

Photochemistry of VOCs in the Boreal Zone

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Introduction

The boreal regions are characterised by strong seasonal cycles of both emissions and photochemical activity. The southern parts of the areas between the latitudes 60°N and 70°N are densely forested and even in the very north the land is covered by vegetation. The population is sparse and the anthropogenic activities relatively few and scattered. Thus, in contrast with the industrialised Central European areas, the emission patterns of volatile organic compounds (VOCs) are often dominated by biogenic emissions (e.g. Guenther et al., 1995, Simpson *et al.*, 1995).

In winter, the land is covered by snow, deciduous vegetation is barren, and the availability of solar radiation is very limited - north of the Arctic Circle (66°30'N) the sun does not even rise above the horizon for time periods that may last from a few days to almost two months, depending on the latitude. Because their photochemical cycles are stopped, volatile organic compounds and other anthropogenic emissions accumulate in the high latitude regions of the northern atmosphere. When the sun returns in spring, the onset of photochemistry leads to the rise of the background ozone concentration (e.g. Derwent *et al.*, 1998). The seasonal cycle of biogenic emissions is also profoundly affected by the shortness of the vegetation period at the more northern latitudes. However, the biogenic VOCs are highly reactive (e.g. Hakola *et al.*, 1993; Hakola *et al.*, 1994), and their emissions tend to peak under sunny high pressure conditions, which are also favourable for photochemical ozone formation. In general, the formation of photochemical ozone in the boreal regions is considered to be limited by the availability of nitrogen oxides, but when polluted plumes from the more industrialised areas are carried over the boreal forests, the biogenic VOCs emitted by the vegetation add to the hydrocarbon supply in the air mass. Kleinman (1991) has shown that at lower UV-radiation

levels, typical of the higher latitudes, ozone production tends to be more sensitive to the VOC emissions because radical production is limited under these conditions.

Photochemistry in the boreal atmosphere

In the background boreal atmosphere, the most important photochemical cycles are the oxidation of isoprene (C_5H_8) and monoterpenes ($C_{10}H_{16}$), all of which are emitted in copious amounts by the boreal vegetation, as shown in the BIPHOREP project. The isoprene emissions are believed to be under enzymatic control, and they are strongly dependent on leaf temperature and visible light intensity. Terpene emissions are mainly regulated by leaf temperature. Thus, unlike isoprene whose emissions are practically nonexistent at night, monoterpenes can also be emitted in the dark. Once emitted, the biogenic VOCs quickly react with ozone and the hydroxyl and nitrate radical which contributes to the formation of ozone and influences the photochemical reaction cycles. They also produce organic acids, contributing to the deposition of acids, and are involved in the generation of organic nitrates and the formation of organic aerosols. The main atmospheric oxidation pathways of isoprene are presently quite well understood (e.g. Carter, 1996), and isoprene oxidation is included in several tropospheric chemistry models (e.g. Derwent *et al.*, 1996, Stockwell *et al.*, 1997, and models included in the CMWG Intercomparison of Kuhn *et al.* (1998)). Many aspects of terpene oxidation, however, are still unclear, although considerable progress has been made recently, even in establishing the aerosol formation rates (Becker, 1997, Hjorth *et al.*, 1997).

The application of photochemical models in the boreal regions is complicated by the often extremely low concentrations of key photochemical species in these clean background areas. Even though the photochemical models are developed according to best available laboratory knowledge of the reaction pathways and oxidation products of the various organic compounds, and may be tested rigorously against a wide spectrum of experimental smog chamber data, their performance under such extreme conditions remains an open question. Especially the smog chamber data bases are often inherently representative of highly polluted urban conditions, whereas in Europe long range transport, with several days of photochemical activity over rural areas, is considered to be more important than urban scale ozone formation (e.g. Derwent *et al.*, 1996). In the boreal regions, with NO and NO_x concentrations in the pptv range, the crucial role of NO_x concentration and the NO_x/VOC ratio in the photochemical oxidation (e.g. Madronich and Calvert, 1990, Kleinman, 1994) is even more pronounced. Also

other mechanisms or interactions that can be considered insignificant in more polluted chemical environments, may become important. Thus, the evaluation of the performance of photochemical models under these conditions is a complex task, requiring not only model runs and test scenarios, but also actual chemical and meteorological data representative of the local and regional emissions, chemical concentrations, and the photochemical capacity of the atmosphere.

