Final Report

EMISSION TESTS OF THE BIOCAP™ BIOCOVER INSTALLED ON A COLORADO SWINE LAGOON

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EXCEUTIVE SUMMARY

The objective of this study was to perform compliance monitoring under the State of Colorado animal agriculture emission testing guidelines to evaluate the effectiveness of the BioCap™ permeable biocover toward reducing the emission of ammonia, hydrogen sulfide, and total volatile organic compounds from a swine lagoon. Emission comparisons were performed between treatment areas that were covered with the BioCap™ biocover, and an uncovered area, on the same waste management system, consisting of an 11-meter square opening cut through the cover.

Emission tests showed that the BioCap™ biocover achieved an average abatement efficiency for hydrogen sulfide, ammonia, and total VOCs of 81%, 96%, and 90%, respectively, during the December 1999 sample collection period. Flux assessments for hydrogen sulfide, ammonia, and total VOCs during the April 2000 (98%, 74% and, 88%, respectively) and June 2000 (97%, 61% and, 79%, respectively) showed that the BioCap™ biocover achieved a level of performance that was similar to the December 1999 testing period. This result indicated that biocover abatement performance was independent of seasonal conditions.

Analysis of key odorant compounds associated with swine odor (Zahn et al., 2000b) showed that the assessment of total VOC emissions underestimated the performance of the Biocap™ biocover. Analysis of the concentration of VOCs associated with swine odor intensity, showed that the abatement efficiency achieved by the Biocap™ biocover exceeded 94% for a majority of malodorous VOCs tested during the December 1999, April 2000, and June 2000 sample collection periods.

MATERIALS AND METHODS

Capture and Analysis of Air Pollutants from Swine Waste Management Systems.

Volatile organic compounds (VOC) were captured on a multibed adsorbent tube containing a combination of Tenax TA and Carboxen-569 (Supelco, Bellefonte, PA), according to the low-volume sampling method developed by Zahn et al (1997). Glass fritted tubes (0.6 x 11.5 cm O.D.) were packed and then thermally-conditioned for 1 hour at 230° C using a Dynatherm six tube conditioner (Supelco, Bellfonte, PA). Nitrogen flow was maintained at 20 mL min^{-1} for individual tubes during thermal conditioning. For air sampling of VOC, flow rate through individual thermal desorption tubes was regulated at 0.50 to 0.60 L min^{-1} using a Supelco Model 1064 air sampler that was calibrated with a Supelco bubble flow meter. After sampling, tubes were removed from the pump, sealed in Teflon storage tubes, and transported to the laboratory on ice. Tubes not analyzed immediately were stored at minus 20° C for a period up to 2 months with little or no decomposition of analytes. Chemical analysis of trapped analytes on the thermal desorption tubes was performed using a Dynatherm ACHEM 900 thermal desorber coupled to a Hewlett-Packard model 5890 gas chromatograph equipped with an FID. Tubes were desorbed at 260° C for 3 minutes at a carrier flow rate of 2.2 mL min^{-1}. Analytes were transferred from the desorber oven to a 30m x 0.25mm Innowax Cross-linked PEG column through a nickel transfer line heated at 240° C. Program parameters for the Innowax column were as follows: rate = 12°

C min^{-1}., initial temp. = 40° C, final temp. = 230° C, initial time = 2.5 min., final time = 1 min., and detector temp. = 240° C. Analytes were adequately focused on the front of the column using an initial oven temperature of 40° C. Chemical identity was based on retention times of authentic chemical standards purchased from Aldrich Chemical Co. (Milwaukee, WI) and confirmed by electron-impact ionization mass spectrometry as previously described (Zahn et al., 1997).

Ammonia (NH_3) was collected from air using a glass impinger (125ml internal volume). Air samples were drawn by vacuum through a submerged fritted glass diffusion disk into 40 ml of 0.2M boric acid (pH 5.0) using a 12V. DC Gilian GilAir personal sampling pump (product # 800508) or a 110V AC Cole Parmer vacuum sampling pump (catalog # P-79200), operated at 1.5 to 2.0 L min^{-1}. A Supelco bubble flow meter was used to calibrate sampling pumps on a daily basis. The HACH Company Portable Colorimeter System with the Nessler Ammonia method was used to determine ammonium concentration in the Boric acid sample. This method (HACH, #8038) is adapted from Standard Methods for the Examination of Water and Wastewater and is U.S. EPA approved for reporting ammonium concentration.

