**Tropospheric ozone metrics**

Ozone (O3) is a relatively strong oxidizing agent which in sufficient concentrations can be detrimental to human health and inhibit the growth of crops and damages natural ecosystems. Photochemical oxidant formation was first recognized as a pollution problem in Los Angeles in the middle of the 20th Century. In Europe the regional trans-boundary nature of ozone pollution was realized in the last quarter of the century as emissions of NOx and VOC from traffic and industry increased.

Photo-oxidant pollution is now a problem throughout the globe, particularly in the tropical conurbations where uncontrolled emissions are subject to intense sunlight. Ozone is a so-called secondary atmospheric pollutant as it is not emitted but formed photo-chemically in the lower atmosphere by the chemical reactions nitrogen oxides (NO and NO2, referred to as NOx) with volatile organic compounds (VOC) in the presence of sunlight.

While ozone is mainly formed photo-chemically in the lower atmosphere (the troposphere), there is some transfer down from the stratosphere where concentrations are much higher. The magnitude and impact of Stratosphere-Troposphere exchange is still a matter of debate. Since ozone has an appreciable lifetime in the atmosphere it can be transported long distances far from source regions or from the site of a transfer from the stratosphere. There are two main processes that can remove ozone from the troposphere, photochemical loss routes via photolysis and reaction with HOx radicals and (dry) deposition to the Earth’s surface.

The concentration increases on normal summer days but concentrations can increase much more during ozone episodes. In north Western Europe, these usually occur in periods of warm weather which ensue when a zone of high pressure forms over a region and remains nearly stationary. Normally ozone concentrations decrease over night as photochemical production ceases and ozone is removed at the ground, so a marked diurnal variation is observed in the concentrations. During episodes the extent of the variation may diminish and the concentrations remain high throughout the night as well.

The major sources of the ozone precursors (NOx and VOC) are vehicular traffic and industrial processes. The amount of ozone formed depends on the intensity of the light and on the ratio

[VOC]/[NOx]. Ratios between 4 and 10 are favorable for ozone formation at appropriate light intensities. In the centre of conurbations, NOx concentrations are high so little ozone is formed, chemically much of the ozone formed is scavenged by NO. However as an air mass move out into the countryside the NOx concentrations fall and more ozone is formed. Thus high ozone concentrations do not usually occur where one might intuitively expect, in the centre of cities, close to the major sources.

The highest concentrations are found in the hinterland of cities, suburbs and rural areas downwind of the city. This is a practical example of the effect of the non linearity in ozone formation and removal which, together with atmospheric transport, makes it a difficult pollutant to control.

**Metrics**

**Ozone control and modeling**

The acceptable level of tropospheric ozone is 120 μg/ m3(mixing ratio ~60 ppb) for long periods (WHO, 2000). The health effects of ozone are more marked during ozone episodes when ozone can accumulate over a period of days and concentrations can rise well above the apparently acceptable level. Effects on vegetation appear with exposures to ozone at lower concentrations (80 μg /m3, mixing ratio 40 ppb) during the growing season. There will be appreciable economic consequences if background levels rise and crop productivity is affected. Thus there are two different regimes of ozone must be taken into account in attempting to limit or reduce ozone concentrations: the general background of ozone and peak levels which mainly occur in episodes.

**UV photometric measurement of surface ozone**

Surface ozone is routinely measured by ozone analysers, which measure the concentration of ozone in ambient air in situ. The most commonly used instruments for measuring surface ozone are UV photometric ozone analyzers. These instruments measure ozone by UV absorption photometry in a narrow wavelength interval (≈0.5 to 1nm) at 254nm. The dry chemical analyzer which applies the chemi-luminescence method and the wet chemical analyzers used to be in routine operation, but their use is becoming less common because these methods are not as reliable as the UV absorption method. UV absorption photometry is the method recommended by the WMO/global Atmosphere watch (GAW) Scientific Advisory group on Reactive gases.

Surface ozone is routinely measured by in situ techniques; the most commonly used method is UV photometry where ambient air is drawn through a cell in which the absorption of UV radiation is measured at the 254-nm emission line of a mercury lamp. The strong absorption by ozone at this wavelength produces a detectable absorption measurement when ozone is present in the cell. The absorption cell alternately samples ambient air coming directly from the atmosphere and ambient air diverted through a manganese dioxide scrubber that converts ozone catalytically to oxygen but leaves all other trace gases intact and the relative humidity almost constant. The UV irradiance is therefore measured in the presence and absence of ozone in the ambient air. The measured irradiance in the presence of ozone (I) is related to the measured irradiance in the absence of ozone (Io) by the following expression: I= -I0exp(αCL) where α is the absorption cross section of ozone at 254nm (cm2), C is the concentration of ozone in the cell (molecules/ cm3), and L is the length of the cell (cm). By comparing the two irradiance signals it is possible to determine the concentration of ozone in the cell, provided that the length of the cell and the absorption cross-section for ozone are known. Ozone measurements are reported as parts per billion volume or partial pressure. The detectable range is from 1 to 1000ppbv