

10
11
12 **ABATEMENT OF AMMONIA AND HYDROGEN SULFIDE EMISSIONS FROM A**
13 **SWINE LAGOON USING A POLYMER BIOCOVER**
14

15
16
17 J. A. Zahn^{1,2*}, A. E. Tung³, B. A. Roberts³, and J. L. Hatfield⁴
18
19
20

21 National Swine Research and Information Center¹, USDA-ARS, Ames, IA 50011, Department of
22 Microbiology², Iowa State University, Ames, IA 50011, Monsanto, EnviroChem Systems
23 Division³, St. Louis, MO 63178, and National Soil Tilth Laboratory⁴, USDA-ARS, Ames, IA
24 50011
25
26
27
28

29 **Running Title:** Use of a Biocover for Abatement of Gaseous Emissions from a Swine Lagoon
30
31

32 Disclaimer: Names are necessary to report factually on available data; however, the USDA
33 neither guarantees nor warrants the standard of the product, and use of the name by USDA
34 implies no approval of the product to the exclusion of others that may be suitable.
35

36 *Corresponding author:
37

38 Dr. James A. Zahn
39 National Swine Research and Information Center, USDA-ARS
40 2150 Pammel Drive
41 Ames, IA 50011
42 Phone: (515) 294-0201
43 Fax: (515) 294-1209
44 zahn@nsric.ars.usda.gov
45

46 Submitted for Publication in the Journal of Air and Waste Management Association
47 August 2000
48

1 **IMPLICATIONS**

2 Emissions of ammonia (NH₃) and hydrogen sulfide (H₂S) above 45.4 kg*day⁻¹ are subject to
3 reporting requirements under the Comprehensive Environmental Response, Compensation and
4 Liability Act (CERCLA; 40 C.F.R. Part 302). Determination of whether emissions from
5 concentrated animal feeding operations (CAFOs) approach these reporting thresholds depends
6 upon accurate measurement of emission rates under field conditions. Additionally, the
7 development of strategies for abatement of emissions from CAFOs may allow CAFOs with
8 emissions approaching the reporting thresholds to avoid CERCLA reporting requirements.
9 Research results described herein provide important insight into the successful use of
10 micrometeorological methods for monitoring NH₃ and H₂S emissions from animal waste lagoons
11 and for evaluation of emission abatement strategies.

12 **ABSTRACT**

13 The purpose of this research was to determine the efficiency of a polymer biocover for abatement
14 of hydrogen sulfide (H₂S) and ammonia (NH₃) emissions from an east-central Missouri swine
15 lagoon with a total surface area of 7,800 m². The flux rate of NH₃, H₂S, and methane (CH₄) was
16 monitored continuously from two adjacent, circular (d = 66 m) control and treatment plots using
17 a nonintrusive, micrometeorological method during three independent sampling periods that
18 ranged between 52 and 149 hours. Abatement rates were observed to undergo a temporal
19 acclimation event, where NH₃ abatement efficiency improved from 17% to 54% (p<0.0001 to
20 0.0005) and H₂S abatement efficiency improved from 23% to 58% (p<0.0001) over a period of 3
21 months. The increase in abatement efficiency for NH₃ and H₂S over the sampling period was
22 correlated with the development of a stable anaerobic floc layer on the bottom surface of the
23 biocover that reduced mass transfer of NH₃ and H₂S across the surface. Analysis of
24 methanogenesis activity showed that the biocover enhanced the rate of anaerobic digestion by
25 25% when compared to the control. The biocover-enhanced anaerobic digestion process was
26 shown to represent an effective mechanism to counteract accumulation of methanogenic
27 substrates in the biocovered lagoon.

28 **Keywords:** Biofiltration, CAFO, odor, air pollution, ammonia, hydrogen sulfide.

29
30 **Abbreviations:** Concentrated animal feeding operations, CAFOs; comprehensive environmental
31 response compensation and liability act, CERCLA; United States Environmental Protection
32 Agency, U.S. EPA; theoretical-profile shape, TPS.

33

1 ABOUT THE AUTHORS

2 J. A. Zahn is a research scientist at the National Swine Research Center, USDA-ARS, Ames, IA
3 50011, and an assistant professor, Department of Microbiology, Iowa State University, Ames, IA.
4 A. E. Tung is a senior engineer (P.E.) and B. A. Roberts is a research scientist with Monsanto,
5 EnviroChem Systems Division, St. Louis, MO 63178. J. L. Hatfield is the Laboratory Director
6 and meteorologist at the National Soil Tilth Laboratory, USDA-ARS, Ames, IA 50011.

7

8 INTRODUCTION

9 The impact of emissions from concentrated animal feeding operations (CAFOs) on
10 neighboring residences and businesses has received increasing interest in recent years.¹ Air
11 quality studies have shown that animal production facilities have the potential to emit ammonia
12 (NH_3),²⁻⁴ methane (CH_4),⁵⁻⁶ hydrogen sulfide (H_2S),⁷ particulate matter,⁸ and volatile organic
13 compounds.⁹⁻¹¹ More recently, Zahn and coworkers,¹¹ showed that NH_3 emissions from some
14 CAFOs routinely exceeded the $45.4 \text{ kg} \cdot \text{day}^{-1}$ ($100 \text{ lbs} \cdot \text{day}^{-1}$) reporting threshold that is currently
15 enforced under the Comprehensive Environmental Response, Compensation and Liability Act
16 (CERCLA; 40 C.F.R. Part 302) reporting requirements. Development and implementation of
17 efficient strategies for abatement of emissions from animal production systems could reduce or
18 eliminate the burden of CERCLA reporting requirements for CAFOs.

19 Strategies to control the emission rate of gases from swine waste management systems
20 can be functionally categorized into continuous and discontinuous approaches based on the site
21 of emission abatement.¹² With continuous approaches, emission reduction processes are
22 designed to directly influence the anaerobic effluent fraction by decreasing the effluent-phase
23 concentration of one or more solution-phase analytes before they are emitted into the atmosphere.
24 Examples of continuous treatment systems currently used in animal waste management systems
25 include anaerobic digestion, aerobic digestion, biological catalysis (addition of organisms or
26 enzymes), pH adjustment, ferrous ion amendments, and addition of photosynthetic bacteria.¹³⁻¹⁵
27 For the passive manure storage systems that are utilized by more than 75% of the swine industry,
28 performance of the treatment system is strongly influenced by environmental conditions.^{9,11} For
29 example, low microbial activities in lagoons during periods of cold solution temperatures ($<15^\circ$
30 C; i.e., fall, winter, and spring seasons) have been shown to promote accumulation of odorous
31 methanogenic substrates.¹¹ Effort to minimize the effect of seasonal trends on performance of

1 these treatments; however, is often impractical from an economic and management perspective.¹⁵
2 For this reason, continuous treatment systems have not been widely adopted as effective
3 strategies for treatment of passive manure management systems.¹³⁻¹⁵

4 Discontinuous or gas-phase approaches involve decoupling the treatment process from
5 the anaerobic effluent fraction. Biofiltration is a discontinuous treatment process where emissions
6 from a point source pass through a porous filter substrate that is inhabited by microorganisms
7 that utilize air pollutants as a source of carbon, nitrogen, sulfur, and/or energy. Emission
8 reduction strategies employing biofiltration have been effectively utilized in industrial and
9 commercial settings to control hydrogen sulfide and hydrocarbon emissions.¹⁶⁻¹⁷

10 Despite the success of biofiltration systems for abatement of waste gas streams from
11 industrial and commercial point sources, there have been few reports describing economically
12 viable applications of biofiltration for abatement of emissions from CAFOs. Siemers and
13 Vanden Weghe,¹⁸ described a biofilter-wetscrubber combination that achieved between 17 and
14 38% efficiency for the removal of ammonia from swine confinements. However, a cost analysis
15 indicated that the method (U.S.\$3 to \$10*pig⁻¹) was not economically feasible for production
16 scale applications. A biofiltration study by Young et al.,¹⁹ assessed odor emission rate from three
17 pilot-scale biofilters installed in a swine gestation building. Odor intensity, irritation, and
18 unpleasantness for five biofilter tests were reduced by 61% to 84% for the treatment. While
19 biofilters have been shown to be useful in the control of odors, severe airflow limitations have
20 limited their use for production-scale applications. Lais et al.,²⁰ identified technical limitations
21 that were similar to those identified previously,¹⁹ and further concluded that biofilters and
22 bioscrubbers were not economically feasible for the treatment of contaminated air from swine
23 confinements.

24 Miner and Pan,²¹ described a modified biofiltration system that consisted of floating
25 permeable polymeric materials that were placed over the surface of stored swine effluent. These
26 discontinuous treatment systems have since been shown to represent an economically feasible
27 method (U.S.\$0.10 to \$0.30*pig⁻¹) for control of odor and air pollutants from stored animal
28 effluent and have been coined, biocovers based on their assumed mechanistic similarities to
29 biofilters and similarity in appearance to impermeable covers.²² In support of this nomenclature,
30 Miner and Suh demonstrated that the most effective biocover materials were those with sufficient
31 gas permeability to allow gases from anaerobic decomposition to pass into aerobic zones near the

1 surface of the biocover for biotic and abiotic aerobic decomposition.²³ This study provided
2 initial evidence that biocover abatement efficiency was linked to biological and physical factors.
3 More recently Xue et al.,²⁴ showed that wheat straw biocovers, under laboratory conditions,
4 reduced the pH and NH₃ concentration at the solution interface, and reduced the emission rate of
5 H₂S and NH₃ from stored bovine effluent. However, the biological and/or physical mechanisms
6 responsible for these changes were not investigated. Considering the many positive attributes
7 that have been documented for biocover systems under laboratory conditions, a complete
8 literature search by the authors of this article identified no studies that have measured the
9 performance of biocovers under production-scale conditions.