The Minnesota Pollution Control Agency "Hydrogen Sulfide Ambient Air Quality Screening Protocol" was employed in this study for measurements of H_2S. Briefly, an Arizona Instruments Model 631X Jerome H_2S Gas Analyzer was used to determine the concentration of H_2S in the exhaust air stream from the wind tunnel. Reported measurements consisted of mean and standard deviation from duplex measurements taken every two minutes for a period of one hour during the sample collection period ($n \approx 60$ measurements). A duplex measurement is two separate cycles of the Jerome analyzer within a two minute period taken by pressing the "sample" button once, recording that value and then immediately pressing the sample button again and recording the second value within a two minute period. Prior to sampling, the Jerome Gas Analyzer was regenerated and zeroed in an area free of hydrogen sulfide. The analyzer was not zeroed between daily sampling of different sites.

Air velocity inside the wind tunnel was recorded at the center of the chamber for each two-minute sampling period with a hot-wire anemometer (Cole Parmer Instruments, *Tri-Sense* meter kit, product number P-37000-95), and was reported as the mean ± the standard deviation.

Meteorological conditions (wind speed, relative humidity, and air temperature) were recorded at the point of sample collection, in 5 minute intervals, using a hand-held weather station that was positioned 1.5 meters above the ground near the lagoon berm. Meteorological conditions were reported as the mean ± the standard deviation.

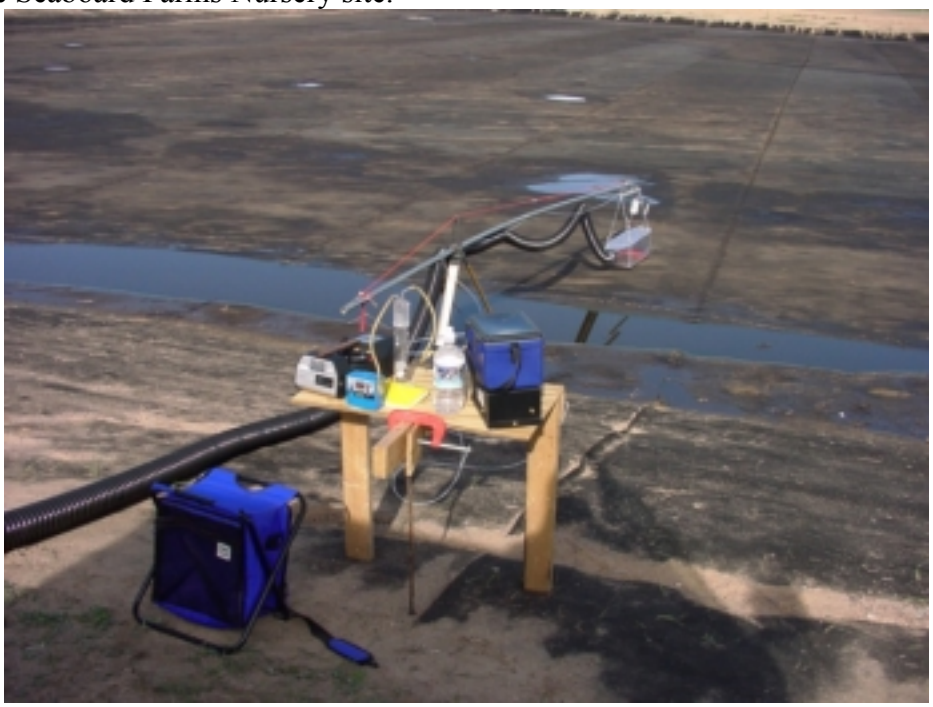
Flux Rate Measurements of Air Pollutants.