Photochemical modeling in BIPHOREP

The field and laboratory measurements carried out in this project have created a unique data base of biogenic VOC and ozone concentrations, together with environmental and meteorological parameters which have been used in the development and testing of atmospheric chemistry models. Ambient measurements have shown that the most important biogenic VOC in the boreal zone are isoprene and terpenes such as pinene and limonene. To simulate the chemical degradation of these compounds in the troposphere and their impact on ozone formation, chemical mechanisms are required. Therefore the participants in the BIPHOREP project developed two new chemical mechanisms for the degradation of isoprene, pinene and limonene in the troposphere. A detailed description of these mechanisms is given in the following. However, the representation of the photochemical processes in these mechanisms varies, due to the lack and uncertainty of kinetic data and the choices of the mechanism developers. Therefore a detailed intercomparison of the two mechanisms with three scenarios was performed and the results are presented in the following. As a next step simple scenario studies were performed to assess the impact of anthropogenic NO_x emissions on the production of ozone and other photooxidants for typical boreal conditions.

Chemical Mechanisms

A new gas-phase chemical mechanism for the modelling of regional atmospheric chemistry, the "Regional Atmospheric Chemistry Mechanism" (RACM) has been developed (Stockwell *et al.*, 1997) by the IFU group. The new RACM mechanism is based upon the earlier Regional Acid Deposition Model chemical mechanism, version 2 (RADM2) (Stockwell *et al.*, 1990). It includes rate constants and product yields from the most recent laboratory measurements and it has been tested against environmental chamber data. The mechanism includes 17 stable inorganic species, 4 inorganic intermediates, 32 stable organic species and 24 organic intermediates. The chemical reactions of these species are treated in 237 reaction equations.

One of the major advantages for the new RACM mechanism is that a new condensed reaction mechanism is included for biogenic compounds: isoprene, α -pinene and d-limonene. Details of these mechanisms are given below. Also the branching ratios for alkane decay were re-evaluated and in the revised mechanism the aldehyde to ketone ratios were significantly reduced. The relatively large amounts of nitrates resulting from the reactions of unbranched alkenes with NO_3 reaction are now included and the production of HO from the ozonolysis of alkenes has a much greater yield. The aromatic chemistry has been improved through the use of new laboratory data. The amount of cresol production has been reduced and the chemistry of the unsaturated dicarbonyl species and the unsaturated peroxyxynitrate has been improved by including HO and NO_3 addition reactions and ozonolysis. The peroxyacetyl nitrate chemistry and the organic peroxy radical - peroxy radical reactions were improved and organic peroxy radical + NO_3 reactions were added.

Isoprene, which is emitted mainly by deciduous trees, is oxidised in the atmosphere through its reactions with HO, NO_3 and O_3 . RACM includes treatment of isoprene ozonolysis, hydroperoxide production and the production of carbonitrates from the reaction of isoprene with NO_3 . During the photochemical degradation of isoprene the secondary products methacrolein, methyl vinyl ketone and $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OONO}_2$ (MPAN) are formed. The reactions of methacrolein and MPAN with HO, NO_3 and O_3 are explicitly included in the new mechanism. The yield of methyl vinyl ketone is grouped with the RACM class for terminal alkenes. For the reaction of isoprene with NO_3 the fractions which add to the $\text{CH}_2=\text{CR}_2$ bond and to the $\text{CH}_2=\text{CHR}$ bond and the yields of 3-methyl-4-nitroso-2-butenal and HCHO were estimated using experimental data. The two reaction channels: (1) the channel that produces mostly carbonyl nitrates and (2) the channel that produces carbonyls and NO_2 are now separately included in the new isoprene mechanism.

