Examples of the importance of trace gas measurements in the Milan ozone plume

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The production rate of ozone depends in a non linear way on NO_x = (NO + NO_2) and VOC (Volatile organic carbon compounds). The analysis of the sensitivity of the ozone production is a prerequest to formulate effective abatement strategies. Analysis of the sensitivity question can be based mainly on two approaches: a) Observation based modelling and b) Chemical transport models. Both ways need a comprehensive data set of gaseous trace compounds in order to successfully address the question.

Ozone and other photooxidants such as H_2O_2 or PAN are secondary pollutants, thus produced in the atmosphere. Ozone is formed from the photochemical oxidation of volatile organic compounds (VOC) in the presence of nitrogen oxides (NO_x = NO + NO_2) and light. The amount of ozone that can be produced is limited by the availability of either VOC or NO_x. Which one is the limiting reagent is a key question that has to be answered in order to design reduction strategies. Measurements of ozone alone cannot answer the question whether NO_x or VOC are limiting the ozone production. Figure 1 shows ozone and H_2O_2 isoplethes as function of the relative VOC and NO_x emissions calculated with a 1-D lagrangian model for the Swiss plateau [1].

Within 50% change of emissions of both VOC and NO_x only a relative small change of ozone is expected. The same ozone concentration occurs for a wide range of VOC and NO_x emissions. This weak dependence of the ozone concentration on the emissions calls for other compounds such as H_2O_2 that react more sensitive to VOC or NO_x emission changes to address the limitation question.

The highest ozone concentrations in Switzerland are found in the Sotto Ceneri. Episodes with peak concentrations above 120 ppb are generally linked with advection

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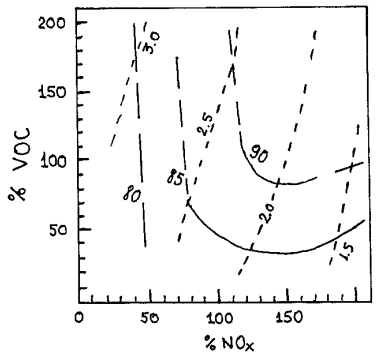

Figure 1. Ozone and H_2O_2 isoplethes calculated for the Swiss plateau. Concentrations are calculated for 16:00 at the second day for clear sky conditions.

from the Po valley [2]. During summer month the Alpine foothills of the Sotto Ceneri are expected to be downwind of the emissions of the Milan metropolitan area due to the thermal induced valley winds.

In several field campaigns POLLUMET (Pollution and Meteorology) 1991-1993, BOCCALINO (Biogenic Organic Carbon Compounds as Leading Indicators of Non-H_2O_2 Peroxides), 1994 and most recently PIPAPO (Pianura Padana Produzione di Ozono) in May and June 1998, ozone plumes and fronts have been found north of Milan with ozone enhancement of 30 to 50 ppb.

Key trace gas species to understand photooxidant formation and model validation

The driving forces of the photooxidant production are the ODD-H radicals (OH, HO_2 and RO_2) that link the oxidation cycle of NO and NO_2 with the oxidation of VOC's.

Preferably the ODD-H radicals should be measured, their low concentrations (in the sub ppt range for OH and sub ppb range for RO_2) makes their measurements costly. The short lifetime results in a large spatial variability of a point measurement. Species with higher concentrations and therefore also longer atmospheric lifetime such as H_2O_2, HCHO, HNO_3, PAN and the sum of oxidised N-compounds, NO_y are key species to be determined. E.g. for VOC sensitive ozone production the ODD-H radical loss mechanism is dominated by the formation of HNO_3 via the combination of NO_2 and OH. For NO_x sensitive conditions the dominante radical loss mechanism is the formation of peroxides (Kleinmann 1986). The ratio of H_2O_2/HNO_3 is therefore a sensible parameter to the chemical regime.

Another characterisation of the photooxidant production is the "chemical age" of an air mass defined as $1 - NO_x/NO_y$. The higher the chemical age the longer the production went on and the larger is the portion of processed NO_x. Because the mentioned gaseous trace species are not regulated in air quality guidelines the measurements of these species are still in the research domain and are not determined in monitoring network. Also no standard quality assurance/quality control procedures have been established. (see e.g. JGR issue 103(D17) september 1998).

Indicator concept to distinguish VOC *versus* NO_x limited ozone production

Sillman [4] introduced a concept to derive VOC and NO_x sensitive ozone production based on measurements of different trace components. He proposed a series of indicator derived from simulations with a 3-D Eulerian model. These indicators are NO_y (= $NO+NO_2+HNO_2+HNO_3$+PAN+PPN+ nitrate and organic nitrates), $O_3/(NO_y–NO)$, $HCHO/NO_y$ and H_2O_2/HNO_3. Table I shows the transition values where the chemical regimes is changing from VOC to NO_x sensitive ozone production.

