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## Nitrous Oxide and Ammonia Fluxes in a Soybean Field Irrigated with Swine Effluent

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### ABSTRACT

In the United States, swine (*Sus scrofa*) operations produce more than 14 Tg of manure each year. About 30% of this manure is stored in anaerobic lagoons before application to land. While land application of manure supplies nutrients for crop production, it may lead to gaseous emissions of ammonia ( $\text{NH}_3$ ) and nitrous oxide ( $\text{N}_2\text{O}$ ). Our objectives were to quantify gaseous fluxes of  $\text{NH}_3$  and  $\text{N}_2\text{O}$  from effluent applications under field conditions. Three applications of swine effluent were applied to soybean [*Glycine max* (L.) Merr. 'Brim'] and gaseous fluxes were determined from gas concentration profiles and the flux-gradient gas transport technique. About 12% of ammonium ( $\text{NH}_4\text{-N}$ ) in the effluent was lost through drift or secondary volatilization of  $\text{NH}_3$  during irrigation. An additional 23% was volatilized within 48 h of application. Under conditions of low windspeed and with the wind blowing from the lagoon to the field, atmospheric concentrations of  $\text{NH}_3$  increased and the crop absorbed  $\text{NH}_3$  at the rate of 1.2 kg  $\text{NH}_3$   $\text{ha}^{-1}$   $\text{d}^{-1}$ , which was 22 to 33% of the  $\text{NH}_3$  emitted from the lagoon during these periods. Nitrous oxide emissions were low before effluent applications (0.016 g  $\text{N}_2\text{O-N}$   $\text{ha}^{-1}$   $\text{d}^{-1}$ ) and increased to 25 to 38 g  $\text{N}_2\text{O-N}$   $\text{ha}^{-1}$   $\text{d}^{-1}$  after irrigation. Total  $\text{N}_2\text{O}$  emissions during the measurement period were 4.1 kg  $\text{N}_2\text{O-N}$   $\text{ha}^{-1}$ , which was about 1.5% of total N applied. The large losses of  $\text{NH}_3$  and  $\text{N}_2\text{O}$  illustrate the difficulty of basing effluent irrigation schedules on N concentrations and that  $\text{NH}_3$  emissions can significantly contribute to N enrichment of the environment.

IN THE UNITED STATES, swine operations produce more than 14 Tg of manure each year (Sweeten, 1992) and much of the manure is generated in relatively small geographic areas. Land application is the preferred method of manure management but high concentrations of animals may lead to excessive applications. Application of organic waste materials on agricultural land has received considerable attention in recent years because of potential environmental problems such as water quality degradation, air pollution through N gas emissions, odors, and dispersal of pathogenic organisms (Dosch and Gutser, 1996; Edwards et al., 1996; Paul and Zebarth, 1997).

Gaseous emissions of N from waste applications generally occur through volatilization of  $\text{NH}_3$  and loss of  $\text{N}_2$  and  $\text{N}_2\text{O}$  through nitrification-denitrification processes. These emissions are affected by waste characteristics,

method of application, climatic conditions, and chemical and physical soil properties (Misselbrook et al., 1996; Lowrance et al., 1998). As much as 13% of applied  $\text{NH}_4$  can be volatilized during irrigation before the effluent reaches the soil, with an additional 10 to 70% lost within 48 h after irrigation (Sharpe and Harper, 1997; Schilke-Gartley and Sims, 1993). Large losses of  $\text{NH}_3$  can result in insufficient N availability for plant uptake or environmental degradation. Ammonia is the primary neutralizing agent for acid gases in the atmosphere and is a common component of atmospheric aerosols. Volatilization of  $\text{NH}_3$  may result in eutrophication of natural ecosystems. Natural ecosystems are thought to be net sinks for  $\text{NH}_3$  (Denmead et al., 1976; Hutchinson et al., 1972; Van Hove et al., 1987) and cropping systems have shown significant absorption capacity (Harper et al., 1987). Atmospheric  $\text{NH}_3$  from agricultural sources has been implicated in forest decline (McLeod et al., 1990; Nihlgard, 1985) and species changes in European heathlands (Van Hove et al., 1987).

Nitrous oxide is a radiatively active trace gas that contributes to global warming and to the destruction of atmospheric ozone when it is converted to nitric oxide (Crutzen, 1981). Anthropogenic sources account for about 41% of total  $\text{N}_2\text{O}$  emissions, but the strength of individual sources is uncertain (Intergovernmental Panel on Climate Change, 1996). Consequently, better source strength estimates are required for all systems. Atmospheric concentrations of  $\text{N}_2\text{O}$  are increasing at about 1.5  $\mu\text{g m}^{-3}$   $\text{yr}^{-1}$  and stabilization of  $\text{N}_2\text{O}$  concentrations at current levels would involve reductions in anthropogenic emissions of more than 50% (Sanhueza and Zhou, 1996). The primary biogenic sources of  $\text{N}_2\text{O}$  are nitrification and denitrification of soil N (Knowles, 1982; Poth and Focht, 1985). Nitrous oxide emissions are favored by low oxygen ( $\text{O}_2$ ) concentrations, high soil organic C, and  $\text{NO}_3$  (Payne, 1981).

