Test of Odour Control System using Ozone on a Commercial Scale Mushroom Farm
AAC Project 8519-1

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ABSTRACT

An ozone generating system was installed at a commercial mushroom farm in Ontario in order to control the emission of odorous compounds during the Phase I preparation of mushroom substrate. This ozone system was custom designed and adapted to operate in conjunction with an existing forced aeration Phase I bunker facility. A ventilation system with manifold and ductwork was installed to direct the compost gases containing odour compounds into a reaction unit consisting of two mixing tanks connected in series. Ozone is produced by applying a corona discharge to oxygen concentrated from air and drawn into the reaction unit using a variable frequency fan, and mixed with the substrate gases. This system provides for an odour control system with facile operation and minimal maintenance. Chemical analysis was performed on samples of substrate gases collected in Tedlar bags taken before and after contact with the ozone. Reductions in odorous sulfur compounds of the gases in the range of 20-60% were obtained with the ozonation. Large variations in the sulfur compound content of both the pre- and posttreatment samples were observed, resulting in the observed range of reduction. The extent of the reduction appears to be dependent upon the operating conditions of the aerated bunker such as operation of the aeration fan, which generally results in increased input of odour compounds. Increasing the amount of ozone introduced into the system appears to increase the efficacy of the system for reducing sulfur compound levels.

INTRODUCTION

Commercial white mushrooms *(Agaricus bisporus)* are commonly cultivated on a substrate prepared from composting a mixture of materials, which typically includes hay or wheat straw, horse manure, poultry litter and gypsum. The initial preparation of mushroom substrate is traditionally undertaken outdoors in a process known as Phase I composting. In the Phase I process, the ingredients are mixed together, and watered with recycled water in a process known as the pre-wet stage, which normally lasts for 5 to 7 days. At the end of the pre-wet stage in traditional Phase I composting, the pre-wet material is formed into windrows that are watered at regular intervals to maintain adequate moisture in the compost, and turned to mix and aerate the compost. Alternatively, Phase I composting can be undertaken using forced aeration, whereby the pre-wet material is loaded into bunkers or tunnels in which the compost is aerated by blowing air through it using a system of nozzles or jets. The Phase I composting process, including the initial material preparation and pre-wet operations, normally lasts for a period of 14 to 21 days. After the initial Phase I preparation, the compost is subjected to a second (Phase II) composting stage that occurs in a controlled environment, where the compost is pasteurized and conditioned prior to use as a substrate for mushroom growth (Rinker, 1993).

Phase I substrate preparation typically occurs under largely uncontrolled conditions, and as a result may undergo considerable variations in temperature and oxygen content, thereby creating anaerobic conditions in the compost . As a consequence, offensive odours may be produced during the Phase I process (Miller *et al.,* 1988). Composting odours are increasingly becoming a problem for mushroom farms as well as for other outdoor composting operations. This is due largely to a combination of residential encroachment into rural areas, and the heightened sensitivity of the general population to environmental issues (Vaserstein and Kelsey, 2000). **In** certain cases, problems related to composting odours have resulted in the passage of restrictive legislation or legal litigation (Anonymous, 1999).

Studies of Phase I mushroom substrate odours have shown that the composting odours may contain several types of malodorous chemicals. Included among these are reduced organic sulfur compounds (mercaptans and sulfides), amines and ammonia, volatile fatty acids, and compounds with less offensive odours such as alcohols and ketones (Miller *et al.,* 1988; Derikx *et al.,* 1990; Duns *et al.,* 1997; Noble *et al.,* 2001). The reduced sulfur compounds are considered to be the most problematic of the above, due to their characteristically offensive odors combined with their low odour thresholds, although several compounds or classes of compounds may combine to produce offensive odours (Miller *et al.,* 1988).

The possible adverse affects on the mushroom industry, as well as to the environment, by offensive odours produced during mushroom substrate preparation, has necessitated a search for solutions to the composting odours problem. Several odour reduction measures have accordingly been investigated. These methods include simply altering the choice and/or quantity of raw materials that are suspect sources of odour, such as reducing the

amount poultry manure (Miller and Macauley, 1989; Pecchia *et al.,* 2001) or gypsum (Beyer *et al.,* 2002) as possible sources of odorous reduced sulfur compounds. These alterations of formulation have met with varying degrees of success in reducing odour emissions, but the possible detrimental effects of such alterations on compost quality and mushroom yield are always a concern to the grower. Semi-permeable coverings of compost piles, which purportedly retain odour compounds while allowing the release of ammonia and respiratory gases, have been investigated as a means for reducing odours (Beyer *et al.,* 1997). The feasibility of biofilters for removing malodorous compounds from mushroom compost emissions has been demonstrated (Op den Camp *et al.,* 1995). However, methods such as pile coverings and biofilters may require periodic maintenance and adjustment, thereby becoming an investment of time and expense on behalf of the mushroom farm.

The use of forced aeration technology to aerate the compost in tunnels or "bunkers" has become the most popular method for reducing mushroom substrate odour emissions. The compost in the bunkers or tunnels is periodically aerated by the forced passage of air through the compost from slatted floors or nozzles or spigots located on the floor of the bunker (Miller et al., 1990; Noble and Gaze, 1994). Several studies have indicated that forced aeration may have varying degrees of effectiveness in reducing mushroom substrate odour emissions (Noble *et al.,* 2001, Perrin and Macauley, 1995; Duns *et al.,* 2003). Reductions in the emission of odorous compounds in the range of 75-90% have been reported, although other studies have actually indicated an increase in the levels of odorous compounds in mushroom substrate treated by forced aeration (Op den Camp *et al.,* 1995). Thus, additional and/or alternative and practical techniques for reducing odour emissions from mushroom substrate preparation are required.

Ozonation is one such alternate method for odour control. The principal of treatment of odours by ozonation involves the addition of ozone (0_3) diluted in air to the system containing odour compounds. Ozone is a powerful oxidant and a very reactive and unstable chemical. Ozone treats odours by oxidizing odour compounds to form chemicals with less offensive odours or possibly no odour at all. In theory, at long contact or mixing times between ozone and odour compounds and with sufficiently high ozone dosage levels, the ultimate products of the ozonation of hydrocarbons are carbon dioxide and water, but in most cases the ozonation products are less odorous oxygenated chemicals (Nebel and Gottschling, 1975). For example, the reaction between dimethyl sulfide, a known component of mushroom compost odour (Duns *et al.,* 1997; Noble *et al.,* 2001) and municipal composts (Day *et al.,* 1998) results in the formation of inoffensive-smelling dimethyl sulfoxide and oxygen:

$$CH_3\text{-}S\text{-}\ CH_3 + 0_3\ a\text{--}\ CH_3\ \text{-}SO\text{-}\ CH_3 + 02$$

The use of ozone for the successful treatment of odours from various sources has been documented for some time. Ozonation odour treatment has been applied to many industries or processes, including rendering plants, fish processing plants, sewage treatment plants (Unangst and Nebel, 1971), rubber compounding plants and paint spraying facilities, as well as numerous other applications (Nebel and Gottschling, 1975).