The new oxidation mechanisms for α -pinene and d-limonene are based upon the limited available experimental data for terpene reactions. Because many of the reactions for α -pinene and d-limonene oxidation are unknown, our mechanism was completed by using reactions that were analogous to known reactions for lower alkenes. To include the large number of different monoterpenes in the mechanism it was necessary to group the individual monoterpenes into a few groups. This grouping was done according to similarities in rate constants and structure. Structure and rate constants of sabinene and Δ^3 -carene are similar to those of α -pinene,

Table 1. Meteorological conditions specified for all BIO scenarios.

Temperature:	298.15 K
Pressure:	1013.25 mbar
Simulation period:	5 Days, starting at noon of 1st day.
Photolysis frequencies:	prescribed for July 1, 45°N

therefore those terpenes are treated as α -pinene. Similarly terpinene and phellandrene are treated as limonene.

The FMI photochemical model is based on the U.K. photochemical trajectory model (U.K. PTM, Derwent *et al.*, 1996). The chemical mechanism describes the atmospheric oxidation of methane and 97 other VOCs, three of which are biogenic, together with CO, SO₂, and NO_x. In the FMI model version, the inorganic reactions and some of the light alkane oxidation pathways of the original U.K. PTM have been revised according to Saunders *et al.* (1997), Simpson *et al.* (1997), and Stockwell *et al.* (1997). The photolysis frequencies and special rate coefficients are calculated identically to the MCM mechanism (Atkinson *et al.*, 1997; Jenkin *et al.*, 1997). The rate coefficients of some key reactions have been updated (DeMore *et al.*, 1994). The FMI model version also includes a revised isoprene oxidation scheme based on Carter (1996), Saunders *et al.* (1997), and Simpson *et al.* (1997), and a simplified treatment of the oxidation of alpha-pinene and limonene, according to Atkinson (1994) and Stockwell *et al.* (1997). The mechanism development is aimed at model application to relatively clean (low-NO_x) background conditions, typical of the boreal vegetation zone.

The present version of the FMI photochemical model has 556 chemical species, which participate in over 1000 chemical and photochemical reactions. Time integration in the model is done by the variable time step method (Gear, 1971) using the commercial FACSIMILE v. 4.01 software package (© AEA Technology, Harwell, U.K.).

Scenarios for mechanism intercomparison

Based on the CMWG Intercomparison (Kuhn *et al.*, 1998) we have developed three scenarios that can be used to compare different mechanisms for the degradation of biogenic VOCs: BIO-ISO includes emissions of isoprene and NO_x while in BIO-POLLUTED and BIO-REMOTE

Table 2a. Initial concentrations identical for all BIO scenarios.

BIO (all)	
Initial concentrations:	
H ₂ O	1.0 %
O ₃	30 ppb
NO	0.1 ppb
NO ₂	0.1 ppb
HNO ₃ :	0.1 ppb
CO	100 ppb
CH ₄	1700 ppb
H ₂	500 ppb
H ₂ O ₂	2 ppb
HCHO	1 ppb

(Identical to the LAND scenario in CMWG intercomparison.)

Table 2b. Initial concentrations and emissions for the BIO scenarios.

BIO-:	ISO	REMOTE/POLLUTED
Initial concentrations:		
Isoprene	1.5 ppb	0.1 ppb
Limonene	0	0.05 ppb
α-pinene	0	0.5 ppb
EMISSIONS (cm⁻³ s⁻¹)		
Constant part		
NO	1.1E5	1.1E4 / 1.1E5
Limonene	0	4.1E4
α-pinene	0	1.6E5
Variable part	J(NO ₂) in s ⁻¹	M = 2.46E19 cm ⁻³
Isoprene	2.0E-11 x J(NO ₂) x M	2.0E-12 x J(NO ₂) x M
Limonene	0	1.0E-12 x J(NO ₂) x M
α-pinene	0	6.0E-12 x J(NO ₂) x M

isoprene, α-pinene, limonene and NO_x are emitted. The meteorological conditions (Table 1) and initial concentrations for all scenarios are identical to the LAND scenario of the CMWG Intercomparison except that additional initial biogenic VOCs are specified (Table 2); the temperature is 298 K. The emission rate of isoprene is a function of the photolysis frequency of NO₂, while for the terpenes an additional constant emission rate is superimposed to reflect the non-zero terpene emissions during the night. Emissions of NO are constant and are specified to be 1/10 of the PLUME1-scenario emissions for the BIO-ISO and BIO-POLLUTED scenario and 1/100 for the BIO-REMOTE scenario.

