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ESTIMATING LONG TERM POPULATION EXPOSURE TO OZONE
IN URBAN AREAS OF EUROPE

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Abstract   Tropospheric ozone concentrations regarded as harmful for human health are frequently encountered in central Europe in summertime. Although ozone formation generally results from precursors transported over long distances, in urban areas local effects, such as reactions due to nearby emission sources, play a major role in determining in ozone concentrations. Europe-wide mapping and modeling of population exposure to high ozone concentrations is subject to many uncertainties, because small-scale phenomena in urban areas can significantly change ozone levels from those of the surroundings. Currently the integrated assessment modeling of European ozone control strategies is done utilizing the results of large-scale models intended for estimating the rural background ozone levels. This paper presents an initial study on how much local nitrogen oxide (NO_x) concentrations can explain variations between large-scale ozone model results and urban ozone measurements, on one hand, and between urban and nearby rural measurements, on the other. The impact of urban NO_x concentrations on ozone levels was derived from chemical equations describing the ozone balance. The study investigated the applicability of the method for improving the accuracy of modeled population exposure, which is needed for efficient control strategy development. The method was tested with NO_x and ozone measurements from both urban and rural areas in Switzerland and with the ozone predictions of the large-scale photochemical model currently used in designing Europe-wide control strategies for ground-level ozone. The results suggest that urban NO_x levels are a significant explanatory factor in differences between urban and nearby rural ozone concentrations and that the phenomenon could be satisfactorily represented with this kind of method. Further research efforts should comprise testing of the method in more locations and analyzing the performance of more widely applicable ways of deriving the initial parameters.

Keywords: tropospheric ozone, health effects, nitrogen oxides, titration, Switzerland

1   INTRODUCTION

Elevated concentrations of ozone at ground-level are known to cause negative impacts on human health, ecosystems and materials. Average ozone concentrations in the troposphere have been rising

during this century as a result of increased input of the precursors of ozone, nitrogen oxides (NO_x) and volatile organic compounds (VOC), into the atmosphere. Today the lowest annual average tropospheric ozone concentrations in remote background areas in Europe range between 20-45 nmol mol^{-1}. During local short-time episodes concentrations of about two hundred nmol mol^{-1} can be encountered, whereas for example in the 1870's the yearly average concentrations measured around Paris were 10 nmol mol^{-1} or less (Anfossi, 1997*)*. In recent years there has been an increased concern about European population and vegetation being exposed to harmful ozone concentrations. Reviewing existing scientific literature, the World Health Organization (WHO) and the Working Group on Effects of the UN/ECE Convention on Long-range Transboundary Air Pollution have established threshold values for the protection of human health and vegetation, respectively (Fuhrer *et al.,*1997; WHO, 1995). With these levels, of all the compounds present in troposphere, ozone has the smallest margin between natural background levels and those considered harmful to human health and ecosystems.

In brief, ozone levels experienced at a certain location are influenced by

(i)   the hemispheric concentrations of ozone in the free troposphere (resulting from emissions in the northern hemisphere),

(ii)   the ozone generated by long-range transport of the precursor emissions over a scale of several hundreds to thousand of kilometers,

(iii)   locally increased ozone production downwind of sources of precursor emissions (in sunny weather),

(iv)   local destruction of ozone (titration) due to nearby NO_x emissions (particularly important at sites close to high NO_x emissions, *i.e.* in urban areas),

(v)   deposition of ozone to the ground, which depends on surface roughness and turbulent movement of the lowest part of the atmospheric boundary layer.

The lifetimes of many precursor emissions and their conversion products in the atmosphere are sufficiently long to be transported over long distances in the atmosphere. Consequently, the large-scale 'background' level of ozone has a strong long-range transport component determined by a wide range of emission sources. On the other hand, the modifying factors listed above (plumes, titration, deposition) depend strongly on small-scale geographical and meteorological conditions and superimpose local variations on the large-scale background level. Local emissions (*e.g.* in urban areas) decrease ozone close to the sources and increase ozone levels in the downwind plumes. At mountain tops reaching into the atmospheric mixing layer, the absence of local NO_x emissions and the minor importance of deposition to the ground as ozone removing mechanisms lead to less ozone destruction. Meteorological conditions at coastal sites (land-sea circulation of polluted air masses) and low ozone deposition over the water surface often lead to locally increased ozone levels compared to large-scale background.