10 The purpose of this research was to determine the efficiency of polymer biocovers for
11 abatement of H₂S and NH₃ emissions from swine lagoons under production-scale conditions.
12 The biocover tested in this study differed from previously studied biocovers,²¹⁻²⁴ in that the filter
13 substrate was specifically developed for resistance to ultraviolet or biological decomposition
14 processes, and was supplied and installed as a commercial product that was manufactured under
15 controlled specifications. Biocover abatement efficiency was tested under production-scale
16 conditions using a nonintrusive approach for direct measurement of H₂S, NH₃, and CH₄ flux
17 rates through continuous gas monitoring and micrometeorological flux calculations. We further
18 describe application of this direct flux measurement method to: (1) evaluate temporal changes in
19 the efficiency for abatement of CH₄, NH₃, and H₂S emissions from a biocovered swine lagoon,
20 and (2) to elucidate mechanisms responsible for the biocover-mediated reduction of H₂S and
21 NH₃ emissions.

22 23 **MATERIALS AND METHODS**

24 **Description of the Swine Lagoon and Biocover Design**

25 Flux measurements were conducted at an east-central Missouri farrow-to-finish swine
26 operation with an annual production of 5400 finisher pigs. Approximate capacity numbers for
27 each production phase and at any time point during the study were: farrowing - 42 sows; nursery
28 - 645 pigs; grower - 1260 pigs; and finisher - 1800 pigs. Manure from shallow pits was emptied
29 once each week into a lagoon with a surface area of 7,800 m² and a maximum depth of 3.8
30 meters. Wastewater analysis of lagoon effluent was completed weekly for chemical oxygen
31 demand (COD), total solids (TS), volatile solids (VS), total suspended solids (TSS), total

1 Kjeldahl nitrogen (TKN), ammonia-N ($\text{NH}_3\text{-N}$), total phosphorous, ortho-phosphate, pH, H_2S -
2 sulfide ($\text{H}_2\text{S-HS}$), and calcium (Ca) according to U.S. EPA methods for wastewater analysis
3 (410.1; 160.3; 160.4; 160.2; 351.3; 350.3; 365.1; 365.1; 150.1; 375.3; 215.1), respectively.²⁵
4 Effluent samples (100 ml) were collected weekly, unless stated otherwise, from the surface of the
5 lagoon (~0.5 cm depth) at the center of each sampling plot using glass serum vials. The vials
6 were filled to exclude air from the headspace and then were sealed with silicone-Teflon septa and
7 aluminum crimp rings. The vials were shipped and stored on ice (0 to 4° C) until wastewater
8 analysis was completed.

9 The commercial biocover tested in this study (Biocap II™, Baumgartner Environics) was
10 manufactured by Monsanto, EnviroChem Systems Division (St. Louis, MO) and was distributed
11 by Baumgartner Environics (Olivia, MN). The biocover consisted of a proprietary polymer
12 composite composed of 0.3 mm geotextile (Shell Chemical Co., Deer Park, TX) and 0.32 cm
13 closed-cell polypropylene foam (Dow Chemical Co., Midland, MI). The panels were perforated
14 with a 0.32 cm roller-punch on 10.2 cm centers down the length of the panels. Spun
15 polyethylene fiber (ASPUN 6835A fiber grade resin, Dow Chemical Co., Midland, MI) was
16 laminated to the top surface of the geotextile-polypropylene foam composite to increase the
17 aerobic surface area of the biocover (Fig. 1). The biocover was installed as 2.0 m x 38.0 m
18 panels that were approximately 2.0 cm thick and were connected every 0.4 m by 0.635 cm
19 stainless steel eyelets. The biocover was deployed over the south half of the lagoon (3,889 m²)
20 on August 2, 1999 and the first tests of biocover abatement efficiency commenced on August 3,
21 1999.

22 Measurements of $\text{NH}_3\text{-N}$ and $\text{H}_2\text{S-HS}$ stratification in the biocover were completed by
23 removing the liquid film layer on the upper surface of the closed-cell polypropylene-geotextile
24 layer using a 60 mL syringe at the central edge (middle lagoon location) of the biocover.
25 Samples from the free effluent below the biocover were collected by drawing effluent through a
26 large-bore catheter tube that was inserted through one of the 0.32 cm roller-punch perforations in
27 the biocover. Samples were transferred into a glass serum vial and sealed as described above.
28 The weight of biosolids that were attached to the biocover was measured in triplicate by
29 removing pre-cut patches (100 cm x 100 cm) at the central edge of the biocover. The patches
30 were turned up side down and blotted for 15 minutes on layers of Whatman #1 filter paper to
31 remove excess liquid. The blotted samples were then weighed and recorded.

1
2 **Capture and Quantification of Ammonia, Hydrogen Sulfide, Methane, and Volatile**
3 **Organic Compounds from Air**

4 Control, treatment, and background air samples were continuously drawn at a flow rate of
5 $5.0 \text{ L}\cdot\text{min}^{-1}$ into a climate-controlled mobile laboratory, via 0.953 cm i.d x 45 m flexible Teflon
6 tubing. Vacuum pressure inside individual sampling lines was maintained at -4.5 kPa using a
7 vacuum gauge and needle valve attached to the vacuum pump manifold. An inline 47mm
8 diameter, 3-5 μm Zitex Teflon filter membrane (Cole-Parmer, #E-06623-41) was placed on each
9 sample line as it entered the mobile laboratory to prevent particulate matter from plugging
10 transfer capillaries in the gas analyzers. Analytes in the air from the collection points were
11 sampled in 30 minute intervals by using a Valco 0.32 cm multiposition valve to divert air flow
12 from individual sampling lines through a Teflon sampling manifold. Gas analyzers were
13 connected directly to the Teflon sampling manifold and each gas analyzer sampled from the
14 manifold at a flow rate of $1.0 \text{ L}\cdot\text{min}^{-1}$. Equilibration of common flow path surfaces following
15 the valve switching event was completed in less than 3 minutes (~15 liters of gas flow). The first
16 five minutes of gas concentration data that were collected following the valve switching event
17 (pre-equilibration period) were discarded. Other air samples for VOC concentration and odor
18 concentration were collected by connecting grab sampling devices (i.e., Supelco, model 1063 air
19 samplers, Bellefonte, PA) to the sampling manifold just prior to sample collection. The flow rate
20 for grab sampler was adjusted so that air samples were collected from the sampling manifold
21 over a 25 minute sampling period. Grab sampling flow rates for VOC concentration
22 measurements were maintained at $1.2 \text{ L}\cdot\text{min}^{-1}$.

23 Analyte concentration of H_2S was determined in real-time using a Thermal
24 Environmental Instruments, Inc. (TEI) model 340 H_2S converter and TEI model 43C Pulsed
25 Fluorescence sulfur dioxide (SO_2) Analyzer (TEI, Franklin, MA). The SO_2 analyzer had a
26 measurement range of $0.00071 - 14.2000 \text{ mg}\cdot\text{m}^{-3}$ and an accuracy of 0.5% of the H_2S reading.
27 Ammonia concentration was determined in real-time using a TEI model 17C chemiluminescence
28 NH_3 analyzer and a model 17 converter module. The NH_3 analyzer had a measurement range of
29 $0.0003 - 14.8000 \text{ mg}\cdot\text{m}^{-3}$ and an accuracy of 0.5% of the NH_3 reading. The concentration of
30 CH_4 was determined in real-time using a Mine Safety Appliances Co. (MSA, Pittsburgh, PA),
31 model 3800 photoacoustic infrared gas sensor (MSA, Pittsburgh, PA). The MSA instrument had

1 a sensitivity of $0.70 \text{ mg}\cdot\text{m}^{-3}$ and an accuracy of $0.70 \text{ mg}\cdot\text{m}^{-3}$ over the range from 0.70 to 70.00
2 $\text{mg}\cdot\text{m}^{-3}$. The concentration of CH_4 in air was also confirmed by collecting grab samples from
3 the sampling manifold into triple-evacuated Teflon sampling bags and then analyzing the
4 contents of the bag by gas chromatography according to the method of Chan et al.²⁶ The TEI gas
5 analyzers were calibrated every 7 days with certified calibration standards (Matheson Gas
6 Products, Joliet, IL) consisting of 0.070, 0.430, 4.260, and 14.210 $\text{mg}\cdot\text{m}^{-3}$ H_2S or NH_3 . The CH_4
7 gas analyzer (MSA) was calibrated every 7 days with zero and span gases that were supplied by
8 the manufacturer.

9 Volatile organic compounds (VOC) were captured by low-volume grab sampling method
10 of Zahn et al.,⁹ on a multibed adsorbent tube containing Tenax TA and Carboxen-569 (Supelco,
11 Bellefonte, PA), and were thermally desorbed into a gas chromatograph equipped with a flame
12 ionization detector or electron-impact ionization mass spectrometer as previously described.⁹

13 Statistical evaluation of data and experimental designs were performed with JMP version
14 3 statistical discovery software (SAS Institute, Inc., Cary, NC).