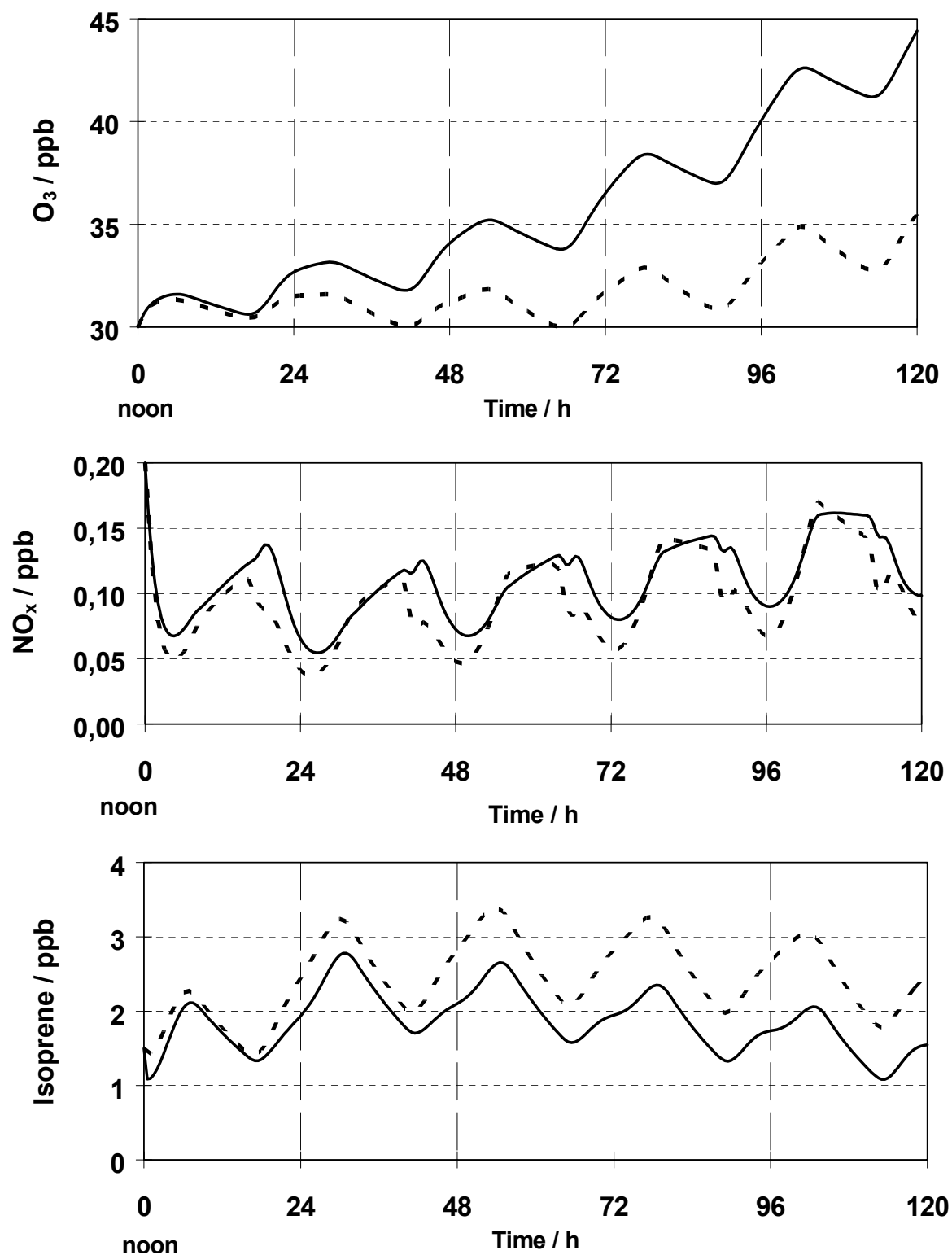


Figure 1. Mixing ratios of ozone, NO_x and isoprene for simulations of the BIO-ISO scenario for the RACM (black straight) and FMI (black dotted) chemical mechanisms.

