REDUCTION OF ORGANIC AND INORGANIC EMISSIONS FROM ANAEROBIC LIVESTOCK WASTE LAGOONS USING THE BIOCAPTM BIOCOVER

James A. Zahn, Ph.D. Livestock Emission Solutions 3733 Branch Way Indianapolis, IN 46268

Phone: (317) 876-1963 Fax: (317) 276-5281 Email: j5zahn@aol.com

and

Alan A. DiSpirito, Ph.D. Department of Microbiology Iowa State University Ames, IA 50011

June 1, 1999

PROBLEM STATEMENT

Anaerobic processing of livestock wastes results in the production of air pollutants including volatile organic compounds, methane, hydrogen sulfide, ammonia, and carbon dioxide. Recent studies have shown that the emission rate of U.S. Environmental Protection Agency priority pollutants are of significant concern(Zahn et al., 1997; Zahn, 1999). A subset of the EPA priority pollutants and non-regulated volatile organic compounds released from stored swine wastes have been shown to strongly contribute to odors associated with concentrated animal feeding operations (Zahn, 1999).

The present regulatory, social, health, and environmental problems associated with animal production emphasize the necessity for the development of emission reduction strategies that are customized to both the economic and engineering design requirements of present day CAFOS. Commercialization of specific emission reduction solutions is needed, since integration of specific emission reduction practices is anticipated to be a future requirement for operation CAFOS in many states (Progressive Farmer, 1998).

SUMMARY

The main objective of this study is to determine the effectiveness of BioCap™, a synthetic, permable biocover, toward reducing the off-site emission of organic and inorganic gases from animal waste storage systems. Specific objectives were:

- To determine the effect of BioCap[™] on emission rate of odorous gases, including hydrogen sulfide, ammonia, and volatile organic compounds, from stored swine wastes.
- 2) To compare the emission rates of odorous gases (hydrogen sulfide, ammonia, volatile organic compounds) from swine waste storage systems using the BioCap™ biocover to an uncovered swine waste storage system.

Emission testing was conducted during the month of May (1999) on four swine waste basins located in south-central Minnesota. The four swine waste basins evaluated in this study were chosen based on similarity of waste management system, production, genetics and nutrition. All tested sites are owned by ValAdCo, Renville, MN. Wind speed, ammonia, hydrogen sulfide, and volatile organic compound emissions were monitored on the downwind edge of the swine waste basins as described in the Material and Methods section, and were converted to flux density using micrometerological methods. In addition to chemical analyses, scentometry and dynamic dilution olfactometry were performed on the control site and on site B, a site which employed the BioCapTM biocover.

Emission rate testing showed that the BioCap™ biocover reduced the combined emission rate of odorous gases (hydrogen sulfide, ammonia, and volatile organic compounds) between 60% and 90%, when compared to the control site (Table 1).

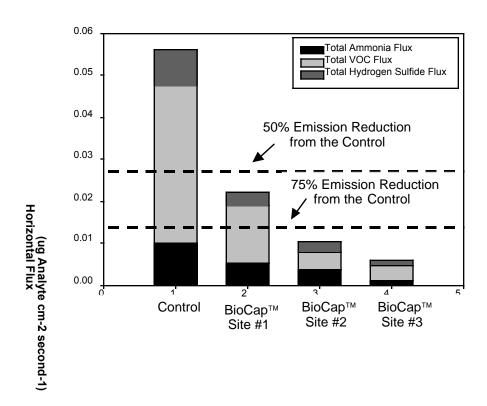
TABLE 1. The effect of BioCap[™] on air pollutant emission rate from swine waste basins in Minnesota. Measured horizontal flux rate for air pollutants collected in air samples from swine waste basins. Values reported represent the average air concentration of air pollutants over a one hour sampling period with sampling variation reported as the standard error of the mean.

