Modified Tobacco Warehouse Aerations For Lowered Acute Emissions of Phosphine Into Surrounding Environs[1]

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Abstract Regulations of atmospheric emissions of phosphine have been enacted by a number of states in the U.S. The maximum concentration allowed at the property of fumigated sites addresses not environmental contamination, but rather the health and safety of citizens in the proximity of warehouse fumigations. In a warehouse fumigation, phosphine is most rapidly vented just after opening the warehouse for aeration. Therefore, alternative aeration techniques were tested with the objective of minimizing peak concentrations outside the warehouse through a slower and more uniform emission rate. Three types of warehouse aerations were tested: (1) a standard aeration with all doors and vents open for 3 d, (2) a modified aeration with only roof vents open for 1 d and then all doors and vents open for the following 2 d, and (3) a second modified aeration with only one large door open for 1 d and then all doors and vents open for the following 2 d. Rates of phosphine emission from the warehouses throughout aeration, gas concentrations downwind from the warehouse, and the adequacy of aeration in both the commodity and warehouse freespace were determined. Modified aerations greatly reduced phosphine peak emission rates, adequately aerated the warehouse freespace, and for most application situations, adequately aerated the tobacco. At one warehouse complex, the three types of aeration (Standard, Roof-Vent-Only and Door-Only) released 45.7, 8.5 and 9.7%, respectively, of the available gas during the first 30 min of aeration. Compared with the Standard aeration, both types of modified aeration delayed aeration of both freespace and tobacco by less than 24 h. Outside downwind concentrations of phosphine were greatly reduced by the modified aerations, especially the Roof-Vent-Only in which downwind concentrations were virtually undetectable.

Key Words Phosphine, fumigation, aeration, emissions, tobacco.

Several methods are used to control the cigarette beetle, *Lasioderma serricorne* (F.) (Coleoptera: Anobiidae), in stored tobacco. Methoprene is widely used to inhibit the increase of cigarette bettle populations in stored tobacco, carbon dioxide is being used to a limited extent to disinfest small volumes of tobacco, and pyrethroids are being studied for adulticidal efficacy against stored-tobacco insect pests. However, fumigation with phosphine is currently the only method widely acceptable in the United States, and much of the world, for rapidly disinfesting tobacco warehouses of the cigarette beetle (Anonymous 1995). Therefore, it is important to maintain the option of using phosphine while at the same time protecting people in the surrounding community from phosphine released during aeration.

Most tobacco warehouses were built well away from surrounding communities, but

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in many cases community expansion has reached the warehouses. Therefore, the standard practice of aerating tobacco warehouses by immediately opening all doors and vents can sometimes release large concentrations of phosphine toward nearby homes, yards, and streets. Phosphine dissipates rapidly (Fluck and Novobilsky 1973) and has not been known to be a serious health threat, but concern for the community's health is still in order.

In response to such concerns, states have enacted regulations on phosphine emissions from fumigation sites. The North Carolina Air Pollution Control Requirements (Section 15 NCAC 2D) has been amended to regulate the emission of 93 chemicals including phosphine. The phosphine standard ($\leq$ 0.1 ppm at the property boundaries) was established for the health and safety of citizens in the proximity of warehouse fumigations rather than environmental contamination.

The total amount of phosphine released during an aeration is the same regardless of how aeration is accomplished. However, with standard aerations the most rapid release of phosphine is during the first few minutes after a warehouse is opened. This is the time that concentrations downwind from the warehouse will be the greatest, and regulatory compliance will be the most difficult. Therefore, the maximum concentration in the surrounding air for the entire aeration period can be minimized by a more gradual release of phosphine. Computer models to be used in assessing regulatory compliance ("SCREEN", Version 1.1) (Brode 1988) directly and linearly correlate gas concentration at a distance from a warehouse to the mass of gas released from the warehouse.