Several studies have shown that land application of animal waste increases both  $\text{NH}_3$  (Lockyer et al., 1989; Whitehead and Raistrick, 1992) and  $\text{N}_2\text{O}$  emissions (Cabrera et al., 1994; Stevens and Cornforth, 1974; Egginton and Smith, 1986). These studies dealt with cattle and poultry manure or slurry applications and there is little information available concerning  $\text{NH}_3$  and  $\text{N}_2\text{O}$  emissions associated with application of waste lagoon effluent. Our objectives were to quantify gaseous losses of

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NH<sub>3</sub> and N<sub>2</sub>O after effluent application with a traveling gun irrigation system and relate N<sub>2</sub>O emission rates to soil water content and soil temperature.

## MATERIALS AND METHODS

This research was conducted on a 1200 sow, farrow-to-finish swine farm located in the Coastal Plains of North Carolina. The waste management system was a "flush" type with recycled water from the lagoon used to flush the pits beneath slatted floors. There were two pits beneath each house. The pits were flushed in a 4-h cycle: one pit being flushed and 4 h later a second pit was flushed. The waste from all the houses was flushed into a single 2.7-ha anaerobic lagoon. Effluent from the lagoon was applied to the field by a traveling big gun sprinkler system. The experimental site was an 11-ha field with sandy loam soils of the Norfolk (fine-loamy, kaolinitic, thermic Typic Kandiudult)–Rains (fine-loamy, siliceous, semiactive, thermic Typic Paleaquult)–Goldsboro (fine-loamy, siliceous, subactive, thermic Aquic Paleudult) series (Brandon, 1986). Soil characteristics are shown in Table 1. Soybean was planted in 18-cm rows on 17 July 1997 and the only N fertilizer applied was through three effluent applications during the growing season.

Effluent was applied through the irrigation system three times during the summer growing season. Quantities applied, total N, and inorganic N contents for each application are shown in Table 2. Effluent pH at time of applications was 8.0. Most of the N in the effluent was NH<sub>4</sub>-N with only small amounts of NO<sub>3</sub>-N and organic N. Effluent application was about twice as large in the first irrigation as in the last two. Nitrogen applied in the three irrigation events was 144.6, 59.1, and 70.8 kg N ha<sup>-1</sup>, respectively. Total applications during the study were 274.6 kg ha<sup>-1</sup> of total N and 239.2 kg ha<sup>-1</sup> of NH<sub>4</sub>-N. Initial effluent application was relatively late in the growing season (day of year [DOY] 237), thus there was limited opportunity for plant uptake.

Soil N (0- to 0.1- and 0.1- to 0.2-m depths) measurements were made through the season. Soil samples were taken from 10 areas in the field and each sample consisted of four cores. Soil temperatures (0.05-, 0.10-, and 0.15-m depths) were measured every 15 min using copper-constantan thermocouples. Total plant N was measured using Kjeldahl digestion, and soil N (NH<sub>4</sub> and NO<sub>3</sub>) was determined colorimetrically in a 2 M KCl soil extract. Losses of effluent NH<sub>3</sub> during the irrigation events were calculated by collecting effluent samples in glass containers and comparing N concentrations in the catchment samples to samples collected directly from the lagoon close to the irrigation pipe.

Micrometeorological instrumentation was located near the center of the field to obtain a minimum fetch of 100:1 (upwind canopy distance to measurement height) in all directions for wind profile development. Micrometeorological data and atmospheric NH<sub>3</sub> and N<sub>2</sub>O concentrations were determined throughout the season starting on DOY 200 (20 July) and ending at harvest on DOY 250. Windspeed (sensitive cup anemometers; Model 106-LED-DC, Thornthwaite & Assoc., Pittsgrove, NJ) and air temperature (aspirated thermocouples;

**Table 1. Soil properties prior to irrigation.**

Property	Value
Sand/silt/clay, %	64/23/13
Bulk density, g cm <sup>-3</sup>	1.5
pH	6.3
Organic matter, %	3.2
NH <sub>4</sub> -N, μg g soil <sup>-1</sup>	8.2
NO <sub>3</sub> -N, μg g soil <sup>-1</sup>	6.1

Model ASPTC, Campbell Scientific, Logan, UT) profiles were measured at six heights (plant height plus 0.2, 0.4, 0.6, 0.8, 1.6, and 2.7 m). Atmospheric concentrations of NH<sub>3</sub> and N<sub>2</sub>O were measured at plant height plus 0.6 and 1.6 m using tunable diode laser spectroscopy (TDL). The TDL (Model TGA100, Campbell Scientific) technique is based on infrared spectroscopy (Dias et al., 1996; Edwards et al., 1994). The diode laser is mounted in a liquid nitrogen cooled dewar and a heater in the dewar gives precise control of the laser in the 78- to 110-K region. The laser was operated in the IR spectral region between 3000 and 3025 cm<sup>-1</sup>. The sample and reference cells are 1.54 m and 0.05 m long, respectively. Both sample and reference detectors were Peltier-cooled mercury-cadmium-tellurium IR detectors (EG&G Judson, Montgomeryville, PA). The instrument had a short-term (sample period) total noise of about 10 ppbv. The TDL's electronics were integrated with a PC for software control of the digital signal processing, laser function, real-time display of laser-operating functions, and for data storage. Atmospheric gas concentrations were measured 10 times per second. Delta N<sub>2</sub>O concentrations (concentration differences between the two sampling heights) were calculated every minute, and delta NH<sub>3</sub> concentrations were calculated every two minutes. Delta concentrations were averaged over 30-min periods for use in the flux gradient technique. Mylar balloons were used to transport reference gases to the field to calibrate the laser spectrometers.