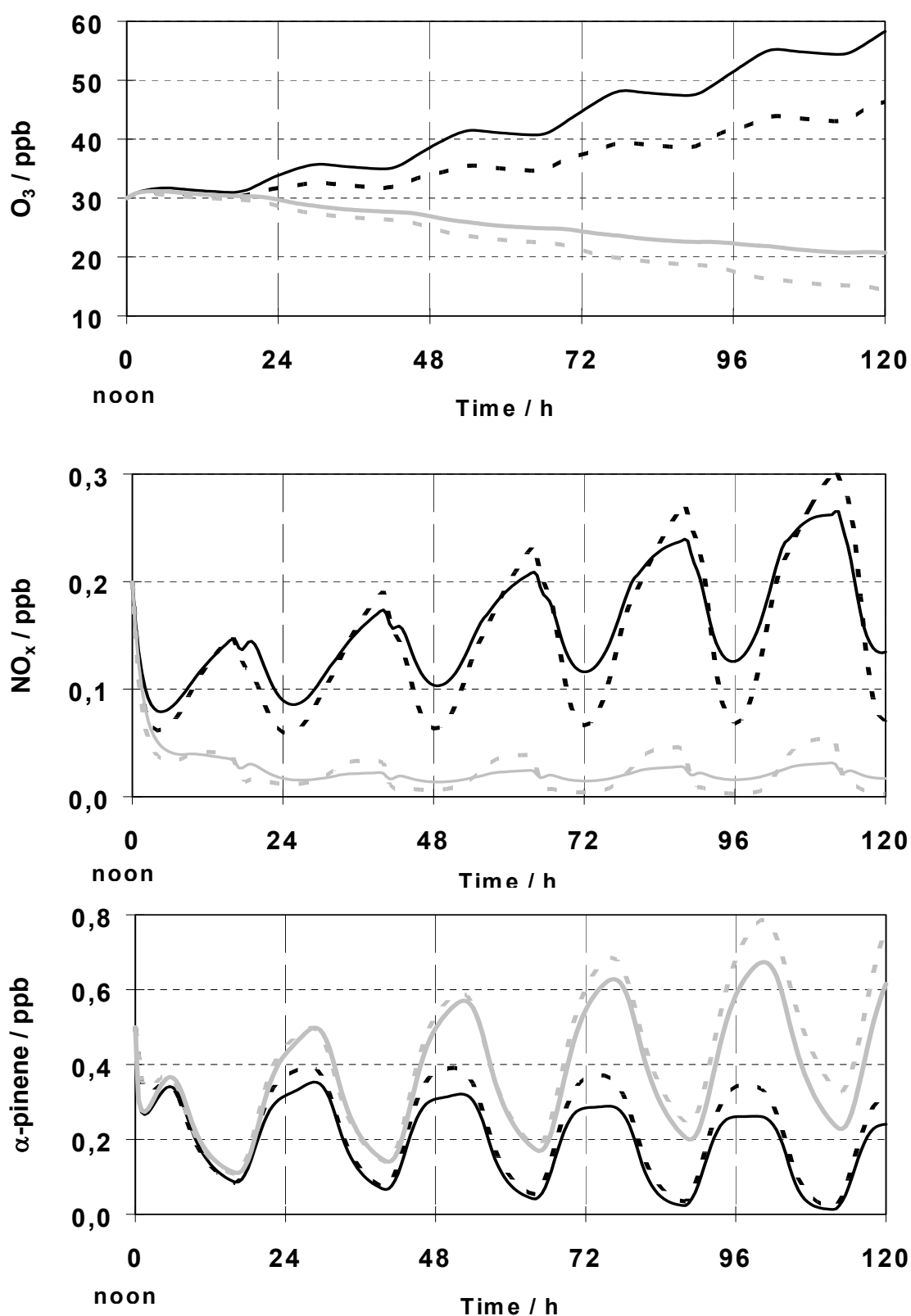


Figure 2. Mixing ratios of ozone, NO_x and α-pinene for simulations of the BIO-REMOTED (grey) and BIO-POLLUTED (black) scenarios for the RACM (straight line) and FMI (dotted line) photochemical mechanisms.