16 **Measurement of Gas Flux Rates and the Experimental Design of Sampling Plots**

17 A traverse cable (0.635 cm braided stainless steel) was installed across the center of each
18 circular sampling plot for suspension of air sample inlet ports, solution thermocouples, and cup
19 anemometers above the lagoon surface. Height of the cable at the center of the each sampling
20 plot was monitored by observing the position of the lower end of a 126 cm plastic chain that was
21 attached to the traverse cable at the center of each plot. The height of the sampling inlet was
22 checked every two days and adjusted if necessary with a mechanical winch. A polymer-coated
23 copper-constantan thermocouple (Type T, Campbell Scientific, Inc., Logan, UT) was attached to
24 the bottom of a 25 cm x 25 cm x 5.1 cm closed-cell foam insulation board and tethered from the
25 traverse cable at the center of each sampling plot for measurement of the solution interface
26 temperature. Other measurements, collected at a height of 126 cm on the west berm of the
27 lagoon included irradiance (Type SZ, Li-Cor, Lincoln, NE), air temperature and relative humidity
28 (Model HMP45C, Campbell Scientific, Inc., Logan, UT), and wind direction (Model 03301-5,
29 Campbell Scientific, Logan, UT). Output from the micrometeorological sensors, gas analyzers,
30 and the multiposition valve were monitored every 5 seconds and a sample mean was recorded
31 every 5 minutes ($n = 60$) using two Campbell CR10X data recorders (Campbell Scientific, Inc.,

1 Logan, UT). The multiposition valve was computer-controlled and was automatically cycled
2 between various sampling positions to permit unattended, continuous sampling.

3 The flux of NH₃, H₂S, CH₄, and volatile organic compounds (VOC) from the lagoon were
4 measured using the theoretical profile shape (TPS) method described by Wilson et al.²⁷ The TPS
5 method employs the trajectory-simulation model of turbulent dispersion described by Wilson and
6 coworkers,²⁷ to assign a sampling height, referred to as ZINST, above the center of a circular-
7 shaped source where the flux rate of a gas can be determined from measurements of wind speed
8 and the gas concentration. The emission rate of gases from a circular source plot was calculated
9 with the following equation:

$$10 \quad (1) \quad \bar{F}_z(0) = \frac{(uc)^{measured}}{\Phi}$$

11 Where $F_z(0)$ is the vertical flux rate in $\mu\text{g}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$, Φ is the non-dimensional normalized
12 horizontal flux predicted by the trajectory simulation model and $(uc)^{measured}$ is the product of the
13 measured average wind velocity and air concentration of analyte in $\text{m}\cdot\text{s}^{-1}$ and $\mu\text{g}\cdot\text{m}^{-3}$,
14 respectively.²⁸ Flux measurements were completed at the center of two adjacent circular plots (d
15 = 66.0 m) on the surface of a swine lagoon. The surface roughness was determined on three
16 separate occasions (August 3, September 25, and October 14, 1999) by performing mean wind
17 velocity profile measurements at 0.2, 0.5, 1.0, 2.0, and 3.0 m for a period of 1 hour at the center
18 of the lagoon with cup anemometers (model 03101-5, R.M Young Co., Traverse City, MI).²⁹
19 The value for roughness length at the surface of the lagoon, during periods of neutral atmospheric
20 stability (mid-morning), was 0.09 ± 0.01 cm (mean \pm std. error). A measurement height of $z =$
21 ZINST (0.09, 3,300) = 126 cm was determined by the trajectory-simulation models using the
22 radius of the emitting area (3,300 cm) and the surface roughness (0.09 cm). Error in
23 measurement height that was associated with temporal changes in roughness length for the
24 lagoon surface was estimated to cause a maximum error of 7% in the height parameter for
25 emission measurements.

26 In an effort to reduce the contribution of background gas concentrations on flux
27 calculations, data acquisition was restricted to data sets with wind velocities that were in excess
28 of $0.2 \text{ m}\cdot\text{s}^{-1}$ and those that had a wind direction between 225° and 315° (north = $0^\circ/360^\circ$, east =
29 90° , south = 180° , and west = 270°). These precautions minimized background contributions
30 from the adjacent plot or from the swine confinement that was located 34 meters south of the

1 lagoon. All sample sets collected in this study had less than a 10% rejection rate for exclusion of
 2 data points based on wind velocity and wind direction criteria. Background gas concentrations of
 3 NH₃, H₂S, and CH₄, were measured for 25 minute intervals every 4 hours at the west edge of the
 4 lagoon at a height of 126 cm above the earthen berm (Fig. 1). The concentration of gases
 5 acquired over the surface of the lagoon was corrected before flux calculations were performed,
 6 by subtracting the background concentration values. Typical background concentrations ranged
 7 between 0.0007 to 0.0200 mg*m⁻³ for H₂S, 0.0003 to 0.2150 mg*m⁻³ for NH₃, and 1.20 to 1.70
 8 mg*m⁻³ for CH₄.

9 The flux rate of NH₃ was also estimated for uncovered areas of the lagoon using the NH₃
 10 mass transfer model described by Monteny and coworkers:³⁰

$$(2) \quad E = \left(\frac{(48.4 * v^{0.8} * T^{-1.4}) \left(\frac{1}{\left(1 + \frac{10^{(-pH)}}{0.81 * 10^{-10} * 1.07^{(T-293)}} \right)} \right) (TAN)}{1.384 * 10^3 * 1.053^{(293-T)}} \right) * 1.0^5$$

12 Where E = NH₃ flux in µg*cm⁻²*s⁻¹, pH = pH at the solution interface (0.5 cm depth), T =
 13 solution interface (0.5 cm depth) temperature in Kelvin, v = wind velocity at solution level in
 14 m*s⁻¹, and TAN = total ammoniacal nitrogen in the slurry in kg*m⁻³. This model has been
 15 shown to provide accurate estimates of NH₃ emissions from mechanically-ventilated bovine
 16 confinements and from slurry pits beneath slatted floors.³⁰⁻³¹

17

18 RESULTS AND DISCUSSION

19 Comparison of Direct and Modeled NH₃ Flux Measurements from the Swine Lagoon

20 A comparison between direct flux rate measurements of NH₃ from the uncovered, north
 21 sampling plot on the lagoon and modeled NH₃ flux rates was performed between October 20 and
 22 October 23, 1999 to validate the use of the TPS method for use in the direct flux measurements
 23 of gases emitted from the surface of swine lagoon. Measured parameters for the model included
 24 solution temperature, wind velocity, pH and NH₃-N concentration at the solution-air interface.

25 The greatest range in measured values for the model occurred with wind velocity (95%) and

1 solution interface temperature (32%), while no significant temporal or spatial differences in
2 measurements for pH (pH 8.11) or NH₃-N concentration (931.5 mg*L⁻¹) were observed in
3 effluent samples (n = 6) that were collected during the three-day sampling period (2
4 samples*day⁻¹). Figure 2A shows the temporal changes in the measured and modeled NH₃ fluxes
5 during the 103 hour sampling period. In general, there was good agreement between the model
6 estimates of NH₃ flux and those measured by the TPS method. The best agreement between field
7 observations and modeled NH₃ flux occurred during lagoon cool-down periods, when there was a
8 decrease in solution-temperature or irradiance. The most dramatic differences between measured
9 and modeled NH₃ flux occurred during mid-morning periods (Fig. 2A), or during periods when
10 the wind velocity exceeded 4 m*s⁻¹. Modeled NH₃ flux was observed to be lower (~34%) than
11 the measured flux during periods of lagoon warming and higher than measured NH₃ fluxes
12 during periods of high wind velocity (>4 m*s⁻¹). One possible explanation for the observed
13 differences in the response of modeled NH₃ flux to measured NH₃ flux was that the methods
14 used to measure boundary interface temperature were not adequate, or that other parameters
15 including irradiance (sun light intensity) need to be included in the model to improve accuracy
16 for outdoor measurements of NH₃ flux.

17 The mean and standard error for modeled estimates (n = 517*plot⁻¹) of NH₃ flux during
18 the three-day sampling period was 4.48 ± 0.17 ng NH₃*cm⁻²*s⁻¹, while the mean and standard
19 error for measured fluxes (n = 517*plot⁻¹) was 4.26 ± 0.16 ng NH₃*cm⁻²*s⁻¹. A statistical
20 analysis of these data by a paired t-test (Fig. 2B) showed that the differences in flux rates were
21 not statistically-different (p = 0.329, α = 0.05). The TPS method has previously been verified for
22 measuring NH₃ emissions from soils,³² flooded fields,³³ and for measuring low vapor pressure
23 (<10⁻² Pa) semi-volatile organic compounds from soils.²⁸ The fact that good agreement in NH₃
24 flux rates was achieved between the TPS method and the NH₃ flux predicted through modeled
25 estimates provides evidence that the TPS method is also suitable for direct measurements of gas
26 flux from the surface of a swine lagoon.

27

28 **Flux Measurements of NH₃, H₂S and CH₄ Are Independent of the Spatial Positioning of Air** 29 **Sample Inlets Over the Lagoon Surface**

30 Direct comparisons between gas flux measurements from control and treatment sampling
31 plots were utilized in this study to measure the abatement efficiency of a commercial biocover.

