Indicator species for 0_3 sensitivity relative to NO_x and VOC in Switzerland and their dependence on meteorology

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Abstract

Ozone sensitivity can be determined by identifying individual species or species ratios that are consistently different under conditions of NO_x-sensitive and VOC-sensitive ozone formation. These indicator species may provide a useful tool in the assessment of the relative effectiveness of VOC versus NO_x controls. Following this approach, the model predictions for O_3 sensitivity relative to NO_x and VOC levels in Switzerland are correlated to the afternoon concentration ratios of indicator species such as O_3/NO_z, O_3/NO_y, $HCHO/NO_y$ and H_2O_2/HNO_3. These correlations are based on a series of simulations with varying rates of emissions and two different wind conditions. A base case in summer 1993 with light west wind was compared with a case having a stagnant meteorology. Results showed that the correlations varied when the meteorology is different. In a stagnant meteorology, VOC-sensitive chemistry is predicted to be linked to afternoon ratios approximately $O_3/NO_z < 10$, $O_3/NO_y < 8$, $HCHO/NO_y < 0.3$, and $H_2O_2/HNO_3 < 0.5$. Higher ratios correspond to NO_x sensitive ozone formation. In a light west wind situation, these ratios were shifted to higher values. Correlations were established also on the basis of a simulation for the year 2000 using a standard development of emissions. These results indicated that the correlations between NO_x-VOC sensitivity and indicator species remain the same for 1993 and 2000 although the emission rates are different.

1 Introduction

Recent investigations showed that ozone pollution in Switzerland is declining in rural areas and increasing slightly in urban agglomerations. Modelling studies indicated that ozone formation in rural areas is mainly determined by NO_x supply, whereas in the cities VOC plays a comparable role [1]. However, the highways crossing the rural areas might have some effect on the sensitivity of ozone to NO_x and VOC levels in the regional scale.

In recent years, a new approach indicated that ozone sensitivity can be determined by identifying individual species or species ratios that are consistently different under conditions of NO_x-sensitive and VOC-sensitive

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ozone [2]. If these types of indicator species can be identified, then ozone sensitivity to NO_x and VOC could be determined directly from measurements rather than models. These indicator species may provide a useful tool in the assessment of the relative effectiveness of VOC versus NO_x controls. Following this approach in this paper, the model predictions for O_3 sensitivity relative to NO_x and VOC in Switzerland are correlated to the afternoon concentrations of indicator species such as O_3/NO_y, O_3/NO_z, $HCHO/NO_y$ and H_2O_2/HNO_3 ($NO_y = NO_x + PAN + HNO_3$ + other nitrates, $NO_z = NO_y - NO_x$).

2 Methodology

The three-dimensional Urban Airshed Model (UAM) is used for the simulations [3]. The chemical reactions are described by the Carbon Bond Mechanism (CBM IV) [4]. The horizontal resolution was 5km x 5km and 5 vertical layers were used. Simulations were performed for July 28-29, 1993 with light west wind. In that period, an air quality field experiment took place providing the most important meteorological and chemical parameters. The first 12 hours of the simulation served to initialize the parameters. The base case model results were validated with the field measurements [5]. VOC and NO_x emissions were reduced by 35 % and simulations were repeated for each case. Calculations were carried out also for a stagnant meteorological case [6]. Results in the first layer at the time of ozone peak, between 16:00 and 17:00 (central european time) were used for the evaluations. Some simulations were carried out for the year 2000 using a standard development of emissions published by BUWAL [7]. Similar emission reductions were performed for this case as well.

