Reports

Ammonia Flux into the Atmosphere from a Grazed Pasture

Abstract. *A micrometeorological technique has been used to measure the flux of ammonia and related gaseous nitrogen compounds into the atmosphere from a pasture grazed by sheep. During 3 weeks in late summer, the average daily flux density of nitrogen in these forms was 0.26 kilogram per hectare. This is a substantial part of the nitrogen turnover in grazed pastures.*

Ammonia is present in the air in very small concentrations (a few micrograms per cubic meter), but its manner of transfer to the atmosphere and its subsequent dispersion are of interest in many earth sciences. In a meteorological context, for instance, Healy *et al.* have pointed out that ammonium sulfate produced in the atmosphere from the reaction of ammonia and sulfur dioxide is a major component of aerosols affecting health, corrosion, visibility, and mist formation (*1*). In the context of air and water pollution, it has been suggested that the release of ammonia to the atmosphere from animal feeding lots could lead to eutrophication of nearby lakes and reservoirs (*2*). Some soil scientists suspect that significant losses of soil nitrogen can occur through the production of ammonia in the soil and its transfer to the atmosphere (*3*).

So far as we are aware, no direct measurements of the inputs of ammonia to the atmosphere from extensive land surfaces have yet been reported. We describe here a technique for making such measurements and present observations of the flux densities of nitrogen as ammonia and related gaseous amino compounds from a grazed pasture. These nitrogen losses appear to be a substantial part of the nitrogen turnover of grazed pastures and point to atmospheric transfer as a significant means of redistribution of nitrogen over the land.

Several micrometeorological methods are available for measuring mass transfer between extensive natural surfaces and the atmosphere in a nondisturbing way. The method we have employed, based on the energy balance at the ground surface, is much used in micrometeorology, and a formal description of its application to the measurement of gas (carbon dioxide) exchange has been given by Denmead and McIlroy (*4*).

The technique relies on the conservation of energy at the ground surface. The net gain or loss of radiant energy at the surface, the net radiation R, is balanced by a change in heat storage in the ground G and by energy exchanged with the air in the form of convected and latent heat. The sum of the flux densities of convected and latent heat is proportional to the gradient (change with height) of the equivalent temperature T_e, a linear function of air temperature T and vapor pressure e:

$$T_e = T + \frac{0.622\,L\,e}{c_p\,p}$$

where L is the latent heat of vaporization of water, c_p is the specific heat of air at constant pressure, and p is the atmospheric pressure. From these considerations, a transfer coefficient h can can be calculated for a layer of air near the ground from the relationship:

$$h = \frac{R - G}{\rho\,c_p\,\Delta T_e} \qquad (1)$$

where ρ is the density of air and ΔT_e is the difference in equivalent temperature between the bottom and the top of the layer. A formulation similar to Eq. 1 can be developed for the transport of other atmospheric constituents. Thus for ammonia we write:

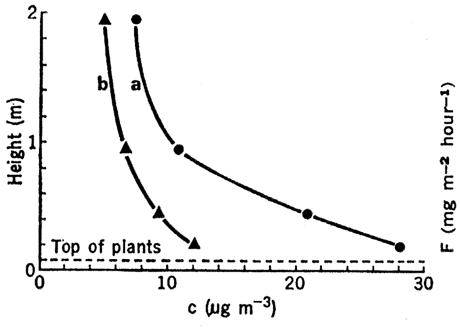
$$F = h\,\Delta c \qquad (2)$$

where F is the vertical flux density of ammonia and Δc is the difference in the ammonia concentration across the air layer. In application, h is calculated from measurements of the quanties on the right side of Eq. 1, and this value is used to compute F from Eq. 2.

With the technique we have carried out several calculations of ammonia flux over a grazed alfalfa pasture near Canberra during March 1974. The field had an area of approximately 4 ha, and during the measurement period it was evenly grazed by 200 sheep. The surface layers of soils in the area were slightly acidic (*5*). The net radiation over the pasture and the soil heat flux were measured with standard instruments, and air temperatures and vapor pressures were determined with aspirated, radiation-shielded, dry- and wet-bulb platinum resistance thermometers at heights of 0.20, 0.45, 0.95, and 1.95 m above the ground surface. Atmospheric ammonia concentrations were measured by drawing air from the same heights through absorption traps at approximately 12 liter/min. The actual flow rate for each level was monitored with a flowmeter. The traps were Plexiglas cylinders, 24 cm long and 2 cm in internal diameter, filled with 3-mm glass beads held between plugs of glass wool. Each trap contained 5 ml of 2 percent phosphoric acid. Connecting lines between the air intakes and the traps were interchanged periodically to make sure that no contamination occurred in the lines. At the end of a sampling period, the traps were removed. The acid was eluted with water, and the amount of ammonia was determined with an ammonia-specific ion electrode.

Although we speak here in terms of ammonia nitrogen, our tests have shown that the electrode is also sensitive to amines. Use of a technique specific for ammonia (*6*) in parallel with the ammonia electrode indicated that, under some conditions, up to half the nitrogen collected in the traps was in the form of other volatile basic compounds, presumably amines. The proportion of ammonia varied from day to day, and in cool, humid weather virtually pure ammonia was found. We are investigating this aspect further to identify the sources of volatile nitrogen [see (*7*)].

