

## Gaseous Nitrogen Emissions from Anaerobic Swine Lagoons: Ammonia, Nitrous Oxide, and Dinitrogen Gas

Lowry A. Harper,\* Ron R. Sharpe, and Tim B. Parkin

### ABSTRACT

Seventy-five percent of swine (*Sus scrofa*) production systems in North America use anaerobic or liquid-slurry systems for waste holding or disposal. Accurate emissions data and emission factors are needed for engineering, planning, and regulatory agencies. These data are used for system design and evaluation of the effect of animal concentrations on the regional soil, surface and ground waters, and atmospheric environments. Noninvasive techniques were used to evaluate trace gases without disturbing the meteorology or lagoon system being measured. Micrometeorological and gas sensors were mounted on a submersible barge in the center of the lagoon for use with flux-gradient methodology to determine trace gas fluxes, without disturbing atmospheric transport processes, over extended periods. Collateral measurements included lagoon nutrient, dissolved gas concentrations, and sludge gas mass flux. Ammonia emissions varied diurnally and seasonally and were highly correlated with windspeed and water temperature. Nutrient loading measurements showed that mobile ions, which were nonvolatile, were constant throughout four successive lagoons. Immobile ions concentrated primarily in the sludge layer of the first lagoon. Measurements of denitrification  $N_2$  losses suggest as much  $N_2-N$  lost as from  $NH_3-N$ . Ammonia gas emissions are not as large a percentage of total nitrogen input to the lagoons as previously thought but unaccounted-for nitrogen requires further research.

AMMONIA ( $NH_3$ ) is the most abundant alkaline component in the atmosphere that neutralizes sulfur dioxide ( $SO_2$ ) and N oxides. Consequently,  $NH_4^+$  is a major component of atmospheric aerosols (particulate matter) and rainfall (Asman, 1994). When  $NH_3$  and  $NH_4^+$  are deposited onto the soil, nitrification occurs and (in this oxidation process) acid is formed, causing soil acidification (van der Molen et al., 1990) and possible plant nutrient imbalances of Ca, K, and Mg. Ammonia and  $NH_4^+$  deposition can play an important role in natural ecosystems. Many natural systems such as forest and heath are adapted to low nutrient conditions (Nilsson and Grennfelt, 1988) and when large quantities of N are deposited onto the landscape, nitrophilous species are better competitors. For large parts of northern Europe the N critical loading for many plant species is being exceeded, causing species replacement (Bobbink et al., 1992). In cropping systems, atmospheric  $NH_3$  and  $NH_4^+$  may be beneficial by adding N during critical times of the day (Harper et al., 1987) and during periods of

soil N deficiency (Sharpe et al., 1988; Harper et al., 1996). Crop canopies may also remove significant quantities of  $NH_3$  released to the atmosphere from nearby sources (Harper and Sharpe, 1995; Harper et al., 1996; Bussink et al., 1996).

Increased animal concentrations result in increased efficiency, improved economics, and a better industry support system; however, concentrated livestock production can represent a significant source for  $NH_3$  emissions to the atmosphere in a relatively small geographic area. Seventy-five percent of swine production systems in North America use anaerobic or liquid-slurry systems for wasteholding, which is a source for  $NH_3$  emissions (Safley et al., 1992b). Ammonia emissions from concentrated animal production sites may influence landscapes and their use (such as forestry, water management areas, fisheries, structural corrosion, aquatic ecosystems) even though the landscape sites may range from a few kilometers to the next state or country from the emission sources. Adverse effects may be due to the direct and indirect effects of  $NH_3$  (which has a shorter residence time of hours) and/or  $NH_4^+$  aerosols of nitrate ( $NO_3^-$ ) and sulfate ( $SO_4^{2-}$ ), which may have a residence time of 5 to 9 d (Crutzen, 1983). Reduction of N losses are also significant economically since the original source was synthetic or biologically fixed N at considerable expense, providing strong motivation from the animal producer's viewpoint to promote reduction or prevention of these losses.

In order to evaluate the effect of animal concentration on the local and regional soil, ground water, and atmospheric environments, accurate nutrient dynamics and emissions and emission factors (emissions per animal unit per year) are needed by planning and regulatory agencies. The purpose of this research was to evaluate climatic influence on emissions from concentrated swine production on a seasonal and annual basis using noninvasive techniques and to determine the effect of multiple lagoons on nutrient loading and management of the lagoons.

### MATERIALS AND METHODS

The swine production unit used in this study is a 12 000 animal facility located in the Coastal Plains of Georgia. The waste disposal system is a series of four lagoons with the animal house waste emptied into the first lagoon. The lagoons are 3.5-, 1.3-, 3.5-, and 1.3-ha for Lagoons 1 through 4, respectively, and the effluent is gravity fed in succession to each of the lagoons. The production facility uses about 300 000  $m^3$  water annually for cleaning and flushing with 82% of the water recycled from Lagoon 4. The balance of the water is from fresh ground water. Effluent from Lagoon 4 (about 29 000  $m^3$

L.A. Harper and R.R. Sharpe, Southern Piedmont Conservation Research Unit, USDA-ARS-JPCSNRCC, 1420 Experiment Station Road, Watkinsville, GA 30677; and T.B. Parkin, National Soil Tilth Lab., 2150 Pammel Drive, Ames, IA 50011. Contribution from the USDA-ARS-JPCSNRCC, the National Soil Tilth Lab., and Univ. of Georgia Agricultural Experiment Station. Received 30 Sept. 1998.  
\*Corresponding author (lharper@arches.uga.edu).

yr<sup>-1</sup>) is applied to crops and/or pastures through solid-set or center pivot irrigation systems (Sharpe and Harper, 1997). Although trace gases are emitted from all of the lagoons, most of the trace gas measurements for this study were made from the primary lagoon (Lagoon 1).

Micrometeorological instrumentation was located in the center of the lagoon to obtain a minimum fetch of at least 50:1 (upwind lagoon distance to measurement height) in any direction for wind, temperature, and gas concentration profile development. The 50:1 fetch length was marginal in some directions; however, a larger ratio was obtained in the direction of the prevailing winds. Windspeed and NH<sub>3</sub> concentration profile analysis was used to evaluate profile development. Instruments were affixed to a platform "barge" with flotation tanks. The barge with micrometeorological equipment, already mounted and tested, was floated to the center of the lagoon, secured into place with adjustable legs extending to the bottom and guylines attached to the shore. The barge was then sunk to about 50-mm below the water surface to minimize structural interference of windflow patterns by the platform itself. Windspeed (using sensitive cup anemometers, Thornthwaite Associates, Pittsboro, NJ<sup>1</sup>), air temperatures (using aspirated thermocouples, Campbell Scientific, Logan UT, Model ASP-TC), and NH<sub>3</sub> concentration profiles were measured above the lagoon at vertical heights of 0.2-, 0.4-, 0.6-, 0.8-, 1.6-, and 2.7-m above the water surface. Ammonia concentrations were obtained by drawing unfiltered air through gas washing bottles containing 80 mL of 0.1 M H<sub>2</sub>SO<sub>4</sub> at a known rate (6 L min<sup>-1</sup>) for 4 h, then transferring it to storage bottles for refrigeration until analysis of NH<sub>4</sub><sup>+</sup> (by Wards Laboratories, Kearney, NE) concentration by a colorimetric technique similar to that of Weier et al. (1980). Water temperature was measured with thermocouples at three vertical depths, at the surface (about -0.05 m), in the sludge layer (about 3 m), and at a midpoint between the two layers. All electronic data was sampled every minute and averaged over 15 min using a Campbell Scientific Model 21-X data acquisition system.

