Sensitivity of photooxidant production in the Milan Basin: An overview of results from a EUROTRAC-2 Limitation of Oxidant Production field experiment

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[1] The international field experiment Pianura Padana Produzione di Ozono (PIPAPPO) studying the volatile organic compounds (VOC)/NO_x ozone production sensitivity took place in May and June 1998 downwind of the metropolitan area of Milan. The project was embedded in the framework of the EUROTRAC-2 Limitation of Oxidant Production (LOOP) subproject. Several ground stations between the city of Milan and the Alps north of Milan combined with airborne measurements delivered a comprehensive data set suitable for observation-based analysis and validation of chemical transport models. The special section devoted to the PIPAPPO project contains 10 contributions on the characterization of secondary aerosol formation, and radical precursors, and the characterization of ozone production sensitivity based on field measurements and numerical model simulations. In this paper the scientific background and the major objectives of PIPAPPO are described. An overview of the field measurement program, the study site, and the meteorological conditions prevailing during the experiment are given. A general conclusion of the combined results is that under typical summer conditions in the Milan area with clear skies, low wind speeds and high temperatures, the transition from VOC- to NO_x-sensitive ozone production occurs a few tens of kilometers downwind of the strongest emission sources in the city of Milan.

INDEX TERMS: 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; **KEYWORDS:** tropospheric ozone production, photochemical smog, NO_x-VOC sensitivity of ozone production, urban pollution, Milan, EUROTRAC-2

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1. Introduction

[2] Over the last 20 years, the understanding of the chemical mechanisms leading to photooxidant episodes has been developed and is now on a sound base (see, e.g., NARSTO Synthesis Team, An assessment of tropospheric ozone pollution, July 2000, <http://odysseus.owt.com/Narsto/index.html>). The degree of photooxidant formation in the planetary boundary layer is determined by the meteorolog-

ical conditions and the emissions of volatile organic compounds (VOC) and NO_x (sum of nitric oxide and nitrogen dioxide). The photooxidant formation process is nonlinear with respect to emission strength. This makes the development of abatement strategies to meet air quality standards complicated.

[3] High levels of aerosols parallel the occurrence of photochemical episodes. However, photooxidants and aerosols have often been studied separately. Air pollution directives are being developed for either one or the other, even though the formation of photooxidants and aerosols is tightly linked through atmospheric chemical processes. Emission reduction strategies for photochemical oxidants and aerosols should be evaluated together, as a strategy that is optimum for aerosols may interfere with an ozone reduction strategy, and vice versa [Meng *et al.*, 1997].

[4] The EUROTRAC-2 subproject Limitation of Oxidant Production (LOOP) studies the VOC and NO_x sensitivity of ozone production and evaluates the temporal and spatial behavior of photochemical regimes. We distinguish between

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two sensitivity measures. The local ozone production sensitivity is defined as the response of the O_3 production rate ($P(O_3)$) to a change in the concentration of either NO_x or VOCs. The integrated ozone concentration sensitivity is the response of O_3 concentration to a change in the emissions of either NO_x or VOCs. For the local ozone production the transition from one chemical regime to the other (i.e., the transition from VOC-sensitive to NO_x -sensitive production) is defined as the point at which a relative decrease in both NO_x and VOC concentrations has the same effect on $P(O_3)$ (see for example, Kleinman [1994], Kleinman *et al.* [1997], and Sillman [1995]),

$$\frac{\partial P(O_3)}{\partial [VOC]} [VOC] = \frac{\partial P(O_3)}{\partial [NO_x]} [NO_x]. \quad (1)$$

[5] The sensitivity of the ozone concentration is related to the local sensitivity [Spirig *et al.*, 2002] upwind, mixing processes, and deposition integrated over the atmospheric lifetime of ozone. This sensitivity has to be evaluated by varying the emissions in numerical models. The evaluation of abatement strategies also needs to be based on numerical model simulation, ideally with a validated three-dimensional (3-D) model.

2. Pianura Padana Produzione di Ozono Project

[6] Within the EUROTRAC-2 subproject Limitation of Oxidant Production (LOOP) we conducted a field campaign in May and June 1998 devoted to the evaluation of the temporal and spatial dynamics of the VOC versus NO_x sensitivity around Milan. Because the Milan region has a photochemical oxidant and aerosol problem, and because the chemistries of these substances are so tightly linked, the LOOP project included cooperation with the AEROSOL subproject of EUROTRAC-2.