Results

The results for the BIO-ISO scenario (Figure 1), which is designed to test the isoprene degradation scheme in the two mechanisms of interest, show an ozone production for both mechanisms. The NO_x concentrations are lower than 200 ppt, which is typical for the boreal zone (Laurila et al., this volume). The isoprene concentrations in the BIO-ISO scenario are higher than usually observed in the boreal zone, but given the fact that in this scenario isoprene is the only biogenic VOC and therefore represents a whole range of compounds the concentrations are reasonable. The results of the two mechanisms agree quite well for ozone, NO_x and isoprene.

The BIO-REMOTE scenario is designed to be comparable to remote conditions as found in the remote boreal zone (Laurila et al., this volume). The NO_x mixing ratios are lower than 50 ppt and the concentrations of terpenes are below 1 ppb (Figure 2). Under these conditions ozone is depleted due to reactions with the biogenic VOCs which are not favoured by photochemical ozone production. Increasing the NO_x emissions by a factor of ten leads to a substantial increase in the photochemical ozone production, which results in increasing ozone mixing ratios in the BIO-POLLUTED scenario. This reveals that on the background of biogenic VOC emissions, anthropogenic NO_x emissions lead to a substantial production of O₃ and other photooxidants. Due to the higher oxidant concentrations in BIO-POLLUTED the mixing ratios for the biogenic VOC are lower as in BIO-REMOTE although the emissions are identical. Also for these scenarios with terpene and isoprene emissions the results of the two mechanisms agree very well considering the many unknowns in the photochemical degradation of complex biogenic VOCs like pinene and limonene.

Conclusions

The photochemical mechanisms of FMI and IFU lead to similar results with respect to the concentration levels and the temporal behaviour of key photochemical and biogenic compounds. While the inorganic reactions are rather identical in both mechanisms, they have a different representation of the degradation of biogenic VOCs and their reaction products. Based on the results of the BIPHOREP scenario test runs, we may, however, conclude that the degradation of biogenic VOCs and their impact on tropospheric chemistry is described consistently in both mechanisms. Sensitivity studies to the influence of NO_x on the ozone mixing ratios show that under low NO_x conditions (BIO-REMOTE scenario) ozone is depleted

in the boreal atmosphere, while with additional NO_x emissions the ozone concentration increases (BIO-POLLUTED scenario).

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References

Atkinson, R., 1994. Gas-phase tropospheric chemistry of organic compounds. *Journal of Physical and Chemical Reference Data*, Monograph No. 2, 1-216.

Atkinson, R., Baulch, D. L., Cox, R. A., Hampson, R. F., Kerr, J. A., Rossi, M. J., and Troe, J., 1997. *Journal of Physical and Chemical Reference Data* 26(3), 521-1011.

Becker, K.H. , 1997, Final report of the EC-Project The European Photoreactor EUPHORE, Contract EV5V-CT92-0059.

Carter, W. P. L., 1996. Condensed atmospheric photooxidation mechanisms for isoprene. *Atmospheric Environment* 30(24), 4275-4290.

DeMore, W. B., Sander, S. P., Golden, D. M., Hampson, R. F., Kurylo, M. J., Howard, C. J., Ravishankara, A. R., Kolb, C. E., and Molina, M. J., 1994. Chemical kinetics and photochemical data for use in stratospheric modeling, Evaluation number 11. JPL Publication 94-26, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA.