Control of ground-level ozone in Europe has been the subject of international emission reduction agreements within the European Union and the UN/ECE Convention on Long-range Transboundary Air Pollution (European Commission, 1999; UN/ECE, 1999). Both processes have derived their quantitative emission reduction targets from an 'effects-based' rationale. While the environmental objectives (protection levels for human health and nature) were decided on a political basis, integrated assessment models were used to identify the set of cost-effective measures to reduce the emissions of the various substances to achieve the environmental objectives (Amann, 1995).

Due to the large geographical area in concern, present integrated assessment models work with a relatively coarse spatial resolution and put their focus on large-scale (rural background) ozone concentrations. While they (have to) ignore small-scale variations in ozone levels caused, *e.g.* by local

meteorological effects or near-by emission sources, they emphasize the reduction of large-scale background ozone to be achieved by internationally coordinated measures down to levels at which local measures can be effective to eliminate remaining local problems. On the other hand, this limited spatial resolution of the modeling exercise introduces certain inaccuracies when estimating population exposure to elevated ozone levels. 'Rural background' ozone as calculated by the present integrated assessment models tends to overestimate ambient levels in urban areas, and underestimate ozone concentrations prevailing in urban plumes. Accurate modeling of these small-scale and short-term effects posing risk to human health is a demanding task and requires detailed atmospheric models. The demand for high-quality input data and computer time imposed by such models makes it impractical to apply them for a continental scale analysis.

Recognizing the practical difficulties in large-scale modeling of these small-scale effects, this paper explores possible improvements of large-scale estimates by superimposing some of the 'local' factors. With an emphasis on health effects, the paper concentrates on the 'titration effect', *i.e.* the destruction of ozone by fresh NO emissions. The key question is to what extent titration can explain differences between rural background and observed ozone levels in urban areas, and how small-scale information on urban NO_x levels could be used to improve the accuracy of population exposure estimates derived from large-scale modeling. Section 2 of this paper summarizes the basic chemistry of ozone formation and highlights the role of titration, and Section 3 introduces the hypothesis of this study. Section 4 reviews the monitoring database and the large-scale ozone model, the EMEP ozone model, underlying the assessment. Results of the calculations are presented in Sections 5 and 6. Section 7 examines the results of the study in terms of the long-term accumulated ozone exposure index, which was used in the international control strategy development, and conclusions are drawn in Section 8.

2   BASIC OZONE CHEMISTRY IN THE TROPOSPHERE

Ambient levels of ozone are a result of complex chemistry with several thousands of known chemical reactions (*e.g.* Colbeck and McKenzie, 1994). Essentially, increased ozone levels occur in the presence of NO_x , VOC and sunlight. An ozone molecule is produced through the recombination of molecular oxygen (O_2) and atomic oxygen ($O(^3P)$). In the presence of solar energy, hν, the NO_2 molecule may dissociate into NO and O as follows:

$$NO_2 + h\nu \quad \rightarrow \quad NO \quad + O(^3P) \tag{1}$$

Then the recombination of O and O_2 will occur:

$$O(^3P) + O_2 + M \quad \rightarrow \quad O_3 \quad + M \tag{2}$$

where M is any inert molecule. On the other hand, the NO molecule may undergo a rapid reaction with ozone molecule:

$$NO \quad + O_3 \quad \rightarrow \quad NO_2 \quad + O_2 \tag{3}$$

The balance of these reactions is dependent on the solar energy and NO_x available. In the presence of VOC, there may occur series of chemical processes, which will convert NO to NO_2 and therefore reduce the possibility for reaction (3), resulting in net ozone production. If there is initially a lot of NO in relation to NO_2 , reaction (3) will be more dominant. A new equilibrium state with decreased ozone concentration will emerge. This is often referred to as the titration of ozone. It is known to be a significant factor diminishing ozone levels near NO_x emission sources and it has often been observed in urban ozone measurement studies. Titration is independent of solar energy and therefore reduces

ozone concentrations also during nighttime together with deposition to ground. Nitrogen oxides are mainly emitted as NO, most of which oxidizes in the atmosphere within a few minutes to form NO_2. Therefore, in the immediate surroundings of emission sources the share of NO in total NO_x (NO_x = sum of NO and NO_2) is higher than further away from the sources.