Ozonation has also recently been applied to the treatment of odours from agricultural sources, such as swine production (Van Sickle, 1999; Kim-Yang *et al.,* 2002).

Despite the use of ozone to treat offensive odours in many areas, the method has yet to be adapted by mushroom growers. Preliminary studies have indicated that ozone has potential in treating odours from mushroom substrate. Nebel and Gottschling (1975) reported an early attempt to treat odours from mushroom substrate preparation, while Finney (1999) reported the successful removal of odours from traditional windrow mushroom composts from a mushroom farm in British Columbia as determined by an odour panel, using a temporary treatment facility. Ozonation also has an advantage as a method of odour treatment in that ozone can be generated on site from ambient air and thus requires only the initial investment of ozone generation equipment and a ventilation system to collect gases for treatment. Further research into the feasibility of ozone for reducing odours produced during the preparation of mushroom substrate is accordingly required to determine if ozonation can be used as an alternative or supplementary method of odour control.

The objectives of this research project were to install and test the efficacy and practicality of ozone treatment as a viable means of reducing odours from mushroom substrate preparation on a commercial mushroom farm. This is essentially a pilot project undertaken on a commercial scale. An ozone odour treatment system was designed, and installed on an existing aerated bunker Phase I facility at a mushroom farm in Ontario. A ventilation system was constructed on the bunker facility to collect and contain mushroom substrate gases produced by the composting process for treatment by ozone. The ozone is generated on site by applying a corona (electrical) discharge to oxygen concentrated from ambient air, and injected into the ventilation system together with the compost gases, where they are combined to react in a series of mixing chambers. Samples of gases were taken before and after contact with the ozone and tested for specific odorous compounds in order to test the efficacy of the system by determining if levels of the odour compounds were reduced as a result of the ozone treatment. The ozonation system was investigated by testing samples for odour compounds under varying operational conditions of the system including during the operation and cessation of the aeration fan, changing the frequency of the exhaust fan, and increasing the amount of ozone entering the system.

MATERIALS AND METHODS

Mushroom Substrate Preparation

A mushroom farm in southern Ontario (Greenwood Mushroom Farm, Ashburn, ON) was selected as the site at which to perform this study. This mushroom farm prepared substrate using an aerated bunker Phase I process and the Phase I bunker facility at this

farm was determined to be readily suitable for the installation of an ozonation odour control system. The mushroom substrate at this farm consisted of the following components and approximate composition, on a percent dry weight basis: wheat straw (32%), hay (21%), poultry manure (17%), horse manure (13%), ground corncob (12%), gypsum (4%), and commercial nitrogen supplement (1%). The substrate was prepared by firstly laying out the bales of straw or hay and covering them with the remaining substrate components. The bales were then watered with recycled water, and left for a day. On the following day, the bales were broken and watered with recycled water using a pre-wet machine, and formed into long heaps. The pre-wet period lasted for approximately 5 days, during which the pre-wet piles were turned and watered 5 times. The pre-wet material was loaded into a bunker to initiate the aerated Phase I process.

The forced aeration of the mushroom substrate was undertaken in a facility containing three separate bunkers enclosed on 3 sides by concrete walls and covered by a roof, with open front ends that can be covered after filling. Each bunker was equipped with floor-based microprocessor-controlled nozzle aeration that permitted the aeration to operate at timed intervals. The compost was transferred to a different bunker every 3 days, and held in the bunkers for a total of 9 days, after which the compost was filled into the Phase II tunnels. The Phase I bunker schedule is given in Table 1. The pre-wet material is first placed in Bunker 3 to initiate the aerated Phase I process. In order to keep the production of compost continuous, two batches of compost were in preparation at a given time at the mushroom farm. One batch was at the beginning stages of preparation, while the other batch was near the end of the Phase I stage. These two batches of compost are present in different bunkers simultaneously on Tuesday and Wednesday as shown in Table 1.

The bunker aeration fan was turned on for approximately 2 minutes and switched off for 5 minutes during the aeration cycle for the first day the compost was placed in the bunker. For the remaining time the compost was in the bunker, the aeration fan was turned on for 1 minute and switched off for 6 minutes.

Ozonation Odour Control System

A commercial scale ozone generating odour control system was custom designed and provided by Mainstream Water Solutions Inc. (Regina, SK). This system was designed to operate in conjunction with the aeration bunker facility by adapting the bunker system to allow for collection of the substrate gases and operate with the ozone generating system. Each of the three bunkers was equipped with an odour control system. The ozone generating system consists of a single oxygen concentrator and three ozone-generating units, one for each bunker. In the oxygen concentrator, oxygen is concentrated from ambient air to provide sufficient oxygen for an adequate supply of ozone. The oxygen emitted from the concentrator at a constant flow rate (22 L/min) and could be split three ways for introduction into the ozone generator for each bunker, in which ozone is generated by corona discharge through application of a high voltage to the oxygen. The ozone is generated at constant concentration (2% ozone in oxygen).

A ventilation system was installed external to each bunker to permit collection and treatment of the odorous compounds in the mushroom substrate gases. A sheet metal manifold and ductwork was constructed around a vent port at the back and near the top of each bunker. A variable frequency (12-60 Hz) exhaust fan of 10,000 cubic feet/min capacity was installed on top of each bunker. The ductwork from the rear of each bunker was constructed to conduct the substrate gases from the bunker to the fan. Ozone from each of the generators was introduced at the top of the ductwork from tubing (1/4") encased in protective cable (Figure 1). The ozone was injected adjacent to the fan in order to be drawn through the fan together with the compost gases, for mixing purposes. Once the gases and ozone were contacted by being drawn through the ventilation system by the fan, they were introduced into a mixing or reaction system located on top of the bunker containment building, consisting of two 2,500 gallon plastic water tanks which served as mixing chambers. The tanks were connected in series by means of 3' diameter metal tubing. A capped exhaust stack was installed on the second tank in order to vent the treated gases to the atmosphere (Figure 2). Each bunker was equipped with a mixing unit.

The ozonation odour control system was designed primarily to treat odorous reduced sulfur compounds and accordingly set to operate with a mixing time of approximately 5 seconds, which was considered an adequate mixing time in order to react the sulfur compounds with ozone (A. Finney, personal communication). The duration of this mixing time includes the time of initial contact of ozone with the compost gas until exit from the final mixing tank. The variable-frequency exhaust fan operates continually, pulling the gases through the mixing unit, with the system operating under negative pressure. When the microprocessor-controlled aeration fan of the bunker is operational, the exhaust fan is set by microprocessor to ramp to high frequency (60 Hz) in order to increase fan speed to handle the anticipated higher volume of gases released from the substrate. After the aeration fan is switched off, the exhaust fan frequency reduces to lower operating frequency or fan speed.