1 A fundamental concern with this experimental approach was the possibility that gas flux rates
2 were not spatially uniform across the two sampling plots under uncovered conditions. For
3 example, variation in depth of the lagoon due to localized accumulation of biosolids could be
4 expected to contribute to spatial differences in methanogenesis activity (flux rates for CH₄) over
5 the lagoon surface due to uneven distribution of methanogenic substrates. Direct comparisons
6 between control and treatment sampling positions would not be appropriate if spatial non-
7 uniformity existed in measured flux rates. Therefore, an experiment was conducted to confirm
8 whether flux rates of NH₃, H₂S and CH₄, were independent of the spatial positioning of the
9 sampling plots on the lagoon surface. Two adjacent circular sampling plots, each of 66 m in
10 diameter, were established over the open lagoon surface (Fig. 1). The area covered by the two
11 sampling plots (6,860 m²) accounted for approximately 88% of the total lagoon surface area
12 (7,800 m²). Gas concentrations (H₂S, NH₃, and CH₄), micrometeorological conditions, and
13 solution-phase analytes in lagoon effluent samples that were collected from the center of each
14 plot were measured for a period between July 17 and July 24, 1999. There were no significant (α
15 = 0.05) spatial differences detected in micrometeorological measurements (n = 918*plot⁻¹), gas
16 concentration measurements (n = 918*plot⁻¹), or the wastewater analysis measurements (n =
17 3*plot⁻¹) that were collected during this period. The mean and standard error for measured fluxes
18 of H₂S (n = 918*plot⁻¹) from the plots during the eight-day sampling period was 1.16 ± 0.03 ng
19 H₂S*cm⁻²*s⁻¹ for the north plot and 1.14 ± 0.03 ng H₂S*cm⁻²*s⁻¹ for the south plot (Fig. 3). The
20 mean and standard error for measured fluxes of NH₃ (n = 918*plot⁻¹) and CH₄ (n = 918*plot⁻¹)
21 from the north and south plots were 18.0 ± 0.7 ng NH₃*cm⁻²*s⁻¹ vs. 16.4 ± 0.6 ng NH₃*cm⁻²*s⁻¹
22 and 162 ± 3 ng CH₄*cm⁻²*s⁻¹ vs. 160 ± 0.03 ng CH₄*cm⁻²*s⁻¹, respectively. Statistical analyses
23 of H₂S data (Fig. 3B) or NH₃ and CH₄ data (not shown) by a paired t-test revealed that there was
24 no significant differences in the flux of H₂S, NH₃, or CH₄ from the two areas (α = 0.05). This
25 result provided evidence that direct comparisons could be made between control and treatment
26 positions for measurement of biocover abatement efficiency.

27

28 **Effect of the Biocover on the Emission Rate of H₂S, NH₃, and CH₄ from the Lagoon** 29 **Surface**

30 The flux rate of NH₃, H₂S, and CH₄, was continuously monitored from two adjacent,
31 circular (d = 66 m) control and treatment plots during three independent sampling periods that

1 ranged between 52 and 149 hours. Nutrient analyses of effluent samples that were collected
2 weekly during the course of the study are shown in Table 1. No significant changes occurred in
3 the composition of the effluent fraction during the 3-month study (Table 1). Results for the flux
4 rate of gases from control and treatment plots and the statistical analysis of data collected during
5 the three sampling periods are shown in Table 2. The flux rates of NH_3 and H_2S from the
6 biocovered area were statistically lower ($\alpha = 0.05$) than the control for each of the three sampling
7 periods. Abatement rates were observed to undergo a temporal acclimation event, where NH_3
8 abatement efficiency improved from 17% to 54% ($p < 0.0001$ to 0.0005) and H_2S abatement
9 efficiency improved from 23% to 58% ($p < 0.0001$) over a period of 3 months. Figure 4 shows the
10 differences in flux rates for NH_3 and H_2S between control and biocovered areas for the October
11 14-16 sampling period and the statistical analysis of differences in gas flux rates using the t-test.
12 The traces of flux values over time for control and treatment areas had similar line shapes;
13 however, the abatement efficiency achieved by the biocover for H_2S or NH_3 generally increased
14 as the control flux rate increased (Fig. 4).

15 Physical parameters governing the mass transfer of NH_3 and H_2S from liquid surfaces
16 include temperature, pH, wind velocity, and analyte concentration at the air-solution interface.^{31,}
17 ³⁴ The mean solution interface temperature and pH for the three sampling periods was $2.2 \pm$
18 0.06°C ($p = 0.002$) and 0.9 ± 0.01 pH units ($p = 0.006$) lower for the biocovered area than the
19 control area. However, these differences in solution interface temperature and pH remained
20 essentially constant for each sampling period, thus indicating that neither parameter was
21 significant in the temporal acclimation event. Further evidence for this conclusion is provided by
22 the fact that modeled estimates of NH_3 and H_2S flux respond inversely to changes in pH, since
23 NH_3 is a weak base and H_2S is a weak acid.^{31, 34} The observed difference in solution interface
24 temperature ($\Delta \text{Temp} = 2.2 \pm 0.06^\circ \text{C}$) for control and treatment areas was estimated by
25 modeling, to reduce NH_3 emission by 22% during the October 14-16 sampling period. The
26 average reduction in modeled NH_3 emission due specifically to solution interface temperature
27 effects of the cover was 20%. In addition to lowering the solution interface temperature, the
28 biocover also minimized daily fluctuations in solution interface temperature due to the apparent
29 reflective and heat retention properties of the biocover. While solution interface temperature
30 appeared to contribute to the overall abatement efficiency achieved by the biocover, it was not
31 considered an important factor in the observed temporal acclimation event, since the difference

1 in solution interface temperature (Δ Temp) between control and treatment remained constant for
2 the three sampling periods.

3 The concentration of NH_3 and H_2S at the boundary between emitting surfaces and the air
4 has previously been shown to be a major factor in the rate of volatilization from liquid
5 surfaces.^{31,34} Therefore, measurements of $\text{NH}_3\text{-N}$ and $\text{H}_2\text{S-SH}$ concentration on the upper, liquid
6 surface of the biocover and the free effluent fraction below the cover were completed to test for
7 stratification of analytes in the biocover. Table 2 shows the concentration ratio for analytes
8 present as a thin liquid film above the closed-cell polypropylene layer of the biocover vs. analyte
9 concentration in the free effluent fraction below the cover. No significant stratification of
10 analytes was detected for the first sampling period (Aug. 3-6) that started approximately 18 hours
11 after the installation of the biocover. However, a significant level of stratification was observed
12 in measurements 25 days after biocover installation. This stratification in $\text{NH}_3\text{-N}$ and $\text{H}_2\text{S-SH}$
13 concentrations became highly significant by the September 25 ($p=0.007$) and October 14
14 ($p=0.002$) sampling periods (Table 2). The difference in concentration of $\text{NH}_3\text{-N}$ and $\text{H}_2\text{S-SH}$
15 across the surface of the biocover (top to bottom) was $663 \pm 9 \text{ mg NH}_3\text{-N}\cdot\text{L}^{-1}$ vs. $931 \pm 11 \text{ mg}$
16 $\text{NH}_3\text{-N}\cdot\text{L}^{-1}$ and $10 \pm 3 \text{ mg H}_2\text{S-SH}\cdot\text{L}^{-1}$ vs. $17 \pm 2 \text{ mg H}_2\text{S-SH}\cdot\text{L}^{-1}$ for the September 25 to
17 October 1 sampling period, and $573 \text{ mg NH}_3\text{-N}\cdot\text{L}^{-1}$ vs. $924 \text{ mg NH}_3\text{-N}\cdot\text{L}^{-1}$ and $10 \pm 1 \text{ mg H}_2\text{S-}$
18 $\text{SH}\cdot\text{L}^{-1}$ vs. $18 \pm 1 \text{ mg H}_2\text{S-SH}\cdot\text{L}^{-1}$ for the October 14 to 16 sampling period. The modeled
19 difference in NH_3 flux rate that resulted from the combined effects of NH_3 stratification and the
20 2.2°C reduction in solution temperature for the biocovered area was estimated to lower NH_3 flux
21 by 45% ($33.5 \text{ ng NH}_3\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ vs. $18.6 \text{ ng NH}_3\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$) for the September 25 to October 1
22 sampling period and 52% ($29.5 \text{ ng NH}_3\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ vs. $14.2 \text{ ng NH}_3\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$) for the October 14 to
23 16 sampling period. These modeled values for NH_3 flux were similar to the observed abatement
24 efficiencies of 50% and 54% for the September 25 to October 1 sampling period and the October
25 14 to 16 sampling period, respectively.

26 The rate of NH_3 and H_2S volatilization from liquid surfaces is in part dependent upon
27 mass transfer of the analyte through the liquid-gas boundary at the surface of the liquid.³¹ For
28 NH_3 , the effect of boundary wind velocity and temperature on mass transfer is represented by the
29 following equation:

30 (3)
$$k = 48.4 * v^{0.8} * T^{-1.4}$$

1 Where k is the mass transfer coefficient for NH_3 in m^*s^{-1} , v is the wind velocity in m^*s^{-1} , and T is
2 the solution interface temperature in Kelvin.³¹ As noted previously, the differences observed
3 between control and treatment areas for solution interface temperatures remained constant
4 throughout the three sampling periods. This difference in solution interface temperature was
5 considered an important factor in the overall performance of the biocover and therefore, was
6 included in the modeled estimates of biocover abatement efficiency that were described above.
7 However, solution interface temperature was not considered to be an important factor in the
8 temporal acclimation event, since differences in solution interface temperature remained constant
9 for the three sampling periods.