3   HYPOTHESIS OF THE STUDY - THE 'TITRATION MODEL'

Within the first few minutes after release, emissions of nitrogen oxides (NO_x) change the equilibrium ozone concentration from that of the surroundings. In the absence of other processes to convert NO to NO_2 and assuming steady state conditions, reactions (1), (2) and (3) can be written as

$$[O_3] = \frac{K \cdot [NO_2]}{[NO]} \tag{4}$$

with

$$K = \frac{j}{k} \tag{5}$$

j = photolysis rate coefficient (reaction (1)),

k = rate coefficient for reaction (3) and

where it is assumed that K is constant with height in the lower troposphere.

Following (Eleveld, 1997), the effect of titration on observed ozone concentrations due to local NO_x emissions can be quantified by assuming that the local ground-level NO_x concentration at an urban location $[NO_{x,U}]$ is the sum of background concentration found in rural areas $[NO_{x,R}]$ and the concentration induced by local emission sources $[\Delta NO_x]$:

$$[NO_{x,U}] = [NO_{x,R}] + [\Delta NO_x] \tag{6}$$

The share of NO_2 in NO_x concentrations resulting from nearby emissions can be assumed to be small, and written as:

$$[\Delta NO_2] = \alpha\,[\Delta NO_x], \tag{7}$$

with α=0.1 as a generally used value.

From equations (1) - (3) it can be concluded that the sum of oxidizing compounds $[O_x]=[O_3]+[NO_2]$ and $[NO_x]$ are constant. Therefore it can be stated that:

$$[O_{x,U}] = [O_{x,R}] + \alpha[\Delta NO_x] \tag{8}$$

Thus the new equilibrium ozone concentration due to the presence of $[NO_{x,U}]$ can be written as:

$$[O_{3,U}] = K \cdot \frac{[O_{x,U}] - [O_{3,U}]}{[NO_{x,U}] - [O_{x,U}] + [O_{3,U}]} \tag{9}$$

which yields only one non-negative solution for $[O_{3,U}]$.

In this study this equation (the 'titration model') was applied to both measured and modeled time series of NO_x and O_3 concentrations to explore to what extent it can explain (i) differences in measured ozone concentrations between urban and rural areas, and (ii) between measurements and the large-scale predictions of a continent-scale model.

Obviously, the estimation of K-factor is important for the application. The purpose of this study was to make initial testing of how significant explanatory factor titration is in the differences between ozone concentrations in urban and nearby rural locations and whether this kind of formulation would be able to represent the effect. Thus the K-factor was approximated from the available rural measurement data. For this we assumed that the concentration of VOC at the rural (background) stations is rather small, so that one can neglect the chemical reaction of VOC and assume that the reactions (1)-(3) will be in steady state for these stations. Under this assumption, equation (4) holds and one can approximate K as

$$K \approx \frac{[O_3].[\overline{NO}]}{[\overline{NO_2}]} \qquad (10)$$

where $[\overline{NO_2}]$ and $[\overline{NO}]$ represent the approximate rural concentrations, estimated from the monitored NO_x and NO_2 concentrations at the rural stations, and $[O_3]$ designates either the monitored rural ozone concentrations or the EMEP model's ozone prediction. The means of three-hour averages at the nearby rural stations were used in order to estimate the average rural conditions surrounding the urban stations. The averaging over three hours monitored data served to reduce the number of non-available measurements, and the purpose of averaging in general was to reduce the effects of local site-specific impacts and of individual errors in the monitoring data.

This initial estimation of K requires good-quality rural NO_x measurements, which are not available throughout Europe. For a wider integrated assessment modeling application the method should be further developed and tested. The estimation of K could be done for example by calculating the reaction rates from the actual radiation and temperature conditions, this urban 'down-scaling' perhaps being coupled with the large-scale models.

4   DATA USED IN THE STUDY

Due to the ready availability of detailed data on ozone and NO_x concentrations from a dense monitoring network, the study tested the hypothesis of the titration model for Switzerland. The study focused on ozone at rural and urban stations in the largest geographically and meteorologically uniform area in Switzerland, the central plateau area.