	Swine Production Site			
	\mathbf{A}	В	C	D
Parameter	(Control Site 1)\$\phi\$	(BioCap Site 1)	(BioCap Site 2)	(BioCap Site 3)
Wind Speed (m/s)	5.0 ± 0.2	5.8 ± 0.17	3.8 ± 0.13	2.4 ± 0.1
NH ₃ Concentration in	183.3 ± 8.9	82 ± 3.3	86 ± 5.1	41 ± 2.0
Air (μg NH ₃ m ⁻³)				
NH ₃ Horizontal Flux (μg NH ₃ cm ⁻² s ⁻¹)	0.0102	0.0053	0.0036	0.0011
Total Volatile Organic Compound (VOC) Concentration in Air (µg VOC m ⁻³)	670	210	102	134
Total VOC Horizontal Flux (μg VOC cm ⁻² s ⁻¹)	0.0372	0.0135	0.0043	0.0036
H ₂ S Concentration in Air (μg H ₂ S m ⁻³)	155.5 ± 14	51 ± 3.2	58 ± 3.1	40 ± 2.1
H ₂ S Horizontal Flux (μg H ₂ S cm ⁻² s ⁻¹)	0.0087	0.0033	0.0025	0.0011

φ = Sampling location; (A) ValAdCo farm #3; (B) ValAdCo farm #1; (C) ValAdCo NW Finisher; (D) Lippert Finisher Site.

Results reported in this study describe functional characteristics of the BioCap™ biofilter on reducing the emission rate of odorous gases from anaerobic/slurry waste management systems. These results indicate that the biocover is effective in reducing the air pollution potential of outdoor swine waste management systems. In addition to the impacts on reducing the emission rate of odorous gases, odor measurement methods based on direct human evaluation of air samples (sentometry and dynamic dilution olfactometry), and indirectly on VOC concentration (Zahn, 1999), show that the BioCap ™ biocover reduces odor by 72% to 95% when compared to the control site.

The Effect of a BioCap Cover on the Release of Air Pollutants From Swine Waste Basins



RATIONALE

Outdoor basins and manure storage tanks provide conditions of high manure loading rates and low surface area. Under conditions of high loading rates it is often more efficient to treat emissions in an aerobic process that is decoupled from the highly anaerobic waste storage system. Biofiltraton, is an aerobic process where emissions from the storage system pass through a porous filter material inhabited by aerobic bacteria which utilize odorant and other chemicals present in the emission stream as carbon, nitrogen, sulfur, and energy sources. Because this treatment method is decoupled from the anaerobic waste, the nutrient value of the manure is not changed and at the same time, air quality of emissions is improved by removal of odors and other chemical compounds. Biofiltration stratigies are currently in use in industrial and commercial settings to control hydrogen sulfide and hydrocarbon emissions. Several groups of aerobic and microaerophilic prokaryotic microorganisms are known to catalyze the degradation of organic and inorganic air pollutants that pass through the biofilter (Leson and Winer, 1991). For experimental systems, optimum performance and loading parameters for biofilters have been correlated to growth and metabolic activity of microorganisms inhabiting the biofilter (Yang and Allen, 1994). Additionally, the supply of oxygen, the waste gas flux rate, and the availability of other nutrients required for growth are also limiting factors in the

reduction of organic and inorganic air pollutants passing through the filter material. Biofiltration relies on primarily bacteria and fungi, immobilized on the surface of the filter substrate, that utilize organic emissions in the gas streams as carbon, nitrogen, sulfur, and energy sources. The large number of bacteria found to inhabit the filter material include genera of the chemolithotrophic bacteria including ammonia-oxidizing bacteria (*Nitrosomonas*), hydrogen sulfide-oxidizing bacteria (*Thiobacillus*), genera of heterotrophic bacteria including methane oxidizing bacteria (*Methylomonas*), cresol-degrading bacteria (*Pseudomonas*), and other hetrotrophic bacteria using carbon compounds as energy sources. In the aerobic environment provided by the filter material, inorganic and organic emissions, including the malodorous swine waste emissions, may be oxidized to provide cellular energy, assimilated into cellular material, or co-metabolized in reactions providing no energy or nutrient value to the organism.

The use of floating, porous covers on basin and tank waste storage systems is a successful modification to the idea of biofiltration. The idea for placing floating, porous material on top of manure storage systems to reduce odor is based on an observation that dairy manure storages with floating scum layers had less odor than with a free water surface (Miner, 1995). Floating, porous covers represent an attractive treatment strategy for swine waste emissions, since the processes of anaerobic decomposition that occur in the stored waste and the aerobic treatment of the gaseous pollutants evolved from the anaerobic treatment are decoupled in two separate processes. Because these processes are decoupled, odor reduction is not dependent on reducing the nutrient value of the manure; as is the case with digestive or biological system additives.

