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On the determining role of CO in local ozone production

I. Coll (1), F. Lasry (1), S. Fayet (2), M. Samaali (3), J.L. Ponche (3) and R. Vautard (4)

(1) Laboratoire Interuniversitaire des Systèmes Atmosphériques, CMC, Université Paris12 - 61 av. du Général de Gaulle - 94010 Créteil Cedex, France, (2) AIRMARAIX, 67-69 avenue du Prado - 13286 Marseille Cedex 06, France, (3) Laboratoire de Physico-Chimie de l'Atmosphere - Centre de Geochimie de la surface - 1, rue Blessig - 67084 Strasbourg, France, (4) Laboratoire de Meteorologie Dynamique, Ecole Polytechnique, 91128 Palaiseau CEDEX, France

Carbon monoxide is one of the most largely distributed air pollutants. Each year, more CO is released into the atmosphere than any other pollutant, excluding CO2. In large urban cities, CO mixing ratios may fall in the range of 1 to 10 ppmv. The evolution of CO is considered as being relevant to climate change : indeed, carbon monoxide is known to play a primary role in governing OH abundances in the troposphere, notably affecting that of methane. The oxidation of carbon monoxide can also affect radiative forcing indirectly through its production of carbon dioxide and tropospheric ozone. Nevertheless, due to a slow photochemistry, CO is known to play a role in O3 formation mainly at the large scale, in the free atmosphere, while VOCs are believed to dominate ozone production at local scale.

Recently, the impact of CO on local air quality has become a pressing current research question. Recent studies are suggesting that due to the intensity of its emissions, carbon monoxide is becoming more and more responsible for generating ground-level ozone. The 1999 american National Research Council's report confirmed the importance of carbon monoxide in the formation of urban ozone, concluding that as much as 20% of the ozone coming from automobile was attributable to carbon monoxide emissions. This has implications for example on the evaluation of ethanol as a reformulated gasoline, as a significant reduction in CO emissions is provided by the high oxygen content of ethanol. However, the California regulations have yet to account for new studies on CO high ozone-forming potential. In Europe, at the present time, the impact of CO on ozone production at local scale is not recognized, and the evolution of CO is currently not regulated in the European protocol of Göteborg aiming to improve air quality for year 2010.

The study presented here points out the determining participation of CO oxidation in local ozone production through a eulerian modelling study of photochemical episodes on a European site in the mediterranean area. This works first reveals that carbon monoxide can be one of the 3 organic compounds most influent on local ozone production. It finally concludes, through a detailed model chemical analysis, that CO can be responsible for 25% of total ozone production and 50% of ozone formation from anthropogenic VOCs on the first 50kms of the secondary plume formation.

Simulations with the CHIMERE model have been conducted over 24 days with significant photochemical pollution. The site of the study is the region of Fos-Berre-Marseille, a well-developped industrial and urban area on the French Mediterranean coast submitted to a strong occurrence of severe ozone events. Sensitivity tests consisting in emission reduction of 5% of individual VOC, including CO, have been conducted on a selected episode. The participation of VOCs and CO to ozone formation was ranked according to their impact on the ozone daily maximum. CO appears to be the third compound implicated in ozone formation, after aromatic compounds and ethene. The spatial and temporal influence of CO was then analysed under the form of 2D maps of CO impact on ozone. Tracers have then been included in the chemical scheme. They were implemented in order to follow the decomposition of 7 classes of VOC and primary CO up to the formation of ozone molecules. We have been analysing the evolution of these marked ozone molecules along the path of the ozone plume from the urban and indutrial centers to the rural inland areas. The diurnal evolution of these ozone molecules reveal the predominant role of CO all along the path, making up to 7ppbv of ozone on a total production of 28 ppbv on a 50km scale.

Such an impact is attributed to the elevated and punctually intense CO emissions coming from industrial processes on the site. This phenomenon is not an isolated case. In France, emission inventories indicate that the Paris region, as well as 2 other regions in the North and East of France, are submitted to very high CO emissions either due to industrial processes or an intense traffic net. Such conclusions may also be extended to all the large industrial and urban places of Europe, suh as the Milan region, industrial sites of Eastern Europe, or large cities of North and central Europe.