4.1   Monitoring sites

Monitoring results for total nitrogen oxides (NO_x), nitrogen dioxide (NO_2) and ozone (O_3) were provided by the Swiss national air pollution monitoring network NABEL. Data were available on an hourly basis, covering the six-month period from April to September 1994. A detailed description of monitoring stations and techniques is given in (BUWAL, 1997).

The locations of 10 monitoring sites were found useful for the purpose of this study. Four stations, Chaumont, Lägeren, Payerne and Rigi, are situated in rural background areas. Lägeren, however, is located about three kilometers from significant emission sources. Two stations, Härkingen and Sion, are located in countryside but close to freeways. The station in Basel is situated in a suburban surrounding and the Zürich station is representative for urban background situation. In addition to these eight stations which are located in the EMEP model's grid cell 23-13, two other stations in the neighboring EMEP grid cell 23-14 (Dübendorf and Tänikon) were included to enable inter-grid comparisons for similar geographical conditions. Tänikon is considered a rural station and Dübendorf is located in an agglomeration area about ten kilometers from Zürich.

Stations with special locations were left out of the study. Stations in Lausanne and Bern were excluded since they are located in street canyons, where micro-meteorological conditions are very different from those in more open areas, and accurate modeling of these effects would require a separate study with more monitoring sites. The mountain station at the Jungfraujoch (located 3600 m above sea level) and the station in Davos (1640 m) can not be considered to represent the conditions in the Swiss plateau region. Table 1 presents a description of the stations used in this work. The locations of the stations are shown in Figure 1 together with the EMEP model's grid system. Table 2 presents the annual volumes of NO_x emissions within five kilometer circles around each monitoring station in 1995, distinguishing four source categories.

4.2 Measured NO_x and ozone concentrations

In the monitoring data for 1994, large differences in the ratio of NO to total NO_x concentration occurred between the stations. At stations close to highways, there was a lot of NO in relation to NO_2, whereas especially at the rural stations the share of NO in total NO_x concentrations was quite small. As suggested by the hypothesis of this study, the differences in NO to NO_x ratios were clearly correlated with the observed patterns of ozone concentrations. Figure 2 shows typical distributions of hourly ozone data for (a) suburban (Basel), (b) roadside (Härkingen) and (c) rural (Payerne) stations. The graphs display the frequency distributions of all hourly monitored data including night hours (solid line) and of the 12 and 18 GMT values (dotted line). The figures indicate higher frequencies of low ozone concentrations in urban areas (Basel) and for stations close to highways (Härkingen) than for the rural stations (Payerne). In urban areas the lowest ozone concentrations (below 10 nmol mol^{-1}) occurred mainly during nighttime and in the early morning, when titration with NO and deposition to the ground are effective factors for destruction of ozone. This diurnal variation was also observed at rural sites, although due to less titration the daily minimums were somewhat higher than in urban areas (typically between 5 and 30 nmol mol^{-1}). At freeway stations the average O_3 concentrations were considerably lower than at the other locations because of the high NO concentrations.

4.3 Modeled ozone concentrations

In addition to observed ozone concentrations, this study also tested the hypothesis (the 'titration model') using modeled large-scale background concentrations of ozone. To this end, the analysis was based on results obtained from the photochemical model of the Meteorological Synthesizing Centre – West of the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP/MSC-W). It has developed a Lagrangian-type photochemical oxidant model covering the whole of Europe (EMEP/MSC-W, 1997; Andersson-Sköld and Simpson, 1999). This model is intended to estimate ozone levels in Europe over long periods of time (up to one year), and its results have been used in the development of the emission control agreements of the UN/ECE and the EU.

In the EMEP model, emission fields are represented by a 50 km $\times$ 50 km grid resolution, based on the EMEP emission database. The temporal variation of emissions is extracted from results of the GENEMIS (Generation of European Emission Data for Episodes) project. Meteorological data are taken from the Norwegian Numerical Weather Prediction (NWP) model (Grønås, 1982), (Grønås, 1986), (Nordeng, 1986). The EMEP model calculates photochemical reactions and transport of air pollutants in a single atmospheric layer with a horizontal resolution of 150 km $\times$ 150 km, applying a chemical scheme with about 140 reactions and 70 species. Ground-level ozone concentrations throughout Europe are computed with a 6-hour time-step, at 0, 6, 12 and 18 GMT. Due to its coarse spatial resolution, the model is mainly designed for estimating ozone values in rural background areas and it is not suited for describing phenomena occurring in cities.