10 No significant differences were observed in wind velocity measurements for control or
11 treatment sampling positions at the sampling height of 126 cm, nor were there any differences in
12 roughness length measurements between the two areas. While these observations provided a
13 basis for comparison of flux values between control and treatment areas, they provided no insight
14 into the actual differences in boundary layer wind velocity for the two areas. The observation
15 that biocover abatement efficiency increased nearly proportionally to wind velocity
16 measurements (collected at 126 cm above the emitting surface) provided evidence that boundary
17 layer wind velocity was an important factor in biocover performance (Table 2). However, direct
18 measurements of solution interface wind velocity for biocovered areas could not be performed
19 because the solution interface was positioned between the geotextile and open polyethylene fiber
20 layers of the biocover. The biocover provided an undetermined level of shielding that could not
21 be quantified using the meteorological sensors chosen for this study. Future studies must focus
22 on assessing the microclimate (air pressure and wind velocity) at the air-solution interface of
23 biocovered lagoons. Furthermore, the differences between measured and modeled NH_3 flux
24 rates, which were calculated using only the temperature and analyte stratification effects was
25 small (2% to 5% discrepancy). This result indicated that boundary layer wind velocity may be
26 less significant in the overall performance of the biocover. Additional studies are needed to
27 investigate the effects of boundary layer wind velocity on biocover abatement performance.

28 These data provide evidence that the temporal increase in biocover abatement efficiency
29 is due to the reduction in analyte concentration at the boundary layer. Other factors that may
30 contribute to the overall performance of the biocover include boundary layer temperature and
31 wind velocity. While these data do not provide insight into the mechanisms responsible for

1 analyte stratification in the biocover, two mechanisms under current investigation include: 1)
2 chemical stratification results from the disassimilatory (i.e., autotrophic or heterotrophic
3 nitrification, anaerobic NH₃ oxidation,³⁵ and sulfide oxidation) or assimilatory metabolism of
4 NH₃ or H₂S by microorganisms residing in the upper aerobic-microaerophilic layers of the
5 biocover, 2) chemical stratification results from a physical barrier that impedes diffusion of
6 analytes into the boundary layer, or possibly, 3) a combination of these processes. The fact that
7 higher CH₄ flux rates were observed for the biocovered areas provides some evidence that the
8 biocover is not a significant physical barrier in the diffusion of analytes into the boundary layer.
9 However, gas transfer coefficients between CH₄ and NH₃, or CH₄ and H₂S are known to differ by
10 several hundred-fold and therefore,^{31, 34} CH₄ may not be an adequate indicator for estimating the
11 effectiveness of the biocover as a physical barrier.

12

13

Biocover-Enhanced Methanogenesis

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

29

30

Analysis of CH₄ fluxes from control and treatment areas showed that biocover areas exhibited significantly higher fluxes rates of CH₄ than control areas during the September 25 and October 14 testing periods (Table 2). The difference in measured flux rates for CH₄ from control and treatment areas increased throughout the length of the study; however, this increase was inversely proportional to the temporal acclimation event observed for NH₃ and H₂S fluxes. The anaerobic digestion of organic materials into carbon dioxide (CO₂) and CH₄ occurs only under highly anaerobic (< 100 mV) conditions, in a variety of ecosystems including aquatic sediments, soils, intestinal tracts of animals and some insects, and waste management or waste storage systems.³⁶ Methanogens catalyze the reduction of simple one and two carbon compounds into CH₄ and are often isolated from anaerobic sediment or sludge layers.^{36, 37} Analysis of changes in the structure of biocover test strips (100 cm x 100 cm) revealed that there was a temporal accumulation of biomass attached to the underside of the biocover (Table 2). The rate of biomass accumulation correlated strongly with the temporal increase in CH₄ production that was observed for the biocover: This correlation was: % Δ CH₄ flux_(treatment-control) = -0.91 + 9.29* (biocover wet wt.*cm⁻²); r² = 0.98. Additional studies of methanogenic activity (CH₄ flux) and methanogen population dynamics are needed to determine if biocover-enhanced methanogenesis results from an increase in methanogenic activity due to changes in temperature, bulk redox

1 potential, substrate availability, or from changes in the population or diversity of methanogens
2 associated with the biocover.

3 The methyl group of acetate has been shown to be the precursor for more than 70% of
4 methane produced from digestion of animal manures.³⁶ This form of methylotrophic
5 methanogenesis has been shown to produce one mole of CO₂ and CH₄ for each mole of acetate
6 reduced.³⁶ Using the study mean for the difference in CH₄ flux rates between control and
7 treatment areas (143 ng CH₄*cm⁻²*s⁻¹ minus 125 ng CH₄*cm⁻²*s⁻¹), the daily increase in CH₄
8 emission due to the effect of the biocover was calculated to be 121 kg CH₄*day⁻¹ (18 ng
9 CH₄*cm⁻²*s⁻¹). In addition to CH₄, methylotrophic methanogenesis produces CO₂ from acetate at
10 the rate of 70% (by mole volume) of the CH₄ emission rate, or 233 kg CO₂*day⁻¹. These
11 emission values indicate that the biocover-enhanced methanogenesis phenomenon can improve
12 the efficiency of anaerobic digestion processes that occur in stored swine effluent by
13 approximately 25%. This improvement in anaerobic digestion efficiency may represent an
14 effective mechanism to counteract accumulation of methanogenic substrates in biocovered
15 lagoons.

16 17 **CONCLUSIONS**

18 Biocovers are permeable organic or inorganic materials and have a limited adsorption
19 capacity for gases emitted from the surface of animal lagoons. Thus, it is often assumed that the
20 effectiveness of biocovers for the abatement of gaseous emission results from: 1) the inhibition
21 of volatilization mechanisms, and 2) the establishment of microbial consortiums that degrade
22 organic and inorganic compounds that enter the porous material. This study shows that element
23 cycling in biocovers is not restricted to those compounds that are present in the gas phase, but
24 also occurs within the anaerobic, solution-phase layers associated with the biocover. Parameters
25 that regulate biocover abatement efficiency were shown to include analyte concentration at the
26 boundary layer and the solution interface temperature. In addition, this study provided indirect
27 evidence that the biocover reduced the effects of wind on volatilization of gases from the surface
28 of the lagoon.

29 Micrometrological flux comparisons between control and biocovered areas of the swine
30 lagoon showed that polymer biocovers could reduce the rate of NH₃ and H₂S emission from the
31 lagoon surface by up to 58% when compared to control areas. Accumulation of methanogenic

1 substrates in the lagoon effluent due to the inhibition of volatilization mechanisms was
2 minimized by biocover-enhanced anaerobic digestion. This process was shown to enhance
3 anaerobic digestion occurring in the lagoon by approximately 25% and therefore, the biocover
4 was shown to represent an effective mechanism to prevent accumulation of methanogenic
5 substrates in biocovered lagoons.

6 The cost for materials and labor for installation of the biocover (U.S.\$2.37 m²) on the
7 lagoon were significantly less than impermeable covers (U.S.\$16.15 m²) that are currently
8 marketed to the animal production industry, but similar in cost to competing biocover products
9 that consist of a single layer of geotextile (U.S.\$1.62 m²; Baumgartner Environics, Olivia, MN).
10 The cost analysis for the biocover tested in this study was U.S.\$1.14*finisher pig⁻¹. This cost
11 analysis is based on the facility evaluated in this study, which produced 5,400 finisher pigs*yr⁻¹
12 (3.0 pigs*pig space⁻¹*yr⁻¹; mean of 109 kg finishing pig), full coverage of the lagoon with a
13 surface area of 7,800 m², and assuming a biocover life expectancy of 3.0 years. A 3.0 year life
14 expectancy for the product was considered conservative based on field trials of the product over a
15 3 year evaluation period.

16 Many swine manure management systems are designed to release gases produced in
17 anaerobic decomposition processes into the atmosphere. Within these systems, a complex
18 consortium of microorganisms (anaerobic food chain) decompose complex biological waste
19 material to end products including CH₄, H₂S, CO₂, and NH₃.³⁸⁻⁴¹ The anaerobic food chain is
20 often functionally separated into microorganisms catalyzing acid-producing reactions from
21 complex organic substrates and *Archaea*, that catalyze CH₄-producing reactions from products
22 formed in the breakdown of complex organic substrates.^{41,42} The emission rate of CH₄ and
23 partially decomposed microbial substrates (volatile fatty acids) has been previously employed as
24 an indicator to assess functional coupling between processes in the anaerobic food chain in
25 anaerobic digesters.⁴³ Overloaded anaerobic digestion processes have been correlated with high
26 emission rates of volatile organic compounds and low emission rates of CH₄, while optimum
27 loading rates promote high bioconversion efficiencies of complex organic matter into CH₄.⁴³
28 Results of this study show that biocovers can significantly enhance the bioconversion efficiency
29 of manure entering the manure management system and thus, the type of cover evaluated in this
30 study can enhance the rate of digestion of manure into stabilized biosolids, while minimizing the
31 accumulation of malodorous methanogenic substrates in the liquid phase of stored effluent.