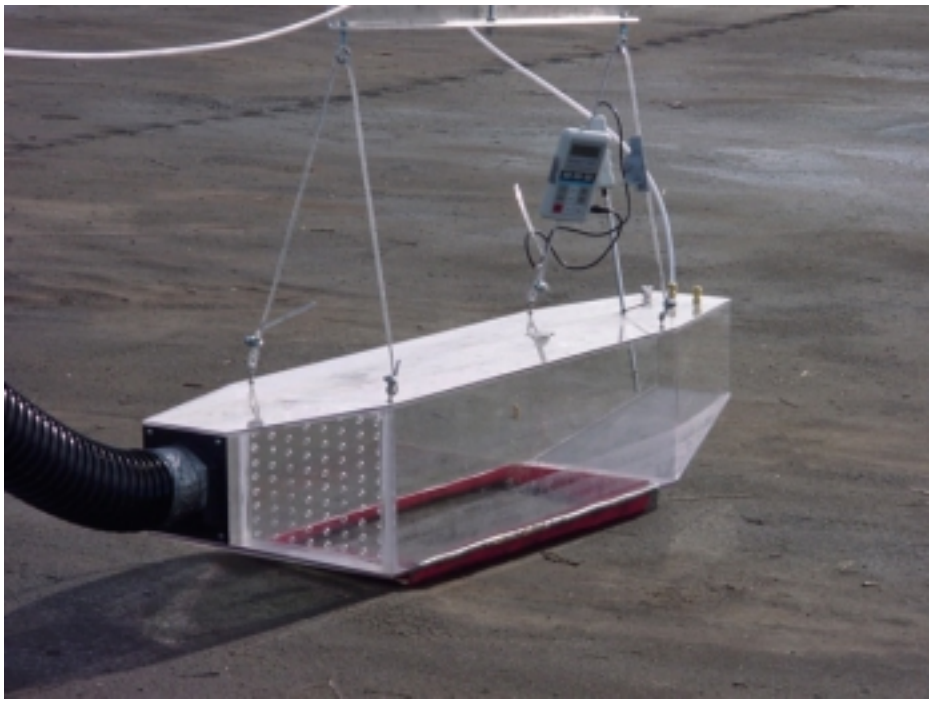
Flux rates of ammonia, hydrogen sulfide, and volatile organic compounds were determined using the dynamic flux chamber described by Schmidt et al., (1999; Fig 1). Analytes were removed from the inlet air by adsorption on 6-14 mesh, activated charcoal (Fisher #05-685B). The air concentration of analytes present in the exit stream from the wind tunnel were converted to flux rate through the following equation:

$$F = (v/a_s) * C \qquad \text{where:}$$

F = gas flux rate in $\mu g*m^{-2}*s^{-1}$; v = air exchange rate in wind tunnel in m^3*s^{-1}; a_s = basal area of the wind tunnel in m^2; and C = concentration of analyte in exit air stream.

FIGURE 1. Photographs showing the construction, location of gas measurement instrumentation, and typical placement of the wind tunnel over the covered surface of the swine lagoon at the Seaboard Farms Nursery site.





RESULTS AND DISCUSSION

December 1999 (below 40° F) Flux Assessments

Effect of the Biocap™ Biocover on Emission Rate of Hydrogen Sulfide, Ammonia, and Total Volatile Organic Compounds.

The objective of this study was to perform compliance monitoring under the State of Colorado animal agriculture emission testing guidelines to evaluate the effectiveness of the BioCap™ permeable biocover toward reducing the emission of ammonia, hydrogen sulfide, and total volatile organic compounds from a swine lagoon. Emission testing was performed on a swine lagoon at Seaboard Farms nursery site near Julesburg, Colorado on December 8 and 9, 1999. Gas fluxes of ammonia, hydrogen sulfide, and total volatile organic compounds were measured using the dynamic flux chamber method previously described by Schmidt et al., 1999. Weather conditions during the emission testing period consisted of overcast skies with ambient air temperatures between 28° to 44.2° F. Emission comparisons were performed between treatment areas that were covered with the BioCap™ biocover, and a separate uncovered area that consisted of an11 meter square opening cut through the cover.

TABLE 1. Operational properties of the wind tunnel during the three sampling trials for control and treatment sampling positions over a Colorado swine lagoon during the December 1999 (below 40° F) sample collection period. Values reported represent the mean ± the standard deviation.