This study uses model calculations conducted for the meteorology of the 1994 summer period (April 1st – September 30th) as input. In order to treat the measurement data in a comparable way with the EMEP model output, the average of the measurements at noon, 1 pm and 2 pm, was assumed to represent the EMEP 12 GMT value. Correspondingly, the average of the measurements at 6 pm, 7 pm and 8 pm was used to represent the EMEP 18 GMT value. The monitoring data used in Sections 5 and 6 refer to these values.

5 CASE 1: TEST OF THE TITRATION MODEL WITH OBSERVED BACKGROUND DATA

A first analysis tested the hypothesis of the titration effect with observed rural background ozone levels as a starting point. The time series representing the mean concentration of the four rural stations in the EMEP grid cell 23-13 (Chaumont, Lägeren, Payerne and Rigi) was assumed to reflect the daytime ozone background levels. Time series of NO and NO_2 concentrations observed at the urban monitoring sites were taken as the second explanatory variable. With this set of data, ozone concentrations at the four urban or roadside stations of the grid cell 23-13 were calculated using the titration model (equation 9) and compared with the monitoring results. Overall, application of the titration model significantly improved the correlation (r^2) between observed rural background ozone and locally observed ozone. For the urban stations, the correlation coefficient increased from 0.80 to 0.89 (Basel) and from 0.83 to 0.94 (Zürich). More significant improvements were achieved for the freeway stations, where the nearby NO_x emissions are bigger. The correlation coefficients are given in Table 3.

Figure 3.(a) shows the calculated and observed frequency distributions at the Zürich station. Measured rural background ozone used as the starting point for the calculation is displayed with a dashed line. The calculated ozone derived from the monitored rural ozone with local NO_x concentrations is drawn with a solid line, while ozone observed at the site is plotted with a dotted line. It is interesting to note that the inclusion of the titration effect improves the fit over the entire range of ozone concentrations. While the frequency of lower concentrations is somewhat overestimated, the approach misses some individual concentration peaks. The results indicate that the titration effect as characterized in equation (9) could be used to improve the quality of high-resolution ozone mapping exercises, which are relevant for determining the potential health hazards from elevated ozone levels. While at present most mapping activities conduct a 'simple' spatial interpolation of ozone observed at the available monitoring sites, this method could improve the accuracy of these estimates.

6 CASE 2: TEST OF THE TITRATION MODEL WITH MODELED BACKGROUND DATA

6.1 Urban ozone measurements and large-scale model predictions

A second test was performed to determine to what extent local NO_x concentrations could explain differences between background ozone predicted by the large-scale model and the observed ozone levels in urban areas. For this purpose, the EMEP ozone predictions for 12 and 18 GMT were used as the initial time series [$O_{3,R}$] for the calculations. Equation (9) was used to quantify changes in ozone concentrations induced by titration with local NO_x emissions.

Also in this case the introduction of the titration effect improved the correlation between observations and large-scale model results at all stations. The correlation coefficients are given in Table 3. Figure 3.(b) compares the calculated frequency distributions against the large-scale model data and the observations at the Zürich station. Calculated ozone concentrations (derived from the modeled

background ozone and observed local NO_x concentrations) are plotted as a solid black line and the site observations with a dotted line. For reference, the modeled background ozone concentrations (for EMEP cell 23-13) are provided with a dashed line.

The results of the analysis support the hypothesis that titration with NO is an important factor responsible for small-scale variations in ozone levels and that it could be represented with this kind of method. Though the resulting overall match between locally observed and modeled background concentrations is not as good as in the first case, significant improvements were achieved by the introduction of the titration effect.

6.2   Sensitivity of the method to starting-point data

The above analysis used the background concentration calculated for the EMEP grid cell 23-13, in which the test sites are located. However, some of the urban and roadside stations investigated are situated close to the borders of the grid cell. Consequently, a sensitivity analysis was conducted in which the rural background ozone concentration was calculated as the average ozone time series of the two neighboring grid cells. In all cases the correlation between the site measurements and the modeled data was further improved (Table 4). Figure 4 shows the correlations between the ozone measurements and the various calculated time series for the Zürich station. The relative importance of each of the initial concentrations and of the assumed reaction parameters was also determined analytically with typical summer day parameter values. The rural background ozone concentration $[O_{3,R}]$ and the reaction rate term K were the most significant variables. Next were $[NO_U]$ and $[NO_{2,R}]$, while the other variables had considerably less significance.

