Determination of mass balances of chemically reactive air pollutants over Baden-Württemberg (F.R.G.) - Study for the regions around the cities of Stuttgart and Freudenstadt

H.-J. Panitz, K. Nester, F. Fiedler

Institut für Meteorologie und Klimaforschung, Forschungszentrum Karlsruhe, Postfach 3640, D-76021 Karlsruhe
E-Mail: hans-juergen.panitz@imk.fzk.de

Abstract

Mass balances of chemically reactive air pollutants have been calculated and analysed in a mesoscale area and two subregions, an industrialized urban centre with large emissions, and a rural region in a mountainous area with high percentage of agriculture and forestry. The vertical and horizontal dependencies of the contributions of different mass budget components are shown. Chemical reactions of ozone are only of importance inside the PBL where the precursors have the highest concentrations. In the upper layers the balance of ozone is dominated by horizontal and vertical advective processes. Horizontal differences are due to the different emission conditions which mainly influence the chemical transformation as well as due to the different topographical structures which influence the deposition and the balance of the different advective transport processes of ozone. To quantify the maximum effects of local emission reduction measures, a 100% reduction of anthropogenic emissions is assumed in both subregions. The contributions to the mass balances in these regions are analysed.

1 Introduction

The air pollution of a region depends on several production and loss processes: emission, deposition, chemical transformation, and advective and turbulent atmospheric transport. Usually, these processes are analysed at individual locations. But it is of increasing interest, e.g. in the context of emission reduction measures, to quantify the contributions of the
different mass budget components to the pollution of a larger volume and to understand and explain the chemical formation processes of secondary species like O₃ in the mesoscale (Jang et al. [1], Schwartz [2]). The mass budget equation for a chemically reactive air pollutant can be written as

\[
\frac{\partial M}{\partial t} = (P_{ADV} + P_{TRB} + P_E + P_{CH}) - (L_{ADV} + L_{TRB} + L_{DEP} + L_{CH}).
\]

It describes the temporal change of the mass \( M \) of a species which is determined by production (P) and loss (L) processes due to horizontal and vertical advective transport (ADV), horizontal and vertical turbulent transport (TRB), emission (E), deposition (DEP), and chemical transformation (CH). Mass balances have been calculated for a mesoscale domain which encloses South-west Germany including the Upper Rhine Valley, the Black Forest, and parts of Alsace (France) with the Vosges Mountains as well as for two smaller subregions around the cities of Stuttgart and Freudenstadt (Figure 1). The Stuttgart area is densely populated and highly industrialized with large NOₓ and VOC emission rates. The Freudenstadt area, which has a rural character, is located in the mountainous region of the Black Forest. The mass balances have been analysed in four vertical layers of different depth (Table 1) between the surface and 8000 m Above Sea Level (ASL). Approximately, the lowest layer 4 represents the Planetary Boundary Layer (PBL). The paper focuses on the results achieved for ozone. In addition it is investigated, how a 100% reduction of anthropogenic emissions in the subareas effects the mass balance of ozone.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Upper Boundaries (m ASL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>2000</td>
</tr>
<tr>
<td>3</td>
<td>3700</td>
</tr>
<tr>
<td>2</td>
<td>5300</td>
</tr>
<tr>
<td>1</td>
<td>8000</td>
</tr>
</tbody>
</table>

Table 1: Upper boundaries of integration volumes

2 Simulations

The calculations have been performed for September 16th, 1992, a day of the TRACT experiment (Zimmermann [3]), using the mesoscale model system KAMM/DRAIS (Adrian & Fiedler [4], Schwartz [2]) which includes the chemical transformation mechanism RADM2 (Stockwell et al. [5]). The non-hydrostatic meteorological model KAMM simulates the space and time dependent distributions of the wind field, the temperature field, and the turbulence field. It is forced by a geostrophic and hydrostatic basic state which is derived from radiosonde data measured during the TRACT campaign and which represents the large scale meteorological conditions. The DRAIS model calculates the concentration and deposition distributions and the mass budget components of 59 chemically reactive species. The initial and boundary data for all substances have been derived.
from contemporary results of the EURAD model (EURopean Acid Deposition model, Hass [6]) using a nesting procedure which has been developed by Nester et al. [7] to couple the KAMM/DRAIS system to the EURAD model. The emission data which have been used, comprise anthropogenic and biogenic emissions (Vogel et al. [8]). During the simulation day about 139 tons of NOx and 217 tons of VOC were emitted throughout the region of the urban centre Stuttgart. The fraction of biogenic VOC emissions was 14%. In the rural region Freudenstadt the amounts of emitted mass were about 40 tons of NOx and 77 tons of VOC with 52% being biogenic VOCs. The whole model area covers 260 km × 240 km. The two subregions have horizontal extensions of 50 km by 50 km each (Figure 1). The horizontal resolution of the model grid is 5 km. In the vertical, the model domain between the ground and 8000 m ASL is divided into 35 terrain following levels.