Ammonia and N<sub>2</sub>O gas flux densities above the canopy were determined during the measurement seasons using gas concentrations and the flux gradient gas transport technique using the momentum balance transport coefficient. The relationship for gas flux density is:

$$F = K_{mb} \frac{\Delta n}{\Delta z} \quad [1]$$

where  $F$  = gas flux densities (kg<sub>gas</sub> ha<sup>-1</sup> d<sup>-1</sup>),  $n$  = atmospheric gas concentration (μg gas m<sup>-3</sup>),  $z$  = gradient measurement height (cm), and  $K_{mb}$  = momentum balance transport coefficient. A negative  $F$  value indicates absorption and a positive value emissions from the field. The momentum coefficient ( $K_{mb}$ ) is determined from the relationship:

$$K_{mb} = \frac{-k^2(\mu_2 - \mu_1)}{\{\ln[(z_2 - z_d)/(z_1 - z_d)]\}^2 \Psi^2} \quad [2]$$

where  $k$  = von Karman constant,  $\mu$  = windspeed (cm s<sup>-1</sup>) at upper height ( $\mu_2$ ) and lower height ( $\mu_1$ ),  $z_d \cong 0$  (cm) for a water surface, and  $\Psi$  = stability correction factor (Dyer and Hicks, 1970). Errors associated with the flux gradient gas transport technique have been discussed by Harper (1988) and

**Table 2. Quantity of effluent, effluent concentrations, and total N, NH<sub>3</sub>-N, and NO<sub>3</sub>-N applied in each irrigation. DOY = day of year.**

Irrigation event	Quantity	Effluent concentration			Amount applied		
		Total N	NH <sub>4</sub> -N	NO <sub>3</sub> -N	Total N	NH <sub>4</sub> -N	NO <sub>3</sub> -N
		μg g <sup>-1</sup>			kg ha <sup>-1</sup>		
1 (DOY 237)	2.6	556 ± 56	501 ± 56	0.39 ± 0.14	144.6	130.5	0.1
2 (DOY 242)	1.1	537 ± 97	465 ± 59	0.91 ± 0.20	59.1	51.2	0.1
3 (DOY 246)	1.2	590 ± 167	479 ± 131	0.86 ± 0.27	70.8	57.5	0.1

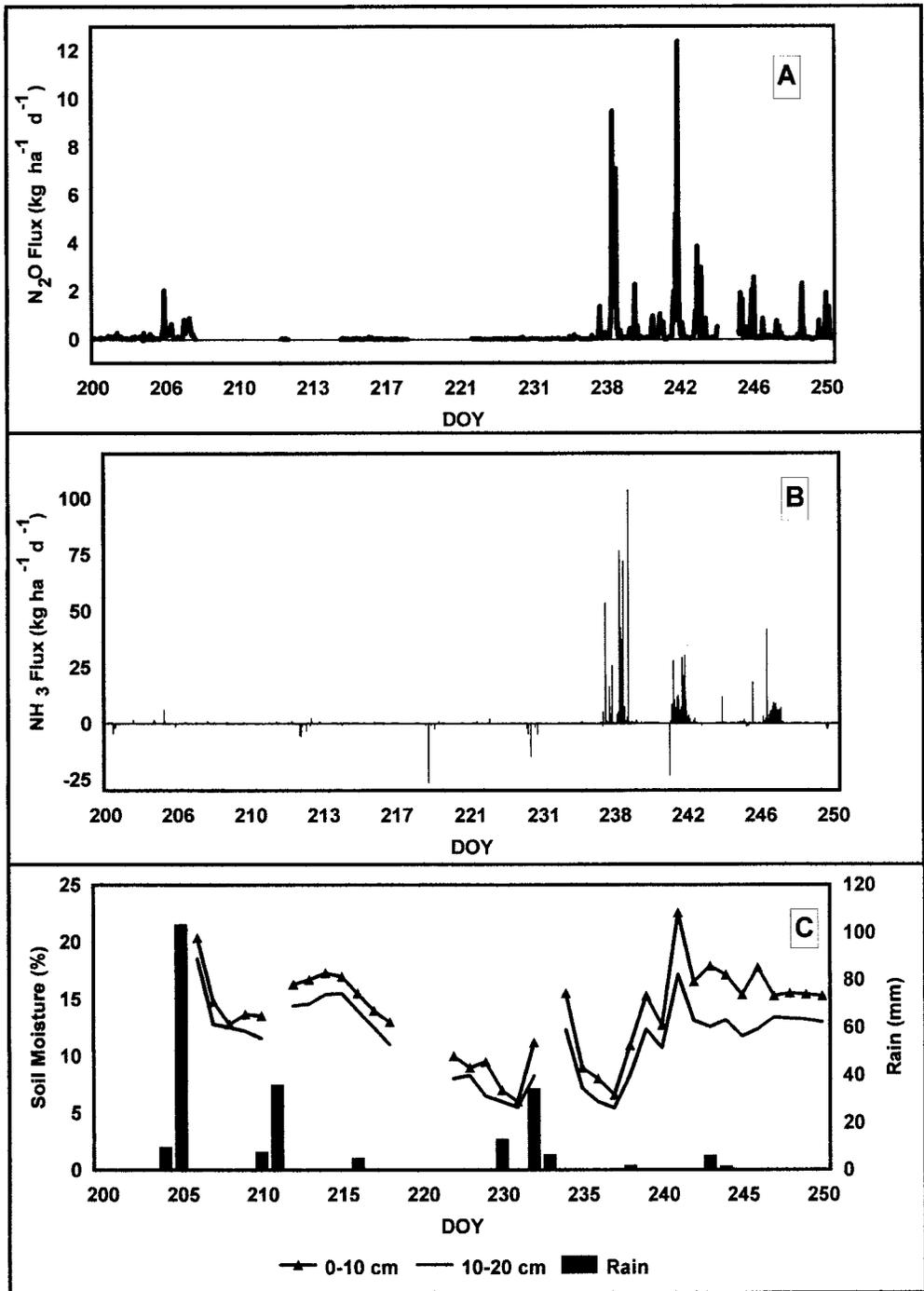


Fig. 1. Nitrous oxide flux and rainfall from a soybean field before irrigation with swine waste effluent, day of year (DOY) 200 to 236.