[7] The Milan metropolitan area, located in the Po Basin, the most industrialized and populated area in northern Italy, is regularly affected by high ozone levels, especially during the late spring and summer months. The entire Milan metropolitan area can be considered as a single urban area, with a population of approximately 3.8 million. The expansion of the urban area during the last few decades has been paralleled by the development of a dense road network. Inside the area there are about 580 km of highways and 1740 km of secondary roads.

[8] The region between the industrialized area of Milan and the Alps represents a very interesting natural laboratory, with a high variability in emission strength and emission patterns. The region exhibits frequent stagnant meteorological conditions associated with relatively high insolation. In this case the meteorology of the area is dominated by low wind speeds subject to mesoscale breeze circulations. Winds near the ground typically blow from north to south during the night and in the early hours of the morning. The wind direction changes to southerly in the late morning and remains that way until sunset. Typical residence times of air masses transported between the center of Milan and the foothills of the Alps some 40 km to the north are 3–5 hours, thus representing rather short processing times. Concentrations of ozone up to 185 ppb have been reported [Prévôt *et*

al., 1997]. Despite this short time period, field and model studies indicate that integrated ozone production is NO_x sensitive only a few tens of kilometers north of the urban area of Milan [Staffelbach *et al.*, 1997a, 1997b].

[9] Model studies accompanied the experimental activities from the start of the program. A modeling community interested in doing three-dimensional simulations for the Milan area in the Po Basin was established, and had several workshops to coordinate and intercompare their efforts.

[10] The PIPAPO campaign was organized as a pure bottom-up project without central funding. Close cooperation with local authorities was established from the beginning. All information of the PIPAPO project is collected on a CD. This CD contains an ACCESS database with all measurement data as well as a visualization tool.

2.1. Outline of the PIPAPO Campaign

2.1.1. Milan Basin as Natural Photoreactor

[11] The PIPAPO field campaign was basically set up as a Lagrangian experiment with several stations within the so-called Milan plume, that is, downwind of Milan. During two intensive observation periods (IOPs, 12 and 13 May, 1–10 June 1998), surface station and aircraft measurements were performed. Observational stations at Bresso, Seregno, and Verzago were established downwind of Milan, hypothetically located in different chemical regimes according to earlier investigations with a one-dimensional Lagrangian model [Staffelbach *et al.*, 1997b].

[12] Figure 1 illustrates the evolution of O_3 sensitivity in a typical Milan urban plume as determined by Staffelbach *et al.* [1997b]. The red color stands for VOC-sensitive ozone production, purple for the transition (about equal sensitivity to VOC and NO_x), and yellow for NO_x -sensitive ozone production. The calculations are based on an air mass that starts at 0700 LST (local standard time, UTC + 1 hour) in Milan and arrives at 1500 LST in Verzago.

2.1.2. Intensive Observation Periods (IOP)

[13] Meteorological criteria for an IOP were (1) a high-pressure situation lasting for several consecutive days, (2) high insolation producing strong thermally driven circulations and intensive photochemical activity, (3) weak synoptic winds aloft and southerly winds near the surface, and (4) absence of precipitation. Because ozone episodes often occur in spring and early summer, this time of the year was selected over the better known midsummer episodes.

[14] The first IOP lasted from 12 to 13 May 1998 and was embedded in a period of exceptionally warm, dry, and sunny weather. The synoptic situation showed a stationary high-pressure ridge at 500 hPa extending from northern Africa to southern Scandinavia (Figures 2a and 2b). Milan reported daily maximum temperatures of 31°C on 12 May and 32°C on 13 May. The Po Basin was free of clouds on both days, while in the afternoon of the second day convective clouds developed in the mountains east of the Lake of Como, which led to thunderstorms that terminated the IOP. A heat low over the Alps was well established on both days. The pressure gradient induced a weak south-to-north flow over the study area, and the ideal flow configuration for PIPAPO was realized on 13 May. High insolation and high temperatures were very favorable for photochemistry in the plan-

Figure 1. Modeled sensitivity of O_3 concentration to NO_x/VOC emissions in the Milan plume. The red area is VOC sensitivity, purple marks the region with about equal sensitivity, and yellow the NO_x -sensitive area. The trajectory passed the city of Milan between 0700 and 1000 indicates local standard time LST.

etary boundary layer (PBL), and the winds supported the transport of polluted air from the basin toward the Alps. Ozone concentrations reached values of 190 ppb during this IOP.

[15] The second IOP took place from 1 to 10 June 1998. The 500 hPa charts show a consistent southwesterly flow across the Alps for the whole period, while the surface charts exhibit various frontal systems which remained north of the alpine crest.

