Atmospheric Environment Vol. 11, pp. 1209–1211. Pergamon Press 1977. Printed in Great Britain.

A FAST RESPONSE SENSOR FOR OZONE EDDY-CORRELATION FLUX MEASUREMENTS*

J. A. EASTMAN and D. H. STEDMAN

Department of Atmospheric and Oceanic Science, University of Michigan, Ann Arbor, Michigan 48109, U.S.A.

(*First received* 12 *July* 1976 *and in final form* 10 *May* 1977)

Abstract—The measurement of fluxes of gaseous pollutants to the ground may be made using eddy-correlation techniques. The application of a chemiluminescent and other fast response detectors is discussed. As an example, a specific study of ozone fluxes is described.

INTRODUCTION AND BACKGROUND

Several techniques have been employed to measure fluxes of various atmospheric components. We will discuss ozone in particular. One of the first methods used the hypothesis that under appropriate conditions the transfer processes of ozone and momentum are identical, so that the momentum eddy diffusivity theory is valid (Regener, 1957; Galbally, 1968, 1969, 1971; Galbally and Allison, 1972; Kelly and McTaggert-Cowan, 1968). These authors applied one of the following equations, depending on their ability to measure the vertical wind profile:

$$F = \frac{k^2 \Delta u \Delta c}{\left[\ln \frac{z_2}{z_1}\right]^2} = \frac{U_*^2 \Delta c}{\Delta u} = \frac{\tau \Delta c}{\rho \Delta u},$$

where F is flux in molecules/cm^{-2}/s^{-1}, k is Von Karman's constant, Δu is wind speed difference at two heights, z_1 and z_2, Δc is concentration difference at two heights, z_1 and z_2, U_* is friction velocity, ρ is air density, τ is shearing stress in dynes/cm^{-2}.

Another flux measuring scheme, known by the author as the box method (Aldaz, 1969) finds the ozone flux by injecting ozone into a box having nearly inert Mylar walls with the bottom open to the ground.

Kroenig and Ney (1962) studied the depletion of ozone from a layer close to the ground after sunset. They found the flux by multiplying the initial ozone concentration by the height at which ozone is no longer present and the inverse of the time required to deplete ozone to that height.

Some of these methods are limited to unrealistic meteorological regimes, others by the inherent slowness and inaccuracy of the ozone sensors employed. None of the above methods can measure instantaneous and variable fluxes.

In the atmosphere, the ozone flux is caused by eddies, individual fluid elements transporting the gas. The flux of material, F, across a horizontal plane is given by the product of the concentration, c, and the vertical velocity w, $F = cw$. If the concentration and wind velocity are thought of as the sum of an average value and perturbation, the product becomes $F = (\bar{w} + w')(\bar{c} + c')$. The average vertical flux simplifies to an eddy dispersion term:

$$\bar{F} = \overline{c'w'},$$

since in vertical dispersion $\bar{w} = 0$ so only the $\overline{c'w'}$ term is non-zero. Attempts to measure fluxes of heat, momentum, and, more recently, water vapor by this method have proven successful (Hicks, 1970; Hicks and Dyer, 1970). Extension of this technique to other air pollutants such as SO_2 and O_3 demands fast response chemical instrumentation. Typically, with a 4 m tower, the flux will be adequately determined only with sensors having a time response faster than 1 s. For lower heights still faster response is required (Garratt, 1975). We demonstrate herein the application of chemiluminescence to determine ozone fluxes, and discuss the advantages and limitations of this technique.

OZONE FLUX OBSERVATIONS

The chemiluminescent ozone meter used was a modified Thermo-Electron model 12A chemiluminescent NO meter. The modifications are as described by Stedman *et al.* (1972). In brief, the detector is a vacuum pumped flow system in which pure nitric oxide from a cylinder is mixed with the incoming sample stream in a reactor viewed by a red sensitive photomultiplier tube. To achieve high speed and sensitivity the sample inlet is under vacuum to the sampling point 4 m in height. The flow is restricted to 500 ml min^{-1} with a stainless steel capillary. Laboratory measurements showed a flow delay time of less than 0.1 s and a response time of less than 0.2 s with a 4 m inlet tube. With full scale corresponding to

* Contribution No. 232 from Department of Atmospheric and Oceanic Science.

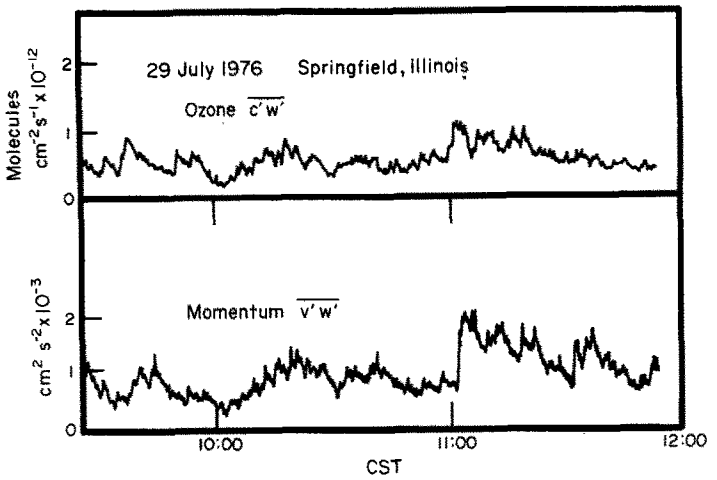

Fig. 1. Correlation between ozone and momentum fluxes.