A schedule of twenty-three, 24- to 48-h data collection periods were made throughout six measurement seasons over the primary lagoon (two each in winter, summer, and spring) to evaluate differences in losses related to microclimate and lagoon seasonal variations. Ammonia flux densities were determined during the measurement seasons above the lagoon surface from profile gradients of NH<sub>3</sub> concentrations and the momentum balance transport coefficient.

$$N = K_{mb} \frac{\Delta n}{\Delta z}$$

The momentum balance transport coefficient ( $K_{mb}$ ) is determined from the relationship,

<sup>1</sup> Mentioning of trade names is for information purposes and not an endorsement by the USDA.

<sup>2</sup> The momentum balance relationship is valid theoretically only during adiabatic conditions that prevail briefly in the early morning and late afternoon. Stability corrections have been employed for unstable conditions by Dyer and Hicks (1970) and Panofsky (1963). A discussion of these corrections can be found in Thom et al. (1975) and Denmead (1983). The Dyer-Hicks profile correction function is the more elaborate correction (Denmead, 1983) with corrections on the eddy diffusivity and the gas, and was the correction function used in these studies. The need for stability corrections at times other than neutral conditions (where Richardson number is zero) can be evident when highly unstable conditions prevail. It should be noted that with stability corrections, the momentum balance technique is valid at all times of the day.

$$K_{mb} = \frac{-k^2(u_2 - u_1)}{\left[ \ln \left( \frac{z_2 - z_d}{z_1 - z_d} \right) \right]^2} \psi^2$$

where  $N$  = NH<sub>3</sub> flux density (kg ha<sup>-1</sup>d<sup>-1</sup>),  $n$  = atmospheric NH<sub>3</sub> concentration (μg m<sup>-3</sup>),  $k$  = von Karman constant,  $u$  = windspeed (m s<sup>-1</sup>),  $z$  = gradient measurement height (m),  $z_d$  = effective vegetation height (m) (note:  $z_d$  is very small over water and was treated as 0), and  $\psi$  = stability correction factor (no dimensions).<sup>2</sup> This flux-gradient micrometeorological technique was used since it does not interfere with the convective or turbulent transport processes involved in trace gas emissions (Denmead and Raupach, 1993) and has been used and described previously (Harper et al., 1973; Denmead et al., 1978). Errors associated with the micrometeorological technique have been discussed by Harper (1988) and Denmead and Raupach (1993) and error attributed to the technique is ±15%.

Spatial sampling of the lagoon, both horizontally (in three to four random locations) and vertically (at the surface, the vertical midpoint [about 1.5 m], and in the sludge layer), was accomplished using a remotely actuated, closed sampler to obtain samples representative of each of the vertical layers. The sample containers were lowered from a boat to the appropriate depths, opened for sample collection, then closed before bringing them to the surface for sample retrieval and storage. The samples were frozen immediately and shipped to a laboratory (Ward Laboratories, Kearney, NE) for analysis of total nitrogen (TKN), NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, pH, P, K, S, Ca, Mg, Na, Zn, Fe, Mn, and Cu. For NH<sub>4</sub><sup>+</sup>-N, a weighed portion of slurry suspension (2 g) was extracted with 2 M KCl. The filtrate was analyzed by flow injection analysis with salicylate-nitroprusside color reagent (Lachat Instruments, Milwaukee, WI, QuikChem Method 12-107-06-2-A, ammonia [salicylate] in 2 M KCl soil extracts [Anonymous, 1983]). A portion of the slurry suspension was cleared for NO<sub>3</sub><sup>-</sup>-N with calcium oxide (CaO) and analyzed by flow injection analysis by cadmium reduction (Lachat Instruments, Milwaukee, WI, QuikChem Method 10-107-04-1-A, Nitrate/Nitrite, Nitrite in Surface Water, Wastewater [Anonymous, 1992a]). For total N, a weighed portion of slurry suspension (about 0.25 g) was placed in a combustion boat with a nickel boat liner and combustion catalyst (tungsten oxide). The combustion boat was then loaded into a Leco (St. Joseph, MI) FP-2000 N analyzer (Padmore, 1990). For P, K, Ca, Mg, Zn, Fe, Mn, Cu, and Na, a weighed portion of slurry suspension was treated with 10 mL nitric acid. After boiling to reduce the volume to approximately 2 mL, 3 mL of perchloric acid (70%) was added. The solution was heated until it cleared and then was allowed to fume for an additional 20 min. Deionized water was added to the flask while the solution was still hot to bring all minerals into solution. The final volume was brought to 50 mL with deionized water. Phosphorous was determined by developing the meta-mandate yellow and reading color intensity with a colorimeter (Anonymous, 1992c). Potassium (Anonymous, 1992b) and sodium (Anonymous, 1992f) were measured by flame emission. Calcium and Mg were determined by atomic absorption after diluting with lanthanum solution (Anonymous, 1992d). Zinc, Fe, Mn, and Cu were measured by atomic absorption (Anonymous, 1992d). The pH of the solution was measured on a 2-g portion of the slurry suspension diluted to 10 mL with deionized water and then read with a glass electrode (Anonymous, 1992e). All lagoons were sampled similarly.

Gas bubbles emitted from each of the lagoons were trapped in three to four collectors in each lagoon below the lagoon surface. The collectors were made of 20-L open-bottom car-

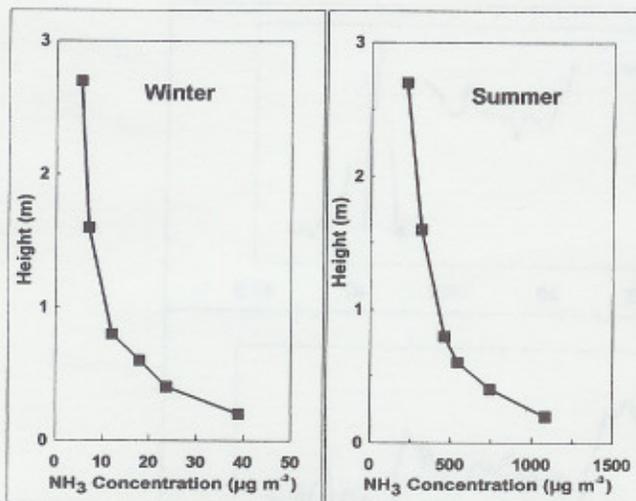


Fig. 1. Ammonia concentration gradients measured above a swine lagoon between 1200 and 1600 EDT on 12 Feb. and 9 Aug. 1996.

boys (0.275-m diameter) with flotation collars, tethered to the lagoon bottom, for collection of the mass-flow gases (bubbles) before they reached the water–air interface. Gases were collected from the samplers using evacuated sample lines and evacuated SUMA canisters (B.R.C. Rasmussen, Portland, OR). Eight-milliliter gas samples were transferred to evacuated glass autosampler vials capped with butyl rubber stoppers. The samples were analyzed for  $N_2$  and  $O_2$  using a thermal conductivity detector (Tracor Model 540, Austin TX) at 200°C and a molecular sieve column; for  $CH_4$  using a flame ionization detector (Tracor Model 540) with the detector at 200°C. Samples were analyzed for  $N_2O$  using an electron capture detector (Shimadzu Mini-2, Columbia, MD) with the detector at 300°C, column temperature of 80°C, a Porapak Q column (Alltech Associates, Deerfield, IL), and  $N_2$  as the carrier gas at 30 mL  $min^{-1}$ . Samples were analyzed for  $CO_2$  using an infrared gas analyzer (Model 880A, Rosemont Analytical, LaHabra, CA) by passing the effluent from the electron capture detector. Gas fluxes were determined by measuring the amount of gases collected over time and then multiplying the emissions by the measured concentrations.

## RESULTS AND DISCUSSION

### Ammonia Emissions

Ammonia concentration gradients varied considerably, depending on climatic and lagoon conditions: Figure 1 gives some gradients measured during different seasonal conditions. Windspeeds during the summer period were about 50% higher but there was no difference in Richardson's number (stability). Although a large difference in above-surface concentration is observed between winter and summer, other factors than temperature influence the concentration gradients, including windspeed, water pH, and water nutrient concentration (see below). Normal background  $NH_3$  concentrations varied between 0 and 20  $\mu g m^{-3}$  (Sharpe and Harper, 1997).