[16] Winds aloft were mostly southwesterly, while surface winds showed variable directions. Very frequently thunderstorms and scattered intermittent, heavy showers developed during the second IOP. In contrast to the first IOP, Milan always reported moderate cloudiness around noon. The ideal flow situation for the second IOP lasted from 2 to 4 June, before a cold front approached the Alps (Figures 3a and 3b). The front then became stationary and soon dissolved. The

days were warm and sunny, but haze started to accumulate in the PBL, and visibility became poorer with time. In this period, maximum ozone concentrations increased from day to day, reaching peak values of 140 ppb on 4 June. Rain was falling on the morning of 5 June, and the winds became northerly for a while. Wind speeds were rather low. A frontal system moved across the continent and the Alps on the night of 7–8 June, thereby interrupting the second IOP. Behind the front, winds turned to northerly directions at all levels for some time. Generally, the surface wind field of the second IOP was quite inhomogeneous.

[17] The days that have been chosen as the ideal days for the application of the Eulerian models are 12 and 13 May.

2.1.3. QA/QC of PIPAPO

[18] The quality assurance, quality control (QA/QC) within PIPAPO is based primarily on the conscientiousness of the individual contributors. An overview of the measure-

Figure 2. (a) The 500 hPa geopotential height contours and (b) surface pressure analysis for 13 May 1998, 1200 UTC. Notice that the two charts cover a slightly different geographical area. Charts provided by MeteoSchweiz.

Figure 3. (a) The 500 hPa geopotential height contours and (b) surface pressure analysis for 3 June 1998, 1200 UTC. Notice that the two charts cover a slightly different geographical area. Charts provided by MeteoSchweiz.

Table 1. Measurements Overview

Species/Parameter	Technique	Reference
<i>Ground Based Measurements</i>		
H ₂ O ₂	Nafion scrubber with fluorescence	<i>Spirig et al.</i> [2002]
HCHO	coil collection with fluorescence	<i>Spirig et al.</i> [2002]
HCHO, HONO, O ₃ , NO ₂ , SO ₂	differential optical absorption spectrometer (DOAS)	<i>Alicke et al.</i> [2002]
Vertical gradients of HONO, NO ₂ , SO ₂	differential optical absorption spectrometer (DOAS)	<i>Stutz et al.</i> [2002]
HONO, HNO ₃	parallel plate denuder with ion chromatography	<i>Spirig et al.</i> [2002]
Hydrocarbons (C ₄ –C ₁₀)	gas chromatograph with flame ionization detector (FID)	<i>Thielmann et al.</i> [2001]
NO, NO ₂ , NO _y	chemiluminescence with photolytical/molybdenum converter	<i>Thielmann et al.</i> [2002]
O ₃	UV absorption	<i>Thielmann et al.</i> [2002]
Peroxy radicals	chemical amplifier	<i>Spirig et al.</i> [2002]
Radiation/J _{NO2}	radiometer	<i>Thielmann et al.</i> [2002]
Aerosol compounds	cellulose and quartz fiber filters in virtual impactors for ionic and carbonaceous species, respectively.	<i>Puteaud et al.</i> [2002]
Aerosol absorption coefficient	Aethalometer [®]	<i>Puteaud et al.</i> [2002]
Aerosol size distributions	differential mobility analyzers	<i>Puteaud et al.</i> [2002]
PM _{2.5}	betameter	<i>Baltensperger et al.</i> [2002]
BC mass concentration	aethalometer	<i>Baltensperger et al.</i> [2002]
Volatility	thermodesorber SMPS (scanning mobility particle sizer)	<i>Baltensperger et al.</i> [2002]
Hygroscopic growth	tandem differential mobility analysis (TDMA)	<i>Baltensperger et al.</i> [2002]
Nitrate, sulfate, gaseous HNO ₃	WEDD/AC (wet effluent diffusion denuder/aerosol collector)	<i>Baltensperger et al.</i> [2002]
<i>Aircraft Measurements</i>		
H ₂ O ₂	chemiluminescence	<i>Dommen et al.</i> [2002]
HCHO	Hantzsch-fluorescence	<i>Dommen et al.</i> [2002]
Hydrocarbons (C ₄ –C ₁₀)	gas chromatograph with FID	<i>Dommen et al.</i> [2002]
NO _x	chemiluminescence	<i>Dommen et al.</i> [2002]
O ₃	UV absorption	<i>Dommen et al.</i> [2002]

ments is given in Table 1. The data have been compiled on an MS ACCESS database, including tools for extracting and visualizing of data (The CD can be ordered at FAL, P.O. Box, CH 8046 Zürich, Switzerland.). Figure 4 shows an example for the representation of the flight data. The user can, for example, scan the flight for any measured species, and then the height above ground, the geographical location, and the concentration are shown.