Sampling of Compost Gases for Chemical Analysis

Samples of gases were obtained for analysis before and after contact with the ozone. Bulkheads were installed in the ventilation system in the manifold at the back of the bunker and also in the exhaust stack constructed on the final mixing tank. Valves were installed in these bulkheads (1/2" compact ball valve, PVC threaded) and 1/4" OD threaded nipples fitted to the valves in order to facilitate attachment of tubing for sample collection. These sampling valves for the input (pre-ozone contact) and output (post-ozone contact) are shown in Figures 1 and 3 respectively. The gas samples were collected in Tedlar bags (8.1 L volume, 2 mm PVF, 15" x 15", 2 mm barrier thickness) equipped with nickel-plated brass on/off valves (Chromatographic Specialties, Brockville, ON). The pressure and flow of gases through the odour control system were found to be insufficient to adequately fill the Tedlar bags, thereby necessitating the use of pumps to

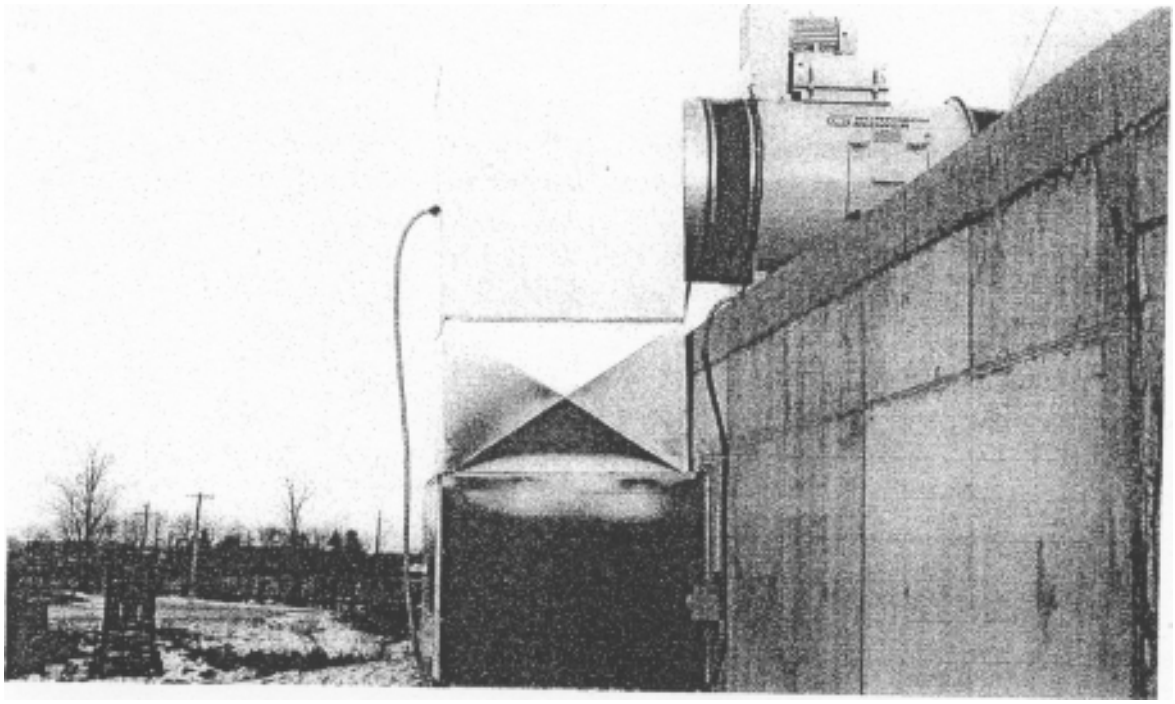

Figure 1. Photograph showing manifold at back of aerated bunker for collecting odorous mushroom substrate gases for treatment by ozonation. The line carrying ozone with connection point to the manifold is evident, and the exhaust fan for mixing gases with ozone is mounted on top of the bunker. The white valve located at the front of the bottom section of the manifold is for sampling input (pre-ozone contact) gas samples for chemical analysis.

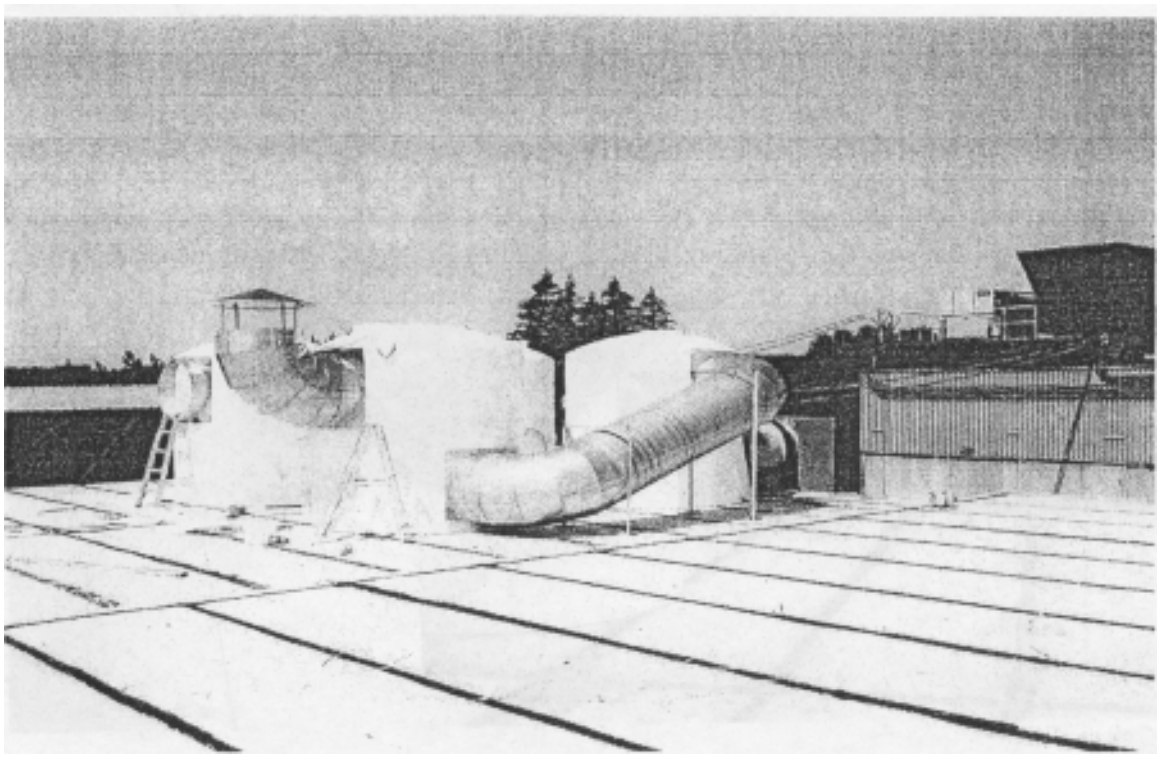

Figure 2. Ozonation odour control system mixing unit consisting of two mixing tanks and connecting tubing, located on roof of aerated bunker Phase I facility. The exhaust stack for emitting treated substrate gases to the atmosphere is shown on the second mixing tank of the nearest unit. The mixing unit for the ozone system for another bunker is still under construction in the background in the photograph.