Figure 1: Terrain height (m ASL) of model domain and locations of subregions

3 Results

The results of the meteorological and dispersion simulations have been described by Panitz et al. [9]. They showed that the simulated
flow and concentrations fields agree well with measurements recorded contemporarily. Mass balance calculations of O₃, NOₓ, and VOC for the whole area of Baden-Württemberg revealed vertical dependencies of the contributions of the different budget components (Panitz et al. [9], [10]). In the following the net contributions of each budget component to the O₃ balance are presented. They have been normalized by the size of the corresponding integration volume. Therefore, they are presented as volume averages in concentration units.

3.1 Mass balances for Stuttgart and Freudenstadt

The Figures 2 and 3 show the diurnal variations of the total ozone concentration changes and of the changes due to advective transport, deposition, and chemistry inside the PBL. The contributions of the turbulent transport are of minor importance and they have been omitted. The diurnal variations of the changes due to chemical transformations show the typical behaviour. The production of O₃ starts after sunrise. Its maximum of about 2.3 ppb/h around noon is nearly identical in both areas. In the afternoon the chemical production of ozone weakens. After 5:00 p.m. the contribution of the chemistry changes from gain to loss because of the titration of ozone by NO which has a secondary emission maximum at this time. The loss of mass is more pronounced in the urban centre of Stuttgart where the emissions are much larger than in the rural Freudenstadt region. This results in a smaller net chemical production of ozone in the area around Stuttgart (Figure 4 (left), Figure 5 (left)). Chemical transformations of ozone are only important in the lowest layer. In the upper atmospheric layers above both regions, the contribution of the chemistry to the production and loss of ozone is less than 5% (Table 2, Table 3).

The deposition of O₃ is more pronounced in the Freudenstadt area. (Figure 4 (left), Figure 5 (left)). This region is characterized by farming and forestry. Therefore, the deposition velocity of ozone is larger than in the urban centre of Stuttgart (Baer & Nester [11]). The maximum deposition velocities vary between 0.9 cm/sec and 1 cm/sec in the rural region, in the urban area they range from 0.6 cm/sec to 0.7 cm/sec. In general, the effects of horizontal and vertical advection are counteracting (Figure 2, Figure 3). Nevertheless, they dominate the mass balances of ozone in all layers. Even inside the PBL, the contributions of both advective transport processes considerably exceed the contribution of the chemistry (Table 2, Table 3). In the Freudenstadt area (Figure 4, left) the net vertical outflow (27.2 ppb) into the layer above nearly compensates the increase of the ozone concentration due to the horizontal inflow (17.8 ppb) and the chemical production (11.4 ppb). Together with the loss due to deposition and a small negative contribution of the vertical turbulent transport, this
advective outflow causes a net decrease of 7 ppb of the ozone concentration.

Figure 2: Hourly changes of mass budget components for O₃ Region Freudenstadt, Layer 4

Figure 3: Hourly changes of mass budget components for O₃ Region Stuttgart, Layer 4
Around the City of Stuttgart (Figure 5, left), vertical inflow alone would increase the ozone concentration by 22.3 ppb which is more than half of the total ozone concentration prevailing at the end of the day. This gain is nearly counteracted by a loss of 18.5 ppb due to horizontal transport. Nevertheless, the net contribution of both advective transport processes (3.8 ppb) is responsible for the change of the ozone concentration, because the positive contribution of the chemical transformations is even overcompensated by the deposition.

### 3.2 The effects of local emission reduction measures

In the regions being considered, emissions are the only noteworthy sources of the ozone precursors NO\textsubscript{x} and VOC. In order to investigate the effect of local emission reduction measures on the O\textsubscript{3} concentrations, all anthropogenic emissions have been omitted in both subregions as the
maximum measure which could be taken. Outside the regions the emission conditions are not changed.