2.2. Emissions

[19] The emission inventory for the LOOP project was compiled by *Maffei et al.* [1999]. Unfortunately, different methodologies were used for the Italian and Swiss part of the domain. In the small Swiss part of the domain, a spatial disaggregation of only 5 km × 5 km gridding was available. The Swiss inventory includes two source categories, traffic and industry.

[20] The pollutants considered in the Italian inventory are sulfur dioxide (SO₂), nitrogen oxides (NO_x), carbon monoxide (CO), and nonmethane volatile organic compounds (NMVOC), while the Swiss inventory considers VOC speciation into 32 classes. Lombardy and Piedmont VOC estimates were speciated in 32 classes, according to EPA's SAROAD (Storage and Retrieval of Aerometric Data) scheme, on the basis of 11 different profiles (eight anthropogenic and three biogenic [*Carter, 1995; Derwent et al., 1996*]). The Swiss part of the inventory considers a typical summer profile for the temporal distribution of emissions. In Piedmont and Lombardy the emission estimate algorithms used meteorological parameters that are specific to the hour, day, and area considered. This means that the calculation of isoprene (and other biogenic compounds) for a certain hour of the simulation and in a certain town is

based on interpolated temperature and radiation. The same applies for traffic and evaporative emissions.

[21] It should be noted that the inventories are based on indicators and emission factors referenced to the year 1995. This introduces other sources of uncertainty including (1) new important infrastructure construction (e.g., the Malpensa airport), (2) strong car fleet renewal during the past few years, and (3) changes in industry processes and their decentralization from the main cities.

3. Occurrence of Photosmog Episodes in the Milan Area

[22] Occurrences of elevated ozone concentration in the region between Milan and the Alps are strongly related to the meteorological conditions. As an example, Figure 5 shows the variability of late afternoon concentration in Verzago as a function of the prevailing meteorological conditions. Daily average global radiation and daily temperature maxima were calculated from representative ground stations. The prevailing wind conditions were derived from wind profiler measurements at Seregno, which is located between Milan and Verzago. The best correlation is found between temperature and ozone concentrations in Verzago in the late afternoon (1730 Central European Daylight Time, equal to LST + 1 hour or UTC + 2 hours) during the PIPAPO campaign. Ozone increases from around 45–70 ppb at 20°C to 80–145 ppb at 30°C. The main reasons for this relationship are higher biogenic emissions, higher chemical reaction rates, and usually higher global radiation at higher temperatures, yielding higher ozone production. However, taking only temperature into account, a great part of variability in the ozone concentration remains unex-

Figure 4. Visualization of aircraft data. (left) Flight path. (right) Time series of the height above ground, the concentration of a selected species, and the vertical profile are represented. The flight can be traced with a ruler (dots in the time series plots).

plained. Ozone does not exhibit a consistent dependence on global radiation. On days with low radiation (less than two thirds of typical clear days), ozone concentrations do not exceed 80 ppb (crosses in Figure 5). Assuming the wind profiler data to be representative for the region around Milan, we can deduce the influence of the air mass origin on the ozone concentrations in Verzago. The highest concentrations in a particular temperature range are found for the cases when southerly winds prevail, transporting the Milan plume to Verzago (circles in Figure 5). In the case of strong winds (several hundred kilometers transport distance within 10 hours) and no development of thermally induced winds toward the Alps, low ozone concentrations are found in the corresponding temperature range (squares in Figure 5). On days with thermally induced winds not originating from Milan (usually southwesterly or southeasterly wind directions), the ozone concentrations were close to the linear correlation fit (diamonds in Figure 5).

[23] In summary, the ozone concentrations in Verzago in the late afternoon typically increase by about 6 ppb ozone per 1°C daily maximum temperature. On days with low global radiation, ozone concentrations do not exceed 80 ppb. When the air originates from Milan, we find around 20–30 ppb higher ozone concentrations than the concentration typical for the prevailing temperature. This is similar to what was found in cross sections of the plumes,

where the maximum ozone concentrations are often 20–40 ppb higher than in the adjacent air masses [Dommen *et al.*, 2002]. For conditions with strong winds or no development of southerly thermally induced winds, ozone concentrations are 20–30 ppb lower than typical for the prevailing temperature.

4. Overview of Scientific Outcomes

[24] In this section we give a brief overview on the most important scientific findings of the papers of this special section.