Property	Trial 1		Trial 2		Trial 3	
	Treatment	Control	Treatment	Control	Treatment	Control
Date	12-07-99	12-09-99	12-08-99	12-09-99	12-08-99	12-09-99
Sampling duration (hr)	15:00 to 16:00	11:04 to 12:04	15:38 to 16:38	12:18 to 13:18	17:16 to 18:16	14:26 to 15:26
Linear air velocity ($m*s^{-1}$), (mean ± std. dev.), (n = 32 obs.)	2.7 ± 0.04	2.7 ± 0.06	2.2 ± 0.03	2.2 ± 0.07	1.2 ± 0.05	1.2 ± 0.08
Chamber air exchange rate (m^3*s^{-1})	0.189	0.189	0.154	0.154	0.084	0.084
V/A_s ($m*s^{-1}$ / m^2)	0.88	0.88	0.72	0.72	0.39	0.39
Chamber basal area (m^2)	0.213	0.213	0.213	0.213	0.213	0.213

Flux measurements for control and treatment sampling positions were performed consecutively during a three-hour period from initiation of air sampling on the treatment position to completion of air sampling on the control position. Wind tunnel air velocities were varied for each individual trial to evaluate the influence of air exchange rate on emission rate. To complete this objective, linear air velocity within the chamber was varied over a velocity range from 0.3 $m*s^{-1}$ to 0.9 $m*s^{-1}$ (Table 1). During each of the 1 hour flux determinations, wind tunnel air velocity was monitored continuously at the center of the chamber using a hot-wire anemometer and

recorded in two minute intervals. Purified sweep gas was supplied to the wind tunnel in a positive pressure mode after passage through a bed (800 cm^3) of activated carbon. This helped insure that the air passing though the wind tunnel was free of background analytes. Analyte sampling was performed in the exit stream from the wind tunnel as previously described by Baumgartner et al. (1999), or Schmidt et al. (1999).

TABLE 2. The effect of the BioCap™ biocover on the flux rate of air pollutants from a Colorado swine lagoon during the December 1999 (below 40° F) sampling period. Measured flux rate for air pollutants collected in air samples from the wind tunnel. Values reported represent the mean air concentration of air pollutants over a one-hour sampling period. Standard errors for means were less than or equal to 2% of the mean.

	Sampling Position					
Property	Trial One (12-07/09)		Trial Two (12-08/09)		Trial Three (12-08/09)	
	Control	Treatment †	Control	Treatment	Control	Treatment
H_2S conc. ($\mu g*m^{-3}$)	17.5	5.7	42.6	5.0	21.7	5.7
H_2S flux ($\mu g*m^{-2}*s^{-1}$)	15.6	5.1	30.8	3.6	8.6	2.2
H_2S reduction (%)	67%		88%		74%	
NH_3 conc. ($\mu g*m^{-3}$)	8.1	< 2.0	122	< 2.0	32.6	< 2.0
NH_3 flux ($\mu g*m^{-2}*s^{-1}$)	7.2	< 1.8	88.3	< 1.5	12.9	< 0.8
NH_3 reduction (%)	75%		98%		94%	
Total VOC conc. ($\mu g*m^3$)	1995	2055	1856	229	1493	127
Total VOC flux ($\mu g*m^2*s^{-1}$)	1770	1787	1343	166	589	50
Total VOC reduction (%)	-0-%		88%		92%	

† = Improper support of the wind tunnel during the treatment sampling period caused submersion the Biocap™ biocover and loss of emission abatement efficiency.

Abatement efficiency of the biocover was negatively influenced by the unintentional submersion of the biocover during trial one, due to improper support of the wind tunnel (Table 2). Submersion of the biocover, coupled with the extremely low emission rates for ammonia and hydrogen sulfide decreased the data quality acquired for trial one. Chromatographic profiles of VOCs present in air samples taken from control and treatment positions for trial one provided the strongest evidence that the cover was fully submerged during a significant portion of the sampling period. Henry's law constants for VOC emissions are on average, four orders of magnitude lower than either ammonia or hydrogen sulfide (Zahn, 1997b). Therefore, the

evaluation VOC fluxes offered a more sensitive and reproducible means to evaluate the degree of cover submersion for this example. The lack of detectable VOC oxidation products associated with the treatment in trial one provided evidence that the biocover had been fully submerged during sampling. Therefore, flux data collected for trial one were omitted from the combined abatement efficiency calculations. Examination of trial two and three showed average abatement efficiencies for total VOC, ammonia, and hydrogen sulfide 90%, 96% and, 81%, respectively (Table 2).