Therefore, two modified aeration methods were compared with the most commonly used one (fully opened doors and vents throughout the aeration). The rate of phosphine emission from each warehouse was indirectly determined by subtracting the amount of phosphine in the warehouse at any given time from the amount inside at a previous time. Phosphine concentrations downwind from each warehouse were monitored.

Materials and Methods

Warehouses holding tobacco owned by Flue-Cured Tobacco Cooperative Stabilization Cooperation (FCSC) were selected for the testing. Two different tests were conducted, one in Fuquay-Varina, NC, and one in Oxford, NC.

Fuquay-Varina test. Three test warehouses were fumigated and aerated. Seven other non-test warehouses on the site were fumigated and aerated at the same time. Within this complex, 20 m separates adjacent warehouses. The three test warehouses are separate structures with no common walls. Each warehouse has 8 side vents (1.2 by 1.2 m each), 4 cylindrical roof vents (61.0 cm diam), and a large door on each end of the warehouse (4.9 by 4.3 m each). The width, length, eave height, and center height, respectively, are 38.1, 58.5, 8.8, and 10.4 m for test warehouses #22 and #23, and 38.1, 58.5, 7.9, and 9.4 meters for warehouse #15. Volumes of the warehouses are 21,407 m^3 for warehouses #22 and #23 and 19,484 m^3 for warehouse #15. The numbers of tobacco hogsheads and cases stored were 2128 and 2039 (warehouse #22), 2332 and 2620 (warehouse #23), and 2392 and 2206 (warehouse #15). These commodity volumes constituted 20.4 to 24.9% of the total warehouse volumes.

Each test warehouse was aerated in a different manner. Warehouse #23 (= Standard) was aerated in the conventional manner in which all roof vents, side vents and

the door on each end of the warehouse are opened at the beginning of the 3-day aeration period. Warehouse #15 (= Door-Only) was aerated by opening only one of the large end doors for the first day and then opening all vents and the other end door for the remaining two days of aeration. Warehouse #22 (= Roof-Vents-Only) was aerated by opening the four roof vents for the first day and then opening all other vents and the two end doors for the remaining two days of aeration. Therefore, both modifications were used for one day only, followed by two days of conventional aeration. Doors of all three warehouses were closed nightly from approximately dusk to 9 A.M. the following morning which is normal procedure for aeration of those warehouses.

During aeration phosphine concentrations were monitored both inside each warehouse, to assess the rate of emission from the warehouse, and downwind from the warehouse to assess concentrations that would be subject to regulation. Polyethylene gas-sampling lines (6.4 mm ID) were run from eight sites within the warehouse to the outside where the gas concentration was to be measured with Drager® (Degesch America Inc., Weyers Cave, VA) tubes. Four of the sampling sites were in the warehouse freespace, and were (1) either high (4.9 m above the floor) or low (1.8 m above the floor), and (2) either centered (1.0 m from the center alley) or off-centered (9.0 m from the center alley). The four specific freespace sites were (1) low, centered, and 12 m in from the front door, (2) high, centered, and 12 m in from the front door, (3) low, off-centered, and 33 m in from the front door, and (4) high, off-centered, and 33 m in from the front door. Of the remaining four sampling sites, two were in the center of hogsheads and two were in the center of cases, all 3 m above the floor. One case and one hogshead site were located approximately 17 m in from the front door and 2 m from the center alley, and another case and hogshead site were located approximately 37 m in from the front door and 6 m from the center alley. Hogsheads (28.5 m^3 each) and cases (13.2 m^3 each) aerate more slowly than does the freespace of the warehouse because they are packed tightly with tobacco.