Figure 2 shows the relationship between windspeed and  $NH_3$  flux density during summer 1994 when water temperatures were reasonably constant. Within the

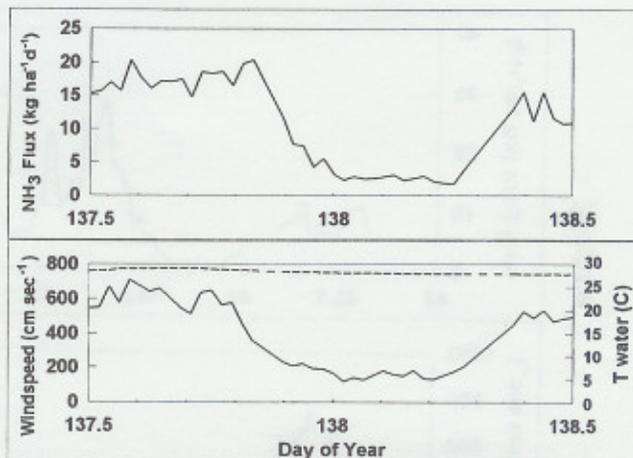


Fig. 2. Lagoon ammonia emissions in relation to windspeed at 1.6-m above the water surface (solid line) and water temperature at 0.05-m below the water surface (dashed line), Georgia Coastal Plains, summer, 1995.

summer season, a 40% daily decrease from maximum to minimum windspeeds was followed by a 46% decrease in the  $NH_3$  flux density; however, the small decrease in daily surface water temperature (from 29 to 28°C) could have contributed to a slight decrease in flux density, since colder water results in a reduced gas vapor pressure in the water (about 3%). Figure 3 relates  $NH_3$  emissions to windspeed and water temperature during a period of large weather variation in winter (1996). The general increase in water temperature on day of year (DOY) 45 was due to the passing of a "warm front" moving through the local area. Average daily windspeeds on DOY 43 through 46 were not significantly different, but effluent temperature increased about 10°C during measurement. This increase in temperature resulted in average  $NH_3$  emissions approximately three times larger on DOY 46. During this winter period  $NH_3$  emissions were highly correlated with surface (about -0.05-m deep) water temperature ( $r^2 = 0.84$ ) but poorly correlated with windspeed ( $r^2 = 0.45$ ), indicating that the winter season emissions were influenced primarily by water temperature during this time period.

Ammonia emissions were quite variable among seasons (Table 1). The emissions' driving forces (independent effects) were interrelationships of physical and chemical factors. The largest emissions (summer, 1996) occurred during periods of high windspeed and effluent temperature but during relatively low  $NH_4^+$  effluent concentration. The next highest emissions occurred during periods of moderate windspeeds but higher effluent concentration (spring, 1995). Although winter windspeeds in 1996 were quite high, water temperature was lowest of all measurement periods, resulting in the lowest emissions period. Windspeed and effluent temperature had the highest correlation with  $NH_3$  emissions ( $r^2 = 0.86$  and 0.45, respectively) based on nineteen, 24-h measurements, with minor correlation with effluent concentration and pH ( $r^2 = 0.15$  and 0.13, respectively). The large

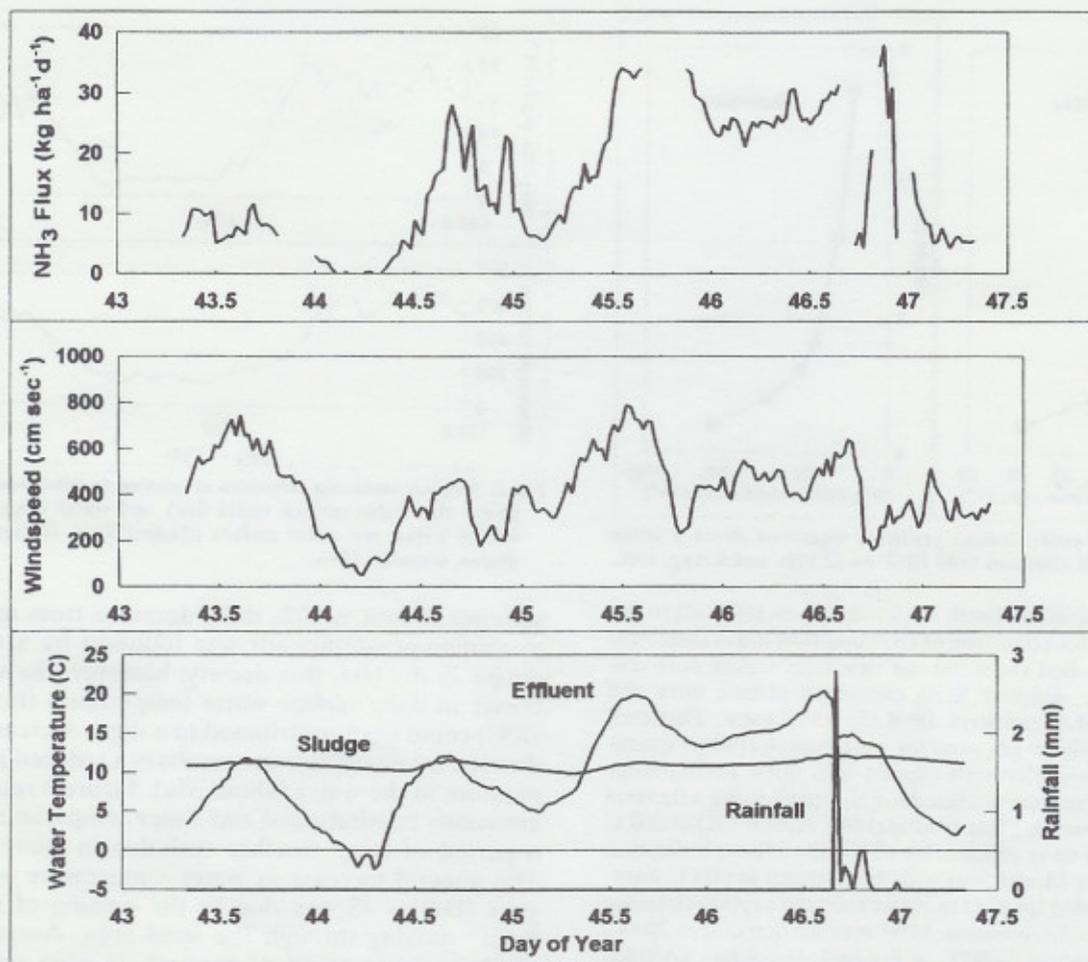


Fig. 3. Lagoon ammonia emissions in relation to windspeed (at 1.6-m above the water surface), water temperature (at 0.05-m below the water surface), and to sludge temperature (located within the sludge layer usually around 3.0-m deep, depending on seasonal lagoon storage requirements), Georgia Coastal Plains, winter, 1996.

effect of windspeed on emissions can be illustrated by comparing the partial pressure of  $\text{NH}_3$  at the effluent surface during the summers of 1994 and 1996. Although the partial pressure of  $\text{NH}_3$  in 1994 was almost twice as high as 1996 (about 0.57 and 0.31 Pa, respectively, and primarily due to a difference in effluent pH), emissions were 12.7 times higher in 1996 with a seasonal average windspeed of 6.7 times higher (Table 1). The low statistical influence of effluent concentration and pH was prob-

ably due to small variations in the chemical makeup of the lagoon that resulted from one management system. Combined multiple regression analysis of the six seasons' daily average emissions gave a very good statistical model ( $r^2 = 0.94$ ,  $N = 19$ ) for emissions on the primary lagoon from this management system, of the form

$$\text{NH}_3 \text{ flux density (kg NH}_3 \text{ ha}^{-1} \text{ d}^{-1}) = -275.2817 \\ + \text{windspeed (cm s}^{-1}) \times 0.0510$$

Table 1. Lagoon ammonia emissions and environmental conditions for a swine production system located in the Coastal Plains of Georgia.