3 Results

Ozone concentrations as a function of NO_y, NO_z, and correlations between HCHO and NO_y, and H_2O_2 and HNO_3 are shown in Figures 1 and 2 for the west wind case and for the stagnant meteorology, respectively. Straight lines indicate the threshold ratios given by Sillman [2] ($NO_y = 20$, $O_3/NO_z = 7$, $HCHO/NO_y = 0.28$, $H_2O_2/HNO_3 = 0.4$). The regions above the lines are considered as NO_x sensitive, below the lines VOC sensitive. In Figure 1 (the west wind case) ozone concentrations plotted against NO_y and NO_z concentrations show that all the points are in the NO_x sensitive region using the ratios given by Sillman. On the other hand, some points are also in the VOC sensitive region for the stagnant meteorological case (Figure 2). Stagnant meteorology and associated high NO_x, VOC and NO_y cause an increase in the photochemical lifetimes of NO_x and VOC therefore an aging urban plume remains in the VOC sensitive regime for a longer time. With more vigorous meteorological dispersion and lower NO_x, VOC and NO_y an aging urban plume would rapidly become NO_x sensitive [8]. Figures 1 and 2 indicate that there is a rather high correlation between O_3 and NO_z. The slopes and the correlation coefficents of a linear fit are 4.1 and 0.70 for west-wind case and 2.9 and 0.79 for the stagnant meteorological case, respectively. These figures include the model results for all Switzerland. They may also be grouped into more than one straight line with

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different slopes for different regions [1]. NO_z has an advantage over NO_y as an indicator because NO_y measurements in urban locations may be affected by NO_x emission sources.

HCHO increases with increasing NO_y, and data cover both NO_x and VOC sensitive regions in west wind case as well as in the stagnant meteorological case. Finally, there is no consistent correlation between H_2O_2 and HNO_3.

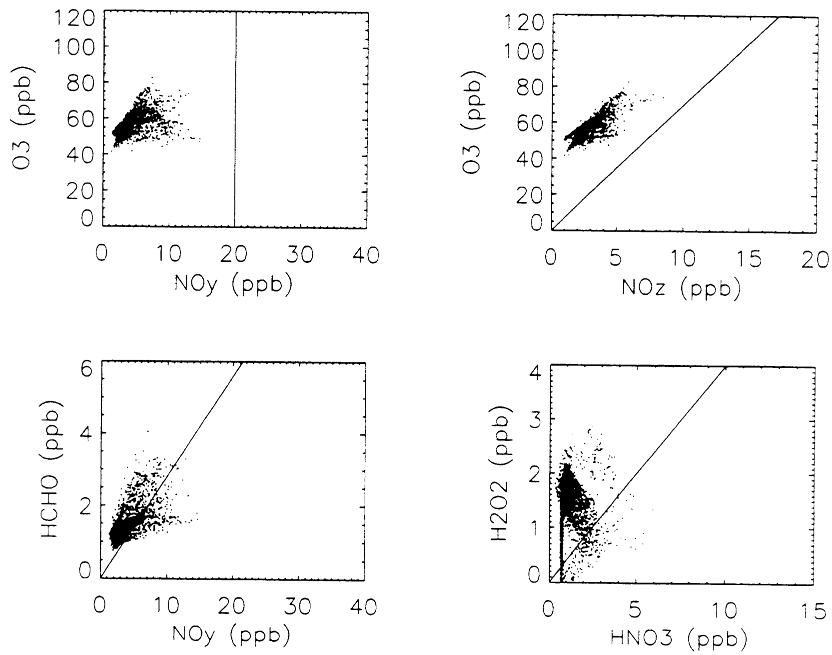


Figure 1 Predicted concentrations and correlations of some species for the west wind case. Straight lines show the ratios given by Sillman [2].

In Figures 3 and 4, predicted reductions in ozone concentrations were plotted against the indicator species ratios for the west wind case, for 35 % reduction in NO_x emissions and 35 % reduction in VOC emissions, respectively. When VOC emissions are reduced (Fig. 4), there is only a decrease in predicted ozone concentrations within a certain range of indicator ratios. However, ozone concentrations increase at low ratios when NO_x emissions are reduced (Fig. 3). This fact is more remarkable for the stagnant meteorological case (see Figures 5 and 6). Increase in ozone concentrations when NO_x emissions are reduced indicates VOC sensitivity of ozone formation.

Low HCHO/NOy is associated with VOC sensitive ozone since production of HCHO is roughly proportional to the summed rate of reactions of

VOC with OH. NO_x-VOC sensitivity is linked to the relative rates of formation of peroxides and nitric acid and to their role as sinks for odd hydrogen.

The distribution of VOC and NO_x sensitive regions in Switzerland can be seen in Figure 7 for the stagnant meteorological case. This figure shows the changes in ozone concentrations when the NO_x emissions were reduced by 35 %. The regions where ozone concentrations decreased are NO_x sensitive (in the rural areas and alpine regions). On the other hand, VOC sensitive regions are those where ozone concentrations increased and they are mainly around the big cities.