Denmead and Raupach (1993). Data were analyzed using the stepwise regression procedures of SAS (SAS Institute, 1991).

**RESULTS AND DISCUSSION**

Nitrous oxide flux measurements were taken during three periods prior to effluent applications. In general,  $N_2O$  fluxes were small ( $\leq 0.016\ kg\ ha^{-1}\ d^{-1}$ ) before effluent applications except for DOY 206.5 to 207.5 (Fig. 1A), when average  $N_2O$  flux was about  $0.25\ kg\ ha^{-1}\ d^{-1}$ . The increased emissions of  $N_2O$  during this period

were probably due to saturated soil conditions caused by 60 mm of rain on DOY 204 and 205 (Fig. 1C). Assuming an  $N_2O$  emission rate of  $0.016\ kg\ ha^{-1}\ d^{-1}$  during periods when fluxes were not measured, total emission would have been about  $0.53\ kg\ N\ ha^{-1}$  from planting until the first irrigation.

Nitrous oxide flux rates were substantially greater after effluent application than before (Fig. 2A). Average  $N_2O$  emission rate on DOY 236 was about  $0.01\ kg\ N_2O\ ha^{-1}\ d^{-1}$ . After Irr 1 on DOY 237, average  $N_2O$  emissions increased to  $0.5\ kg\ N_2O\ ha^{-1}\ d^{-1}$  within 6 to 8 h.

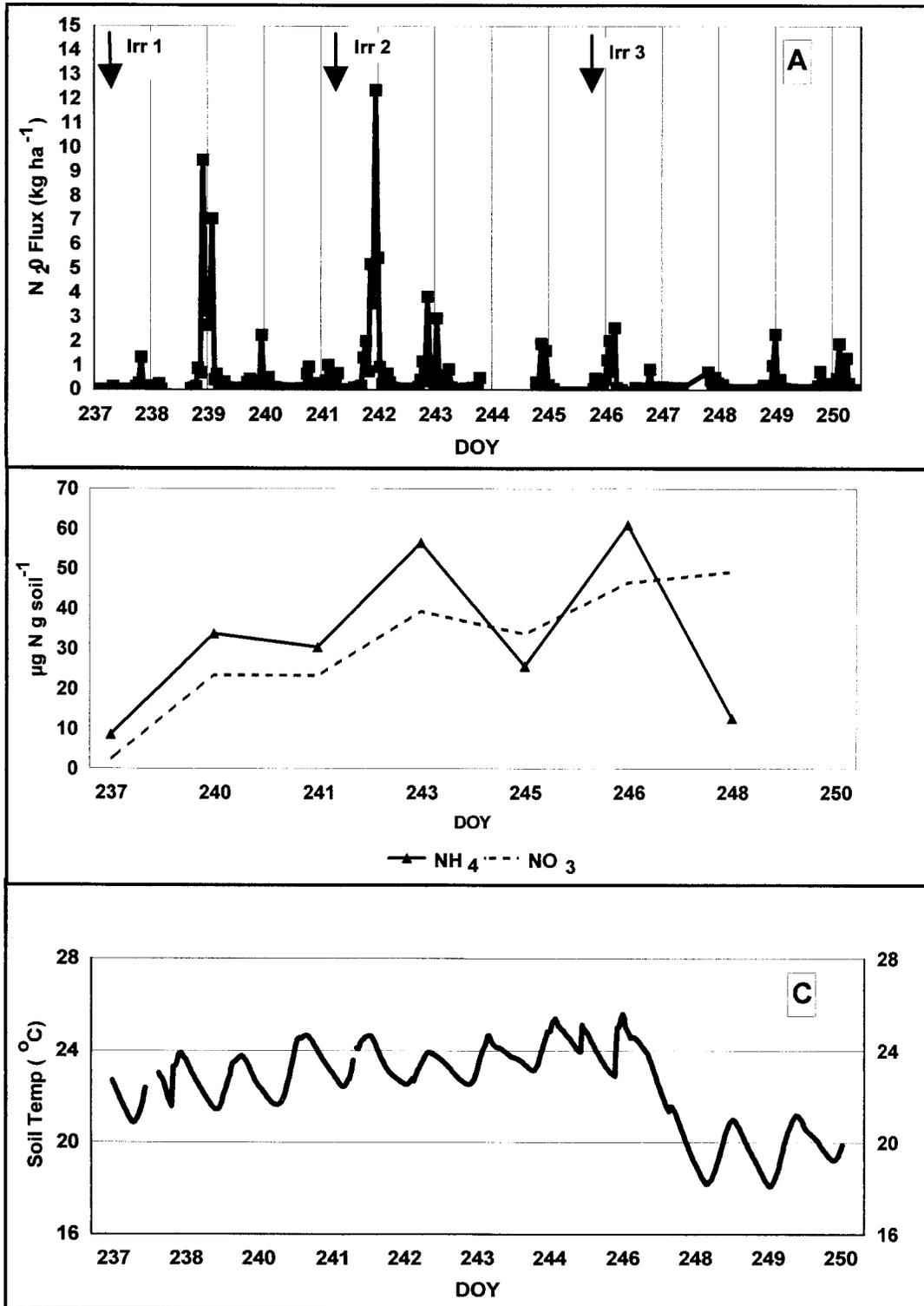


Fig. 2. Time course for (A) N<sub>2</sub>O flux and irrigation (Irr) with effluent, (B) soil moisture and rainfall, and (C) soil temperature from a soybean field.