Season	Year	Begin DOY‡	Air temperature °C	Windspeed cm s <sup>-1</sup>	Effluent temperature† °C	Effluent NH <sub>4</sub> † mg L <sup>-1</sup>	Effluent pH†	NH <sub>3</sub> flux kg ha <sup>-1</sup> d <sup>-1</sup>
Summer	1994	242.0	26.9	168.6	29.5	229.5	8.0	3.88
Winter	1994	340.5	14.8	159.8	15.4	269.0	7.7	2.35
Spring	1995	138.3	26.2	286.7	27.8	290.8	7.6	11.93
Winter	1996	44.5	10.0	470.8	10.3	238.6	7.4	1.56
Spring	1996	137.7	24.6	191.3	27.1	277.5	7.5	3.79
Summer	1996	221.5	25.8	1128.5	29.5	237.5	7.7	48.88
Average			21.4	401.0	23.3	257.2	7.7	12.06
Standard deviation			6.5	342.4	7.6	23.0	0.2	16.81

† At -0.5 m depth.

‡ Day of year.

Table 2. Mass flux of gases emitted from the sludge layer of a four-stage swine waste lagoon system, Cordele, GA.

Lagoon	Gas flux kg gas ha <sup>-1</sup> d <sup>-1</sup>	N <sub>2</sub> % kg N <sub>2</sub> ha <sup>-1</sup> d <sup>-1</sup>	N <sub>2</sub> flux kg N <sub>2</sub> ha <sup>-1</sup> d <sup>-1</sup>	N <sub>2</sub> O % kg N <sub>2</sub> O ha <sup>-1</sup> d <sup>-1</sup>	N <sub>2</sub> O flux kg N <sub>2</sub> O ha <sup>-1</sup> d <sup>-1</sup>	CH <sub>4</sub> % kg CH <sub>4</sub> ha <sup>-1</sup> d <sup>-1</sup>	CH <sub>4</sub> flux kg CH <sub>4</sub> ha <sup>-1</sup> d <sup>-1</sup>	O <sub>2</sub> † % kg O <sub>2</sub> ha <sup>-1</sup> d <sup>-1</sup>	O <sub>2</sub> flux† kg O <sub>2</sub> ha <sup>-1</sup> d <sup>-1</sup>	CO <sub>2</sub> ‡ % kg CO <sub>2</sub> ha <sup>-1</sup> d <sup>-1</sup>	CO <sub>2</sub> flux‡ kg CO <sub>2</sub> ha <sup>-1</sup> d <sup>-1</sup>	TKN‡ mg N kg <sup>-1</sup> d <sup>-1</sup>	Ammonium mg NH <sub>4</sub> -N kg <sup>-1</sup> d <sup>-1</sup>	Nitrate mg NO <sub>3</sub> -N kg <sup>-1</sup> d <sup>-1</sup>	Dissolved oxygen mg L <sup>-1</sup>	pH
1	159.0	14.6	23.1	0.0	0.0	79.1	125.8	0.6	0.9	4.6	7.3	283.6	238.6	0.0	0.7	7.44
2	21.0	53.9	11.3	0.1	0.0	26.1	5.5	1.5	0.3	1.7	0.4	224.3	194.7	0.0	8.0	7.70
3	20.0	59.1	11.8	2.5	0.5	13.1	2.6	2.2	0.4	1.3	0.3	104.3	102.0	16.7	18.8	7.50
4	17.0	69.4	11.8	18.4	3.1	7.6	1.3	7.5	1.3	0.7	0.1	38.7	29.0	34.0	20.0	7.30
Sum	217.0	58.1	58.1	3.6	3.6	135.2	135.2	3.0	3.0	8.0	8.0	36.7	29.0	34.0	20.0	7.30

† We think the concentrations of O<sub>2</sub> and CO<sub>2</sub> in the mass flux gas analyses are probably influenced by algae growing in the gas collectors.

‡ Total nitrogen.

+ lagoon temperature (°C) × 0.1791

+ effluent Concentration (mg kg<sup>-1</sup> NH<sub>4</sub><sup>+</sup>)

× 0.2235 + effluent pH × 26.8137 [1]

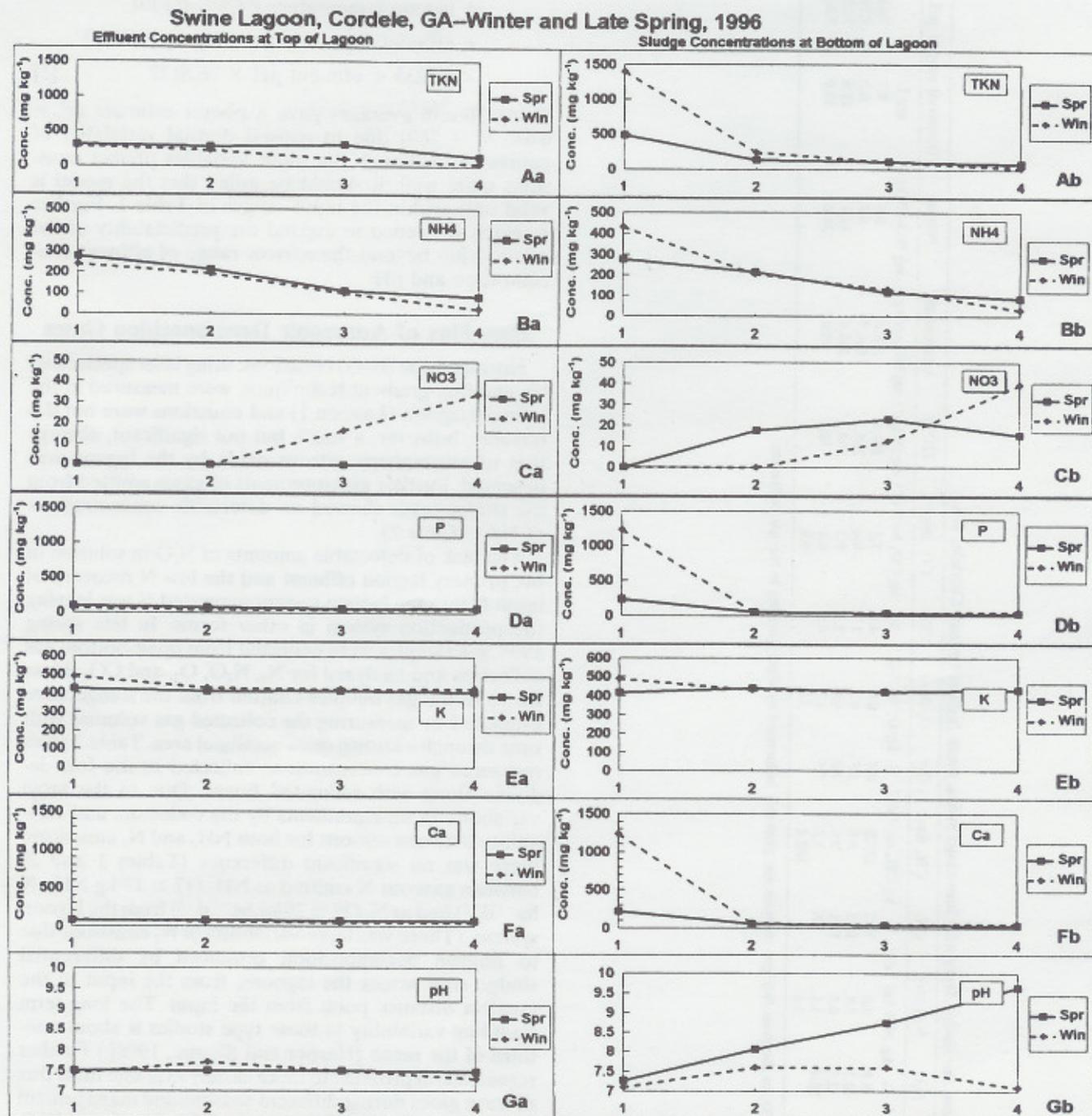
Using 30-min averages gave a poorer estimate ( $r^2 = 0.61$ ,  $N = 769$ ) due to natural diurnal variability of emissions. Although the input variables predict emissions quite well, it should be noted that the model is valid only within the input ranges of Table 1. Further research is needed to expand the predictability of the relationship beyond the narrow range of effluent concentration and pH.