4.1. Aerosol Measurements

[25] Two papers discuss the aerosol measurements that have been performed in Bresso and Verzago. Primary aerosols in Bresso are strongly related to traffic density, with peak values during the morning rush hour. A large fraction consists of hydrophobic organic material. PM_{2.5} values, on the other hand, do not show a diurnal variation and are therefore not directly linked to primary aerosols. There is a higher percentage of secondary aerosols in Verzago compared to Bresso, in accordance with a generally higher photochemical age of the air masses in Verzago. However, secondary aerosol formation cannot be described using a simple flow reactor picture during transport to

Figure 5. Late afternoon ozone concentrations in May and June 1998 in Verzago versus the daily maximum temperature in Milan. The crosses are days with low global radiation. The large circles are cases with air masses originating from Milan. The small circles are days with incomplete or missing data from the wind profiler. The squares are days with very high wind speeds or no thermally induced southerly winds. The diamonds are cases with thermally induced winds, not originating from Milan.

Verzago. Both dilution and additional emission influence the level of secondary aerosols in the plume. *Baltensperger et al.* [2002] showed that a large part of the HNO_3 formed over Milan during the morning hours was transformed rapidly to aerosol nitrate, and was transported away by thermally induced winds.

[26] *Puteaud et al.* [2002] showed that ammonium nitrate and ammonium sulfate contribute roughly 50% to the submicron aerosol fraction; particulate organic matter contributes 32% at the urban site and 39% at the rural site. They concluded also that NH_3 is not the limiting factor for NH_4NO_3 production in the Po Basin in summer.

4.2. Gas Phase Measurements in Bresso, and Verzago, and by Aircraft

[27] Three papers present in detail the measurements of gas phase species at the urban site of Bresso. *Alicke et al.* [2002] and *Stutz et al.* [2002] reported differential optical absorption spectroscopy (DOAS) measurements of the important odd-H radical precursors HCHO and HONO, together with O_3 , NO_2 , SO_2 , and NO measurements. In the heavily polluted area of Milan, photolysis of HONO and HCHO are the most important OH sources at ground level for clear days, more important than the photolysis of ozone. DOAS was also used to determine fluxes with the gradient technique. With this approach it can be shown that for HONO an equilibrium between deposition and emission (a kind of compensation point, related to the HONO/ NO_2 ratio) is established. The measurements show a HONO formation rate of the order of a few percent of the NO_2 concentration, as a consequence of NO_2 dry deposition.

Thielmann et al. [2002] discussed the sensitivity of the ozone production rate based on time series of O_3 , NO, NO_2 , HNO_3 , NO_y , and H_2O_2 measurements in Bresso and Verzago. The analysis shows a predominantly VOC-sensitive ozone chemistry in Bresso and both VOC- and NO_x -sensitive ozone chemistry in Verzago. VOC-sensitive ozone chemistry in Verzago is always associated with polluted air masses from the Milan area.

[28] *Spirig et al.* [2002] determined the odd-H radical levels and the local ozone production from measurements in Verzago and Bresso. On the basis of a steady state analysis, the VOC/ NO_x sensitivity was determined. In cases where air masses have been advected directly from the south, the local production in Verzago during the afternoon was determined to be VOC sensitive. The measurements suggest an additional strong emission source between the city of Milan and Verzago that is not adequately represented in the numerical simulations. In other air masses the ozone production was NO_x sensitive.

[29] A similar approach was taken by *Dommen et al.* [2002] using measurements from the MetAir aircraft. Their analysis shows that the core of the Milan plume is highly VOC sensitive with a downwind extension of about 40 km and a width of 10 to 20 km. Peroxide and ozone productions rates were calculated from the measurements and also deduced from a local steady state photochemical analysis. The intercomparison of these two approaches yielded reasonable agreement for peroxide and lower ozone productions for the steady state analysis. *Dommen et al.* [2002] concentrated on measurements in the Milan plume owing to their rather high uncertainty for low NO_2 concentrations.

[30] On the basis of previous field campaigns, a gradual increase of biogenic VOC emission in the Milan plume going north was postulated. Isoprene emissions were expected to have the largest influence on ozone production. According to the VOC measurements taken from the aircraft, isoprene contributes only moderately to the total VOC reactivity in the layers where the aircraft was flying, with no clear increase toward the Alps over the Po Basin.

4.3. Model Simulations

[31] Three contributions are based on simulations with chemical transport models. *Dosio et al.* [2002] and *Martilli et al.* [2002] used the TVM-LCC model to simulate the conditions in the Po Basin for 13 May. *Hammer et al.* [2002] used the KAMM/DRAIS model. *Dosio et al.* [2002] concentrated on the meteorological aspects and the associated ozone dispersion in the Po Basin. The mountain-induced circulation extends for about 1000 m in the vertical. The simulations show that at higher altitudes a return current is present that subsides in the middle of the basin.