The Sillman indicators characterise the integrated ozone production sensitivity and reflect therefore more than just a local condition at the specific measuring site. It has to be pointed out that indicator values have not a "universal" range of validity. They can differ from one area to another and do change with season. Indicator transition values are based on a 3-D model, that in turn has to be validated. Such a validation needs a comprehensive dataset of chemical trace species and meteorological information. Such information can only be gained with large scale experiments involving research groups and the local agencies responsible for the air quality monitoring networks.

An air mass loaded with fresh urban emissions will have generally a VOC sensitive ozone production. When the air mass is travelling over a region with lower NO_x emissions, dilution and chemical reactions reduce the precursor concentrations. The ozone production sensitivity will change sooner or later to NO_x sensitive [5]. It was one of the important result of the BOCCALINO study that the transition of the integrated ozone production downwind of the Milan area occurs within a few tens of kilometers only [7]. To get a comprehensive picture of the temporal and spatial extension

Table I. Indicators as defined by Sillman [1995]

Indicator	*NO_x sensitive*	*VOC sensitive*
NO_y	< 20 ppb	> 20 ppb
$O_3/(NO_y - NO_x)$	> 7	< 7
$(O_3 - 40)/(NO_y - NO_x)$	> 5	< 4
$HCHO/NO_y$	> 0.28	< 0.28
H_2O_2/HNO_3	> 0.4	< 0.4

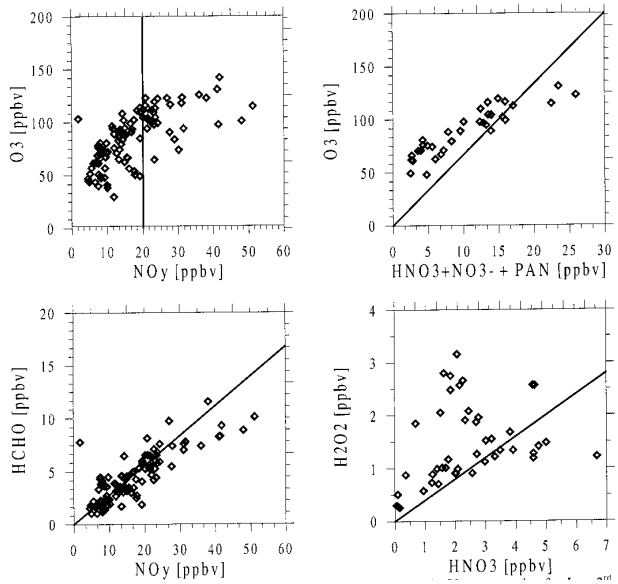

Figure 2. Indicator values evaluated for afternoon concentrations from the Verzago station for June 3rd to June 10th.

of the VOC sensitive area around Milan and eventually along the major traffic routes we initiated within the Eurotrac-2 subproject LOOP (Limiation of oxidant production – http://ww1.psi.ch/~loop/) the PIPAPO experiment.

First data impression from the PIPAPO experiment. An approach to determine the sensitivity of the ozone production with indicator values

Two intensive observation periods have been performed in the PIPAPO experiment. The first IOP lasted from May 12th to May 14th, the second from June 3th to June 10th. Our institute operated in Verzago (a small village 10 km south east of Como) a ground station Ispra together with the ETH-Zürich and a group of the JRC-Ispra. We concentrated on the measurement of O_3, peroxides, HCHO, PAN, HNO_3 and NO_3^-, thus all species related to the evaluation of the Sillman indicator. Figure 2 shows the indicator values calculated for the times between 1330 and 1800 CEST of the second IOP when good vertical mixing is established together with the transition line. We assumed that NO_y – NO_x is well represented by the sum of PAN, HNO_3 and NO_3^-.

Discussion

The afternoon values of the second IOP show no titration effects. The highest ozone values parallel the highest NO_y concentrations. There is a clear tendency that the highest ozone values are associated with VOC limited production regime. Polluted airmasses that are transported to Verzago are still VOC limited and have not reached the NO_x limited status. This differs from the findings of the BOCCALINO study. Most probably lower mixing heights and lower levels of biogenic emissions could be the reason. Further evaluation of data from other stations and simulations with numerical models adapted for the situation in the Milan area have to proof or disproof this hypothesis.

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