7   HARMFUL LONG-TERM OZONE LEVELS

The amount of potentially harmful ozone concentrations to which population is subjected in a certain area can be represented by an index number indicating the total amount of high concentrations over a whole summer period. The index currently used as a surrogate for adverse health effects in the modeling work of the European emission reduction strategies is denoted with a concept called Accumulated Ozone exposure over Threshold of 60 nmol mol^{-1} (AOT60). It reflects the WHO guideline which sets a limit of 120 µg/m^3 (60 nmol mol^{-1}) for possible adverse health effects as an eight-hour moving average, and it attempts to indicate both the amount and the frequency of exceedances of the guideline. For the purposes of this study, it was written as follows:

$$AOT60 = \int max([O_3] - 60 nmol \cdot mol^{-1}, 0) dt \tag{11}$$

where the integral is taken over the whole summer period (April-September) and the unit time step is eight hours.

AOT60 values were calculated from hourly measurement data by using all non-overlapping eight-hour time periods in which the eight-hour average exceeded 60 nmol mol^{-1}. Each such average was weighted by eight hours. The EMEP model produces six-hourly ozone concentrations. AOT60 values were evaluated from the model data by using the 12 GMT and 18 GMT during the period April – September of 1994, assuming that each value represents a six-hour period.

7.1   Variation of AOT60 within the study area

In this study, the highest AOT60 values were observed in rural areas at elevated locations (700 – 1100 meters above sea level), while in urban and suburban areas the AOT60 levels were considerably lower. Lower AOT60 levels in urban areas are a direct consequence of the lower ozone concentrations induced by titration. Table 5 presents the AOT60 values obtained from the measurements (a), and from

the EMEP model predictions (b). At elevated locations, the absence of strong ozone destroying mechanisms (titration with local NO_x emissions, deposition on ground) is known to result in higher ozone concentrations particularly at night time (*e.g.* Achermann and Rihm, 1997; Loibl, 1994). This effect is clearly demonstrated by the high AOT60 values observed in Chaumont at 1140 meters and in Rigi at 1030 meters above sea level. The rural station in Lägeren, situated 45 meters above ground, reflects ozone concentrations in the atmospheric boundary layer rather than at ground-level.

7.2   Urban AOT60 values calculated from background concentrations using the titration model

Figure 5 compares the background AOT60 values with urban site observations and with the AOT60 values derived from background concentrations using the titration model for the Basel, Härkigen, Sion and Zürich sites. In Figure 5.(a) the black bars represent the AOT60 index obtained from the average ozone time series of the four rural stations in the EMEP grid cell 23-13. The gray bars show AOT60 calculated from the hourly site measurements, and the striped bars result from the calculations described in Section 5, utilizing the average rural time series. In Figure 5.(b) the black bars represent the AOT60 index obtained from the modeled time series, averaged over the two closest grid cells for Basel, Sion and Zürich. The gray bars indicate again the AOT60 calculated from the hourly site measurements, and the striped bars are the results of the calculations described in Section 6, using the model data as starting point.

Figure 6 shows that the titration model improves the estimation of the AOT60 index at all sites. In this study, with respect to AOT60 the utilization of average rural observations was less successful than the use of modeled ozone time series as starting point. Especially for Basel, the use of rural time series gave too high results. This is probably because the rural observations used were not fully representative for the lower Plateau region, as discussed above. In addition, the AOT60 index is a very sensitive measure since it incorporates only a minor part of the whole data set. A systematic error of a few percent either in the observed or in the modeled ozone concentrations can result in large deviations of the AOT60 value, as illustrated for example in (EMEP/MSC-W, 1998). Therefore these AOT60 results should be considered only indicative. The results calculated with the whole data sets, as shown in Sections 5 and 6, demonstrate more comprehensively the performance of the tests.