Ranges of indicator ratios where ozone production is predicted to be NO_x or VOC dependent are given in Table 1. VOC sensitive regions are at lower ratios and there is an overlap between NO_x and VOC sensitive regions for each indicator species ratios. These ratios are shifted to slightly higher values in the case of the west-wind situation. Indicator ratios for the stagnant meteorology are similar to those given by Sillman [2]. These ratios cannot be used for other meteorological cases.

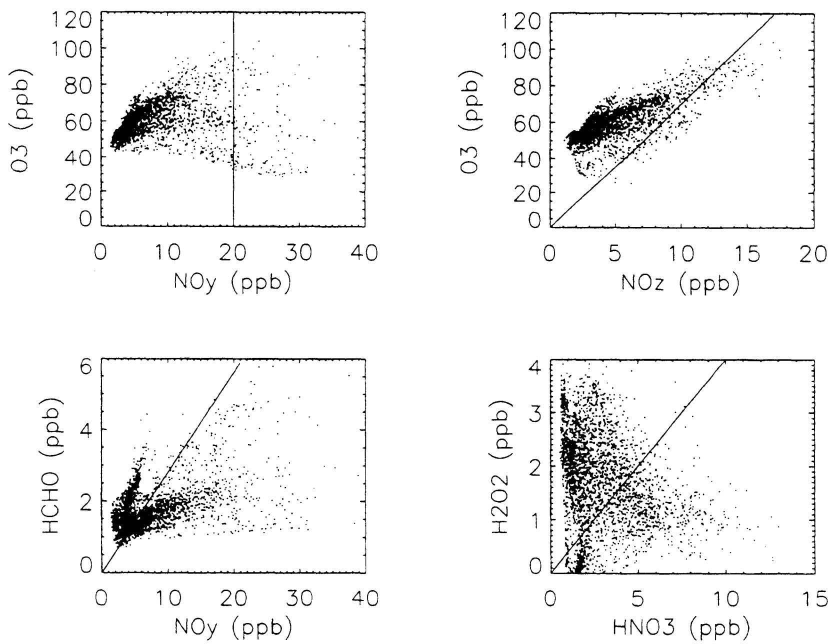
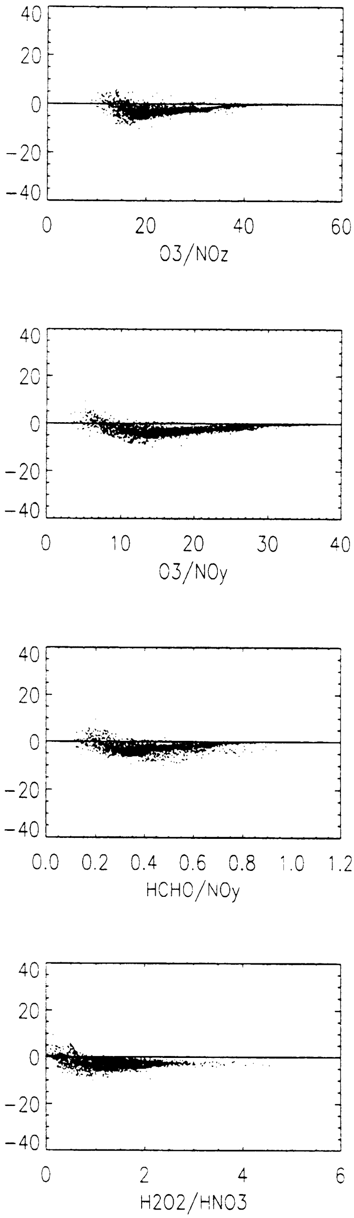


Figure 2 Predicted concentrations and correlations of some species for the stagnant meteorological case. Straight lines show the ratios given by Sillman [2].