Outside downwind concentrations were measured with Drager tubes held in the middle of the airstream 2 m above groundlevel. (Simultaneous concentration assessments via collection of samples with vacuum tubes and subsequent gas chromatography analysis proved ineffective.) Downwind direction was determined with colored smoke released either from a warehouse door or roof. Samples were taken just outside the warehouses, and at 0.5, 1.0, 3.0, and 5.0 building heights away from the warehouses. (The only exception was that for the Roof-Vents-Only warehouse where samples were not taken just outside a door because phosphine was not being released there.) Building heights, instead of absolute distances, were used because the nature of wind currents around a building are strongly correlated to the number of building heights away from the building (Brode 1988). The downwind concentrations were measured by members of the North Carolina Division of Environmental Management.

Outside temperature, relative humidity, solar radiation, wind speed and direction, and the temperatures within the warehouse freespace and the tobacco were monitored throughout the aeration. These data are being used for modeling purposes and will not be reported here.

Oxford test. Two test warehouses were fumigated and aerated. One other non-test warehouse on the site was fumigated and aerated at the same time. The two test warehouses are not separate structures, but rather the middle section and one end section of a three-section building. Each warehouse has 8 side vents (1.4 by 1.4 m

each), 4 cylindrical roof vents (61.0 cm diam), and a large door on each end of the warehouse (4.9 by 4.3 m each). Width, length, eave height, and center height of each warehouse are 39.0, 48.8, 8.8, and 10.4 meters, respectively. The volume of each warehouse is 18,268 m^3. The numbers of tobacco hogsheads and cases stored were 2914 and 875 (warehouse #6) and 3039 and 155 (warehouse #7). These commodity volumes constituted 24.2 to 25.1% of the total warehouse volumes.

Warehouse #7 was aerated in the conventional (Standard) manner. Warehouse #6 was the site of the Roof-Vents-Only aeration, conducted as before in Fuquay-Varina with the four roof vents open for the first 24 h and all other vents and the two end doors open for the remaining 48 h of aeration. A Door-Only aeration was not conducted during this test. Phosphine concentrations were monitored inside each warehouse as in the Fuquay-Varina test. The only difference was that to save time and money a manifold was used outside the warehouse to combine the four freespace sampling lines into one. The same was done to the two case sampling lines and to the two hogshead sampling lines so that only one line was used for each of the freespace, cases, and hogsheads. This allowed the average concentrations of all three sites to be measured with three readings. Prior to using this approach each line was tested to ensure that it contributed an equal amount of gas to the measured concentration. In Oxford, outside downwind concentrations were not monitored.

Doors in both warehouses were closed at night throughout the aeration period. As in the Fuquay-Varina tests, the outside temperature, relative humidity, and temperatures within the warehouse freespace and the tobacco were monitored throughout the aeration. However, solar radiation and wind speed and direction were not monitored because the appropriate instruments were destroyed in a storm just prior to testing.

Results

Fuquay-Varina test. The temperature of the tobacco was 25.0°C and the outside daylight temperatures, when doors were open during aeration, averaged 26.7°C. Wind speeds (mean ± SE in m/sec) during the first hour and the first 24 h post-aeration, respectively, were 1.73 ± 0.06 and 2.82 ± 0.08 outside the Standard warehouse, 2.78 ± 0.17 and 2.96 ± 0.08 outside the Door-Only warehouse, and 2.68 ± 0.14 and 2.78 ± 0.07 outside the Roof-Vent-Only warehouse. Wind speed measurements were taken 50 m upwind of the respective warehouse.

Phosphine concentrations in all sampling lines from the freespace and commodity (cases and hogsheads) in each warehouse were measured 5 to 7 times during the first 2 h post-aeration (i.e., 2 h after initiation of aeration). They were measured at irregular intervals after that, typically every 2 h until 11:00 PM of the first day, and again at approximately 1, 2, 3, and 4 d post-aeration. Mean ± SE pre-aeration concentrations (ppm) in the freespace, cases, and hogsheads were 246 ± 7, 210 ± 31, and 260 ± 10 for the Standard warehouse, 197 ± 13, 185 ± 5, and 195 ± 5 for the Door-Only warehouse, and 310 ± 6, 195 ± 5, and 282 ± 8 for the Roof-Vent-Only warehouse.