1 Although high bioconversion efficiencies are often considered a desirable endpoint in
2 waste management processes, high bioconversion rates can result in the production of the
3 greenhouse gases, CH₄ and CO₂, which are released through the permeable cover into the
4 atmosphere. While the permeable cover tested in this study exhibits several advantages over
5 impermeable covers, namely that: 1) rainwater does not accumulate on the surface of the
6 permeable covers, 2) material and labor costs for installation of the permeable cover (U.S.\$2.37
7 m²) are more than 6-fold less than impermeable covers (U.S.\$16.15 m²), and 3) equipment for
8 combustion or flaring of biogas is not needed for permeable covers, the release of CH₄ and CO₂
9 into the atmosphere from biocovered lagoons could be considered a significant disadvantage of
10 this method. There is, however, some potential to reduce or eliminate CH₄ emissions from
11 biocovered lagoons by promoting the colonization and growth of methanotrophic (methane-
12 oxidizing) bacteria on the upper surface of the biocover. This area of the biocover provides an
13 environment rich in CH₄ and oxygen that would favorably support the growth of these
14 microorganisms. A better understanding of the factors involved in methanotroph colonization
15 and growth on the upper surface of the biocover may be essential for the continued use of
16 biocovers for abatement of H₂S and NH₃ emissions from waste management systems.

17

18

ACKNOWLEDGEMENTS

19

20

21

22

23

24

25

26

REFERENCES

27

28

29

30

1. Anthan, G. *Environment feels the strain*. p. 2J. Nov. 10, 1996. The Des Moines Register, Des Moines, IA.
2. Harper, L.A.; Sharpe, R.R. Climate and water effects on gaseous ammonia emissions from a swine lagoon. In *Proceedings of the southwestern sustainable animal waste*

- 1 *management workshop*; Risse, L.M., Eds.; Univ. of Georgia publication No. ENG97-001:
2 Tifton, GA, Feb. 11-13 1997; pp 223-229.
- 3 3. Sharpe, R.R.; Harper, L.A. “Ammonia and nitrous oxide emissions from sprinkler
4 irrigation applications of swine effluent,” *J. Environ. Qual.* **1998**, 26,1703-1706.
- 5 4. Asman, W.A.H. Ammonia and ammonium in the atmosphere: Present knowledge and
6 recommendations for further research, 1995. In *Acid Rain Research: Do We Have*
7 *Enough Answers*; Heij, G.J., Erisman, J.W., Eds.; Proceedings of a Speciality
8 Conference: ‘s-Hertogenbosch, Netherlands. Elsevier Science B.V., Amsterdam,
9 Netherlands; October 10-12 1994; pp 55-70.
- 10 5. Sharpe, R.R.; Harper, L.A. Atmospheric methane emissions from a swine lagoon. In
11 *Proceedings of the southwestern sustainable animal waste management workshop*; Risse,
12 L.M., Eds.; Univ. of Georgia Publication No. ENG97-001: Tifton, GA, Feb. 11-13 1997;
13 pp 237-241.
- 14 6. Safley, Jr. L.M.; Casanda, M.E.; Woodbury, J.W.; Roos, K.F. *Global methane emissions*
15 *from livestock and poultry manure*. United States Environmental Protection Agency.
16 Washington DC, 1992.
- 17 7. Jacobson, L.D.; Clanton, C.J.; Radman, C.; Schmidt, D.; Nicalai, R.; Janni, K.A.
18 Comparison of hydrogen sulfide and odor emissions from animal manure storages. In
19 *Proceedings of the international symposium on animal and odor control from animal*
20 *production facilities*; Voermans, J.A.M., Monteny, G.J., Eds.; ISBN:90-9011059-3:
21 Vinkeloord, Netherlands, Oct. 6-10 1997; pp 404-412.
- 22 8. VanWicklen, G.L. Air quality in confinement animal facilities. In *Proceedings of the*
23 *southwestern sustainable animal waste management workshop*; Risse, L.M., Eds.; Univ.
24 of Georgia Publication No. ENG97-001: Tifton, GA, Feb. 11-13 1997; pp 231-236.
- 25 9. Zahn, J.A.; Hatfield, J.L.; Do, Y.S.; DiSpirito, A.A.; Laird, D.A.; Pfeiffer, R.L.
26 “Characterization of Volatile Organic Emissions and Wastes from a Swine Production
27 Facility,” *J. Environ. Qual.* **1997** 26,1687-1696.
- 28 10. Zahn, J.A.; DiSpirito, A.A.; Do, Y.S.; Brooks, B.E.; Cooper, E.E.; Hatfield, J.L.
29 “Correlation of human odor responses to airborne concentrations of malodorous volatile
30 organic compounds emitted from swine effluent,” *J. Environ. Qual.* **2001**, 30, 624-634.

- 1 11. Zahn, J.A.; Hatfield, J.L.; Laird, D.A., Hart, T.T., Do, Y.S.; DiSpirito, A.A. "Functional
2 classification of swine manure management systems based on solution-phase chemical
3 and gas emission characteristics," *J. Environ. Qual.* **2001**, 30, 635-647.
- 4 12. Crocker, B.B. Air Pollution Control Methods. In *Encyclopedia of Chemical Technology*
5 4th Ed.; Howe-Grant, M., Ed.; John Wiley & Sons. New York.
- 6 13. Miner, J.R. Controlling odors from livestock production facilities. In *Research results in*
7 *manure digestion, runoff, re-feeding, odors*; Smith, R.J., Eds.; North central regional
8 research publication no. 284: Ames, IA, 1982; pp 30-35.
- 9 14. Miner, J.R. *An executive summary: A review on the literature on the nature and control*
10 *of odors from pork production facilities*. National Pork Producers Council. Des Moines,
11 IA, 1995.
- 12 15. Miner, J.R. "Alternatives to minimize the environmental impact of large swine production
13 units," *J. Anim. Sci.* **1999**, 77, 440-444.
- 14 16. Wani, A.H.; Lau, A.K.; Branion, R.M.R. "Biofiltration control of pulping odors –
15 hydrogen sulfide: Performance, macrokinetics, and coexistence effects of organo-sulfur
16 species," *J. Chem. Technol.* **1999**, 74, 9-16.
- 17 17. Leson, G.; Winer, A.M. "Biofiltration: An innovative air pollution control technology for
18 VOC emissions," *J. Air & Waste Management. Assn.* 41 (8), 1045-1054.
- 19 18. Siemers, V.; Vanden Weghe, H. Biofilter/Wetscrubber Combinations for the Reduction
20 of Ammonia, Odor, and Dust Emissions of Pig Fattening Houses. In *Proceedings of the*
21 *international symposium on animal and odor control from animal production facilities*;
22 Voermans, J.A.M., Monteny, G.J., Eds.; ISBN:90-9011059-3: Vinkeloord, Netherlands,
23 Oct. 6-10 1997; pp 537-544.
- 24 19. Young, J.S.; Classen, J.J.; Bottcher, R.W.; Westerman, P.W. Biofiltration System for
25 Testing the Reduction of Odor from Swine Buildings. In *Proceedings of the international*
26 *symposium on animal and odor control from animal production facilities*; Voermans,
27 J.A.M., Monteny, G.J., Eds.; ISBN:90-9011059-3: Vinkeloord, Netherlands, Oct. 6-10
28 1997; pp 521-528.
- 29 20. Lias, S.; Hartung, E.; Jungbluth, T. Reduction of Ammonia and Odor Emissions by
30 Bioscrubbers. In *Proceedings of the international symposium on animal and odor control*

- 1 *from animal production facilities*; Voermans, J.A.M., Monteny, G.J., Eds.; ISBN:90-
2 9011059-3: Vinkeloord, Netherlands, Oct. 6-10 1997; pp 533-536.
- 3 21. Miner, J.R.; Pan, H. A floating permeable blanket to prevent the escape of odors. In
4 *Proc. 7th Int. Symp. On Agricultural and Food Processing Wastes*; Chicago, IL, June 18-
5 20: American Society of Agricultural Engineers. St. Joseph, MI.
- 6 22. Freese, B. "Manure Storage Covers," *Successful Farming*. 1997, 40-41.
- 7 23. Miner, J.; Suh, K.W. Floating Permeable Covers to Control Odor from Lagoons and
8 Manure Storages. In *Proceedings of the international symposium on animal and odor*
9 *control from animal production facilities*; Voermans, J.A.M., Monteny, G.T., Eds.;
10 ISBN:90-9011059-3: Vinkeloord, Netherlands, Oct. 6-10 1997; pp 435-440.
- 11 24. Xue, S.K.; Chen, S.; Hermanson, R.E. "Wheat straw cover for reducing ammonia and
12 hydrogen sulfide emissions from dairy manure storage," *Trans. ASAE*. **1999**, 42 (4),
13 1095-1101.
- 14 25. U.S. Environmental Protection Agency. "Methods for chemical analysis of water and
15 wastes". USEPA Rep. 600/4-79-020. **1979**. U.S. EPA, EMSL, Cincinnati, OH.
- 16 26. Chan, A.S.K., J.H. Prueger, and T.B. Parkin. "Comparison of closed-chamber and
17 bowen-ratio methods for determining methane flux from peatland surfaces", *J. Environ.*
18 *Qual.* **1998**. 27, 232-239.
- 19 27. Wilson, J.D., G.W. Thurtell, G.E. Kidd, and E.G. Beauchamp. "Estimation of the rate of
20 gaseous mass transfer from a surface source plot to the atmosphere". *Atmos. Environ.*
21 **1982**. 16(8), 1861-1867.
- 22 28. Majewski, M.S., D.E. Glotfelty, and J.N. Seiber. "A comparison of the aerodynamic and
23 the theoretical-profile shape methods for measuring pesticide evaporation from soil".
24 *Atmos. Environ.* **1989**. 23(5), 929-938.
- 25 29. Brutsaert, W. *Evaporation into the atmosphere: Theory, history, and application*. pp.
26 113-127. D. Reidel Publishing Co., London, England, **1982**.
- 27 30. Monteny, G.J. and P.P.H. Kant. Factors influencing air velocity in and ammonia
28 volatilization from a slurry pit in cubicle houses for dairy cows. In *Proceedings of the*
29 *international symposium on animal and odor control from animal production facilities*;
30 Voermans, J.A.M., and G.J. Monteny, G.J., Eds.; ISBN:90-9011059-3: Vinkeloord,
31 Netherlands, Oct. 6-10 1997; pp. 57-67.