Results reported in Table 2 show that the BioCap™ biocover is effective in reducing the emission rate of odorous gases from stored swine manure. These results were further corroborated by 12 scentometry readings that were performed simultaneously to flux rate measurements on the Biocap™ covered swine lagoon. Odor measurement surveys conducted around the perimeter (berm) of the covered lagoon, under ambient wind velocities ranging from 1.4 $m*s^{-1}$ to 11.9 $m*s^{-1}$, showed that there was no detectable odor released from the lagoon during emission sampling periods.

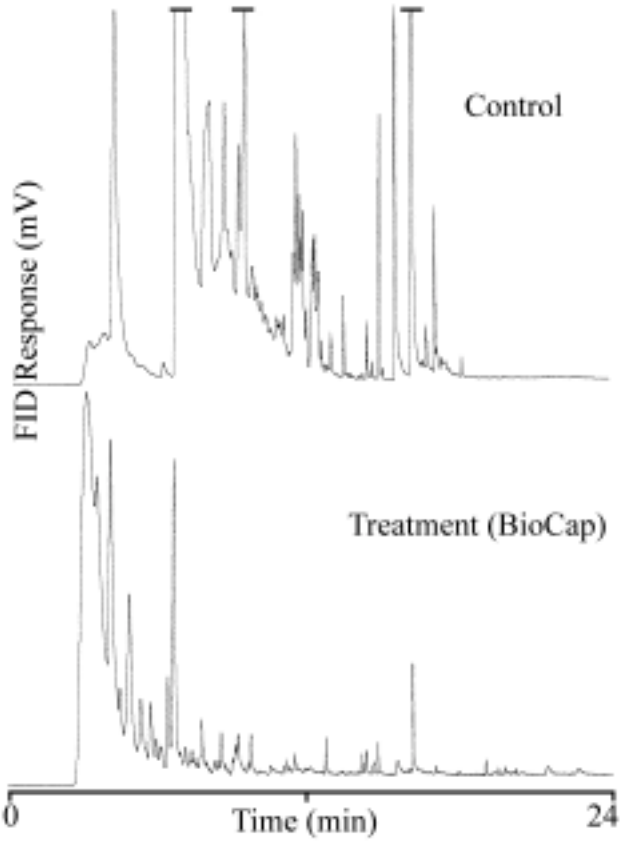
Effect of the Biocap™ Biocover on the Emission Rate of Malodorous Volatile Organic Compounds Associated with Swine Odor.

Flux measurements of VOCs emitted from the control and treatment chambers showed that the average abatement efficiency achieved by the Biocap™ for reduction of total VOC emissions was 90%, when the biocover remained at the air/solution interface. However, analysis of key odorant compounds associated with swine odor (Zahn et al., 2000b) showed that the total VOC emission assessment underestimated the performance of the Biocap™ biocover towards reducing VOC emissions. Analysis of VOCs associated with swine odor intensity showed that the abatement efficiency achieved by the Biocap™ biocover exceeded 94% for a majority of malodorous VOCs. Table 3 and Figure 2 shows the effect of the Biocap™ biocover on emission of indicator VOCs of swine odor for Trial 2. The average abatement efficiency between control and treatment positions for seven indicator compounds of swine odor was observed to be approximately 93%. While physical mechanisms appear to be the most critical factor in emission abatement efficiency associated with the biocover (Zahn, 1997b), VOC data presented in this report provide evidence that 3% to 7% of the total amount of VOCs emitted from the liquid are being transformed to low-odor compounds (i.e., low molecular weight alcohols) by chemical or biological processes occurring in the cover (see Fig. 2).

TABLE 3. Effect of the Biocap™ biocover on the flux rate of selected (partial group) indicator VOCs of swine manure odor.

Organic compound	Abatement efficiency for Trial 2 (%)	Odor characteristic	Odor threshold ($mg*m^3$)
Dimethyl disulfide	97%	Putrid, decayed vegetables	0.0011-0.61
2-Butanol	98%	Alcohol	0.11
Acetic acid	95%	Pungent	0.1-2.5
Propionic acid	97%	Fecal	0.0025
Butyric acid	93%	Fecal, stench	0.00025
Phenol	79%	Aromatic	0.23-0.38
p-Cresol	88%	Fecal	0.0021-0.009
4-Ethyl phenol	94%	Pungent	0.0035-0.01
Mean abatement efficiency	~93%		

FIGURE 2. The effect of the BioCap™ biocover on air concentration of VOCs emitted from control and treatment emission operating at an air exchange rate of chambers from a Colorado swine lagoon during the December 1999 sampling period.