<table>
<thead>
<tr>
<th>Production in Layer</th>
<th>Loss in Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1  2  3  4</td>
</tr>
<tr>
<td>Production and Loss (ppb)</td>
<td>14.6 18.6 20.1 34.2</td>
</tr>
<tr>
<td>Contribution chemistry (%)</td>
<td>3.7 1.9 0.9 40.7</td>
</tr>
<tr>
<td>Contribution advection (%)</td>
<td>96.3 98.1 98.9 59.3</td>
</tr>
<tr>
<td>Contribution diffusion (%)</td>
<td>0.0 0.0 0.2 0.0</td>
</tr>
<tr>
<td>Contribution deposition (%)</td>
<td>- - - -</td>
</tr>
</tbody>
</table>

Table 2: Total production and loss of O₃ in different vertical layers above the Freudenstadt region

<table>
<thead>
<tr>
<th>Production in Layer</th>
<th>Loss in Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1  2  3  4</td>
</tr>
<tr>
<td>Production and Loss (ppb)</td>
<td>24.8 7.3 20.7 55.0</td>
</tr>
<tr>
<td>Contribution chemistry (%)</td>
<td>2.1 4.7 1.2 23.9</td>
</tr>
<tr>
<td>Contribution advection (%)</td>
<td>97.9 95.3 98.6 76.1</td>
</tr>
<tr>
<td>Contribution diffusion (%)</td>
<td>0.0 0.0 0.2 0.0</td>
</tr>
<tr>
<td>Contribution deposition (%)</td>
<td>- - - -</td>
</tr>
</tbody>
</table>

Table 3: Total production and loss of O₃ in different vertical layers above the Stuttgart region

Comparing the results with those of the full emission case, a slight decrease (less than 0.5 ppb) of the O₃ maximum can be observed during the afternoon in the lowest layer of the rural region (Figure 6, left) which is due to a weaker chemical production during daylight (Figure 7, left). This reduced production of ozone leads to an increase of the positive net contribution of horizontal advection because less ozone is transported out of the area (Figure 4). The lack of NO weakens the chemical O₃ depletion during the evening. Therefore, at the end of the day, the ozone level is about 2.3 ppb higher for the case without emissions.
In the urban centre, the increase of the volume averaged $O_3$ level is much more pronounced (Figure 6, right). Due to the lack of the large NO emission peak, the morning minimum of the $O_3$ concentration is about 1 ppb higher than for the case with emissions (in the rural region the difference is only 0.1 - 0.2 ppb). Then the $O_3$ concentration increases up to a maximum of 50 ppb which exceeds the emission case maximum by 3.5 ppb with a time lag of 1 hour. The reason is that, despite the $NO_x$ reduction, chemical production occurs due to the photolysis of $NO_2$ which is horizontally transported into the region. On the other hand, the ozone depletion is reduced because less NO is available. Thus, the chemical gain of $O_3$ starts earlier (immediately at sunrise), it increases more rapidly, and the duration of the maximum production, which is nearly comparable with that of the emission case, is elongated (Figure 7, right). In the late afternoon the chemical production...
of ozone weakens much more slowly and the loss of ozone in the evening is not as pronounced as for the emission case.

In consequence of these relationships, the net chemical production of ozone is about 10.8 ppb higher for the zero-emission case (Figure 5). This gain is counteracted by increased losses due to deposition and horizontal transport, but it still leads to an increase of the initial ozone level of about 9 ppb, in contrast to 3.5 ppb for the full-emission case.

4 Conclusion

Mass balances are a helpful tool to understand the processes influencing the air pollution of a region. For a one day period during the TRACT experiment (September 16th, 1992) the differences between the mass budget components of O₃ have been analysed and quantified for different vertical layers in the atmosphere. Two subregions have been considered which differ with respect to their topographical structure and the emission conditions. The mass balance of ozone shows a strong vertical dependency. Chemical reactions are only of importance inside the PBL where the ozone precursors have the highest concentrations. In the upper layers the contribution of the chemistry to the production and loss of ozone is less than 5%. The horizontal and vertical advective processes dominate the ozone budget in all layers. Short term reductions of anthropogenic emissions of ozone precursors in the subregions are not convenient measures to reduce the ozone level in the regions themselves. In the rural area, the afternoon maximum of the volume averaged O₃ concentration decreases slightly because less ozone is chemically produced during daylight. But the total mass increases because less ozone is titrated in the evening. In the urban centre the ozone maximum and the overall ozone level are increasing due to an enhanced chemical production. The assumption of zero emissions inside the urban region leads to an increase of the ozone concentration beyond the eastern outflow boundary. In contrast to this, the ozone concentration decreases in an area south of the southern outflow boundary. In the future, these results will be analysed in more detail using of mass balance calculations. Additionally, the effects of different local and mesoscale emission reduction scenarios will be investigated.

Key words: mesoscale air pollution, O₃ budget, emission reduction measures

References

422 Air Pollution Modelling, Monitoring and Management


