



Annual and seasonal trends surface ozone background levels at rural French monitoring stations over the 1995-2003 period.

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Ozone is a secondary pollutant that is produced during the atmospheric photooxidation of Volatile Organic Compounds under the presence of nitrogen oxides. O₃ is an important air quality issue due to adverse health effects on humans and plants. Furthermore, O₃ acts as a strong greenhouse gas in the free troposphere. Background O₃ is generally defined as the fraction of O₃ present in a given area that is not attributed to anthropogenic sources of local origin. O₃ background concentrations in the lower troposphere strongly increased within the last century (Volz *et al.*, 1988). There is considerable interest in quantifying surface background ozone concentrations and associated trends, as they serve to define a lower boundary with respect to reductions of ozone by control of anthropogenic precursors.

The data used in this analysis were obtained from the French Background Air Pollution Monitoring Network, called MERA, integrated the EMEP program. An assurance quality plan has been established since 1995s. All sites are located in rural areas and are generally not influenced by local anthropogenic emission sources. Our study examines data from 9 MERA sites well distributed over France during the sampling period from January 1995 to December 2003 and national emissions of NO_x and NMVOC were examined. The non-parametric Mann-Kendall test (MKT) was used to test randomness against trend. The procedure is based on the non-parametric MKT for the trend and the non-parametric Sen's method for the magnitude of the trend. Thus, its use is highly recommended for general use by the World Meteorological Organization (Sirois, 1998). This test is developed for detecting and estimating monotonic trends in the time series of annual values of atmospheric and precipitation concentrations and

includes an important number of applications in air quality. We have applied this test to 9 stations of MERA network in order to bring out spatio-temporal trends and to determine trends surface O₃ background levels in France over the period 1995-2003. Hirsch *et al.* (1991) have extended the MKT to take into account any seasonality in the data. They called this test the Seasonal Kendall test. We considered the monthly and seasonal averages for detecting and estimating trends. The Sen's slope estimator can be extended to take into account the presence of seasonality.

For the whole period an O₃ increasing trend was also observed with an increasing of 0.65%.year⁻¹. The situation in France with respect to near-surface O₃ is comparable to that of other countries in Europe. For most stations, no significantly negative trends of the O₃ concentrations were found despite the significant reduction in the precursor emissions in France over the 1995-2003 period (- 2.8%year⁻¹ for NO_x and - 3.8%year⁻¹ for VOCs) and Europe.

O₃ concentrations declining by 0.13%year⁻¹ in spring and by 0.22%year⁻¹ in summer, seasons in which the main driving mechanism is photochemical production, suggests that the negative trend observed is slightly in line with the reduction in emissions of O₃ precursors during the 1995-2003 period. We obtained significantly positive O₃ trends in the cold seasons, on average + 0.83%year⁻¹ in winter and + 2.01%year⁻¹ in autumn. The positive O₃ trend might be related to the lower effect of the ozone loss by titration through NO as a consequence of the decreased emissions of primary during the 90s (Ordóñez *et al.*, 2005). This effect of titration is especially important at the most polluted sites (Donon and Revin). The decrease of the precursor emissions thus might have led to a significant decrease of ozone only at the Morvan station. Moreover, exists a coherence between the evolution of the concentrations in precursors and O₃ concentrations: when the ratio VOC/NO_x increases, the O₃ concentration decreases.

Keywords: Mann-Kendall test, ozone background, Seasonal Kendall test, Sen's method, spatio-temporal trends.

References:

Hirsch R.M., 1991, "Selection of methods for the detection and estimation of trends in water quality". *Water Resources Research* 27, 803-813.

Ordóñez C. *et al.*, 2005, "Changes of daily surface ozone maxima in Switzerland in all seasons from 1992 to 2002 and discussion of summer 2003". *Atmospheric Chemistry and Physics* 5, 1187-1203.

Sirois A., 1998, "WMO/EMEP Workshop on Advanced Statistical Methods and their application to Air Quality Data sets". Helsinki.

Volz A. *et al.*, 1988, "Evaluation of the Montsouris series of ozone measurements made in the nineteenth century". *Nature* 332, 240-242.