April 2000 (turnover) Flux Assessments

Effect of the Biocap™ Biocover on Emission Rate of Hydrogen Sulfide, Ammonia, and Total Volatile Organic Compounds.

Emission testing was performed on a swine lagoon at Seaboard Farms nursery site near Julesburg, Colorado on April 26 through 28, 2000. Gas fluxes of ammonia, hydrogen sulfide, and total volatile organic compounds were measured using the dynamic flux chamber method as described for the December 1999 measurements. Weather conditions during the emission testing period consisted of overcast skies and variable winds (2-16 miles hr^{-1}), with ambient air temperatures between 51° to 68° F. Emission comparisons were performed between treatment areas that were covered with the BioCap™ biocover, and a separate uncovered area that consisted of an 11 meter square opening cut through the cover. Operating parameters for the wind tunnel during flux measurement periods are described in Table 4.

TABLE 4. Operational properties of the wind tunnel during the three sampling trials for control and treatment sampling positions over a Colorado swine lagoon during the April 2000 (turnover) sample collection period. Values reported represent the mean ± the standard deviation.

Property	Trial 1		Trial 2		Trial 3	
	Treatment	Control	Treatment	Control	Treatment	Control
Date	4-25-00	4-27-00	4-25-00	4-27-00	4-26-00	4-28-00
Sampling duration (hr)	16:28 to 17.28	07:28 to 08:28	17:44 to 18:44	18:04 to 19:04	08:12 to 09:12	08:20 to 09:20
Linear air velocity ($m*s^{-1}$), (mean ± std. dev.), (n = 32 obs.)	0.42 ± 0.04	0.46 ± 0.11	0.37 ± 0.03	0.48 ± 0.04	0.34 ± 0.02	0.51 ± 0.04
Chamber air exchange rate (m^3*s^{-1})	0.0294	0.0322	0.0259	0.0336	0.0238	0.0357
V/A_s ($m*s^{-1}$ / m^2)	0.138	0.151	0.122	0.158	0.112	0.168
Chamber basal area (m^2)	0.213	0.213	0.213	0.213	0.213	0.213

The effect of the BioCap™ biocover on the flux rate of total VOC, ammonia, and hydrogen sulfide, during the April 2000 sample collection period is shown in Table 5. The mean abatement efficiency during the three sampling trials for total VOC, ammonia, and hydrogen sulfide was 88%, 74% and, 98%, respectively (Table 5). The low VOC and ammonia abatement efficiency observed in Trial 1 may have resulted from a wet biocover surface, due to a light (<0.2 inches) precipitation event. Hydrogen sulfide abatement efficiency remained high during the precipitation event and thus, hydrogen sulfide flux appeared not to be influenced by the wetting of the biocover surface (Table 5).

TABLE 5. The effect of the BioCap™ biocover on the flux rate of air pollutants from a Colorado swine lagoon during the April 2000 (turnover) sampling period. Measured flux rate for air pollutants collected in air samples from the wind tunnel. Values reported represent the mean air concentration of air pollutants over a one-hour sampling period. Standard errors for means were less than or equal to 2% of the mean.

	Sampling Position					
Property	Trial One (4-25/27)		Trial Two (4-25/27)		Trial Three (4-26/28)	
	Control	Treatment	Control	Treatment	Control	Treatment
H_2S conc. ($\mu g*m^{-3}$)	348.5	5.8	241.4	2.6	151.4	9.7
H_2S flux ($\mu g*m^{-2}*s^{-1}$)	52.7	0.8	38.1	0.3	25.4	1.1
H_2S reduction (%)	98%		99%		96%	
NH_3 conc. ($\mu g*m^{-3}$)	262.6	97.5	260.2	146.4	650.4	< 2.0
NH_3 flux ($\mu g*m^{-2}*s^{-1}$)	39.7	13.5	41.1	17.8	109	< 0.2
NH_3 reduction (%)	66%		57%		>99%	
Total VOC conc. ($\mu g*m^3$)	1865	560	1728	207	1621	10.1
Total VOC flux ($\mu g*m^2*s^{-1}$)	282	77.3	273	25.2	271.7	1.1
Total VOC reduction (%)	73%		91%		>99%	

June 2000 (above 80° F) Flux Assessments

Effect of the Biocap™ Biocover on Emission Rate of Hydrogen Sulfide, Ammonia, and Total Volatile Organic Compounds.