8   CONCLUSIONS

This study presented the initial results of estimating the impact of local NO_x levels on ozone concentrations in urban areas with a simple chemical equilibrium model together with information about background ozone levels. The aim was to find methods to improve the precision of integrated assessment modeling of population subjected to ozone concentrations regarded hazardous for health in Europe, which is currently done with large-scale models intended for estimating the rural background ozone levels. The method was tested with monitoring data from a dense network in Switzerland. The results suggest that urban NO_x emissions are a significant explanatory factor in differences between urban and nearby rural ozone levels and that it could be satisfactorily represented with this kind of method. In this study the chemical equilibrium coefficient was estimated from background monitoring data. Thus the accuracy of the estimate depended on the quality of the monitoring data. For wider applications in integrated assessment modeling the methodology should be developed towards utilizing calculated parameters to avoid dependence on dense high-quality monitoring networks. Further research efforts should comprise testing of the method in more locations and analyzing the performance of the more widely applicable ways of deriving the initial parameters.

The study indicated that with this methodology, also rural ozone measurements together with the calculated effect of urban NO_x levels could be applied in the mapping of urban population presently exposed to harmful ozone concentrations. The method tested here could be used for extrapolating ozone concentrations from single measurement points together with NO_x concentration information, derived from spatially detailed emission data or from local measurement networks.

In estimating health effects, both ozone and NO_2 levels should be considered. In cities, the titration reaction shifts the oxidant balance towards NO_2. Also in the urban areas studied here exceedances of both WHO ozone guidelines and national NO_2 guidelines were recorded. Moreover, as synergistic interactions in the exposure of respiratory mechanisms to both NO_2 and ozone have been suggested as well (see a review by Kley *et al.*, 1999), the importance of considering these pollutants jointly in the integrated assessment modeling of control strategies is emphasized.

This kind of methodology could also be used in assessing the co-impacts of the international emission reductions and local policies on health risks to population caused by high ozone and NO_2 concentrations. Considerable future improvement in the general background ozone levels is expected as a result of the recent emission reduction plans of the UN/ECE and the EU. This kind of methodology could be applied to predict the combined effects of international emission reductions and changes in local emissions on the future ozone and NO_x levels in urban areas for effective further control strategy development.

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TABLES AND FIGURES

Table 1. Monitoring stations used in the study**.**

Table 2. NO_x emissions in five kilometer radius in 1995 from the measurement stations (ton NO_2).

Table 3: Correlation coefficients between measurements and the calculated ozone time series.

Table 4. Correlation coefficients between observations and the model data, showing the effect of averaging over the two closest grid cells.

Table 5. AOT60 values in 1994 in the study area. (a) Observed values, (b) values from the EMEP model.

Figure 1. The locations of measurement stations used in the study and the EMEP grid.

Figure 2. Typical ozone concentration patterns (a) at a suburban station (Basel), (b) near a major road (Härkingen), and (c) at a rural station (Payerne).

Figure 3. Measured and calculated daytime ozone concentrations in Zürich. Dotted lines represent ozone concentrations measured at the site. (a) Solid line shows the concentrations calculated from equation (9) using the average rural ozone measurements and NO_x concentrations measured at the site. Dashed line designates the average rural ozone time series used as the starting point. (b) Solid line shows the concentrations calculated from equation (9) using the EMEP model's ozone predictions and NO_x concentrations measured at the site. Dashed line designates the EMEP model predictions for the grid cell in concern.

Figure 4. (a) Correlation between daytime measurements and the EMEP grid cell 23-13 ozone predictions, (b) correlation between measurements and the EMEP ozone predictions averaged over the two nearest grid cells, (c) correlation between measurements and the values calculated with equation (9) from EMEP ozone predictions and local NO_x concentrations, and (d) correlation between measurements and the values calculated with equation (9) from rural ozone measurements and local NO_x concentrations. Concentrations are given in nmol mol $^{-1}$.

Figure 5. AOT60 evaluated at urban and freeway stations of the EMEP grid cell 23-13. Gray bars denote AOT60 calculated from the hourly measurements. (a) Black bars show AOT60 evaluated from the average rural ozone time series. Striped bars show the values obtained by applying equation (9) to rural ozone measurements. (b) Black bars show AOT60 evaluated from the modeled data, averaged over two nearest grid cells except for Härkingen. Striped bars show the values obtained by applying equation (9) to the modeled data.