MATERIALS AND METHODS

Proprietary Monitoring System The Zahn Test is a proprietary system to objectively quantify Ammonia (NH3), Hydrogen Sulfide (H2S), and Volatile Organic Compounds (VOC) using established analytical methods. Zahn et al., (1997) "Characterization of Volatile Organic Emissions and Wastes from a Swine Production Facility" [J. of Environ. Qual., 26:1687-1696] describes a US EPA-approved sampling protocol for collection and identification of VOC concentration from the air using gas chromatography (GC) mass spectrometry or GC using flame ionization detection. Tube desorption techniques essential to this method are further summarized in US Patent No. 5,766,551 "Device for quantitation of odors from liquid livestock wastes". Another unpublished report by Zahn describes the relationship between odor magnitude and total concentration of VOC collected in air. This report has been submitted for publication in the Journal of Environmental Quality.

Micrometerological Data Wind speed and direction, temperature and general conditions will be recorded during the testing period. A hand-held weather station will be used for taking these measurements.

General Sampling Protocol All samples will be taken at the shoreline (0 feet) of the primary (most odorous) cell at a height of approximately 70 cm above the slurry surface. Monitoring equipment for each of the three analytes will be operated concurrently to produce good comparative results. Continual monitoring of wind direction will determine the monitoring point. Monitoring will be conducted at the downwind side of the lagoon near the middle of the emission plume. If the wind shifts more than 30 degrees during this time, sampling will be

suspended and then moved into the middle of the odor plume correlating to the new wind direction. Sampling will then commence for the time period discussed below.

Hydrogen Sulfide Measurement Hydrogen Sulfide will be measured using a calibrated and approved model 631-X Jerome Gas Analyzer.

Duplex Measurements will be taken every two minutes for a total 64 in one hour. The Minnesota state approved method for H_2S measurement calls for 2 duplex measurements every two minutes (32 total) for one half hour. This method was simply doubled for this project.

Measurements will be recorded in parts per billion (ppb) and will be averaged over the total test period.

Ammonia Measurement Ammonia will be collected from air using three glass impingers (40 ml internal volume each) arranged in series. The last impinger in the series will be used as a trap to protect the pump from liquid contamination.

Air samples will be drawn by vacuum through submerged fritted glass diffusion tubes into 26 ml of 0.4M boric acid using a GilAir personal sampling pump operated at 2.0 L min⁻¹. The GilAir pump is calibrated with a digital flowmeter.

The sampling period will proceed for one hour and the boric acid will be replaced prior to the next sample.

Ammonium concentration will be determined using the HACH Company Portable Colorimeter System. The Nessler Ammonia method (adapted from Standard Methods for the Examination of Water and Wastewater) will be used. The HACH Method Number is 8038. This test is USEPA approved for reporting.

Volatile Organic Compounds Measurement Volatile organic compounds (VOC) will be captured on a multibed adsorbent tube containing a combination of Tenax TA and Carboxen-569 (Supelco, Bellafonte, PA), according to the low-volume sampling method developed by Zahn et al (1997).

Glass fritted tubes (0.6 x 11.5 cm OD) are packed and then thermally-conditioned for one hour at 230°C using a Dynatherm six tube conditioner (Supelco, Bellafonte, PA). Nitrogen flow is maintained at 20 ml min⁻¹ for individual tubes during thermal conditioning.

For air sampling of VOC, flow rate through individual thermal desorption tubes is regulated at 0.65 L min⁻¹ for one hour using a model 1063 sequential sampler that has been calibrated using a digital flowmeter.

After sampling, tubes will be removed from the sampling unit, sealed in Teflon storage tubes, and transported to the gas chromatograph location on ice. (If stored at -20° C, tubes not analyzed immediately may be stored up to two months with little or no decomposition of analytes.)

Chemical analysis of trapped analytes on the thermal desorption tubes was performed using a Dynatherm model 890 thermal desorber coupled to a Hewlett-Packard model 5890 gas chromatograph equipped with an FID by Dr. Alan DiSpirito at Iowa State University.

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)

VOC concentration is reported as a cumulative number.

Flux Rate Measurements of Air Pollutants from Swine Waste Management Systems

Meteorological techniques employing the Theoretical -Profile-Shape method for determining evaporative fluxes (Majewski, 1990) were used to evaluate VOC, H_2S , and NH_3 emissions at four sites. Measurements were based on the individual and total concentration of airborne analytes present at a measurement height (z) and meteorological data collected on weather stations positioned at the point of air sample collection. Measurement height (z) was associated with system surface area and was calculated through trajectory-simulation models (Wilson et al., 1982). When possible, additional air samples were collected upwind from the waste storage system to document background air concentrations of analytes evaluated in this study and to confirm the source of these emissions.