### Mass Flux of Anaerobic Decomposition Gases

Nitrous oxide (N<sub>2</sub>O) emissions, using laser spectrometry and flux-gradient techniques, were measured in the primary lagoon (Lagoon 1) and emissions were not detectable; however, a small, but not significant, absorption of atmospheric nitrous oxide by the lagoon was observed. Further measurements of gases emitted from the sludge layer showed no detectable concentrations of N<sub>2</sub>O (Table 2).

The lack of detectable amounts of N<sub>2</sub>O in solution in the primary lagoon effluent and the low N recovery of input N into the lagoon system suggested N was leaving the production system in other forms. In late spring 1998, gas samples were collected from open-bottom gas collectors and analyzed for N<sub>2</sub>, N<sub>2</sub>O, O<sub>2</sub>, and CO<sub>2</sub>. Mass fluxes of the gas bubbles emitted from the sludge were estimated by measuring the collected gas volumes with time through a known cross-sectional area. Table 2 gives measured gas concentrations collected in the four lagoons along with estimated fluxes. Due to the large variability in measurements by the collectors and variability between seasons for both NH<sub>3</sub> and N<sub>2</sub> emissions, there was no significant difference (Tables 1 and 2) between gaseous N emitted as NH<sub>3</sub> (12 ± 17 kg NH<sub>3</sub>-N ha<sup>-1</sup> d<sup>-1</sup>) and as N<sub>2</sub> (37 ± 25 kg ha<sup>-1</sup> d<sup>-1</sup>) from the lagoon system. (There was large variability in N<sub>2</sub> emissions due to uneven decomposition produced by differential sludge type across the lagoons, from the input to the greatest distance point from the input. The long-term sampling variability in these type studies is about one-third of the mean [Harper and Sharpe, 1998].) Further research is in progress to more closely evaluate mass flux of trace gases during different seasons and management types (L.A. Harper, R.R. Sharpe, F.M. Byers, and W.P. Robarge, unpublished data, 1999).

Results of Table 2 suggest that some form of denitrification is taking place in the lagoons and that different reactions are involved, depending on the N form and concentration. With higher NH<sub>4</sub><sup>+</sup> concentration and biological activity (i.e., CH<sub>4</sub> production) in the primary lagoon (Lagoon 1) it would appear that denitrification may be chemical denitrification (Van Cleemput, 1997) with minimal N<sub>2</sub>O intermediate loss or biological denitrification by heterotrophs. Thermodynamics and Gibbs free energy for chemical denitrification (Van Cleemput, 1972) suggest that spontaneous conversion of NH<sub>4</sub><sup>+</sup> to

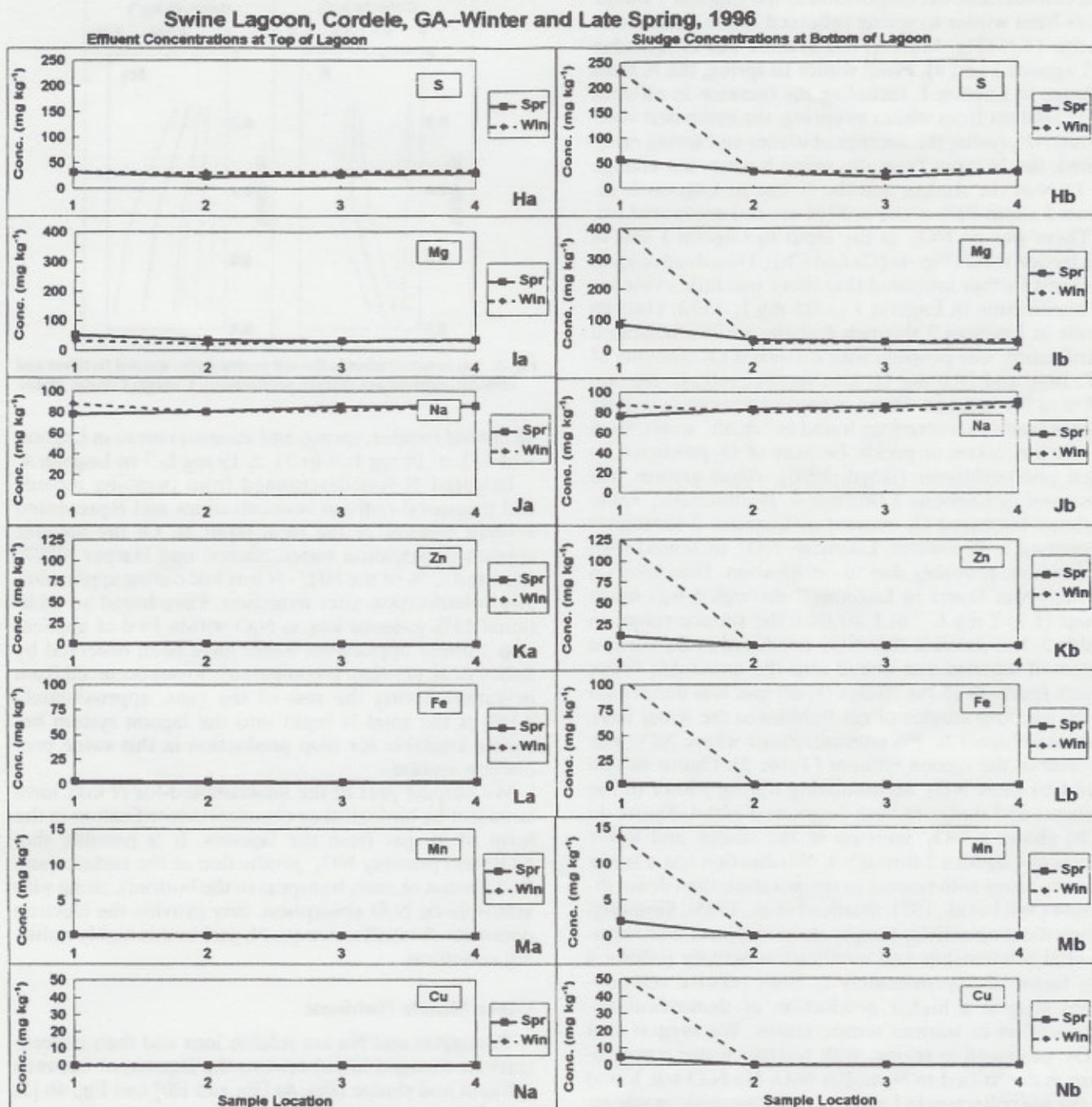


Sample locations: 1 = lagoon #1, 2 = lagoon #2, 3 = lagoon #3, 4 = lagoon #4

Fig. 4a. Swine lagoon nutrient concentrations in the effluent (0.05-m below the water surface) and within the sludge layer (approximately 3.0-m deep) in a four-stage lagoon system, Georgia Coastal Plains.