Peak emission rates, however, were not observed until after about 30 h (DOY 238). Emissions rates decreased after DOY 238 but remained elevated, relative to pre-irrigation rates, until Irr 2. Peak emission rates were observed within 8 h after Irr 2 and 3. Other studies have shown highly variable time courses for peak response following animal waste application. Sharpe and Harper

(1997) and Whalen et al. (2000) reported maximum responses within several hours of swine effluent applications. Studies with cow and poultry manure have shown peak emissions from 1 to 7 d after application (Cabrera et al., 1994; Egginton and Smith, 1986; Lessard et al., 1996). Nitrous oxide is a product of both nitrification and denitrification of soil N. Highest rates of production

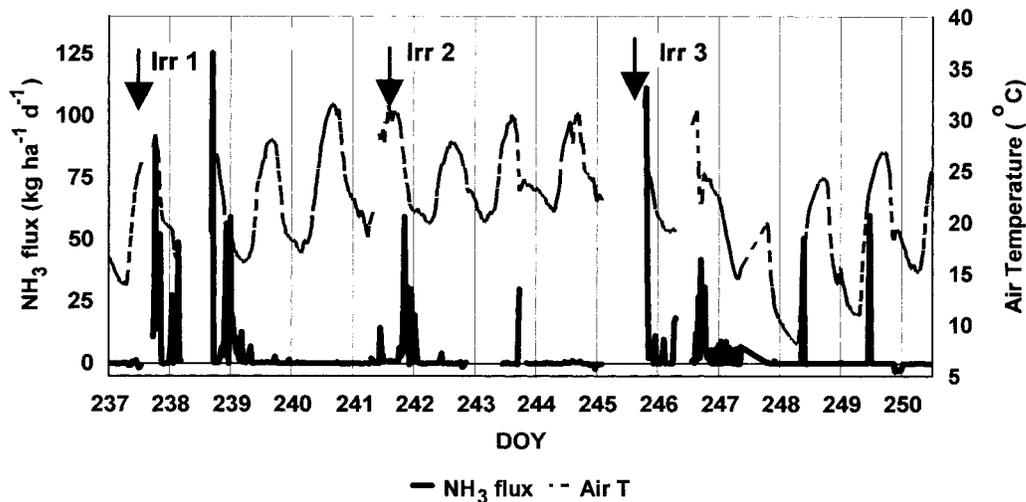


Fig. 3. Time course for  $\text{NH}_3$  flux and irrigation (Irr) with effluent from day of year (DOY) 237 to 250.

would occur at low  $\text{O}_2$  concentrations, which limit use of  $\text{O}_2$  as an electron acceptor in the nitrification process (Klemmedtsson et al., 1988) and inhibit reduction of  $\text{N}_2\text{O}$  to  $\text{N}_2$  in the denitrification process (Focht, 1974). A rapid release of  $\text{N}_2\text{O}$  would be expected from the application of a liquid organic fertilizer such as swine effluent. Swine effluent provides a large source of  $\text{NH}_4$  for nitrification, decreased  $\text{O}_2$  concentration by increasing soil water, and a soluble C source for microbial growth. Nitrous oxide emissions after the first two irrigations averaged about 0.58 and 0.78  $\text{kg ha}^{-1} \text{d}^{-1}$ . Emissions after Irr 3 were smaller, about 0.18  $\text{kg N}_2\text{O ha}^{-1} \text{d}^{-1}$ . The lower response may have been due to a sharp decrease in temperature since soil water content was similar on DOY 242 and 246 (Fig. 1C). Soil temperature decreased about 5°C (Fig. 2C) and air temperature decreased about 15°C (Fig. 3) from DOY 246 to 247. From DOY 237 through 250, total  $\text{N}_2\text{O-N}$  emission was about 4.1  $\text{kg N ha}^{-1}$  or about 1.5% of the applied N.

Before irrigation there was little or no  $\text{NH}_3$  flux from the soil-crop system (Fig. 1B). There were, however, three short periods during which atmospheric  $\text{NH}_3$  was absorbed by the crop. Each period of absorption was associated with periods of high atmospheric  $\text{NH}_3$  concentrations. Two of these periods are shown in Fig. 4 and 5. On DOY 212.5 to 213.5, the differential range in  $\text{NH}_3$  concentrations between the two measurement heights increased to 8 to 32  $\mu\text{g NH}_3 \text{m}^{-3}$  (Fig. 4B). During this time,  $\text{NH}_3$  absorption rate averaged about 1.17  $\text{kg NH}_3 \text{ha}^{-1} \text{d}^{-1}$  (Fig. 4A). Similarly, on DOY 218 to 219 (Fig. 5B), the delta  $\text{NH}_3$  concentration increased to a differential range of 15 to 25  $\mu\text{g m}^{-3}$  with corresponding periods of short-term  $\text{NH}_3$  absorption by the crop (Fig. 5B). During these periods atmospheric concentrations were probably greater than the  $\text{NH}_3$  compensation point (Farquhar et al., 1980) inducing  $\text{NH}_3$  absorption. Numerous studies have shown significant absorption of atmospheric  $\text{NH}_3$  by plants (Hutchinson et al., 1972; Harper and Sharpe, 1995; Parton et al., 1988).