[32] *Martilli et al.* [2002] focused on the VOC/ NO_x sensitivity of the ozone production rate and discussed the influence of the formation of nitrate aerosols on the indicator values. The detailed comparison with field data shows a series of systematic deviations between modeled and measured concentrations. There are two main reasons for this: (1) deviations of the real emissions for 13 May from those used as emission input and (2) a too low vertical exchange during the night between the first few model layers. We believe that these deviations have only a minor influence on the NO_x /VOC sensitivity in the model. This is supported by obser-

vation-based analysis of the local ozone production rate from the field data [see *Spirig et al.*, 2002; *Dommen et al.*, 2002]. Also, the scaling up of the local analysis with simple box and one-dimensional Lagrangian models gives the same picture of a rapid change-over from VOC- to NO_x -sensitive ozone production 20 to 40 km downwind of the city of Milan. The absence of a detailed NH_3 emission inventory and atmospheric measurements (NH_3 concentrations were only measured in Verzaggo) prevents a quantitative validation of the aerosol formation in the TVM-LCC model.

[33] *Hammer et al.* [2002] used the KAMM/DRAIS model to investigate the applicability of the indicator $\text{H}_2\text{O}_2/\text{HNO}_3$ to separate NO_x -sensitive and VOC-sensitive regions in the polluted planetary boundary layer on a regional scale. Three-dimensional model runs were performed for two model domains in Germany and one domain in the Po Valley. These domains differ significantly in the spatial distribution of the emissions, in the absolute values of the emissions, and in the composition of the VOC. The domains also differ in their meteorological conditions and therefore in the involved transport processes. Nevertheless, the transition values of $\text{H}_2\text{O}_2/\text{HNO}_3$ found for the individual domains differ by less than 30% from each other. The VOC-sensitive area is larger in the KAMM/DRAIS model compared to the TVM-LCC model run. The reason for this deviation is the different wind fields of the two models.

5. Summary of Scientific Findings and Outlook

[34] The main goal of the PIPAPO field campaign was to describe the spatial and temporal dynamics of the NO_x/VOC sensitivity in the plume of the Milan metropolitan area. This can only be reached with models that have been proven to reproduce well not only the ozone distribution in space and time, but also the correct sensitivity to changed emission rates. However, a comparison with experimental data has to be based only on the base case model run. Sensitivity runs thus simulate situations that do not correspond to the real situation, and can therefore not be validated with measurements. This situation is a dilemma, as a validation of sensitivity runs with field data cannot be performed.

[35] Reasons for deviations between modeled and measured values must be assessed, and it must be evaluated whether the causes for the deviations affect the sensitivity. We carefully investigated whether the models are producing the right ozone level just by a combination of wrong assumptions that are canceling each other.

[36] Photochemical smog episodes are accompanied by high aerosol loads, with an important contribution from secondary aerosols. The high radical level associated with photochemical smog favors the formation of secondary aerosols, both inorganic and organic. The aerosol measurements have confirmed the large contribution from secondary aerosols. However, a simple description of the aerosol in a kind of a flow reactor downwind of Milan cannot be expected owing to the patchy emissions. Fresh emissions are always mixed into chemically aged air masses. The NH_3 emissions are one of the driving forces for the inorganic aerosol formation. However, an adequate spatially and temporally resolved emission inventory was not available, and atmospheric NH_3 concentration measure-

ments to validate the plausibility of such an inventory do not exist.

[37] Aerosol formation in the model world has a very minor influence on ozone formation. The two most important processes that couple the photooxidant and aerosol formation are not yet in the models: There is no feedback of the aerosol levels on the radiation properties, and there is no reaction of radicals with aerosol surface or within water droplets. For example, the plume that arrived in Verzaggo in the early afternoon caused a 10% drop of the $j\text{NO}_2$ values at the surface [*Thielmann et al.*, 2002].