During Standard aeration phosphine was released rapidly (Fig. 1). With the pre-aeration concentration as a baseline value, the freespace concentration decreased by 45.7% in the first 30 min of aeration and decreased by 87.8% within the first hour. These data demonstrate the initial rapid release of phosphine during standard aeration which must be addressed in complying with regulatory standards. Adequate aeration of the freespace was achieved within 26 h, well before the standard 72 h

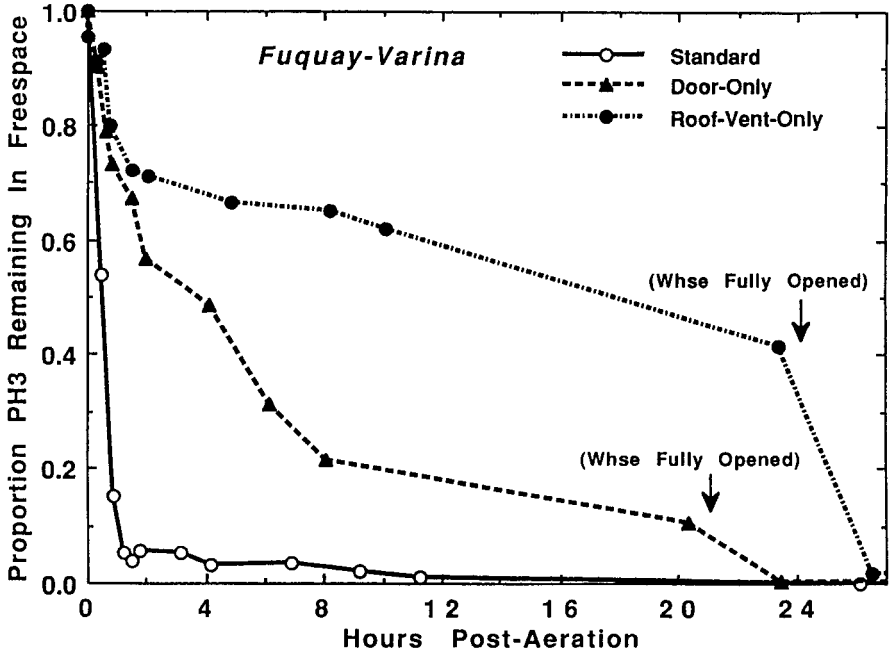

Fig. 1. Release of phosphine from three tobacco warehouses in Fuquay-Varina, NC, during the first 24 h of aeration using one Standard and two modified aeration methods. Each of the two modified aeration warehouses was fully opened between 21 and 24 h post-aeration.

aeration period (Table 1). The <0.1 ppm concentration measurement was well below the maximum allowable reentry level of 0.3 ppm (Table 1). The cases were well aerated at 72 h post-aeration. However, the hogsheads still retained 2.2 ppm, Indicating they could not be moved in marketing channels without further aeration.

During the time prior to complete opening of the warehouse at approximately 21 h post-aeration, the Door-Only aeration (Fig. 1) released phosphine more slowly and uniformly. Only 9.7% of the pre-aeration phosphine in the freespace was released in the first 30 min of aeration and only 21.2% was released in the first hour. Of the pre-aeration concentration, 10.6% remained at approximately 24 h post-aeration just before full opening of the warehouse. Compared with the Standard aeration, the Door-Only aeration released 79 and 76% less of the available phosphine during the first 30 min and 1 h, respectively. Because the fastest emission of phosphine from a warehouse is usually immediately after opening a warehouse (not 30 min post-aeration or later) and because the Standard aeration curve has a steeper slope than the Door-Only curve (Fig. 1), the maximum reduction in the problem of regulatory compliance should be even greater than 79% with the Door-Only aeration modification.