The experimental field was southwest of the 2.7-ha waste handling lagoon supplying the effluent for irrigation and the measurement site was located about 325 m from the lagoon. Using the standard compass conven-

tion of north being 0° and east being 90°, then wind directions of 0 to 60° would indicate wind blowing from the lagoon toward the measurement site. Thus,  $\text{NH}_3$  volatilized from the lagoon was blown toward the experimental site when winds were less than 60°. From DOY 210 through 220, there were several extended periods when the wind was blowing from the lagoon toward the experimental site (Fig. 4C and 5C). However, during most of these periods windspeed was greater than 100  $\text{cm s}^{-1}$  and atmospheric  $\text{NH}_3$  concentrations were not affected (Fig. 4B and 5B) probably due to turbulence and mixing of  $\text{NH}_3$  from the lagoon with the bulk air mass. During periods of low windspeed and wind direction from the lagoon [DOY 212 to 213 (Fig. 4C); DOY 218 to 219 (Fig. 5C)], atmospheric concentration increased and the plants absorbed  $\text{NH}_3$ , as indicated by the negative flux rates. This forced absorption of N can occur in natural systems such as a forest (Nihlgard, 1985). There is no indication for N saturation in leaves (Van der Eerden et al., 1992) and uptake is probably linearly related to atmospheric  $\text{NH}_3$  concentrations. During these periods about 1.2  $\text{kg NH}_3 \text{ha}^{-1} \text{d}^{-1}$  was absorbed by the crop. If the entire field (11 ha) absorbed  $\text{NH}_3$  at a similar rate, then a total of about 39.6  $\text{kg}$  of  $\text{NH}_3$  would be absorbed over the 3-d period. The lagoon emitted 15 to 22  $\text{kg NH}_3 \text{ha}^{-1} \text{d}^{-1}$  during the summer of 1997 (Harper et al., 2002). Over a 3-d period the 2.7-ha lagoon would emit 120 to 178  $\text{kg NH}_3$ . Thus, 22 to 33% of the  $\text{NH}_3$  emitted from the lagoon was absorbed by the crop during these short-term periods.

Ammonia emissions were large immediately after irrigation with effluent, but decreasing to background levels within 24 to 48 h (Fig. 3). There was a large pulse of  $\text{NH}_3$  within 4 h after Irr 1, but the largest emissions were observed 24 to 30 h after irrigation. With Irr 2 and 3, the maximum emission rates were directly following irrigation. Previous research with waste effluent application has shown maximum emission rates directly following applications as in Irr 2 and 3 in this study (Sharpe and Harper, 1997; Smith et al., 1996). The slower maximum response with Irr 1 may have been due to the quantity of N applied and to the small quantity of precipitation on DOY 238. The larger quantity of applied N would