150 ppb, typical values of 0–80 ppb were readily measureable, the baseline noise was about 1.5 ppb.

Studies were conducted in collaboration with Hicks *et al.*, at Argonne National Laboratory and near Springfield, IL. Typical fluctuations of about 10 ppb over a few seconds were observed at 4 m during spring conditions over grass at Argonne. The deposition velocity, $\overline{F}/\bar{c}$, was observed to be about 0.5 cm s^{-1}, consistent with previous observations.

During the study near Springfield, measurements were made on the downwind edge of a corn field. At the time of the study the corn stood about 3 m in height and the wind fetch was at least 1 km. A 4 m tower was erected on a movable trailer, so that when secured, it stood 5 m above the ground. A four-blade Gill propeller anemometer measured vertical wind velocities at the tower's apex. The sampling inlet for the ozone detector was attached to the tower about 0.5 m from the anemometer. The analog signals from the ozone detector and anemometer were fed into a set of covariance analysers (Hicks, 1973). After amplification and removal of mean values by active filters, having a time constant of 100 s, the signals were fed to analog multipliers. The product signals were further amplified and smoothed with time constant of 1000 s for display on chart recorders. Simultaneous measurements of heat and momentum fluxes were also displayed on the chart recorder. Figure 1 is a portion of the Springfield data that shows a good correlation between ozone and momentum fluxes. Determining ozone fluxes by this method are limited by the following factors; level terrain, adequate fetch to avoid terrain-induced vertical velocities, and matching the ozone detector's response to the anemometer's to ensure precise temporal correlation. Past measurements of ozone flux are summarized in Table 1. Note that positive is downward.

The capability of measuring precise real-time instantaneous fluxes makes the eddy-correlation technique a superior flux measuring method. To extend this technique to other gases, fast and sufficiently sensitive instrumentation must be available. The ozone detector described can clearly be used in this application. Other authors have been successful in measuring CO_2 and H_2O. At the present stage of commercial development, instrumentation for NO_x, SO_x and CO is either too slow or inadequate in sensitivity; however, some developmental research equipment may have the necessary characteristics.

Table 1. A compilation of measured ozone fluxes

Author	Site	Ozone flux (10^{11} molecules $cm^{-2} s^{-1}$)
Regener (1957)	O'Neill, NB	0.87–2.50
Kroenig and Ney (1962)	Minneapolis, MN	0.6
Galbally (1968)	Hay, Australia	0.14–3.60
Kelley and McTaggart-Cowan (1968)	Barrow, AK	−1.74 and 6.32
Aldaz (1969)	N.M. (over snow)	0.9
Galbally (1969)	Edithvale, Australia	0.5–6.3
Galbally (1971)	Hay, Australia	1.2–5.0
Galbally and Allison (1972)	Mt. Buller, Australia (over snow)	−22–17
This work	Argonne, IL (over grass)	1.0–40
	Springfield, IL (over corn)	0.5–14

Acknowledgements—We gratefully acknowledge the assistance of the Argonne National Laboratory (ERDA) personnel, and some financial support from NSF under grant No. ATM76-03793.

REFERENCES

Aldaz L. (1969) Flux measurements of atmospheric ozone over land and water. *J. geophys. Res.* **74,** 6943–6946.

Galbally I. E. (1968) Ozone variation and destruction in the atmospheric surface layer. *Nature,* **218,** 456–457.

Galbally I. E. (1969) An evaluation of the Ahmert technique for measuring ozone profiles in the atmospheric surface layer. *J. geophys. Res.* **74,** 6869–6872.

Galbally I. E. (1971) Ozone profiles and ozone fluxes in the atmospheric surface layer. *Q. Jl R. met. Soc.* **97,** 18–29.

Galbally I. E. and Allison I. (1972) Ozone fluxes over snow surfaces. *J. geophys. Res.* **77,** 3946–3949.

Garratt J. R. (1975) Limitations of the eddy-correlation technique for the determination of turbulent fluxes near the surface. *Boundary Layer Met.* **8,** 255–259.

Hicks B. B. (1970) The measurement of atmospheric fluxes near the surface: a generalized approach. *J. appl. Met.* **9,** 386–388.

Hicks B. B. (1973) Eddy fluxes over a vineyard. *Agric. Met.* **12,** 203–215.

Hicks B. B. and Dyer A. J. (1970) Measurements of eddy-fluxes over the sea from an off-shore oil rig. *Q. Jl met. Soc.* **96,** 523–528.

Kelley J. J., Jr. and McTaggart-Cowan J. D. (1968) Vertical gradient of net oxidant near the ground surface at Barrow, Alaska. *J. geophys. Res.* **73,** 3328–3330.

Kroenig J. L. and Ney E. P. (1962) Atmospheric ozone. *J. geophys. Res.* **67,** 1867–1875.

Regener V. H. (1957) Vertical flux of atmospheric ozone. *J. geophys. Res.* **62,** 221–228.

Stedman D. H., Daby E., Stuhl F. and Niki H. (1972) Analysis of ozone and nitric oxide by a chemiluminescent method. *J. Air Pollut. Control Ass.* **22,** 260–263.