REFERENCES CITED AND BIBLIOGRAPHY

- Alarez-Cohen, L. 1993. Application of methanotrophic oxidations for the bioremediation of chlorinated organics. p 337 350. *In*. Microbial Growth on C₁ Compounds. J.C. Murrell and D.P. Kelly. eds. Intercept Ltd., Hampshire, NY.
- Amann, R.I., B.J. Binder, R.J. Olson, S.W. Chisholm, R. Devereux, D.A. Stahl. 1990. Combination of 16S rRNA-targeted oligonucleotide probes with flow cytometry for analyzing mixed microbial populations. Appl. Environ. Microbiol. **56:** 1919 1925.
- Brune, D.C. 1989. Sulfur oxidation by phototrophic bacteria. Biochim. Biophys. Acta **975**: 189 221.
- Caumett, P. 1986. Phototrophic sulfur bacteria and sulfate-reducing bacteria causing red waters in shallow brackish coastal lagoon (Prévost lagoon, France). FEMS Microbiol. Ecol. **38:** 113 124.
- Cotter, PA, S. Darie and R.P. Gunsalus. 1995. The effect of iron limitation on expression of aerobic and anaerobic electron transport pathway genes in *Escherichia coli*. 1992. FEMS Microbiol. Lett. **100**: 227 232.
- DeLong, R.F. 1992. Archaea in coastal marine environments. Proc. Natl. Acad. Sci. USA. **89:** 5685 5689.
- Devereux, R., M.D. Kane, J. Winfrey, and D.A. Stahl. 1992. Genus- and group-specific hybridization probes for determinative and environmental studies of sulfate-reducing bacteria. System. Appl. Microbiol. **15:** 601 609.

- Gibson, J. and C.S. Harwook. 1995. Degradation of aromatic compounds by nonsulfur purple bacteria. *In.* R.E. Blankenship, M.T. Madigan and C.E. Bauer (eds.): Anoxygenic Photosynthetic Bacteria, pp.991 1003. Kluwer Academic Pub., Boston, MA.
- Goldstein, R.M., L.M. Mallory, and M. Alexander. 1985. Reasons for possible failure of inoculation to enhance biodegradation. Appl. Environ. Microbiol. **50:** 977 983.
- Halverson, L., A.A. DiSpirito, D. Bazylinski, J.L. Hatfield and J.A. Zahn. Development of a Development of a diagnostic tool to indicate potential odor emission from anaerobic waste sotrate stystems. proposal currently under review by Iowa Soybean Promotion Board, Iowa Corn Board and Iowa Pork Producers Association.
- Hill, D.T. and R.D. Holmberg. 1988. Long chain volatile fatty acid relationships in anaerobic digestion of swine waste. Biol. Wastes 23: 195 214.
- Imhoff, F.J., 1995. Taxomony and physiology of phototrophic purple bacteria and green sulfur bacteria. *In.* R.E. Blankenship, M.T. Madigan and C.E. Bauer (eds.): Anoxygenic Photosynthetic Bacteria, pp. 1 15. Kluwer Academic Pub., Boston, MA.
- Kobayashi, M. and M. Kobayashi. 1995. Waste remediation and treatment using anoxygenic phototrophic bacteria. *In.* R.E. Blankenship, M.T. Madigan and C.E. Bauer (eds.): Anoxygenic Photosynthetic Bacteria, pp. 1269 1282. Kluwer Academic Pub., Boston, MA.
- Lindley. J.A. 1982. Processing manure for feed components. *In.* Manure digestion, runoff, refeeding, odors. North Central Regional Research Publication No. 2284.
- Majewski, M.S. 1990. Field methods comparisons for estimating evaporative flux densities of pesticides from fallow soil. Order number 9110651. UMI Dissertation Services. Ann Arbor, MI.
- Miner, J.R. 1982. Controlling odors from livestock production facilities. Agricultural Experimental Station North Central Regional Research Publication No. **284:** 30 35.
- Moré, M., J.B. Herrick, M.C. Silva, W.C. Ghiorse, and E.L. Madsen. 1994. Quantitative cell lysis of indigenous microorganisms and rapid extraction of microbial DNA from sediment. Appl. Environ. Microbiol. **60:** 1572 1580.
- Morris, J.G. 1986. Anaerobiosis and energy-yielding metabolism. *In.* Anaerobic Bacteria in Habitats Other than Man. E.M. Barnes and G.C. Mead eds. p. 1 21. Blackwell Scientific Publications.
- Oelze, J. 1985. Analysis of Bacteriochlorophylls. Meth. Microbiol. 18: 257 274.
- Olsen, G.J., D.J. Lane, S.J. Giovannon, N.R. Pace, and D.A. Stahl. 1986. Microbial ecology and evolution: a ribosomal RNA approach. Ann. Rev. Microbiol. **40:** 337 365.
- Pace, N.R., D.A. Stahl, D.J. Lane and G.J. Olsen. 1986. The analysis of natural microbial populations by ribosomal RNA Sequences. Adv. Microbial Ecol. 9: 1 55.
- Phillips, J.A. and T.D. Brock. 1991. Laboratory Manual for Biology of Microorganisms, 6th ed. Prentice-Hall, Englewood Cliffs, NJ.
- Pradasam, T.B.S., and N.C. Dondero. 1967. Aerobic heterotrophic bacterial populations of sewage and activated sludge. Appl. Microbiol. **15:** 461 467.
- Raskin, L., L.K. Poulsen, D.R. Noguera, B.E. Rittmann, and D.A. Stahl. 1994. Quantification of methanogenic groups in anaerobic biological reactors by oligonucleotide probe hybridization. Appl. Environ. Microbiol. **60:** 1241 1248.
- Ritter, W.F. 1989. Odour control in livestock wastes: state-of-the-art in north America. J .Agric. Engng. Res. **42:** 51 62.