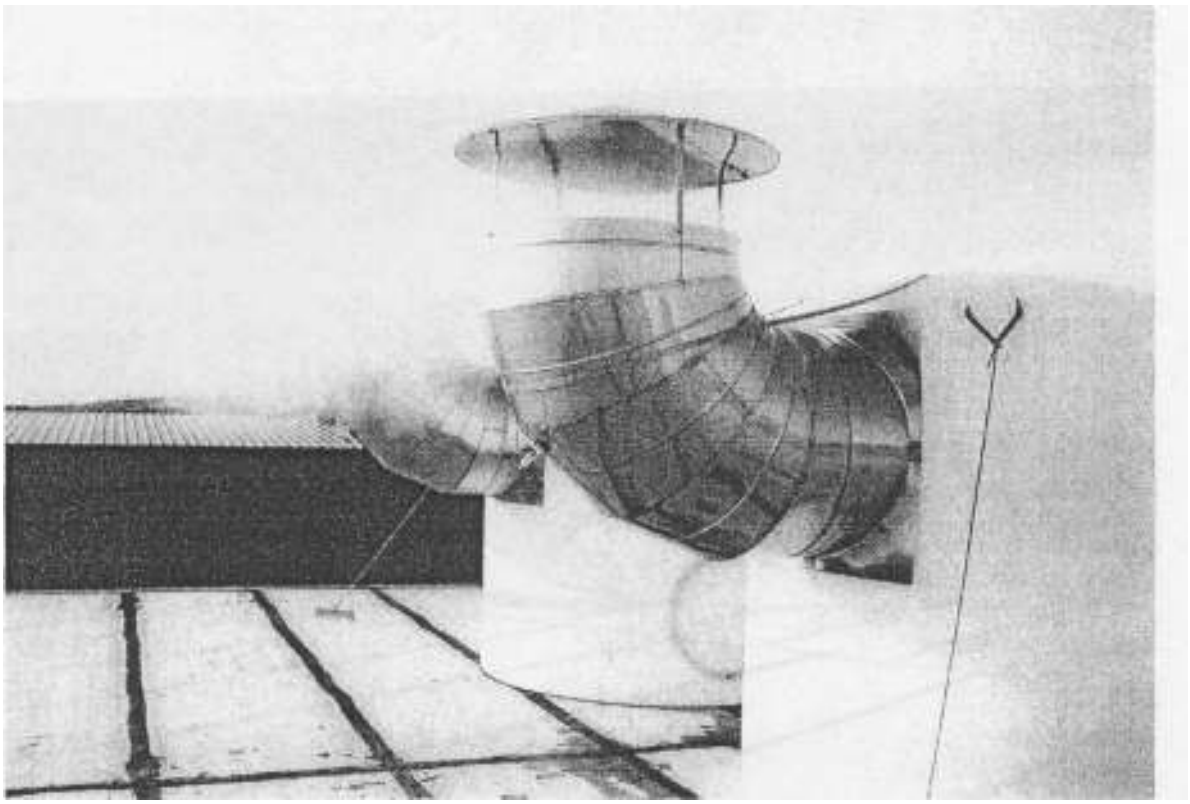

Figure 3. Photograph showing sampling valve for collection of output (post-ozone treated) gas samples on exhaust stacks of second mixing tanks for ozonation systems for two of the three bunkers.

fill the bags. A 70-cm section of 1/4" ID Tygon 83603 tubing was attached to the sampling valves. The other end of the tubing was attached to the inlet port of a portable Gilian HFS-513AUP sampling pump (Sensidyne Inc., Clearwater, FL). A 105-cm piece of 3/16" ID Tygon R3603 tubing was connected to the outlet port of the pump and the other end of this tubing was attached to the valve of the Tedlar bags (Figure 4).

Pre- and post-ozonation substrate gas samples were collected for each bunker several times from September to December 2003. As indicated in Table 1, compost was never contained in all three bunkers simultaneously, requiring bunkers to be sampled on different days. Specific details pertaining to the collection of samples under certain operational conditions of the system are described in the appropriate Results sections. Replicate samples were collected sequentially. Blank air samples were collected at a rural location removed from the mushroom farm site.

Chemical Analysis of Pre- and Post-Ozone Treatment Substrate Gases

Samples of gases collected in the Tedlar bags prior to and after ozone treatment were analyzed for odorous chemical compounds. These included reduced sulfur compounds, which, as mentioned above, are considered to be the major odorous component of mushroom substrate odours, as well as amines and ammonia, which are also odorous components of substrate gases. Analysis was performed using gas detector tubes that are specific for certain compounds or classes of compounds. This method allows for portability and possible on-site measurement of samples and was utilized to compare odours from traditional and forced-aerated Phase I mushroom substrates at various mushroom farms in the U.K. (Noble *et* cd.,2001) and Poland (Szudyga, 2002).

A Gastec GV-100S gas-sampling pump (Gastec Corporation, Kanagawa, Japan) was used to draw gas samples from the Tedlar bags for analysis. A 2-cm piece of Tygon tubing (1/4"-0.6 cm ID) was used to connect the trapping tubes to the barbed on/off fitting of the Tedlar sample bags. The following Gastech detector tubes were used in conjunction with the sampling pump, given as tube identification number with target compound(s), molecular formula and measuring range in parts per million (ppm) or mg/m^3 given in brackets: No.3M (ammonia/NH_3, 10-1000 ppm); No.3La (ammonia/NH_3, 2.5-100 ppm); No.180 (amines/R-NH_2, 5 to 100 ppm); No. 4LL (hydrogen sulfide/ H_2S, 0.25 to 120 ppm); No. 77 (t-butyl mercaptanJ$(CH_3)_3CSH$ + dimethyl sulfide/$(CH_3)_2S$, 1-15 mg/m3); No. 13 (carbon disulfide/CS_2, 0.63 to 100 ppm); No. 70L (mercaptans/R-SH, 0.1 to 8 ppm); No. 70 (mercaptans/R-SH, 0.5 to 120 ppm); No. 71 (methyl mercaptan/ CH3SH, 0.25 to 140 ppm); No. 53 (dimethyl sulfide/$(CH_3)_2S$ + dimethyl disulfide/$(CH_3)_2S_2$, 0.25 to lOppm); No. 18L (ozone/0_3, 0.025 to 3 ppm); No. 18M (ozone/0_3, 0.025 to 3 ppm).