$N_2$  may occur (O. Van Cleemput and L.A. Harper, unpublished data, 1999). However, it is probable that the process requires an enzyme or catalyst for starting the reaction. Van Cleemput (1998) has shown that in the presence of  $Fe^{2+}$  (which is present in the sludge, Fig. 4b [Lb]) and an alkaline pH (Fig. 4a [Ga and Gb]),  $NO_3^-$  can be chemically reduced in soils. It is possible that there is some biological denitrification in Lagoon 1, but we think it is small since we measure no  $NO_3^-$  or

$N_2O$ , nor do we measure dissolved  $O_2$  necessary for autotrophic nitrification. It is also possible that there are some processes occurring such as nitrification-denitrification by methanotrophs (Verstraete and Phillips, 1998) or by heterotrophs not requiring  $O_2$  but using  $NO_2^-$  as an electron acceptor (Strous et al., 1997). In lagoons with the highest amounts of methanogenesis occurring, we found the highest quantities of  $N_2$  emitted in relation to other nitrogenous gases ( $NH_3$  and  $N_2O$ )



Sample locations: 1 = lagoon #1, 2 = lagoon #2, 3 = lagoon #3, 4 = lagoon #4

Fig. 4b. Swine lagoon nutrient concentrations in the effluent (0.05-m below the water surface) and within the sludge layer (approximately 3.0-m deep) in a four-stage lagoon system, Georgia Coastal Plains.

(Harper and Sharpe, 1998). Lagoons 3 and 4 had a higher concentration of  $\text{NO}_3^-$  (Fig. 4a [Ca and Cb]) and  $\text{O}_2$  content in the water surface (stated previously) that may provide conditions more suitable for biological denitrification (Seitzinger, 1990). In these lagoons, a larger percentage of  $\text{N}_2$  gas was produced along with significant amounts of  $\text{N}_2\text{O}$  intermediate gas. We think the concentrations of  $\text{O}_2$  and  $\text{CO}_2$  in the mass flux gas analyses are probably influenced by algae growing in the gas collectors. Further research is needed to evaluate the mechanism of  $\text{N}_2$  and  $\text{N}_2\text{O}$  gas production for use in

better management possibilities in lagoon waste systems.

### Lagoon Nitrogen

Figure 4 shows the comparisons between winter and spring nutrient concentrations in each of the successive lagoons (1 through 4). Average residence times for the effluent were 118 d in Lagoons 1 and 3 and 49 d in 2 and 4. Organic N in the effluent did not change between winter and spring in Lagoon 1 (Fig. 4a [Aa]) but there

was considerable decomposition in the Lagoon 1 sludge layer from winter to spring reflected in the decrease in sludge TKN (Fig. 4a [Ab]) (note: there was little sludge in Lagoons 3 and 4). From winter to spring, the N mass balance in Lagoon 1, including the increase in effluent  $\text{NH}_4^+$  content from winter to spring, the estimated volatilized  $\text{NH}_3$  (using the average of winter and spring emissions), the N input from the swine houses, the change in TKN in the sludge, and the N loss to Lagoon 2, indicated about 30% of the total N was not accounted for.

There was no  $\text{NO}_3^-$  in the input to Lagoon 1 and in the lagoon itself (Fig. 4a [Ca and Cb]). Dissolved oxygen contents further indicated that there was little evidence of nitrification in Lagoon 1 ( $<0.5 \text{ mg L}^{-1} \text{ O}_2$ ). Oxygen levels in Lagoons 2 through 4 at the surface indicated nitrification was possible with dissolved  $\text{O}_2$  contents of 8.7, 18.4, and 20.0  $\text{mg O}_2 \text{ L}^{-1}$ , respectively, in the top 0.5 m of the lagoons. These concentrations were slightly higher than concentrations found in "clean" water, such as streams, lakes, or ponds, because of  $\text{O}_2$  produced by algal photosynthesis (Boyd, 1990). Algal growth was observed in Lagoons 2 through 4. Additionally, Table 2 shows increased  $\text{O}_2$  content as Lagoons 2 through 4 decreased in N content. Likewise,  $\text{NO}_3^-$  increased with  $\text{O}_2$  content, probably due to nitrification. Dissolved  $\text{O}_2$  in the lower layers in Lagoons 2 through 4 was much lower (1 to 2  $\text{mg L}^{-1}$  at 1 m) than the surface values in Table 2. It is possible that  $\text{NO}_3^-$  produced in the surface layers of lagoons was mixed into the anaerobic lower layers (perhaps in the sludge layer) and was denitrified to  $\text{N}_2$  gas. Our studies of gas bubbles in the water have indicated higher  $\text{N}_2$  gas concentrations where  $\text{NO}_3^-$  was present in the lagoon effluent (Table 2). Figure 4a (Ca and Cb) show  $\text{NO}_3^-$  accumulating during winter in the effluent and sludge in both Lagoons 3 and 4. Figure 4a (Cb) shows a  $\text{NO}_3^-$  increase in the sludge and lower layers of Lagoons 2 through 4. Nitrification has a lower activity range with respect to temperature than denitrification (Wild et al., 1971; Stanford et al., 1975). Similarly, denitrification activity temperature response is an exponential relationship and nitrification activity follows a  $Q_{10}$  factor of approximately 2. Both relative relationships suggest a higher production of denitrification-nitrification in warmer temperatures. We suggest that  $\text{NO}_3^-$  produced in spring, with warmer water temperature, is denitrified to  $\text{N}_2$  and/or  $\text{N}_2\text{O}$ . No  $\text{N}_2\text{O}$  was found in the gas collectors in Lagoon 1. Nitrous oxide gradients were measured over Lagoon 1 and were found to be not significantly different from zero. In this lagoon, reduction to  $\text{N}_2$  was complete without release of a  $\text{N}_2\text{O}$  intermediate. Increasing amounts of  $\text{N}_2\text{O}$  were measured from Lagoons 2 through 4, along with increasing  $\text{NO}_3^-$  in the water. We think that increased  $\text{NO}_3^-$  in solution and  $\text{N}_2\text{O}$  produced may be indicative of biological denitrification in these lagoons, particularly Lagoons 3 and 4.

### Lagoon Nutrients

#### Nitrogen

Ammonium concentrations in the lagoons decreased considerably from Lagoons 1 through 4, decreasing from

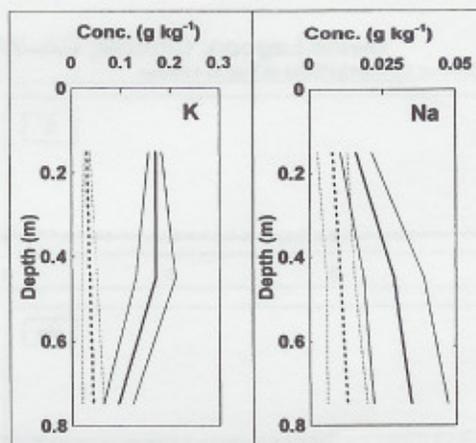


Fig. 5. Ion concentration in the soil profile under normal fertilizer and effluent applications (forage production), Georgia Coastal Plains.

an annual (winter, spring, and summer) mean in Lagoon 1 of  $251 \pm 19 \text{ mg L}^{-1}$  to  $31 \pm 19 \text{ mg L}^{-1}$  in Lagoon 4.

Irrigated N was determined from pumping records and measured nutrient concentrations and represented a small amount of the total input N. Of the amount applied in irrigation water, Sharpe and Harper (1997) reported 82% of the  $\text{NH}_4^+$ -N was lost during application and volatilization after irrigation. They found an additional 13% gaseous loss as  $\text{N}_2\text{O}$  within 15 d of application. Similar application losses have been observed by Safley et al. (1992a). If comparable losses occurred from irrigation during the rest of the year, approximately 0.1% of the total N input into the lagoon system becomes available for crop production in this swine production system.

