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Study of diurnal variation of surface ozone with special emphasis to nocturnal surface ozone in a mountain-valley system

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Ozone (O_3) is a highly reactive secondary photochemical air pollutant and an important greenhouse gas which contributes to global warming and climate change. Long term (2001-2011) analysis of hourly O_3 data has been conducted at 4 background monitoring sites in and around the city of Clermont-Ferrand for diurnal variation as well as variability of O_3. Clermont-Ferrand is located in the high altitude region of the Massif Central in South-central France. This study shows the occurrence of prominent nighttime enhancements, particularly during the winter months (Nov-Feb). Whilst nocturnal surface ozone (NSO) enhancement events have been observed at other locations, this is the first time that frequent NSO enhancement events have been demonstrated to occur in France. We show them to be clearly discernible in monthly diurnal cycles averaged over several years of data. 3 out of 4 background stations (except the Sommet du Puy de Dom site) shows a bimodal diurnal variation with a nighttime peak around 0200 hr in addition to a daytime peak during the winter months. The reasonable explanation for the observed bimodal pattern of surface ozone with a secondary peak around 0100 – 0300 hr (local time) has to be transport processes. In this case, the dominant one being a mountain-valley wind system, as ozone production ceases at nighttime. The frequency distribution analysis of daily maximum NSO concentrations during winter months shows that the daily maxima NSO concentrations during the winter months exceeded 60 μg/m^3 on >30% of the nights and exceeded 80 μg/m^3 on >5% of the nights at urban and suburban sites. This is considerably higher than the winter mean daytime maxima ($\sim$50 μg/m^3). The highest NSO value recorded was 108 μg/m^3 at the Delille site. The Sommet du Puy de Dom site, being a high altitude site, showed minimum variations in diurnal cycle and variability with daily maxima NSO concentrations during the winter months exceeding 80 μg/m^3 on >70% of the nights. The analysis also shows that these NSO enhancements at urban and suburban sites can last for several hours in one night or for several nights.