The sampling pump and tubes were utilized as per operational details given in Anonymous (2002), with temperature corrections for readings applied where appropriate. Samples were typically analyzed within 24 hours of collection.

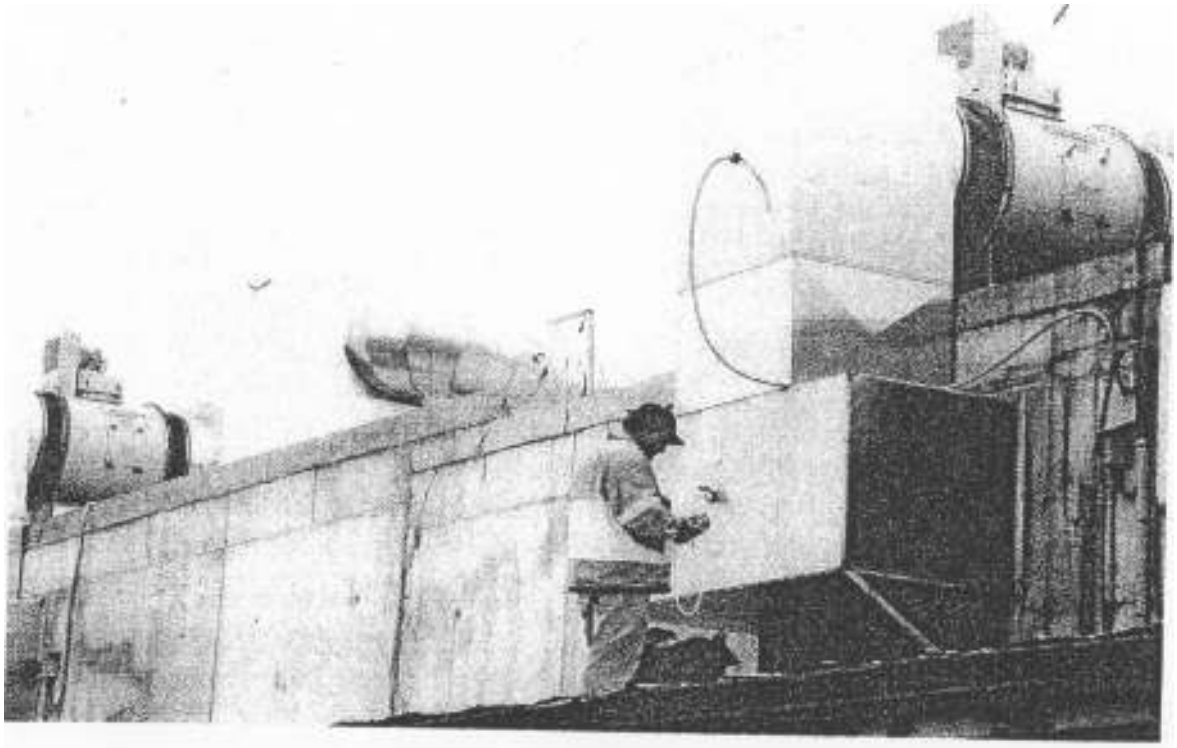

Figure 4, Collection of input gas sample for chemical analysis.

RESULTS AND DISCUSSION

1. Initial (Random) Sampling

It was initially intended that the efficacy of the ozonation odour control system would be evaluated by collecting several input and output samples from each bunker at various times during each site visit. This sampling scheme was essentially random sampling without regard to specific operation details of the bunkers and odour control system. The procedure was repeated so that each bunker could be sampled over several days. Samples were routinely analyzed for ammonia, amines, hydrogen sulfide, mercaptans, and dimethyl sulfide/dimethyl disulfide. Carbon disulfide (CS_2) could not be detected in any of the samples. Previous studies indicated the presence of CS_2 at very low levels in mushroom substrate odours (Op den Camp *et al.,* 1991; Duns *et al.,* 1997) but no CS_2 was detected in a variety of substrate odour samples in a study by Noble and co-workers (2001). Methyl mercaptan appeared to be the predominant mercaptan compound present when mercaptans were detected in the gas samples.

Results from the initial sampling study for all three bunkers are given in Tables 2-4. In these tables are the results for the input (pre-ozone contact) and output (post-ozone contact) samples for ammonia (NH_3), amines ($R\text{-}NH_2$), mercaptans (R-SH), dimethyl sulfide $(CH_3)_2S$/dimethyl disulfide ($(CH_3)_2S_2$) (determined simultaneously), and total reduced sulfur compound concentration (total S), the sum of concentrations of all detected reduced sulfur compounds. Mean values of all compounds for the input (IP) and output (OP) samples in parts per million (ppm) for each sampling day are presented for each bunker. Overall mean values and standard deviations for ammonia, amines and total S for all sampling days combined are also given for each bunker. These tables appear after the main body of the report. Results are given for Bunker 3 first as this bunker is the first one utilized in the aeration process.

When examining the data in Tables 2-4, it is firstly evident that the levels of the odour compounds can vary considerably among input samples or among output samples during each sampling day for each bunker. For example, from Table 2 for Bunker 3, three input samples had total sulfur values ranging from 1.3 to 9.9 ppm. Secondly, odour compound levels also fluctuated overall from one sampling day to the next. Similar fluctuations also observed in total sulfur concentrations and odour panel data in a detailed study comparing odour emissions from aerated and conventional windrow Phase I substrates (Duns *et al.,* 2003). In considering total sulfur compound values, which the system was designed to treat, the overall means comparing input and output sample values for Bunker 3 showed an overall reduction in total sulfur from 3.7 ppm to 3.3 ppm, a slight reduction of approximately 11%. However, when comparing input and output values on a daily basis, some total sulfur reductions are evident for Bunker 3. The September 16 values show a slight reduction of 9% in total sulfur, which is not significant as it is within experimental error limits. A substantial reduction of 61% was achieved for September 30, while a reduction of 26% was obtained for Oct. 22. The overall input and output means are the same within error for both Bunkers 1 and 2. For Bunker 1, a modest total sulfur non-significant reduction of 8% was observed on September 23, while a reduction

of 39% was obtained on October 21. No daily reductions in total sulfur were observed for Bunker 2, which may be due to the fact that gas samples from Bunker 2 were collected on the day that this bunker was being filled. A subsequent study of input total sulfur levels for samples from Bunker 2 taken at intervals throughout a single day showed that levels increased from 0.7 to 4.1 ppm, as both time and the amount of compost in the bunker increased, demonstrating the possible variance of input samples.