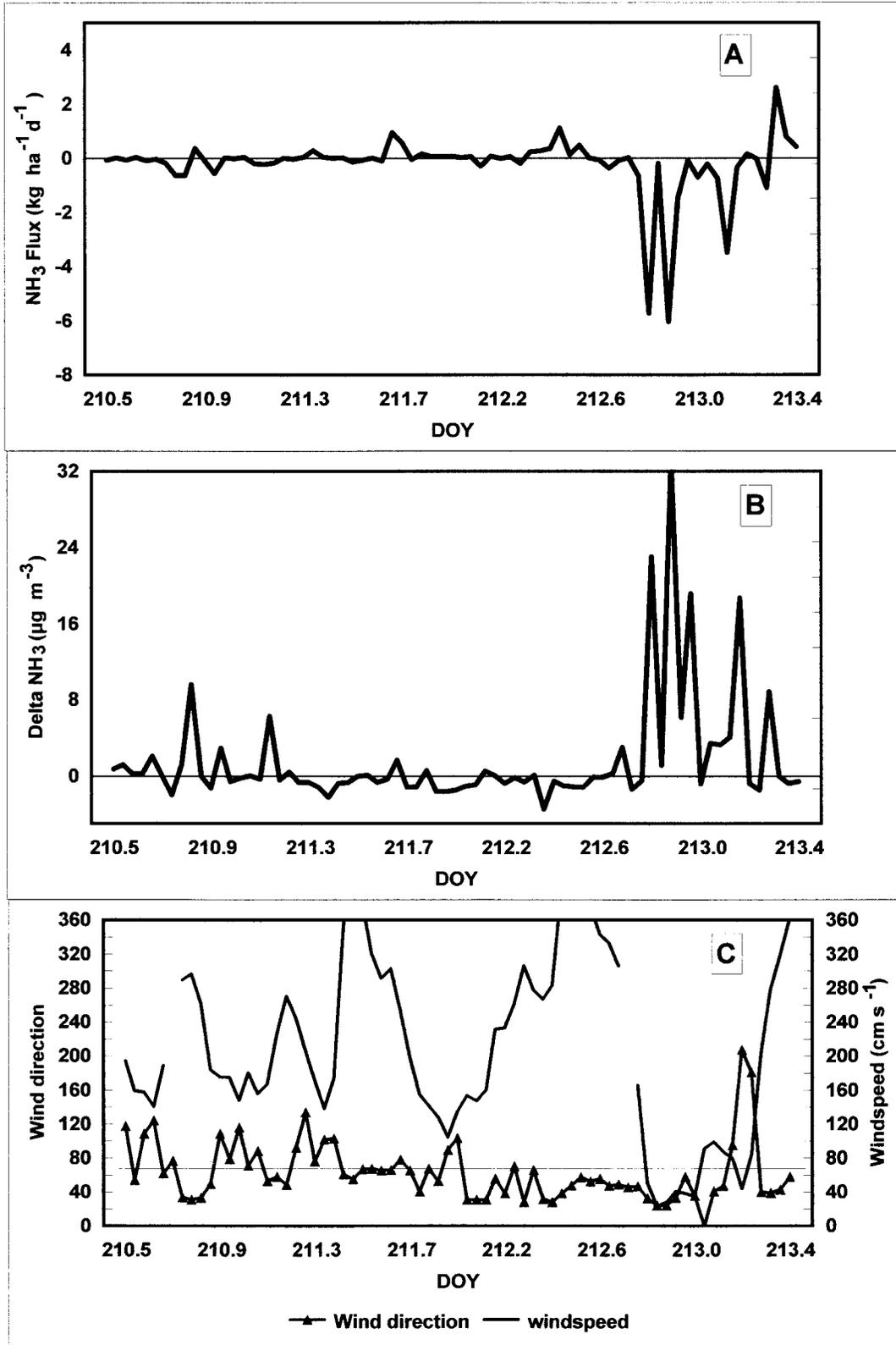


Fig. 4. Time course for (A) NH<sub>3</sub> flux, (B) differential (delta) NH<sub>3</sub> concentrations at 60- and 160-cm heights, and (C) wind direction and windspeed before effluent irrigation from day of year (DOY) 210 to 213.

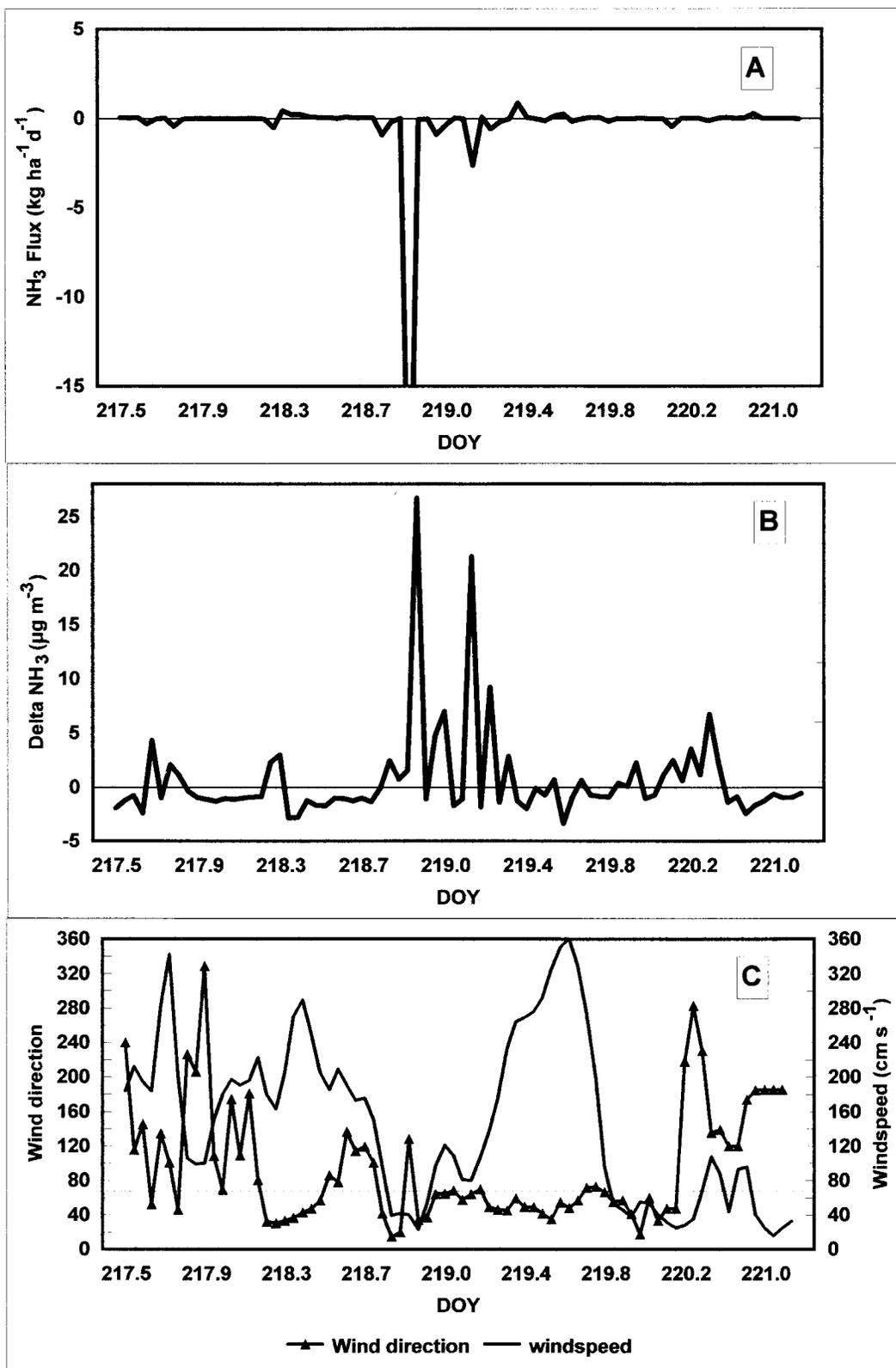


Fig. 5. Time course for (A) NH<sub>3</sub> flux, (B) differential (delta) NH<sub>3</sub> concentrations at 60- and 160-cm heights, and (C) wind direction and windspeed before effluent irrigation from day of year (DOY) 217 to 221.