Emission testing was performed on a swine lagoon at Seaboard Farms nursery site near Julesburg, Colorado on June, 20 through 21, 2000. Gas fluxes of ammonia, hydrogen sulfide, and total volatile organic compounds were measured using the dynamic flux chamber method as described for the December 1999 measurements. Weather conditions during the emission testing period consisted of mostly sunny skies and variable winds (5-25 miles hr^{-1}), with ambient air temperatures between 81° to 96° F. Emission comparisons were performed between treatment areas that were covered with the BioCap™ biocover, and a separate uncovered area that consisted of an 11 meter square opening cut through the cover. Operating parameters for the wind tunnel during flux measurement periods are described in Table 6.

TABLE 6. Operational properties of the wind tunnel during the three sampling trials for control and treatment sampling positions over a Colorado swine lagoon during the June 2000 (above 80° F) sample collection period. Values reported represent the mean ± the standard deviation.

Property	Trial 1		Trial 2		Trial 3	
	Treatment	Control	Treatment	Control	Treatment	Control
Date	6-20-00	6-21-00	6-20-00	6-21-00	6-21-00	6-21-00
Sampling duration (hr)	15:12 to 16:12	12:03 to 1:03	16:27 to 17:27	13:42 to 14:32	09:42 to 10:42	15:08 to 16:08
Linear air velocity ($m*s^{-1}$), (mean ± std. error), (n = 30 obs.)	0.55 ± 0.09	0.60 ± 0.07	0.55 ± 0.07	0.57 ± 0.06	0.72 ± 0.06	0.73 ± 0.07
Chamber air exchange rate (m^3*s^{-1})	0.0385	0.042	0.0385	0.0399	0.0504	0.0511
V/A_s ($m*s^{-1} / m^2$)	0.181	0.197	0.181	0.187	0.237	0.240
Chamber basal area (m^2)	0.213	0.213	0.213	0.213	0.213	0.213

TABLE 7. The effect of the BioCap™ biocover on the flux rate of air pollutants from a Colorado swine lagoon during the June 2000 (above 80° F) sampling period. Measured flux rate for air pollutants collected in air samples from the wind tunnel. Values reported represent the mean air concentration of air pollutants over a one-hour sampling period. Standard errors for means were less than or equal to 2% of the mean.

	Sampling Position					
Property	Trial One (6-20/21)		Trial Two (6-20/21)		Trial Three (6-21)	
	Control	Treatment	Control	Treatment	Control	Treatment
H_2S conc. ($\mu g*m^{-3}$)	161	8.9	215	3.1	197	4.8
H_2S flux ($\mu g*m^{-2}*s^{-1}$)	31.7	1.6	40.2	0.6	47.3	1.1
H_2S reduction (%)	95%		99%		98%	
NH_3 conc. ($\mu g*m^{-3}$)	< 2.0	< 2.0	423.5	68.3	1094.3	< 2.0
NH_3 flux ($\mu g*m^{-2}*s^{-1}$)	< 0.4	< 0.4	79.2	12.4	262.6	< 0.5
NH_3 reduction (%)	-0-%		84%		>99%	
Total VOC conc. ($\mu g*m^3$)	990	146	680	137	735	221
Total VOC flux ($\mu g*m^{2}*s^{-1}$)	195.0	26.4	127.2	24.8	176.4	52.4
Total VOC reduction (%)	86%		81%		70%	

The effect of the BioCap™ biocover on the flux rate of total VOC, ammonia, and hydrogen sulfide, during the June 2000 sample collection period is shown in Table 7. The mean abatement efficiency during the three sampling trials for total VOC, ammonia, and hydrogen sulfide was 79%, 61% and, 97%, respectively (Table 7).

Results reported in Tables 2, 5, and 7 show that the BioCap™ biocover is effective in reducing the emission rate of odorous gases from anaerobic/slurry waste management systems. The results also indicate that the gas abatement performance of the BioCap™ biocover is not adversely influenced by seasonal conditions. Overall mean abatement efficiencies for VOC, ammonia and hydrogen sulfide were 85%, 84% and 90%. This meets minimum efficiency guidelines set forth by the Colorado Department of Public Health and Environment on Alternative Covers used in the state of Colorado.

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