- 1 31. Monteny, G.L., D.D. Schulte, A. Elzing, and E.J.J. Lamaker. "A conceptual mechanistic
2 model for the ammonia emissions from free stall cubicle dairy cow houses" *Transactions*
3 *of the ASAE*. **1998**. 41(1), 193-201.
- 4 32. Wilson, J.D.; V.R. Catehpool; O.T. Denmead; G.W. Thurtell. "Verification of a simple
5 micrometeorological method for estimating the rate of gaseous mass transfer from ground
6 to the atmosphere". *Agric. Met.* **1983**. 29, 183-189.
- 7 33. Freney J.R.; R. Leuning; J.R. Simpson; O.T. Denmead; and W.A. Muirhead. "Estimating
8 ammonia volatilization from flooded rice fields by simplified techniques". *Soil Sci. Soc.*
9 *Am. J.* **1985**. 49, 1049-1054.
- 10 34. Arogo, J.; R.H. Zhang; G.L. Riskowski, and D.L. Day. "Mass transfer coefficients for
11 hydrogen sulfide emission from aqueous solutions and liquid swine manure".
12 *Transactions of the ASAE*. **1999**. 42(5), 1455-1462.
- 13 35. Strous, M., J., J.G. Kuenen, and M.S.M. Jetten. "Key physiology of anaerobic
14 ammonium oxidation". *Appl. Environ. Microbiol.* **1999**. 65(7), 3248-3250.
- 15 36. Sievers, D.M., and E.L. Iannotti. Anaerobic processes for stabilization and gas
16 production. p. 1-10. In *Research results in manure digestion, runoff, refeeding, odors*.
17 R.J. Smith, Ed.; North central regional res. Publ. 284. North Central Regional Res.,
18 Ames, IA. 1982.
- 19 37. Raskin, L., L.K. Poulsen, D.R. Noguera, B.E. Rittmann, and D.A. Stahl. "Quantification
20 of methanogenic groups in anaerobic biological reactors by oligonucleotide probe
21 hybridization". *Appl. Environ. Microbiol.* **1994**. 60, 1241 - 1248.
- 22 38. Gottschalk, G. Bacterial metabolism: Second edition. Springer-Verlag Publishers, New
23 York. 1988.
- 24 39. Lana, R.P., J.B. Russell, M.E. Amburgh. "The role of pH in regulating ruminal methane
25 and ammonia production". *J. Anim. Sci.* **1998**. 76, 2190 - 2196.
- 26 40. Mackie, R.I., P.G. Stroot, and V.H. Varel. "Biochemical identification and biological
27 origin of key odor components in livestock waste". *J. Anim. Sci.* **1998**. 76, 1331 - 1342.
- 28 41. Fenchel, T., and B.J. Finlay. "Evolution of life without oxygen". *Am. Sci.* **1994**. 82, 22
29 - 29.
- 30 42. Deppenmeier, U., V. Muller, and G. Gottschalk. "Pathways of energy conservation in
31 methanogenic archaea". *Arch. Microbiol.* **1996**. 165, 149 - 163.

- 1 43. Hill, D.T. and Bolte, J.P. "Digester stress as related to isobutyric and isovaleric acids".
- 2 *Biological Wastes* **1989**. 28, 33 - 37.
- 3

1 **TABLE 1.** Mean nutrient analysis values of weekly effluent samples collected from the swine
 2 lagoon for the months of August, September, and October, 1999. Reported values represent the
 3 mean \pm the standard error of the mean.
 4

| Analyte | Sampling period | | |
|---------------------------------------------|-----------------|----------------|----------------|
| | August | September | October |
| Sample number (n) | n = 7 | n = 5 | n = 6 |
| pH (-log [H ⁺]) | 8.1 \pm 0.01 | 8.2 \pm 0.02 | 8.1 \pm 0.01 |
| COD (mg*L ⁻¹) | 2130 \pm 107 | 2380 \pm 89 | 2500 \pm 91 |
| TS (mg*L ⁻¹) | 5980 \pm 75 | 6040 \pm 98 | 6404 \pm 102 |
| VS (mg*L ⁻¹) | 1032 \pm 15 | 1040 \pm 18 | 1103 \pm 12 |
| TSS (mg*L ⁻¹) | 83 \pm 20 | 89 \pm 21 | 92 \pm 28 |
| TKN (mg*L ⁻¹) | 968 \pm 11 | 962 \pm 11 | 977 \pm 9 |
| NH ₃ -N (mg*L ⁻¹) | 917 \pm 12 | 934 \pm 8 | 929 \pm 7 |
| H ₂ S-HS (mg*L ⁻¹) | 15 \pm 2 | 17 \pm 3 | 18 \pm 1 |
| Total P (mg*L ⁻¹) | 191 \pm 5 | 196 \pm 2 | 183 \pm 4 |
| Ortho-PO ₄ (mg*L ⁻¹) | 183 \pm 2 | 178 \pm 5 | 179 \pm 6 |
| Ca (mg*L ⁻¹) | 32 \pm 2 | 31 \pm 3 | 34 \pm 2 |

5

1
2 **TABLE 2.** Measured evaporative flux rates of H₂S, NH₃, and CH₄ from a swine lagoon in
3 central Missouri. Flux rates were collected from control and treatment (biocover) emission plots
4 for three individual emission evaluation periods. Reported values represent the mean ± the
5 standard error of the mean.

| Property | Sampling Period | | |
|----------------------------------------------------------------------------------------|---------------------|---------------------|---------------------|
| | Aug. 3-6 | Sept. 25-Oct. 1 | Oct. 14-16 |
| Sample number*plot ⁻¹ (n) | n = 359 | n = 322 | n = 267 |
| Wind velocity (m*s ⁻¹) | | | |
| Control | 1.15 ± 0.05 | 2.31 ± 0.05 | 2.92 ± 0.06 |
| Treatment | 1.14 ± 0.03 † | 2.31 ± 0.03 † | 2.90 ± 0.06 † |
| Solution interface temp. (° C) | | | |
| Control | 25.1 ± 0.2 ° C | 21.3 ± 0.3° C | 20.6 ± 0.3° C |
| Treatment | 22.9 ± 0.1° C | 19.1 ± 0.1° C | 18.4 ± 0.2° C |
| Localized biocover pH (-log[H ⁺]) | | | |
| Bottom (effluent) | 8.1 ± 0.01 | 8.2 ± 0.02 | 8.1 ± 0.01 |
| Top (interface)‡ | 7.3 ± 0.02 | 7.2 ± 0.01 | 7.2 ± 0.01 |
| H ₂ S flux (ng*cm ⁻² *s ⁻¹) | | | |
| Control | 0.73 ± 0.04 | 0.82 ± 0.04 | 2.11 ± 0.06 |
| Treatment | 0.56 ± 0.03 | 0.43 ± 0.02 | 0.88 ± 0.02 |
| Efficiency (%) and level of significance | 23% p<0.0001 | 48% p<0.0001 | 58% p<0.0001 |
| NH ₃ flux (ng*cm ⁻² *s ⁻¹) | | | |
| Control | 18.0 ± 0.6 | 18.4 ± 0.3 | 18.4 ± 0.4 |
| Treatment | 14.9 ± 0.6 | 9.2 ± 0.3 | 8.5 ± 0.4 |
| Efficiency (%) and level of significance | 17% p=0.0005 | 50% p<0.0001 | 54% p<0.0001 |
| CH ₄ flux (ng*cm ⁻² *s ⁻¹) | | | |
| Control | 134 ± 4 | 162 ± 5 | 80 ± 3 |
| Treatment | 137 ± 5 | 181 ± 5 | 110 ± 4 |
| Efficiency (%) and level of significance | (-) 2% † p=0.071 | (-) 11% p<0.0001 | (-) 27% p<0.0001 |
| Ratio NH ₃ -N (top/bottom, mg NH ₃ -N*L ⁻¹) | 0.92 ± 0.01 † | 0.68 ± 0.04 | 0.62 ± 0.07 |
| Ratio H ₂ S-SH (top/bottom, mg H ₂ S- SH*L ⁻¹) | 0.96 ± 0.01 † | 0.59 ± 0.03 | 0.56 ± 0.04 |
| Attached Biomass (g wet weight*cm ²) | 0.2 ± 0.01 † | 2.6 ± 0.03 | 2.9 ± 0.03 |