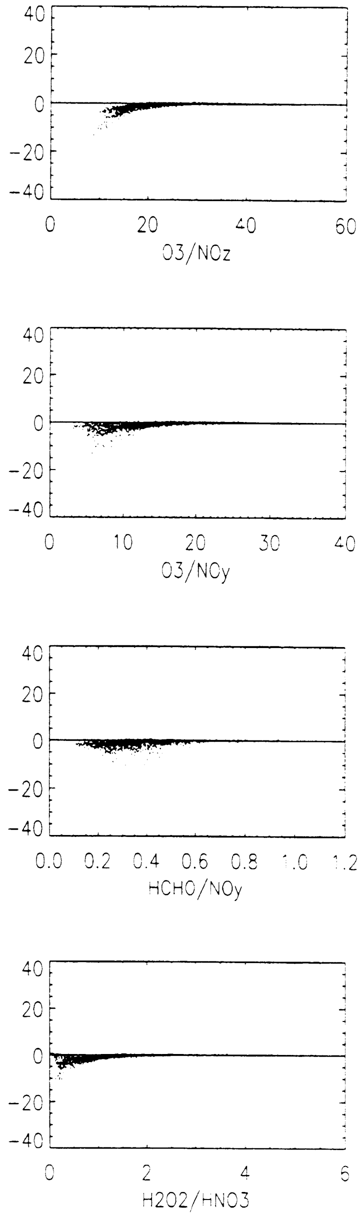


Figure 3 Predicted changes in peak ozone concentrations (ppb) plotted against the indicator species ratios for the west wind case when NO_x emissions are reduced by 35%.

Figure 4 Predicted changes in peak ozone concentrations (ppb) plotted against the indicator species ratios for the west wind case when VOC emissions are reduced by 35%.

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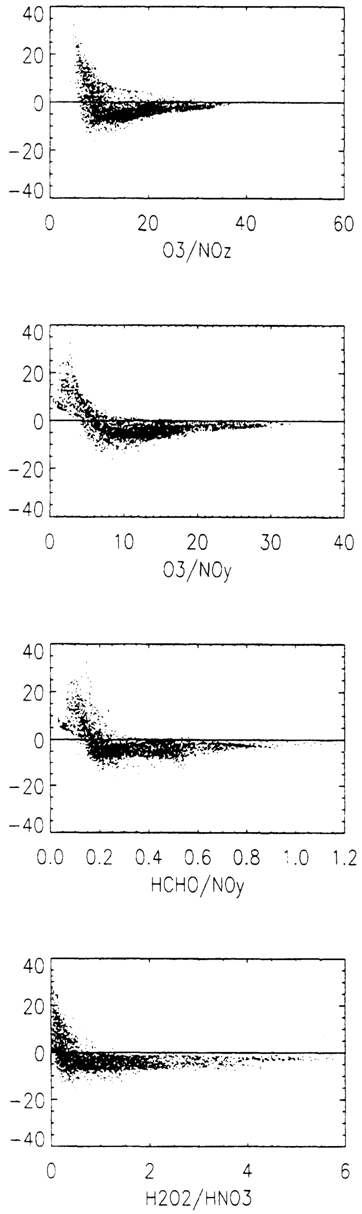

Figure 5 Predicted changes in peak ozone concentrations (ppb) plotted against the indicator species ratios for the stagnant meteorological case when NO_x emissions are reduced by 35%.

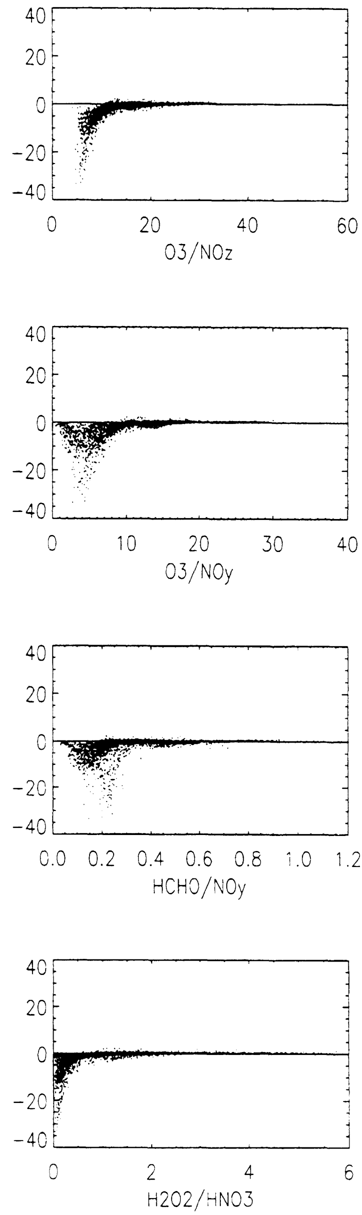

Figure 6 Predicted changes in peak ozone concentrations (ppb) plotted against the indicator species ratios for the stagnant meteorological case when VOC emissions are reduced by 35%.