Derwent, R. G., Simmonds, P. G., Seuring, S., and Dimmer, C., 1998. Observation and interpretation of the seasonal cycles in the surface concentrations of ozone and carbon monoxide at Mace Head, Ireland from 1990 to 1994. *Atmospheric Environment* 32(2), 145-157.

Derwent, R. G., Jenkin, M. E., and Saunders, S. M., 1996. Photochemical ozone creation potentials for a large number of reactive hydrocarbons under European conditions. *Atmospheric Environment* 30(2), 181-199.

Gear, C. W., 1971. *Numerical initial value problems in ordinary differential equations*. Prentice-Hall, Englewood Cliffs, N.J.

Guenther A. B, Hewitt C. N., Erickson D., Fall R., Geron C., Graedel T., Harley P., Klinger R., Lerdau M., McKay W. A., Pierce T., Scholes R., Steinbrecher R., Tallamraju R., Taylor J., Zimmerman P. R., 1995. A global model of natural volatile organic emissions. *Journal of Geophysical Research* 100(D5), 8,873-8,892.

Hakola, H., S. Basima, J. Arey, and R. Atkinson, 1993. Product formation from the gas-phase reactions of OH radicals and O₃ with β -phellandrene. *Environmental Science & Technology* 27, 278-283.

Hakola, H., J. Arey, S. M. Aschmann and R. Atkinson, 1994. Product formation from the gas-phase reactions of OH radicals and O₃ with a series of monoterpenes. *Journal of Atmospheric Chemistry* 18, 75-102.

Hjorth, J. et al., 1997, Aerosol yields and gas-phase products from ozone initiated oxidation of α -pinene, β -pinene, and Δ^3 -carene. Results from the BIOVOC project, experiments made in the EUPHORE photoreactor, to be published.

Jenkin, M. E., Saunders, S. M., and Pilling, M. J., 1997. The tropospheric degradation of volatile organic compounds: A protocol for mechanism development. *Atmospheric Environment* 31(1), 81-104.

Kleinman L., 1991. Seasonal dependence of boundary layer peroxide concentration: The low and high NO_x regimes. *Journal of Geophysical Research* 96(D11), 20,721-20,733.

Kleinman, L. I., 1994. Low and high NO_x tropospheric photochemistry. *Journal of Geophysical Research* 99(D8), 16,831-16,838.

Kuhn, M., Builtjes, P.J.H., Poppe, D., Simpson, D., Stockwell, W.R., Andersson-Sköld, Y., Baart, A., Das, M., Fiedler, F., Hov, Ø., Kirchner, F., Makar, P.A., Milford, J.B., Roemer, M.G.M., Ruhnke, R., Strand, A., Vogel, B., Vogel H., 1998. Intercomparison of the Gas-Phase Chemistry in Several Chemistry and Transport Models. *Atmospheric Environment* 32(4), 693-709.

Madronich, S. and Calvert, J. G., 1990. Permutation reactions of organic peroxy radicals in the troposphere. *Journal of Geophysical Research* 95(D5), 5697-5715.

Saunders, S. M., Jenkin, M. E., Derwent, R. G., and Pilling, M. J., 1997. World wide web site of a master chemical mechanism (MCM) for use in tropospheric chemistry models. *Atmospheric Environment* 31(8), 1249.

Simpson, D., Guenther, A., Hewitt, C.N., and Steinbrecher, R., 1995. Biogenic emissions in Europe 1. Estimates and uncertainties, *Journal of Geophysical Research* 100(D11), 22875-22890.

Simpson, D., Olendrzynski, K., Semb, A., Storen, E., and Steffen, U., 1997. Photochemical oxidant modelling in Europe: multi-annual modelling and source-receptor relationships. EMEP/MSC-W Report 3/1997.

Stockwell, W. R., Kirchner, F., Kuhn, M. and Seefeld, S., 1997. A new mechanism for regional atmospheric chemistry modeling. *Journal of Geophysical Research* 102 (D22), 25847-25879.

Stockwell W. R., Middleton P., Chang J. S., Tang X., 1990. The second generation regional acid deposition model chemical mechanism for regional air quality modeling. *Journal of Geophysical Research* 95, 16343-16367.