N95- 10625

303276

DETERMINATION OF DRY DEPOSITION OF OZONE : COMPARISON OF DIFFERENT MEASURING TECHNIQUES

I COLBECK and A SIMMONS

Institute of Aerosol Science
University of Essex, Colchester CO4 3SQ
UK

ABSTRACT

Five methods were used to investigate the deposition of ozone. The measurements of the eddy diffusivity of heat using the Bowen ratio technique, were slightly higher than but closely matched the measurements made for the momentum eddy diffusivity, measured simultaneously, using the profile technique. Similar flux values were obtained by the profile and eddy correlation method. Deposition velocities determined using the box method were higher than those calculated using an open top chamber.

1. INTRODUCTION

The destruction of ozone at the earth's surface plays an important role in the budget of tropospheric ozone. Dry deposition is the direct absorption/destruction of a gas at the ground. This distinguishes it from removal by precipitation, although water surfaces as well as vegetation and soil may participate. Deposition requires the transfer of ozone through the lower part of the boundary layer to the surface followed by decomposition or chemical reaction on contact with the surface. The first part of the deposition process depends on the nature of the boundary layer whereas the second part depends on the chemical reactivity of the surface with respect to ozone. Not only does dry deposition deplete ozone concentrations directly, but also indirectly through the removal of important precursor species eg NO_2, HNO_3 and PAN.

In studies of dry deposition the rate of transfer, or deposition velocity, v_g is often expressed by

$$v_g(z) = F/c(z) = 1/(r_a+r_b+r_s)$$

where F is the downward flux of the pollutant, which is related to the eddy diffusivity, and c is its concentration at height z. As indicated above, the total resistance to transport to the surface can be written as the sum of the resistances from each of the processes involved where r_a is the aerodynamic resistance, r_b is the resistance in the laminar sublayer next to the surface and r_s is the resistance controlled by the surface itself.

There are several methods routinely used to measure dry deposition in the field and each has its own advantages and disadvantages (Colbeck and Harrison, 1985; Dolske and Gatz, 1985; Kramm et al., 1991). We selected several micrometeorological techniques and the flux chamber method to measure ozone deposition over various types of surface (Simmons, 1992). The micro-meteorological methods chosen were the gradient, Bowen ratio and eddy correlation techniques. Both open- and closed-top chambers were studied.

2. TECHNIQUES

In suitable conditions, micro-meteorological methods permit the vertical flux of species to be determined from measurements made above a surface, by considering the turbulent transfer of that species. The profile method is based on vertical gradients of windspeed, temperature and concentration (Colbeck and Harrison ,1985). In order to calculate deposition velocities this method assumes that in turbulent flow, where mechanical mixing dominates, an eddy transfers atmospheric properties equally so that exchange of all gases, vapours, heat and momentum are expected to be similar. Eddy diffusivities are evaluated as a function of momentum flux, surface roughness and atmospheric stability, which are derived from supporting meteorological data (Hicks et al., 1980). The profile method is straightforward in neutral stability, when profiles of only windspeed and concentration are required. Outside such conditions the wind profile must be corrected, empirically, for the effects of thermal buoyancy. The accepted corrections appear valid over short crops but are less accurate over tall rough crops.

The Bowen ratio determination of flux is derived from the energy balance of the underlying surface. The eddy diffusivities are assumed to be the same as for sensible heat or water vapour and is determined from measurements of vertical gradients of temperature, humidity and ozone concentration as well as the net radiation and soil heat flux. For a flux to be estimated with any accuracy using this technique substantial net radiation fluxes (>50 W m^{-2}) are required. At night, during Winter or in cloudy conditions the available net radiation is often too small for accurate flux determination.

Both the profile and Bowen ratio method are indirect methods of determining the flux since they rely on the measurement of mean potentials and their gradients in the atmosphere. Eddy correlation is a direct method (Monteith and Unsworth, 1990) and requires simultaneous measurement of rapid fluctuations of vertical windspeed in the constant flux region of the surface boundary layer and the associated fluctuations in gas concentration, temperature or humidity. Only stress of the horizontal wind on a horizontal surface together with a mean vertical velocity of zero is assumed. This method requires an extensive uniform upwind fetch so that the flux has equilibrated over the surface being investigated.

The box or decay method enables the surface resistance to ozone uptake of various surfaces to be measured. An inert box, containing a know concentration of ozone is placed with one open side over the surface to be investigated. The rate of decrease of ozone concentration within the box is assumed to be equal to its destruction rate at the surface. Unless atmospheric conditions are simulated in the box, deposition velocities found in this way cannot be compared with field studies. Surface resistances can be compared and, in this case, were obtained by measuring the total surface resistance before and after coating the surface with potassium iodide solution (Simmons and Colbeck, 1990). This has the effect of making the surface resistance negligible. Measurements were made in a 0.5 x 0.5 x 0.5 m teflon lined box. Closed top chambers alter the environment in ways that probably affect the action of pollutant concentrations on the receptor plants (eg raised temperatures within the chamber), however open top chambers provide more natural conditions. The deposition velocity may be determined by the equilibrium method which involves filling the chamber with ozonated air and measuring the ozone concentration entering the chamber and that of the equilibrium mixture. The chamber used had a volume of 1.52 m^3 and the surface area of the base was 0.95 m^2. The advantage of this method is that it can be used under any atmospheric stability. The main disadvantage is that ozone concentrations higher than ambient have to be used in the chamber, to achieve a significant difference in the two concentrations that are measured.

3. RESULTS

Full details of the measurement sites, averaging times, meteorological data (including atmospheric stability) and data selection/rejection criteria are given in Simmons (1992). Of particular importance is the strict requirement on the nature of the upwind fetch. At all sites the fetch was uniform for a sufficient upwind distance to ensure that the boundary layer had equilibrated over the surface of interest. For the profile technique, results were only used when the Richardson number was in the range -0.1 to 0.01.

Figure 1 shows the values of surface resistance obtained by both the profile and box techniques over three days. There is reasonable agreement between the methods although the profile values are highly variable. Measurements were made over short (3

REFERENCES

Colbeck I. and Harrison R.M. (1985) Dry deposition of ozone : some measurements of deposition velocity and of vertical profiles to 100 metres, Atmos. Environ., 19, 1807-1818.

Dolske D.A. and Gatz D.F. (1985) A field intercomparison of methods for the measurement of particle and gas dry deposition, J. Geophys. Res., 90, 2076-2084.

Hicks B.B., Wesely M.L. and Durham J.L. (1980) Critique of methods to measure dry deposition, EPA-600/9-80-050.

G., Muller H., Fowler D., Hofken K.D., Meixner F.X. and Schaller E. (1991) A modified profile method for determining the vertical fluxes of NO, NO_2,ozone and HNO_3 in the atmospheric surface layer, J. Atmos. Chem., 13, 265-288.

Monteith J.L. and Unsworth M.H. (1990) Principles of Environmental Physics, 2nd edition, Edward Arnold, London.

Simmons A. and Colbeck I. (1990) Resistance of various building materials to ozone deposition, Environ. Tech., 11, 973-978.

Simmons A. (1992) Studies of ozone deposition, PhD Thesis, University of Essex.