- Schaefer, J. 1977. Sampling, characterization and analysis of maloddours. Agric. Environ. **3:** 121 128
- Spoelstra, S.F. 1977. Simple phenols and indoles in anaerobically stored piggery wastes. J. Sci. Food Agric. **28:** 415 423.
- Spoelstra, S.F. 1980. Origin of objectionable odorous components in piggery wastes and the possibility of applying indicator components for studying odour development. Agric. Environ. **5:** 241 260.
- Stahl, D.A., B. Flesher, H.R. Mansfield, and L. Montgonery. 1988. Use of phylogenetically based hybridization probes for studies of rumminal microbial ecology. Appl. Environ. Microbiol. **54:** 1079 1084.
- Stahl, D.A. and R. Amann. 1991. Development and application of nucleic acid probes. pp. 205 248. *In.* Nucleic Acid Techniques in Bacterial Systematics (E. Stackebrandt and M. Goodfellow, ed.). John Wiley & Sons, NY.
- Thauer, R.K. 1989. Energy metabolism of sulfate-reducing bacteria pp. 397 414. In. Autotrophic Bacteria. H.G. Schlegel and B. Bowien. eds. Springer-Verlag, New York.
- Tinall, J. and W.D. Grant. 1986. The anoxygenic phototrophic bacteria. pp. 101 156. *In*. Anaerobic bacteria in habitats other than man. E.M. B arnes and G.C. Mead (eds.). Blackwell Scientific Publications, Boston.
- van Gemerden, H., and H.H. Beeftink. 1983. Ecology of phototrophic bacteria. *In* Studies in Microbioloy Vol. 4, The Phototrophic Bacteria: Anaerobic Life in the Light. (J.G. Ormerod, ed.) pp146 185. University of California Press, Los Angeles
- Wagner, M., R. Amann, H. Lemmer, and K.-H. Schleifer. 1993. Probing activated sludge with oligonucleotides specific for proteobacteria: Inadequacy of culture-dependent methods for describing microbial community structure. Appl. Environ. Microbiol. **59:** 1520 1525
- Williams, A.G. 1984. Indicators of piggery slurry odor offensiveness. Agric. Wastes 10: 15 36.
- Williams, A.G. and M.R. Evans. 1981. Storage of piggery slurry. Argic. Wastes 3: 311 322.
- Zahn, J.A. 1999. Air pollution from swine production facilites differing in waste management practice. J. Environ. Qual. *submitted*.
- Zahn, J.A. J.L. Hatfield, Y.S. Do, A.A. DiSpirito, D.A. Laird, and R.L. Pfeiffer. 1997. Characterization of Volatile Organic Emissions and Wastes from a Swine Production Facility. J. Environ. Qual. 26:1687-1696.
- Zahn, J.A. 1997. Swine odor and emissions from pork production. *in* National pork producers council environmental assurance program. Ed. K. McGuire. 122 pages. National pork producers council. Des Moines, IA.