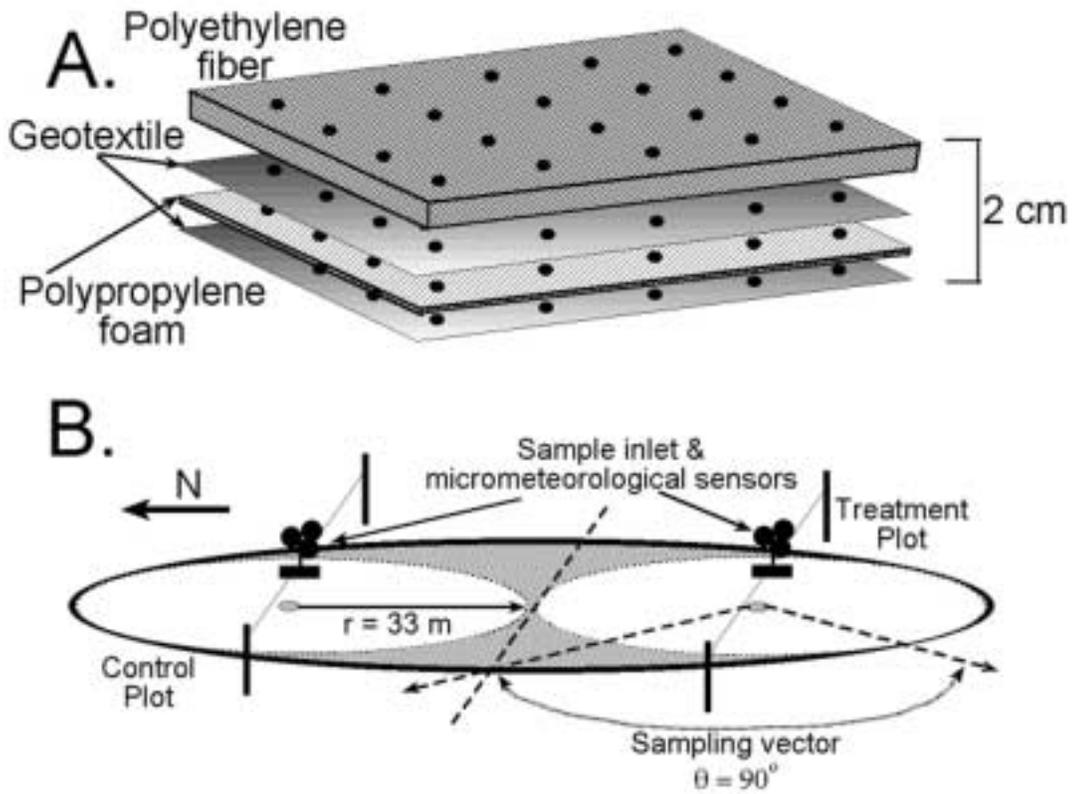
6 † Not significantly different from the control, α = 0.05.

7 ‡ Measured at solution-air interface located between polyethylene fiber and geotextile layers.

8
9

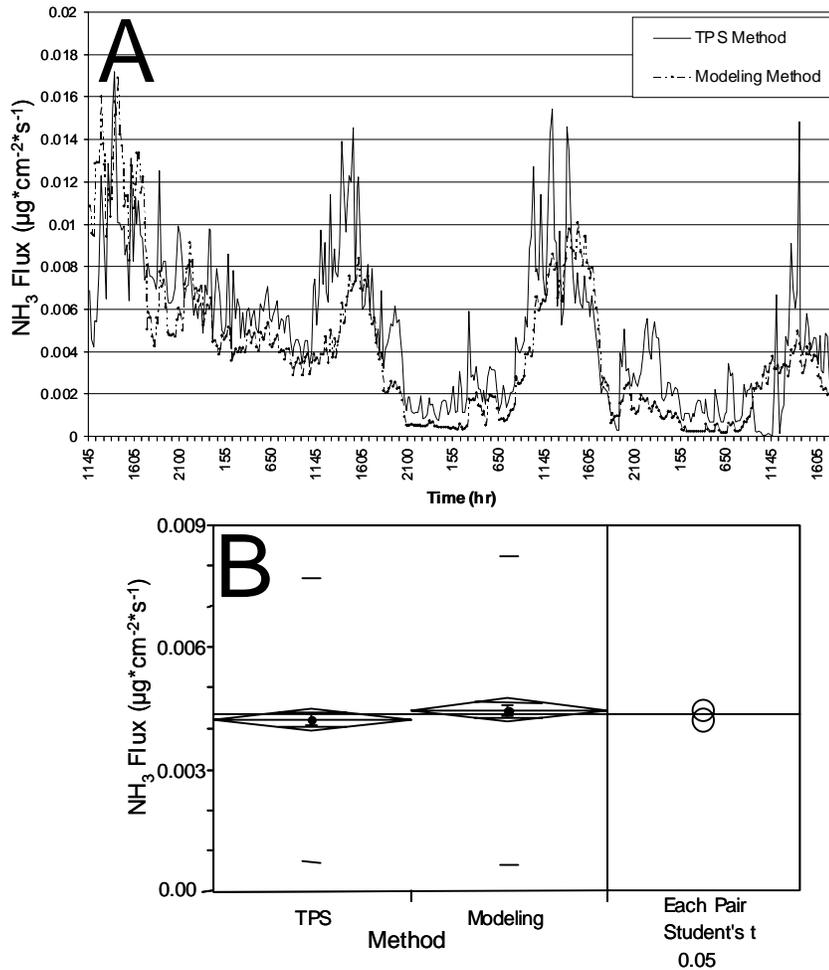
FIGURES

FIGURE 1. Diagrams showing the A) components and design of the commercial biocover and B) the design of the sampling plots and the placement of micrometeorological sensors and air sample inlets above the surface of a swine lagoon.

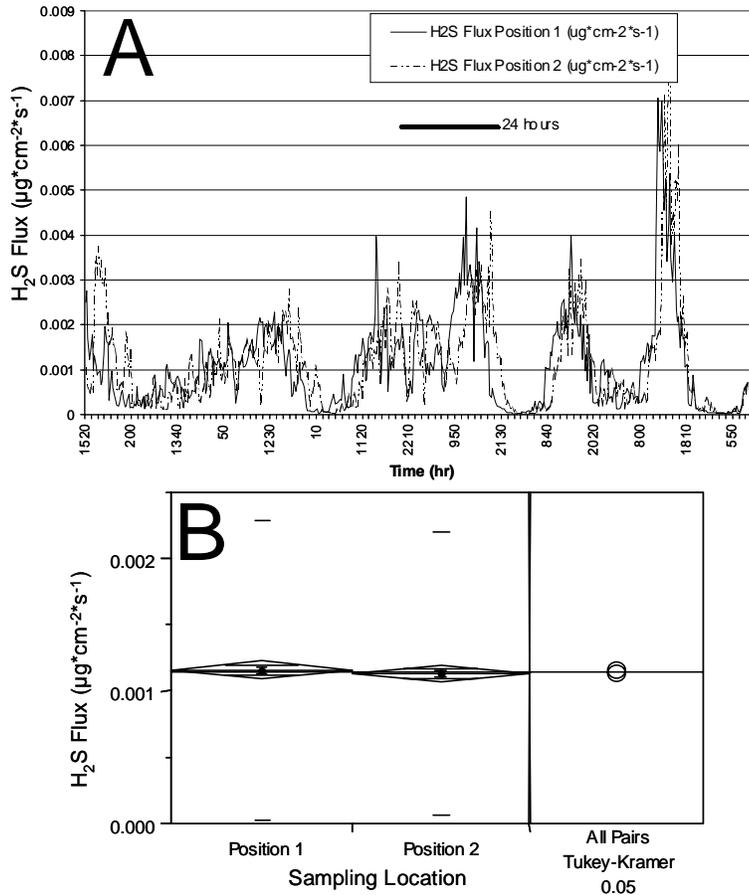


1 **FIGURE 2.** Comparison of methods to measure NH_3 flux rates from a 66 m circular sampling
 2 plot on an east-central Missouri swine lagoon. Evaporative flux rate of NH_3 was calculated by
 3 the theoretical-profile shape method or was simulated by modeling through measured
 4 environmental parameters. The (B) oneway Anova (t-test) for NH_3 flux data and the Tukey-
 5 Kramer HSD means comparison table showing the absolute difference in the means minus the
 6 least significant difference ($\alpha = 0.05$).

7
8
9



1 **FIGURE 3.** A test of spatial variability of H₂S flux from two uncovered sampling plots on a
 2 swine lagoon. Temporal flux rates of H₂S from July 17 through 24, 1999 for two individual 66
 3 meter diameter circular sampling plots on an east-central Missouri swine lagoon. The solid line
 4 represents flux measurements completed over the south sampling plot and the dashed-dot line
 5 represents the flux measurements completed on the north sampling plot. The (B) oneway Anova
 6 (t-test) for H₂S flux data and the Tukey-Kramer HSD means comparison table showing the
 7 absolute difference in the means minus the least significant difference ($\alpha = 0.05$).
 8
 9
 10



1 **FIGURE 4.** Temporal flux measurements of H₂S and NH₃ emissions from a commercial
 2 biocover (treatment) and the uncovered lagoon surface (control) on October 14 through 16, 1999.
 3 The (A`) oneway Anova (t-test) for H₂S flux data, for (B`) NH₃ data, and the corresponding
 4 Tukey-Kramer HSD means comparison table showing the absolute difference in the means minus
 5 the least significant difference ($\alpha = 0.05$).
 6
 7