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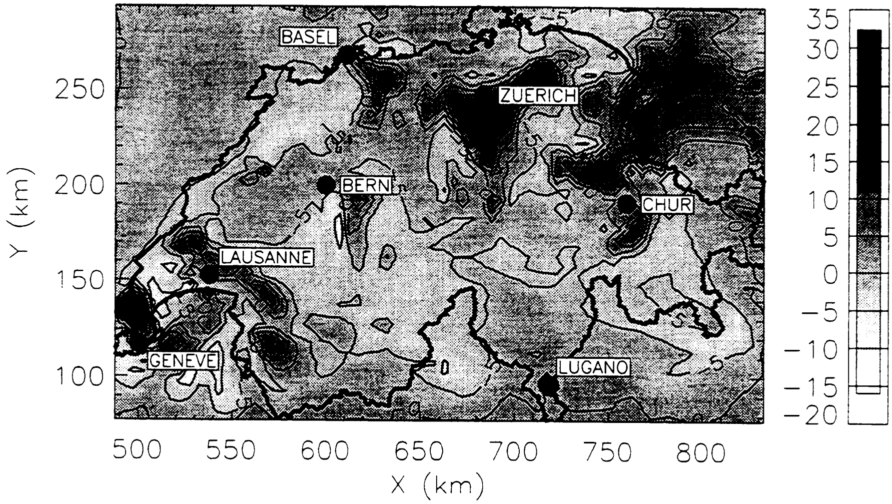

Figure 7 Predicted changes in peak ozone concentrations (ppb) when NO_x emissions were reduced by 35 % for the stagnant meteorological case

Table 1 Indicator species ratios (at the time of peak ozone) calculated by UAM for Switzerland for two different meteorological cases.

	O_3/NO_z	O_3/NO_y	$HCHO/NO_y$	H_2O_2/HNO_3
Stagnant case				
NO_x sensitive	7-30	5-25	0.2-0.7	0.2-4
VOC sensitive	4-10	1-8	0.06-0.3	0.01-0.5
overlap	7-10	5-8	0.2-0.3	0.2-0.5
west-wind case				
NO_x sensitive	13-30	7-25	0.25-0.8	0.25-2.5
VOC sensitive	9-17	3-12	0.1-0.5	0.01-1
overlap	13-17	7-12	0.25-0.5	0.25-1

The results of the simulations for the year 2000 showed that the correlations between NO_x - VOC sensitivity and indicator species remained the same for 1993 and 2000 although the emission rates were different (total emissions of NO_x and VOC are about 25 % and 40 % less than in 1993, respectively).

4 Conclusions

The indicator species proposed by Sillman [2] may be useful for the assessment of the relative effectiveness of VOC versus NO_x controls. Urban Airshed Model predictions for ozone-NO_x-VOC sensitivity for Switzerland have been shown to correlate with simulated values of the indicator species ratios such as O_3/NO_y, O_3/NO_z, $HCHO/NO_y$ and H_2O_2/HNO_3 at the time of the ozone peak. Results showed that the correlations varied when the wind conditions are different. In a stagnant meteorology, VOC-sensitive chemistry is predicted to be linked to the afternoon ratios approximately $O_3/NO_z < 10$, $O_3/NO_y < 8$, $HCHO/NO_y < 0.3$, and $H_2O_2/HNO_3 < 0.5$. Higher ratios correspond to NO_x-sensitive ozone formation. They agree well with the values given by Sillman. In a light west wind situation, these ratios were shifted to higher values. There is always some overlap between NO_x and VOC sensitive regions. Correlations were established also on the basis of a simulation for the year 2000 using a standard development of emissions. These results indicated that the correlations between NO_x-VOC sensitivity and indicator species remain the same for 1993 and 2000 although the emission rates are different.

Keywords : ozone, NO_x-VOC sensitivity, indicator species, modeling

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