ and ozone (30 sec averages) with passing clouds, also LWC (as 10 min averages) on Brocken
Fig. 2 Diurnal variation of concentrations of ozone, SO$_2$ (30 sec averages) and wind direction (30 min averages) with passing clouds on Brocken (LWC as 10 min averages).
Fig. 3 Scheme of chemical interaction between gaseous and liquid phase