We suspect part of the unaccounted-for N may have been lost by biological or chemical denitrification in the form of  $\text{N}_2$  gas from the lagoons. It is possible that  $\text{NO}_2^-$  and possibly  $\text{NO}_3^-$  production at the surface (and its diffusion or mass transport to the bottom), along with atmospheric  $\text{N}_2\text{O}$  absorption, may provide the electron donor for denitrification (to  $\text{N}_2$  gas) in this highly reducing condition.

#### Other Mobile Nutrients

Potassium and Na are soluble ions and their concentrations changed little between the lagoons or between effluent and sludge (Fig. 4a [Ea and Eb] and Fig. 4b [Ja and Jb]). Application of irrigation water to the crops represents 912 and 182  $\text{kg ha}^{-1} \text{ yr}^{-1}$  of K and Na, respectively. After 5 yr of irrigation, concentrations in the soil profile for K and Na were significantly larger than surrounding nonirrigated pasture (Fig. 5).

#### Immobile Nutrients

Immobile nutrients P, Ca, S, Mg, Zn, Fe, Mn, and Cu show little change in concentration in the effluent from Lagoons 1 through 4 (Fig. 4). However, during winter there is a considerable concentration increase in the sludge layer of the primary lagoon (Lagoon 1). We measured increases in concentration in the sludge ranging from seven times higher than effluent concentrations for S (Fig. 4b [Hb]) to 278 times higher for Zn (Fig. 4b

[Ka]). Further evidence of chemical precipitation was observed in the form of crystals attached to the instrument barge and ropes. Analysis of the crystals gave concentrations of P (11.7%), Mg (8.9%), and Ca (1.5%), suggesting crystallization of struvite ( $MgNH_4PO_4 \cdot 6H_2O$ ) and calcite ( $CaCO_3$ ), as found in other studies by Sommer and Hulsted (1995). Calcite and struvite will be present as stable solid phases at  $pH > 7$  and 6, respectively, and our effluent and sludge pH did not fall below 7 in these studies. A decrease in sludge concentration occurred during spring with increase in water temperature from the resulting temperature effect on solution chemistry (Fig. 4). Also, increased temperature promotes an increased decomposition rate of organic matter which was deposited during the winter.

Application of irrigation water to the crops represented application of 110 kg P  $ha^{-1} yr^{-1}$ , 117 kg Ca  $ha^{-1} yr^{-1}$ , 76 kg S  $ha^{-1} yr^{-1}$ , 73 kg Mg  $ha^{-1} yr^{-1}$ , 0.1 kg Zn  $ha^{-1} yr^{-1}$ , 2.3 kg Fe  $ha^{-1} yr^{-1}$ , 0.02 kg Mn  $ha^{-1} yr^{-1}$ , and 0.2 kg Cu  $ha^{-1} yr^{-1}$ . Following 5 yr of irrigation, Mg increased significantly ( $\alpha = 0.95$ ) in the soil horizon from 0 down to 0.6 m but no other nutrients were measured to be significantly higher. Interestingly, Mn significantly decreased in the 0- to 0.3-m soil layer and appeared to decrease in the 0.3- to 0.6-m layer, although due to high variability it was not significant. The soil pH increased significantly on the application sites by one pH unit down to 0.6 m in the soil.

### Emission Factors

Emission factors, generally defined in units of kg  $NH_3$  animal $^{-1} yr^{-1}$ , are used by planners and others to evaluate potential area sources due to concentrated animal production. Emission factors must be used with caution because of variability induced by geography and meteorology, methodology for measurement, type and weight of animals, N content of feedstuffs, housing and management, and, indeed, the lack of use of a standard weight or animal type comparison. Emission factors are generally based on the emissions of a category of swine divided by the number of animals in that category. Asman (1992) developed a composite factor for Europe of 8.5 kg  $NH_3$  animal $^{-1} yr^{-1}$  and Battye et al. (1994), using emissions from Europe and USDA Agricultural Statistics Service animal classifications, developed a similar composite factor for the USA of 9.2 kg  $NH_3$  animal $^{-1} yr^{-1}$ . The lagoon emission factor for the farrow-to-finish (FF) unit in this study is considerably smaller (2.3 kg  $NH_3$  animal $^{-1} yr^{-1}$ ) than the above factors, but it does not include housing emissions that would increase our factor. However, even adding housing losses, preliminary studies suggest that our emission factors will be less than the European and estimated U.S. factors. Further studies are in progress to evaluate  $NH_3$  (L.A. Harper and R.R. Sharpe, unpublished data, 1999) and  $CH_4$  (R.R. Sharpe and L.A. Harper, unpublished data, 1999) emissions from swine production houses.

In conclusion, this study shows that the use of lagoons for waste management may have less environmental impact due to smaller atmospheric emissions of  $NH_3$

than originally thought, with much of the previously estimated N loss from lagoons released to the atmosphere as  $N_2$  gas. A more critical analysis is needed to better understand the N transformations that occur in such complex biological and chemical systems.

### ACKNOWLEDGMENTS

The authors wish to express their appreciation to the project technical assistants, S.E. Norris, J.E. Scarbrough, and M.F. Thorton, for their efforts in these studies. Gratitude is extended to J. Duxbury, J. Lauren, J. Stevens, F. Thornton, and O. Van Cleemput for their assistance in the measurements of some of the trace gases and in the preparation of this manuscript. A special thanks is extended to the Global Climate Change Program, USDA-ARS, and to the host swine producers who provided site locations to make these studies possible.

### REFERENCES

- Anonymous. 1983. Method 351.2. Methods for chemical analysis of water and wastes. EPA-600/4-020. Revised March 1983. USEPA, Washington, DC.
- Anonymous. 1992a. Method 4500  $NO_3^-$ -F automated cadmium reduction method. p. 4-91. In A.E. Greenberg et al. (ed.) Standard methods for the examination of water and wastewater. 18th ed. American Public Health Association, Washington, DC.
- Anonymous. 1992b. Method 3030 H nitric perchloric acid digestion and method 3500-K D flame photometric method. p. 3-6 and 3-80. In A.E. Greenberg et al. (ed.) Standard methods for the examination of water and wastewater. 18th ed. American Public Health Association, Washington, DC.
- Anonymous. 1992c. Method 4500-P B & C vanadomolybdophosphoric acid colorimetric method. p. 4-111 and 4-112. In A.E. Greenberg et al. (ed.) Standard methods for the examination of water and wastewater. 18th ed. American Public Health Association, Washington, DC.
- Anonymous. 1992d. Method 3030 H nitric perchloric acid digestion and method 3111 B direct air-acetylene flame method. p. 3-6 and 3-13. In A.E. Greenberg et al. (ed.) Standard methods for the examination of water and wastewater. 18th ed. American Public Health Association, Washington, DC.
- Anonymous. 1992e. Method 4500-H- B electrometric method. p. 4-65. In A.E. Greenberg et al. (ed.) Standard methods for the examination of water and wastewater. 18th ed. American Public Health Association, Washington, DC.
- Anonymous. 1992f. Method 3030 H nitric perchloric acid digestion and method 3500 Na-D flame emission photometric method. p. 3-6 and 3-93. In A.E. Greenberg et al. (ed.) Standard methods for the examination of water and wastewater. 18th ed. American Public Health Association, Washington, DC.
- Asman, W.A.H. 1992. Ammonia emissions in Europe: Updated emission and emission variations. National Institute of Public Health and Environmental Protection, Bilthoven, the Netherlands.
- Asman, W.A.H. 1994. Emission and deposition of ammonia and ammonium. Nova Acta Leopold. 288:263-297.
- Battye, R., W. Battye, C. Overcash, and S. Fudge. 1994. Development and selection of ammonia emission factors. EPA Contract Number 68-D3-0034, Work Assign. 0-3. USEPA, Research Triangle Park, NC.
- Bobbink, R., D. Boxman, E. Fremstad, G.W. Heil, A. Houduk, and J. Roelofs. 1992. Critical loads for nitrogen eutrophication of terrestrial and wetland ecosystems based upon changes in vegetation and fauna. In P. Grennfelt and E. Thornelof (ed.) Critical loads for nitrogen. Rep. Nord 1992:41. Nordic Council of Ministers, Copenhagen, Denmark.
- Boyd, C.E. 1990. Concentrations of dissolved oxygen. p. 59-65. In C.E. Boyd (ed.) Water quality in ponds for aquaculture. Alabama Agric. Exp. Stn., Auburn Univ., Auburn, AL.
- Bussink, D.W., L.A. Harper, and W.J. Corre. 1996. Ammonia transport in a temperate grassland: II. Diurnal fluctuations in response to weather and management conditions. Agron. J. 88:621-626.