[38] The representation of the vertical mixing in the models has an important influence on the VOC/NO_x sensitivity. In the analysis of *Spirig et al.* [2002], model calculations predicted a NO_x -sensitive O_3 production in the residual layer earlier in the day. Lidar measurements on the Arat aircraft confirm that there was an increase in O_3 concentration above the mixing layer: The analysis of the flight on the morning of June 2 (0930 LST to 1030 LST) indicates a mean net ozone production decreasing from 10 to 2 $\text{ppb}^{-1} \text{ h}$, going from 700 m above sea level (asl) to 1200 m asl. However, these increases are not significant owing to the large scatter of the data. We cannot determine whether the ozone production in the residual layer is due to remaining precursors or due to fresh emissions, because we have no direct information on the vertical profiles of the parameters driving the ozone formation, that is, NO and the Odd-H levels. However, it is evident that ozone produced in the residual layer earlier in the day would influence the sensitivity of the O_3 concentration at the surface in the afternoon, most likely in an accentuation of NO_x sensitivity.

[39] The indicator concept introduced by *Sillman* [1995] and *Milford et al.* [1994] uses simple combinations of concentrations of reasonably long-lived species, such as O_3 , NO_2 , HNO_3 , and H_2O_2 , to discriminate between VOC- and NO_x -sensitive integrated ozone production. These species are well mixed in the PBL in the afternoon. Ground-based measurements can therefore be regarded as representative for the whole boundary layer. The transition values found by the different Eulerian models essentially confirm the values *Sillman* [1995] derived from runs for the eastern part of the United States. However, the transition values are sensitive to the dry removal mechanism in the model that has to be improved in a next model generation. In addition, the transition value of the ratio $\text{H}_2\text{O}_2/\text{HNO}_3$ is probably shifted to slightly lower values owing to an overestimation of the indicator ratio at the inflow borders.

[40] The PIPAPO field campaign showed that the relevant spatial scale for the ozone production in the Milan plume is 10 to 30 km. Peak values of ozone, secondary aerosols, and other photooxidants are reached within a few tens of kilometers from the major emission sources. It is on this scale that reduction strategies have to be assessed. PIPAPO looked at two periods of only a few days. Extrapolation of the analysis to the seasonal scale relevant for reduction strategies and application was not in the scope of the PIPAPO activity. Nevertheless, we are convinced that the model approaches used in the PIPAPO studies can be extended to longer timescales to get the integrated NO_x/VOC sensitivity for the whole summer. The analysis also shows that the measuring network in the Po Basin could be complemented by indicator species in order

to get an independent approach of the spatial and temporal variability of the ozone production sensitivity based on field measurements.

[41] The PIPAPO field campaign has reached its main goal: a consistent description of the VOC/NO_x sensitivity of the ozone production in the Milan plume for typical summer conditions. The findings have to be expanded in five directions.

1. Model simulations must include an aerosol module that treats aerosol—photochemistry—radiation feedbacks, especially the modifications to global radiation due to the aerosol loading.

2. Model simulations must cover a full year in order to get the sensitivities for seasonal averages of ozone and aerosol levels.

3. For the validation of the aerosol module, field data on aerosol speciation and vertical profiles, especially of radiation properties in the lowest layers, must be available.

4. The investigations on the role of biogenic emissions, both VOCs and NO_x, must be improved. Approaches for obtaining regionally integrated fluxes of isoprene, related oxidation products of isoprene, terpenes and carbonyl compounds have to be implemented.

5. Emission inventories must be improved. In particular, spatially highly resolved NH₃ inventories are a prerequisite for a reliable simulation of the aerosol level.

[42] The situation in the Milan area calls for a second project focused on the interaction of secondary aerosol formation and photooxidant production. Because the highest aerosol levels are found during the stagnant winter conditions, the measurements should also include winter campaigns.

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References

Alicke, B., U. Platt, and J. Stutz, Impact of nitrous acid photolysis on the total hydroxyl radical budget during the Limitation of Oxidant Production/Pianura Padana Produzione di Ozono study in Milan, *J. Geophys. Res.*, **107**, 10.1029/2000JD000075, in press, 2002.

Baltensperger, U., et al., Urban and rural aerosol characterization of summer smog events during the Pianura Padana Produzione di Ozono field campaign in Milan, Italy, *J. Geophys. Res.*, **107**, 10.1029/2001JD001292, in press, 2002.

Carter, W. P. L., Computer modeling of environmental chamber measurements of maximum incremental reactivities of volatile organic compounds, *Atmos. Environ.*, **29**, 2513–2527, 1995.

Derwent, R. G., M. E. Jenkin, and S. M. Saunders, Photochemical ozone creation potentials for a large number of reactive hydrocarbons under European conditions, *Atmos. Environ.*, **30**, 181–199, 1996.

Dommen, J., A. S. H. Prévôt, B. Neisinger, and M. Baumle, Characterization of the photooxidant formation in the metropolitan area of Milan from aircraft measurements, *J. Geophys. Res.*, **107**, 10.1029/2000JD000238, in press, 2002.