From the data in Tables 2-4, average total sulfur concentrations generally decrease from Bunker 3 to Bunker 1, or decrease with increasing age of the compost and exposure to aeration. Bunker 3 contains the youngest material which, when sampled, had been in the bunker only for a period of 24 hours from the pre-wet preparation stage. The pre-wet stage, to which the blended materials have been exposed to thorough watering with recycled water, is known to be significant in the production of odorous compounds (Duns *et al.,* 1998). Thus, the emission of relatively high levels of odours in Bunker 3 may be anticipated to occur. Under certain conditions, an increase in ozone concentration or mixing time may further help reduce levels of odour compounds (Nebel and Gottschling, 1975).

Thus, when employing a random sampling scheme, reductions in total sulfur may be achieved on a daily basis, and more daily reductions are apparent with Bunker 3 than with the other bunkers. However, overall, the results are variable. The observed variations are generally greater than any significance in odour reduction obtained by the ozonation process. These variations are likely partially attributable to the composting process producing fluctuating levels of odour compounds and not to the ozonation process, similar to the observations made comparing odour emissions from aerated bunker and traditional Phase I substrates (Duns *et al.,* 2003). However, the sampling process itself may also contribute to the variability of the results, with the collection of samples at random times throughout the day, while not sampling with respect to consideration of the operational details of the compost aeration or ozonation systems. These details are taken into account in the next section of this report.

2. **Systematic sampling-correlation with aeration and ozonation parameters**

In order to investigate the apparent randomness and fluctuations observed in the results from the initial sampling study, a more systematic approach to sampling was undertaken. This approach involved the collection of samples under controlled operating conditions of the aerated bunker and ozonation odour control system, as opposed to random sampling as in the previous section. As described previously, the aerated bunker system does not operate in a constant manner, with the aeration fan and blower system turning on intermittently. While ozone is injected continuously into the ventilation system, the exhaust fan that draws the odours and ozone into the mixing system increases in frequency and therefore fan speed increases accordingly when the bunker aeration fan is turned on. During these changing conditions, the properties of the input and output odorous gases may also change. An experiment was accordingly designed to collect input and output samples in the presence and absence of the aeration fan, and at various frequencies of the exhaust fan. Changing the frequency of this fan may serve to partially

alter the mixing time of the ozone and odours. Four different sets of conditions were investigated in this experiment:

(1) aeration fan off, exhaust fan low speed (12 Hz)
(2) aeration fan off, exhaust fan high speed (60 Hz)
(3) aeration fan on, exhaust fan high speed
(4) aeration fan on, exhaust fan low speed

Input and output samples were collected sequentially, in duplicate, for each of the four sets of conditions. Collection of input samples when the aeration fan was operational was facilitated by the fact that the aeration fan was audible. However, the output sample collection area was physically removed from the aeration fan unit, so that operation of the aeration fan was not always audible. This necessitated the use of a timer to collect the output samples by predicting when the aeration would be turned on according to the programmed fan duration.

This study was initially conducted on Bunker 3, for which the input samples typically exhibited relatively high levels of reduced sulfur compounds. Results of this set of experiments, in terms of total sulfur concentrations and percentage reduction in total sulfur between input and output samples for each set of samples, are summarized in Table 5.

From Table 5, it is apparent that percentage reductions in total sulfur between input and output samples were observed for all four sets of samples. These reductions are greatest when the aeration fan is off, and approached 50% for set (2), with the aeration fan off and the exhaust fan operating on high frequency. It is also noted that the input total sulfur levels with the aeration fan on, are approximately four times greater than those with the fan off, illustrating that the aeration fan in the bunker serves to expel a greater volume of odorous gases from the compost than that occurring naturally when the aeration is off The reduction in total sulfur is, on average, less when the aeration fan is on than when it is off, suggesting that the ozonation odour control system is less able to treat the higher levels of sulfur compounds observed under these conditions. This may be due to the fact that higher levels of other compounds in the gases will also be introduced into the system that could react with the ozone. In the normal operation of the bunkers, aeration occurs only for approximately 20% of the total time of the pre-set aeration cycle, so that for 80% of the time, the conditions leading to higher reduction of sulfur compounds exist in the system.

The frequency of the exhaust or mixing fan appears to have only a small effect on the reduction of sulfur compounds when the aeration is on. There is a greater effect observed with the aeration fan off, with reduction increasing from 33 to 48% at exhaust fan frequencies of 12 and 60 Hz respectively. In this case, the higher exhaust fan frequency may serve to more thoroughly mix the ozone with the odour compounds for treatment than is achievable with the higher input levels of sulfur compounds observed, with the aeration fan turned on.

This set of experiments has correlated the input and output samples to correspondingly observe effects of ozone on the total sulfur levels. Reductions in total sulfur were accordingly obtained under each of the four conditions. By contrast, odour compound reductions were only occasionally observed in the initial random sampling of the previous section. By employing random sampling, the levels of odour compounds are arbitrarily averaged when means are determined for all the input and output samples, regardless of the operational conditions prevailing in the bunker or ozone control system. The results of the present section illustrate the dependence of the levels of sulfur compounds for both input and output samples on the operational parameters of the aeration and ozonation systems and these must be taken into consideration when examining the efficacy of the system for odour reduction.

3. Effect of changing ozone concentration

The ozonation odour treatment system installed and investigated in this report was designed to function at a fixed (60 ppm) concentration of ozone. Ozone levels of approximately 20 ppm were measured near the exhaust stacks of the system and under prevailing wind conditions it was possible to smell ozone in the exhaust air, indicating that ozone present in the odour control system. However, results from the previous system suggest that at certain times, such as during a higher influx of compost gases into the system, either during operation of the aeration fan or during filling of the bunkers, the efficiency of the ozonation process may be reduced. As shown in Tables 2-4, other compounds such as ammonia and amines may be present in the samples at levels 10 or 100 times greater than those of the sulfur compounds, which may also react with the ozone. One possible way to improve the reduction of odours from the compost in the bunkers is to increase the amount of ozone introduced into the system. In order to determine if changing the amount of ozone would have an effect on the reduction of odour compounds, it was necessary to make some physical modifications to the ozonation system. When a bunker does not contain compost, the ozone system for that bunker is not in use. It was accordingly decided to utilize the ozone system for an unused bunker and use it for a bunker containing compost, thereby having two ozone lines injecting ozone into a single bunker, effectively doubling the amount of ozone introduced into the ozonation system. This study was undertaken on Bunkers 2 and 3 on separate days. Samples were collected in duplicate from the input and output sampling points when the aeration fan was on, and the exhaust fan on, to ensure thorough mixing of the additional ozone with the compost gases, and with normal and double amounts of ozone going into the system.