have extended total time of NH<sub>3</sub> volatilization and evaporation of the rain may have resulted in a pulse of NH<sub>3</sub> emissions. Total N applied in Irr 2 and 3 and in the Sharpe and Harper (1997) and Smith et al. (1996) studies was less than half that applied with Irr 1. The larger maximum flux rates after Irr 1 and 3 (125 and 111 kg NH<sub>3</sub> ha<sup>-1</sup> d<sup>-1</sup>, respectively) than for Irr 2 (59 kg NH<sub>3</sub> ha<sup>-1</sup> d<sup>-1</sup>) were probably due to decreased windspeed. After Irr 1 and 3, windspeeds ranged from 150 to 200 cm s<sup>-1</sup> while windspeeds after Irr 2 were 15 to 100 cm s<sup>-1</sup>. Previous research has shown that the NH<sub>3</sub> flux is dependent of both air temp and windspeed (Fenn and Kissel, 1974; Bremner and Mulvaney, 1978).

During the irrigation events, about 12% of the NH<sub>4</sub>-N in the effluent was volatilized as NH<sub>3</sub> before reaching the crop or soil surface. Total emissions after the three irrigations were 42, 11, and 11.1 kg NH<sub>3</sub> ha<sup>-1</sup>, respectively. These losses ranged from 30% of applied NH<sub>4</sub> for Irr 1 to 15% for Irr 3. More than twice as much effluent was applied during Irr 1 than Irr 2 or 3 (Table 1) and this may have resulted in pooling of effluent on the crop and soil surface allowing for greater NH<sub>3</sub> volatilization. In total, about 35.4 and 1.5% of the effluent N was lost to the atmosphere as NH<sub>3</sub>-N and N<sub>2</sub>O-N, respectively.

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## Ecological Risk Assessment

### Industrial Impact on Marsh Soils at the Bahia Blanca Ria, Argentina

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#### ABSTRACT

The Bahía Blanca Estuary is located in southern Buenos Aires province, Argentina. The area is linked to a petrochemical industrial complex, whose raw materials and final products contaminate the surrounding areas via atmospheric pollution and effluents, which are dumped in the estuary waters. To establish the effects of the industrial waste disposal on the nearest coastal soils, 17 samples were taken at different distances from the loading dock and the outfall pipes of the industrial complex. Later, the physicochemical characteristics of the soil samples, their hydrocarbon contents, sulfides, sulfates, Zn, Cu, and Pb were analyzed and a comparison was made to control samples, which were not affected by the industrial outfall. Hydrocarbons, Zn, Cu, and Pb contents were found at levels that modified the physical and chemical characteristics of the soils. The resistance to penetration shows that the thinner the film of water that surrounds the particles or aggregates, the smaller the migration of organic micelle, which settle on the surface of the contact material. This is demonstrated by the degree of cohesion reached by the particles and the strong influence on the index of hydrophobicity. The high porosity shows that the continuity of the porous space of the soil matrix is impeded by the presence of pollutants, which generate areas that are highly limiting to water flow. The oxidation-reduction potential and the low concentrations of soluble forms of Cu and Pb compared with their concentrations precipitated as sulfides confirm the action of the pollutants.

**B**AHÍA BLANCA is a mesotidal estuary located in southern Buenos Aires province, Argentina. A system of northwest-southwest channels separated by islands, low-lying wide marshes, and tidal flats are the principal morphological features. A dense network of minor tidal channels and creeks extensively covers the tidal flats (Aliotta and Perillo, 1990; Gómez and Perillo, 1995).

The Bahía Blanca estuary port system is the most important in the country. Puerto Galvan is located on the northern coast and linked to a petrochemical industrial complex, whose hydrocarbon raw materials and

final products contaminate the surrounding areas via atmospheric pollutants and effluents, which have been dumped in the estuary for almost 30 years. The industrial waste that reaches the sea through atmospheric precipitation and the introduction of urban waste are often responsible for the entry of heavy metals into the marine environment and their incorporation into the soils and sediments (Förtsner, 1989; Giordano et al., 1992; Horning et al., 1989).

Tidal marsh soils are often characterized by low bulk densities, high organic matter content, and high sulfur content. The organic matter accumulated by superficial deposition of marsh grass detritus and the effluents is very important to the fate of trace metals (Griffin and Rabenhorst, 1989). The oxidation status of soils and sediments affects the distribution of some trace metals between bound, unavailable forms and soluble and available forms (Gambrell and Patrick, 1989; Gambrell et al., 1991).

The combination of anaerobic conditions and high organic matter content makes the salt marsh environment ideal for bacterial reduction of sulfate to sulfide (Pons and Van Breemen, 1982). This process of sulfidization plays an important role in the development of marsh sediments and in the control of heavy metal solubility.

This paper reports the influence of industrial pollution on the properties of soils in an estuarine environment. The objectives of this study are to determine the effect of hydrocarbons and waste dumping on the physical properties of soils, the heavy metal content and the relationship of the oxidation-reduction potential to the solubility of heavy metals, and the S-pyrite and sulfate contents.

#### MATERIALS AND METHODS

The sampling site extended 1700 m from the loading dock to the contaminant outfalls. Seventeen soil samples were taken (Thionic Fluvisols), one every 100 m (Fig. 1). The sampling sites were chosen to obtain a representative measure of the pollution conditions in the marsh.

Topsoil (0-30 cm) samples were collected using an Eijkel-

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