NO_x or VOC Limitation in East German Ozone Plumes ?

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Introduction: Enhanced production of O_3 has been found in plumes from cities and power plants in Eastern Germany. Here, we characterize these plumes and analyze what the limiting factors for the formation of O_3 are. Sensitivity test are made with a closed box chemical model with measured concentrations as initial conditions.

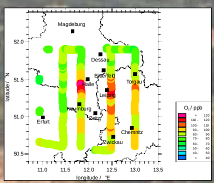


Fig. 1: Ozone concentrations measured during a flight over the densely populated and heavily industrialized region in the south of eastern Germany. Several ozone plumes downwind of cities can be identified [1].

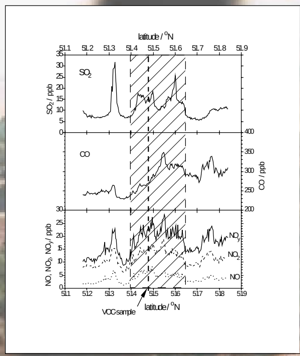


Fig. 2: Data record measured with a research aircraft at 150 m above ground during a N-S-transect along 12.2 °E (*c.f.*, Fig. 1, however, on a different day). The hatched area is the plume from the city of Halle. Apparently, the composition of the plume was not homogeneous. For further analysis, the plume composition that was measured during the 12 seconds of grab sampling for VOC analysis (dashed vertical line) was used.

Ozone formation: For the prediction of O_3 formation the Regional Atmospheric Chemistry Mechanism (RACM) [2] was employed. Starting with the measured chemical composition of the 4 plumes and a sample that is representative for the "clean" background boundary layer in Eastern Germany (see Tab. 1), the production of O_3 was predicted assuming a clear day in September.

NO_x or VOC Limitation:
Scenarios with the input mixing ratios of NO_x and VOCs modified were run. All other parameters were identical to those of the original air samples.

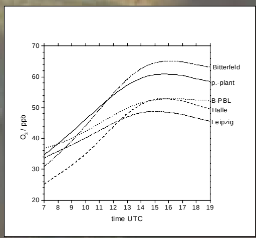
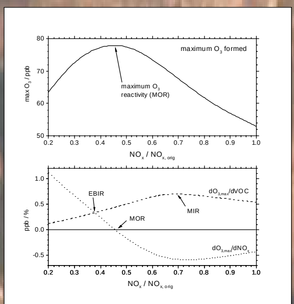
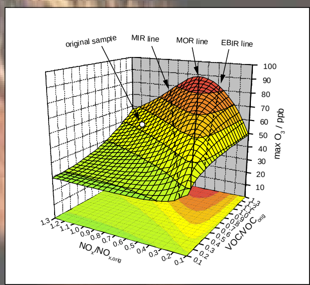


Fig. 3: Simulated ozone mixing ratios for the 5 air masses between 7 hrs and 19 hrs. In all 4 plumes, the net O_3 formation is much more intense than in the background air mass. VOC and NO_x are present in the plumes in concentrations that are 3–4 times (VOC) and 2–3.5 times (NO_x) higher than in the background air mass. The highest maximum O_3 was reached in the Bitterfeld plume (65.1 ppb), being 35 ppb higher than the early morning value. In the other city plumes, 14.6 (Leipzig) and 26.3 ppb O_3 (Halle) were formed during the simulation day.

Fig. 4 (Halle plume, "Carter Plot [3]"): Going from right to left in the upper panel, one reduces the input NO_x mixing ratio and the maximum O_3 increases. At a point of $NO_x/NO_{x,\,orig} = 0.46$, the maximum O_3 formed during a day of simulation reaches a maximum of 77.7 ppb. This maximum point is called the maximum ozone reactivity scenario (MOR).



In the lower panel, the sensitivity of O_3 production versus a reduction of NO_x, $dO_{3,max}/dNO_x$, is presented as dotted line. This line is equivalent to the derivative of the line in the upper panel and it crosses the abscissa at the MOR point. The $dO_{3,max}/dVOC$-line (dashed in the lower panel) defines the incremental reactivity of the O_3 production when the VOC mixing ratios are changed by 1% of the original VOC mixing ratios at a given $NO_x/NO_{x,orig}$ point. This line reaches a maximum (maximum incremental VOC reactivity, MIR) which is, in this case, at $NO_x/NO_{x,orig} = 0.70$. At $NO_x/NO_{x,orig} = 0.38$, the $dO_{3,max}/dVOC$-line intersects the $dO_{3,max}/dNO_x$-line. This intersection is called the scenario of equal benefit incremental reactivity (EBIR), where $\Delta O_3 / \Delta NO_x = \Delta O_3 / \Delta VOC$.



MOR: Maximum Ozone Reactivity
MIR: Maximum Incremental VOC Reactivity
EBIR: Equal Benefit Incremental Reactivity

Fig. 5: 3D-view of the production of O_3 as a response to modifications of the input VOC and NO_x concentrations. Here, MOR, MIR, and EBIR (Fig. 4), represent lines.

All conditions to the right of the MOR line are NO_x-limited ($dO_{3,max}/dNO_x > 0$).

Everything to the left of the MOR line is VOC-limited ($dO_{3,max}/dNO_x < 0$).

The sensitivity of the production of O_3 is defined in a different way [4]. The EBIR line is a separation between areas of VOC-sensitivity of the O_3 production (to the left of the line, $dO_{3,max}/dVOC > dO_{3,max}/dNO_x$) and NO_x-sensitivity.

Note that conditions between the MOR line and the EBIR line (Fig. 5) are both NO_x-limited and VOC-sensitive.

Whichever definition is used, **our original air sample** was clearly **VOC–limitated**, or **VOC–sensitive** with respect to the production of O_3.

Conclusions:

- The **production of O_3 was limited by the amount of available VOC** for all of our air samples from eastern Germany. The slope $dO_{3,max}/dVOC$ in Fig. 5 is positive over the entire range of scenarios.
- The NO_x mixing ratios were high enough to have a limiting effect on the formation of O_3, the NO_x mixing ratios in the plumes must be reduced to about the half of their initial values (35...55%) to reach the maximum ozone reactivity point (MOR). Further reductions of NO_x would bring the air masses into NO_x–limited conditions.
- The background boundary layer air mass was also VOC–limited. In this case, however, the MOR was only negligibly larger than the maximum O_3 in the original case and the MOR was reached already at a NO_x mixing ratio of 73% of the original case.
- In the extreme case of a power plant plume with very high SO_2 mixing ratios (>100 ppb), simulations produce 4.6 ppb (or 21%) more ozone than simulations made for the same conditions without SO_2 (data not shown).

Results:

Table 1		sample				
	unit	background	power plant	Halle	Leipzig	Bitterfeld
NO_x	ppb	4.77	14.15	21.38	17.05	13.38
ΣVOC	ppb	12.64	23.87	41.02	28.76	31.06
$\Sigma VOC/NO_x$	ppb / ppb	2.65	1.69	1.92	1.69	2.32
max O_3	ppb	52.9	60.7	52.9	48.8	65.1
MOR	ppb	53.8	69.5	77.7	66.2	71.7
$NO_{x,MOR}/NO_{x,\,orig}$	ppb / ppb	0.73	0.44	0.46	0.35	0.55
MIR	ppb / 1%	0.144	0.297	0.701	0.405	0.425
$NO_{x,\,MIR} / NO_{x,\,orig}$	ppb / ppb	1	0.65	0.7	0.55	0.8
$NO_{x,\,EBIR} / NO_{x,\,orig}$	ppb / ppb	0.57	0.38	0.38	0.31	0.44

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