The results from the analysis of the samples of this study are given in Table 6. From Table 6, it can be seen that increasing the amount of ozone into the odour control system results in a noted decrease in total sulfur content of the compost gases. For Bunker 3, a total sulfur reduction of 21% with normal ozone was observed, in accordance with the observations of Table 5. The reduction increased to 38% in the presence of the additional ozone. For Bunker 2, a reduction in total sulfur of 22% with normal ozone levels was

observed. It is interesting to note that a reduction in total sulfur was observed for Bunker 2 under these controlled conditions of sampling, while no reduction was observed in the random sampling, as evident in Table 3. The reduction in total sulfur for Bunker 2 increased to 57% when the ozone was increased. Thus, in the present case, increasing the amount of ozone appears to increase the reduction of odorous sulfur compounds by a factor of approximately two or greater.

On occasion, it was found that the ozone input to the ozonation system of certain bunkers had ceased. The ozone generators are designed to operate in a manner that back pressure in the ozone-carrying lines forces the generator to cease operation. Upon removing the ozone line from the ventilation system of the affected unit, it was found that a greenish-white powder had deposited on the end of the tubing, thereby restricting the flow of ozone. This occurrence may lead to certain irregularities in performance of the ozonation unit. Analysis of this powder revealed that it consisted of >99% organic sulfur, with a small amount of nitrogen and trace metals. It is unclear how this substance has entered the system but could possibly be from a reaction product between the ozone and sulfur compounds in the compost gases. The presence in the ozonation system should be further investigated in order to avoid recurrence of the ozone line plugging. Audible ozone alarms could also be installed in the system to alert farm personnel if the ozonation unit is malfunctioning.

CONCLUSIONS AND RECOMMENDATIONS

Overall, the ozonation system installed at Greenwood Mushroom Farm can control the emission of odour compounds. Chemical analysis of samples of mushroom substrate gases taken before and after contact with ozone indicated that levels of odorous sulfur compounds were reduced in the range 20-60% by the ozonation. The extent of this reduction appears dependent on the operating conditions of the bunker. Operation of the aeration fan, for example, tends to increase the volume of gases and odorous compounds entering the treatment system, thereby lowering the efficacy of the treatment system. Increasing the amount of ozone entering the treatment system in certain cases appears to increase the extent of reduction of reduced sulfur compounds. Further research should be undertaken to enhance understanding of this ozonation odour control system and to optimize operational conditions to increase overall reduction of odorous compounds from the compost emissions.

The present study has utilized chemical analysis to test the efficacy of ozonation as a viable means of odour control. The ultimate evaluation of any system for controlling or reducing odours is performed using a combination of chemical analysis and organoleptic or odour panel assessments of the odours (Dorling, 1977; Duns *et al.,* 2003). Relating results from chemical analysis to odour panel measurements converted to odour units is ideally the most informative way to quantitatively relate constituent odour target compounds to human assessment of odours. While the combined use of these two forms of odour evaluation requires further refinement and understanding (Goldstein, 2001;

Zhang *et al.,* 2002), it is recommended that this combination be used to further evaluate the efficacy of the ozone system for controlling the emission of mushroom substrate odours. The ozonation may in fact result in a more substantial reduction in odour units determined by odour panel than was achieved purely by monitoring the levels of reduced sulfur compounds. In addition, several new questions concerning the use of ozonation for the treatment of odours from Phase I mushroom substrate preparation have arisen during the course of this study that can be addressed in future studies. Suggestions for future work include:

1. Use of a combined chemical analysis and odour panel approach to correlate chemical analysis results of pre- and post-ozonation samples with odour panel assessments of the odours and conversion of odour intensities to odour units.

2. Observe the effect of increasing the mixing or contact time between ozone and odours on odour reduction by adding additional mixing tank(s) to the ozonation and optimize reduction of odour compounds under all operational conditions.

3. Undertake a detailed study of the effects of increasing the ozone concentration on odour reduction by generating higher ozone levels than those used in the present study.

4. Investigate possible effects of temperature and relative humidity of compost gases on extent of odour reduction.

5. Employ cumulative sampling methods to collect pre- and post-ozonation samples over periods of several hours or days to average samples over operational effects of ozonation system and, if present, aerated bunker unit.

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Table 1. Phase I aerated bunker schedule for compost preparation

Day of Week	Bunker 1	Bunker 2	Bunker 3
Tuesday	+ (D8)	-	Fill (D1)
Wednesday	+ (D9)	-	+ (D2)
Thursday	Transfer to Phase II tunnels	-	+ (D3)
Friday	-	Fill (D4)	Transfer to Bunker 2 (D4)
Saturday	-	+ (D5)	-
Sunday	-	+ (D6)	-
Monday	Fill (D7)	Transfer to Bunker 1 (D7)	-

+ = compost in bunker
- = no compost in bunker
D(1) = residence time (in days) of compost in bunkers

Table 2. Bunker 3 input (IP) and output (OP) sample analysis results, initial random sampling

Date	Sample	NH_3 Ppm	RNH_2 ppm	H_2S ppm	RSH ppm	DMS/DMDS ppm	Total S ppm
Sept. 9	B3-IP1	18	68	0.85	0.59	0.9	2.3
Sept. 9	B3-1P2	121	>200	0.5	0.99	1.5	3
Sept. 9	B3-IP2 mean	70	-	1.4	0.79	1.2	2.7
Sept. 9	B3-0P1	18	68	3	1.2	1	5.2
Sept. 9	B3-0P2	52	154	0.5	0.8	1.2	2.5
Sept. 9	B3-OP mean	35	111	1.8	1.0	1.1	3.9
Sept. 16	B3-1P1	15	59	0.80	0.5	**1.1**	2.4
Sept. 16	B3-IP2	108	>200	0.90	0.99	2.0	3.9
Sept.16	B3-IP mean	62	-	0.85	0.75	1.6	3.2
Sept.16	B3-0P1			1	0.5	1.4	2.9
Sept. 30	B3-1P2	35	110	0.7	0.6	1.1	2.6
Sept. 30	B3-IP3	18	69	2.5	2.4	2.2	7.1