Dosio, A., S. Galmarini, and G. Graziani, Simulation of the circulation and related photochemical ozone dispersion in the Po plains (northern Italy): Comparison with the observations of a measuring campaign, *J. Geophys. Res.*, **107**, 10.1029/2000JD000046, in press, 2002.

Hammer, M., B. Vogel, and H. Vogel, Findings on H₂O₂/HNO₃ as an indicator of ozone sensitivity in Baden-Württemberg, Berlin-Brandenburg, and the Po Valley based on numerical simulations, *J. Geophys. Res.*, **107**, 10.1029/2000JD000211, in press, 2002.

Kleinman, L. I., Low and high-NO_x tropospheric photochemistry, *J. Geophys. Res.*, **99**, 16,831–16,838, 1994.

Kleinman, L. I., P. H. Daum, J. H. Lee, Y. Lee, L. J. Nunnermacker, S. R. Springston, and L. Newman, Dependence of ozone production on NO and hydrocarbons in the troposphere, *Geophys. Res. Lett.*, **24**, 2299–2302, 1997.

Kleinman, L. I., P. H. Daum, D. G. Imre, J. H. Lee, Y.-N. Lee, L. J. Nunnermacker, S. R. Springston, and L. Newman, Ozone production in the New York City urban plume, *J. Geophys. Res.*, **105**, 14,495–14,511, 2000.

Maffei, G., M. Longoni, A. De Martini, and M. Tamponi, Emissions estimate of ozone precursors during PIPAPO campaign, paper presented at Photochemical Oxidants and Aerosols in Lombardy Region, Milan, Italy, June 1999.

Martilli, A., A. Neftel, G. Favaro, F. Kirchner, S. Sillman, and A. Clappier, Simulation of the ozone formation in the northern part of the Po Valley, *J. Geophys. Res.*, **107**, 10.1029/2001JD000534, in press, 2002.

Meng, Z., D. Dabdub, and J. H. Seinfeld, Chemical coupling between atmospheric ozone and particulate matter, *Science*, **277**, 116–119, 1997.

Milford, J., D. Gao, S. Sillman, P. Blossy, and A. G. Russell, Total reactive nitrogen (NO_x) as an indicator for the sensitivity of ozone to NO_x and hydrocarbons, *J. Geophys. Res.*, **99**, 3533–3542, 1994.

Prévôt, A. S. H., J. Staehelin, G. L. Kok, R. D. Schillawski, B. Neisinger, T. Staffelbach, A. Neftel, H. Wernli, and J. Dommen, The Milan photo-oxidant plume, *J. Geophys. Res.*, **102**, 23,375–23,388, 1997.

Puteaud, J. P., R. Van Dingenen, and F. Raes, Submicron aerosol mass balance at urban and semi-rural sites in the Milan area (Italy), *J. Geophys. Res.*, **107**, 10.1029/2001JD000111, in press, 2002.

Sillman, S., The use of NO_y, H₂O₂ and HNO₃ as indicators for O₃-NO_x-VOC sensitivity in urban locations, *J. Geophys. Res.*, **100**, 14,175–14,188, 1995.

Spirig, C., A. Neftel, L. Kleinman, and J. Hjorth, NO_x versus VOC limitation of O₃ production in the Po valley: Local and integrated view based on observations, *J. Geophys. Res.*, **107**, 10.1029/2001JD000561, in press, 2002.

Staffelbach, T., et al., Photochemical oxidant formation over southern Switzerland, 1, Results from summer, 1994, *J. Geophys. Res.*, **102**, 23,345–23,362, 1997a.

Staffelbach, T., A. Neftel, and L. W. Horowitz, Photochemical oxidant formation over southern Switzerland, 2, Model results, *J. Geophys. Res.*, **102**, 23,363–23,374, 1997b.

Stutz, J., B. Alicke, and A. Neftel, Nitrous acid formation in the urban atmosphere: Gradient measurements of NO₂ and HONO over grass in Milan, Italy, *J. Geophys. Res.*, **107**, 10.1029/2001JD000390, in press, 2002.

Thielmann, A., A. S. H. Prévôt, F. C. Gruebler, and J. Staehelin, Empirical ozone isopleths as a tool to identify ozone production regimes, *Geophys. Res. Lett.*, **28**, 2369–2372, 2001.

Thielmann, A., A. S. H. Prévôt, and J. Staehelin, Sensitivity of Ozone Production derived from Field Measurements in the Italian Po Basin, *J. Geophys. Res.*, **107**, 10.1029/2000JD000119, in press, 2002.

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