Tests of the internal consistency of the data showed that the profiles of T_e and c generated in the air were in equilibrium with the exchanges of energy and ammonia occurring at the ground surface to a height of 0.95 m with a departure from equilibrium at 1.95 m caused by the limited extent of our experimental field. Accordingly, only the data from heights of 0.20, 0.45, and 0.95 m were used to calculate h and F. Net radiation, soil heat flux, and dry- and wet-bulb temperatures were recorded at 4-minute intervals, and half-hourly averages of their values were



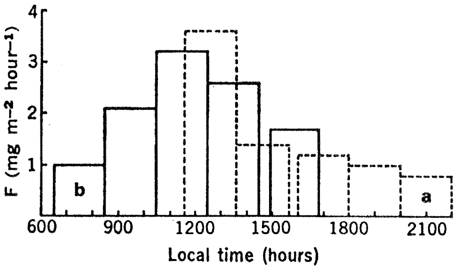


Fig. 1 (left). Profiles of ammonia concentration, *c*, over an alfalfa pasture: profile a, 1600–1800 hours on 14 March 1974; profile b, 1500–1700 hours on 15 March 1974. Fig. 2 (right). Flux densities of nitrogen (as ammonia and related compounds), *F*, from pasture: profile a, 14 March 1974; profile b, 15 March 1974.

used to calculate *h* from Eq. 1. Determination of the ammonia concentration by our absorption method prevented on-the-spot monitoring, and, because of our uncertainty about the concentrations that were likely to prevail from time to time, the sampling periods for this measurement were longer, 1 or 2 hours. Appropriate averages of *h* were then used to calculate *F* from Eq. 2.

There is some ecological interest in the atmospheric concentrations of ammonia and in its flux density. In 28 sampling measurements the average concentration at 0.20 m was 15.7 μg m^{-3} with a range of 3.4 to 51.5 μg m^{-3}. In the same measurements the average concentration at 0.95 m was 10.1 μg m^{-3} with a range of 1.6 to 28.4 μg m^{-3}. Two representative profiles measured at about the same hour on consecutive days are shown in Fig. 1. The very large differences in concentration and gradient were due to differences in the turbulence of the air. Profile a, for instance, was measured in light winds, about 0.9 m sec^{-1} at 1 m above the ground, whereas profile b was measured in strong winds, about 3 m sec^{-1} at the same height. The flux densities of ammonia were similar, however, at about 1.5 mg m^{-2} hour^{-1}. Obviously, little information can be obtained about the magnitude of ammonia exchange from measurements of concentration alone [see, for example, the procedure of Hutchinson and Viets (*2*)].

The general character of the flux determinations is shown in Fig. 2. Those observations were made during a period of 29 hours covering the daylight period and some of the night. A diurnal cycle in the flux is clearly evident with peak flux densities of nitrogen (in excess of 3 mg m^{-2} hour^{-1}) occuring around midday and minimum values (about 0.8 mg m^{-2} hour^{-1}) overnight. Twenty-six calculations were made between 7 March and 29 March on seven separate days. These gave an average daily loss of nitrogen of 0.26 kg ha^{-1}.

Our investigations are still at a preliminary stage, and many aspects remain to be studied, including the seasonal cycle of ammonia exchange. Nonetheless, it is apparent from these measurements that losses of gaseous nitrogen compounds can constitute a large part of the nitrogen turnover in a grazing system. The input of nitrogen to leguminous pastures by symbiotic nitrogen fixation varies with plant species and growing conditions, but annual amounts between 100 and 200 kg ha^{-1} have often been reported (*8*). In addition, rain adds small quantities of nitrogen which we estimate at about 5 kg ha^{-1} year^{-1}. Of these, about 50 kg ha^{-1} remain in the soil (*9*), and the equivalent of about 20 kg ha^{-1} remain in the animals. Thus the annual loss of nitrogen from the system is often of the order of 100 kg ha^{-1} or an average of 0.27 kg ha^{-1} day^{-1}. The almost exact coincidence of this figure with our estimates of ammonia loss must be regraded as fortuitous, but the calculations certainly establish the importance of gaseous losses in the nitrogen economy of grazing systems. In the situation we studied the sheep were returning an estimated 1 kg of nitrogen per hectare per day as urine, which could have been a major source of the observed flux of ammonia (*5*). The data suggest that grazed pastures are important contributors of ammonia nitrogen to the atmosphere and, through it, to other land areas.

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17 April 1974

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Photosynthetic Mechanisms and Paleoecology from Carbon Isotope Ratios in Ancient Specimens of C_4 and CAM Plants

Abstract. *Carbon istotope ratios of modern, 10,000-year-old, and more than 40,000-year-old* Atriplex confertifolia *(C_4) material from Nevada caves indicate that the C_4 photosynthetic pathway was operating in these plants over that period. Samples of a plant with crassulacean acid metabolism,* Opuntia polyacantha, *were also measured, and a shift in the $\delta^{13}C$ value from −21.9 per mil (more than 40,000 years ago) to −13.9 per mil (10,000 years ago) was observed. This provides unique physiological evidence to support the hypothesis that the late Pleistocene pluvial climate in the region already had become drier about 10,000 years ago.*

The carbon isotope ratio technique has been used in paleoecology to follow the photosynthetic pathways in plants throughout geological time (*1*). The proposal that it would be useful to study the past geographical distribution of C_3 and C_4 plants (*1*) has been limited by the scarcity of C_4 remains, but a series of dry caves in the Mohave Desert sector of southern Nevada, western North America, provides this material with ages spanning the past