Sept. 30	B3-IP mean	27	90	1.6	1.5	1.7	4.9
Sept. 30	B3-0P1	30	10	0.5	0.25	0.9	1.7
Sept. 30	B3-0P3	13	48	0.6	0.6	0.9	2.1
Sept. 30	B3-0P3 mean	22	29	0.55	0.43	0.9	1.9
Oct. 22	B3-1P1	16	-	2.5	0.69	0.66	1.3
Oct. 22	B3-1P2	27	-	1.2	0.84	0.99	1.0
Oct. 22	B3-1P3	57	-	4.2	3.0	2.7	9.9
Oct. 22	B3-IP mean	33	-	2.6	1.5	1.4	5.5
Oct. 22	B3-0P1	18	-	2.5	1.2	0.99	4.7
Oct. 22	B3-0P2	32	-	0.73	0.84	0.66	2.2
Oct. 22	B3-0P3	52	-	2.5	2.0	0.82	5.3
Oct. 22	B3-0P3 mean	34	-	1.9	1.4	0.83	4.1
Overall Mean (std dev)	IP:	46 (41)	77 (23)				3.7 (2.9)
	OP:	31 (16)	70 (61)				3.3 (1.5)

Table 3. Bunker 2 input (IP) and output (OP) sample analysis results, initial random sampling

Date	Sample	NH_3 ppm	RNH_2 Ppm	H_2S ppm	RSH ppm	DMS/DMD Sppm	Total S ppm
Oct. 3	B2-IP1	80	>200	0.25	0.25	0.9	1.4
Oct. 3	B2-1P2	68	200	0.5	0.5	0.9	1.9
Oct. 3	B2-1P3	70	>200	0.6	0.5	1.1	2.2
Oct. 3	B2-1P mean	73	-	0.45	0.42	0.97	1.8
Oct. 3	B2-0P1	30	79	0.1	0	0.9	1.0
Oct. 3	B2-0P2	80	190	0.9	0.9	0.9	2.7
Oct. 3	B2-0P3	60	190	0.5	0.5	1.5	2.5
Oct. 3	B2-OP mean	57	153	0.5	0.5	1.1	2.1
Oct. 24	B2-1P1	39	>200	2.4	1.6	0.53	4.5
Oct. 24	B2-IP2	26	98	2.4	2.0	0.69	5.1
Oct. 24	B2-IP3	46	120	1.5	2.0	1.0	4.5

Oct. 24	B2-IP4	55	180	1.5	2.5	0.85	4.9
Oct. 24	B2-IP mean	42	133	2.0	2.0	0.77	4.8
Oct. 24	B2-0P1	17	62	2	1.6	0.47	4.1
Oct. 24	B2-0P2	33	94	3.8	3.1	0.69	7.6
Oct. 24	B2-0P3	56	138	1	2	0.68	3.7
Oct. 24	B2-OP mean	35	98	2.3	2.2	1.8	5.1
Overall Mean (std dev)	IP	55 (19)	150 (48)				3.5 (1.6)
	OP	46 (23)	126 (56)				3.6 (2.2)

Table 4. Bunker 1 input (IP) and output (OP) sample analysis results, initial random sampling

Date	Sample	NH_3 ppm	RNH_2 ppm	H_2S ppm	RSH ppm	DMS/DMDS ppm	Total S ppm
Sept. 9	BI-IP1	41	126	0	0	0.39	0.39
Sept. 9	B1-1P2	57	172	0	0	0.55	0.55
Sept. 9	Bl-IP mean	49	149	0	0	0.47	0.47
Sept. 9	B1-0P1	60	168	0.4	0	2	2.4
Sept. 9	B1-0P2	65	188	0.25	0	1.2	1.5
Sept. 9	**BI-OP** mean	63	178	0.33	0	1.6	2.0
Sept.16	B1-1P1	136	>200	0	0	1.9	1.9
Sept. 16	B1-1P2	57	**191**	0	0	0.48	0.48
Sept. 16	B1-11^{3}3	77	>200	0	0	0.83	0.83
Sept.16	Bl-IP mean	90	-	0	0	1.1	0.66
Sept. 16	B1-0P3	80	>200	0.25	0	0.9	1.2
Sept. 23	B1-IP1	48	154	0.25	0.25	1	1.5
Sept. 23	B1-1P2	16	121	0.25	0.25	0.96	1.5
Sept. 23	B1-1P3	40	122	0	0	0.9	0.9
Sept. 23	B1-IP mean	35	132	0.2	0.2	0.95	1.3
Sept. 23	B1-0p2	42	129	0	0	0.9	0.9
Sept. 23	B1-0P2)	41	137	0.25	0	**1.1**	1.4

Sept. 23	BI-OP mean	42	133	0.13	0	1.0	1.2
Sept. 30	B1-1P1	37	114	, 0	0	0.9	0.9
Sept. 30	B1-1P2	30	86	0	0	0.9	0.9
Sept. 30	B1-IP mean	34	100	0	0	0.9	0.9
Sept. 30	B1-0P1	35	110	0	0	0.9	0.9
Sept. 30	B1-0P2	30	86	0	0	0.9	0.9
Sept. 30	**Bl-OP** mean	33	98	0	0	0.9	0.9
Oct. 21	B1-11[3]1	25	-	0.4	0	0.33	0.73
Oct. 21	B1-1P2	22	-	0.25	0	0.33	0.75
Oct. 21	B1-1P4	25	-	0.35	0	1.3	1.7
Oct. 21	BHP mean	24	-	0.33	0	0.66	1.0
Oct. 21	BI-OP1	23	-	0.5	0	0.33	0.85
Oct. 21	B1-0P2	27	-	0.25	0	0.33	0.75
Oct. 21	BI-OP3	27		0.1	0	0.33	0.43
Oct. 21	B1-OP mean	26	-	0.28	0	0.33	0.61
Overall [r] Mean (std dev)	IP	47 (32)	136			[r]	1.0 (0.49)
	OP	43 (19)	136 (37)				1.1 (0.55)

In Tables 2-4:

NH_3 = ammonia
RH_2 = amines
H_2S = hydrogen sulfide
DMS = dimethyl sulfide
DMDS = dimethyl disulfide
Total S = total sulfur compound concentration
std dev = standard deviation of mean (in brackets below mean value)

Table 5. Input, output and percent change in total sulfur (total S) concentration for samples from with varied aeration and ozonation parameters, Bunker #3

Sample Series	Bunker/Ozonation Parameters			Input Sample Total S (PPm)	Output Sample Total S (ppm)	1 % Change Total S
	floor fan	exhaust fan speed	Ozone			
1	off	low	on	0.36	0.24	33
2	off	high	on	0.44	0.23	48
3	on	high	on	1.1	0.91	17
4	on	low	on	1.9	1.5	21

Table 6. Input, output and percent change in total sulfur (total S) concentration for samples from study changing input ozone amount

Bunker	Bunker/Ozonation Parameters			Input Sample Total S (PPm)	Output Sample Total S (PPm)	% Change Total S
	floor fan	exhaust fan speed	Ozone concentration			
3	on	high	Normal	1.9	1.5	21
3	on	high	Double	1.4	0.87	38
2	on	high	Normal	1.8	1.4	22
2	on	high	Double	1.8	0.78	57