- Crutzen, J. 1983. Atmospheric interactions—Homogeneous gas reactions of C, N, and S containing compounds. p. 67–112. In G. Bolin and R.B. Cook (ed.) *The major biochemical cycle and their interactions*. John Wiley & Sons, Chichester, UK.
- Denmead, O.T. 1983. Micrometeorological methods for measuring gaseous losses of nitrogen in the field. p. 133–157. In J.R. Freney and J.R. Simpson (ed.) *Gaseous loss of nitrogen from plant–soil systems*. Martinus Nijhoff/W. Junk Publ., The Hague, the Netherlands.
- Denmead, O.T., R. Nulsen, and G.W. Thurtell. 1978. Ammonia exchange over a corn crop. *Soil Sci. Soc. Am. J.* 42:840–842.
- Denmead, O.T., and M.R. Raupach. 1993. Methods for measuring atmospheric gas transport in agricultural and forest systems. p. 19–43. In L.A. Harper et al. (ed.) *Agricultural ecosystem effects on trace gases and global climate change*. ASA Spec. Publ. 55. ASA, Madison, WI.
- Dyer, A.J., and B.B. Hicks. 1970. Flux-gradient relationships in the constant flux layer. *Q. J. R. Meteorol. Soc.* 96:715–721.
- Harper, L.A. 1988. Comparisons of methods to measure ammonia volatilization in the field. p. 93–109. In B.R. Bock and D.E. Kissel (ed.) *Ammonia volatilization from urea fertilizers*. Tennessee Valley Authority, Muscle Shoals, AL.
- Harper, L.A., J.E. Box, Jr., D.N. Baker, and J.D. Hesketh. 1973. Carbon dioxide and the photosynthesis of field crops. A tracer examination of turbulent transfer theory. *Agron. J.* 65:574–578.
- Harper, L.A., D.W. Bussink, H.G. van der Meer, and W.J. Corre. 1996. Ammonia transport in a temperate grassland: I. Seasonal transport in relation to soil fertility and crop management. *Agron. J.* 88:614–621.
- Harper, L.A., and R.R. Sharpe. 1995. Nitrogen dynamics in irrigated corn: Soil–plant nitrogen and atmospheric ammonia transport. *Agron. J.* 87:669–675.
- Harper, L.A., and R.R. Sharpe. 1998. Ammonia emissions from swine waste lagoons in the Southeastern U.S. Coastal Plains. Final Grant Report to Division of Air Quality, North Carolina Department of Environment and Natural Resources, Raleigh, NC. USDA-ARS Agreement no. 58-6612-7M-022. North Carolina Dep. of Environment and Natural Resources, Raleigh, NC.
- Harper, L.A., R.R. Sharpe, G.W. Langdale, and J.E. Giddens. 1987. Nitrogen cycling in a wheat crop: Soil, plant and aerial nitrogen transport. *Agron. J.* 79:965–973.
- Nilsson, J., and P. Grennfelt. 1988. Critical loads for sulphur and nitrogen. Rep. 15, 1988. Nordic Council of Ministers, Copenhagen, Denmark.
- Padmore, J.M. 1990. Method 968.06. In K. Helrich (ed.) *Official methods of analysis of the Association of Official Analytical Chemists*. AOAC, Arlington, VA.
- Panofsky, H.A. 1963. Determination of stress from wind and temperature measurements. *Q. J. R. Meteorol. Soc.* 89:85–94.
- Safley, L.M., Jr., J.C. Barker, and P.W. Westerman. 1992a. Loss of nitrogen during sprinkler irrigation of swine lagoon liquid. *Biore-sour. Technol.* 40:7–16.
- Safley, L.M., Jr., M.E. Casanda, J.W. Woodbury, and K.F. Roos. 1992b. Global methane emissions from livestock and poultry manure. EPA/400/1-91/048. USEPA, Washington, DC.
- Seitzinger, S.P. 1990. Denitrification in aquatic sediments. p. 301–322. In N.P. Revsbech and J. Sorensen (ed.) *Denitrification in soil and sediment*. Plenum Press, New York.
- Sharpe, R.R., and L.A. Harper. 1997. Ammonia and nitrous oxide emissions from irrigation application of swine effluent. *J. Environ. Qual.* 26:1394–1398.
- Sharpe, R.R., L.A. Harper, J.E. Giddens, and G.W. Langdale. 1988. Nitrogen use efficiency and nitrogen budget for conservation tilled wheat. *Agron. J.* 52:1394–1398.
- Sommer, S.G., and S. Hulsted. 1995. The chemical buffer system in raw and digested animal slurry. *J. Agric. Sci.* 124:45–53.
- Stanford, G., S. Dezenia, and R.A. van der Paul. 1975. Effect of temperature on denitrification rate in soils. *Soil Sci. Soc. Am. Proc.* 39:867–870.
- Strous, M., E. Van Gerven, P. Zheng, J.G. Kuenen, and M.S.M. Jetten. 1997. Ammonium removal from concentrated waste streams with the anaerobic ammonium oxidation (ANAMMOX) process in different reaction configurations. *Water Res.* 31:1955–1962.
- Thom, A.S., J.B. Stewart, H.P. Oliver, and J.H.C. Gash. 1975. Comparison of aerodynamic and energy budget estimates of fluxes over a pine forest. *Q. J. R. Meteorol. Soc.* 93:494–500.
- Van Cleemput, O. 1972. *Het Denitrifikatieproces in De Bodem (The denitrification process in soil)* (in Flemish). Ph.D. thesis. Faculty of Agricultural and Applied Biological Sciences, University of Ghent, Belgium.
- Van Cleemput, O. 1997. Subsoils: Chemo- and biological denitrification, N<sub>2</sub>O and emissions. (no page numbers). In *Proc. Int. Workshop on Dissipation of N from the Human N-Cycle and its Role in Present and Future N<sub>2</sub>O Emissions to the Atmosphere*, Agric. Univ. Of Norway, Oslo. 22–25 May 1997. Agricultural Univ. of Norway, Oslo.
- Van Cleemput, O. 1998. Subsoils: Chemo- and biological denitrification, N<sub>2</sub>O and N<sub>2</sub> emissions. *Nutr. Cycl. Agroecosyst.* 52:187–194.
- van der Molen, J., A.C.M. Beljaars, W.J. Chardon, W.A. Jury, and H.G. van Faassen. 1990. Ammonia volatilization from arable land after application of cattle slurry. II. Derivation of a transfer model. *Neth. J. Agric. Sci.* 38:239–254.
- Verstraete, W., and S. Philips. 1998. Nitrification–denitrification processes and technologies in new contexts. *Environ. Pollut.* 102, S1:717–726.
- Weier, K.L., V.R. Catchpoole, and L.A. Harper. 1980. An automated colorimetric method for the determination of small concentrations of ammonia in acid. *Tropical Agron. Tech. Mem.* 20. Division of Tropical Crops and Pastures, CSIRO, St. Lucia, QLD, Australia.
- Wild, H.E., Jr., C.N. Savage, and T.C. McMahon. 1971. Factors affecting nitrification kinetics. *J. Water Pollut. Control Fed.* 48:835.