The Roof-Vent-Only aeration (Fig. 1) released phosphine even more slowly and uniformly. Only 8.5% of the pre-aeration phosphine in the freespace was released in

Table 1. Concentration (ppm ± SE) of phosphine at selected times to illustrate the adequacy of aeration. In Fuquay-Varina, n(freespace) = 4, n(case) = 2, and n(hogshead) = 2. In Oxford sampling lines were combined to give only one reading per site, hence no SE. The maximum concentration allowed for re-entry without supplemental breathing apparatus is 0.3 ppm

Type aeration	Hrs post-aeration	Sampling site		
		Freespace	Case	Hogshead
FUQUAY-VARINA:				
Standard	26	0.2 ± 0.1	24.0 ± 14.0	67.5 ± 12.5
	49	<0.1	0.6 ± 0.4	9.0 ± 1.0
	75	<0.1	<0.1	2.2 ± 0.2
	98	<0.1	<0.1	0.6 ± 0.2
Door-Only	23*	1.0 ± 0.2	21.0 ± 11.0	63.5 ± 13.5
	43	0.2 ± 0.1	6.8 ± 5.2	17.5 ± 2.5
	68	<0.1	0.2 ± 0.1	6.0 ± 3.0
	92	<0.1	<0.1	1.3 ± 0.8
Roof-Vent-Only	27*	5.8 ± 0.5	95.0 ± 15.0	190 ± 0.0
	46	1.1 ± 0.5	14.0 ± 1.0	47.5 ± 7.5
	72	<0.1	0.8 ± 0.0	13.5 ± 1.5
	95	<0.1	0.2 ± 0.1	3.5 ± 0.5
OXFORD:				
Standard	22	0.2	5.0	70.0
	47	0.1	0.4	22.0
	71	<0.1	<0.1	7.0
	95	<0.1	<0.1	1.0
Roof-Vent-Only	23**	3.0	70.0	100.0
	45	0.4	9.0	35.0
	75	<0.1	<0.1	5.0
	98	<0.1	<0.1	1.0

* Warehouse had been fully opened for approximately 2.5 h at this time.
** Warehouse had been fully opened for approximately 1.5 h at this time.

the first 30 min of aeration and only 11.0% was released in the first hour. Of the pre-aeration concentration, 41.5% remained at approximately 24 h post-aeration just before full opening of the warehouse. Compared with the Standard aeration, the Roof-Vent-Only aeration released 81 and 88% less of the available phosphine during

the first 30 min and hour, respectively. For reasons stated in the last paragraph, the maximum reduction in the problem of regulatory compliance should be even greater than 81% with the Roof-Vent-Only aeration.

The Door-Only and Roof-Vent-Only aerations provided adequate aeration of the freespace within 72 h (Table 1). Neither procedure adequately aerated either the cases or hogsheads within the same period, and the Roof-Vent-Only commodities were the slowest to aerate. Like the Standard aeration, both modifications failed to adequately aerate hogsheads even after more than 90 h. However, both modifications in aeration were only for the first 24 h, after which the standard method of opening all doors and vents was implemented. Therefore, the maximum delay in aeration, compared with the completely standard method, would be 24 h. The data in Table 1 generally reflect this.

Oxford test. The temperature of the tobacco was 27.8°C and the outside daylight temperatures, when doors were open during aeration, averaged 28.8°C. Phosphine concentrations in all sampling lines from the freespace and commodity (cases and hogsheads) in each warehouse were measured 6 to 7 times during the first 2 h post-aeration. Concentrations were then measured at irregular intervals after the first 2 h, typically every 2 h until 10:00 P.M. of the first day, and again at approximately 1, 2, 3, and 4 d post-aeration. Pre-aeration concentrations (ppm) in the freespace, cases, and hogsheads, respectively, were 185, 170, and 230 for the Standard warehouse and 175, 180, and 210 for the Roof-Vent-Only warehouse. As previously stated, the sampling lines in Oxford were joined to give one line each from the freespace, cases, and hogsheads so the variance in the concentrations was not measured.

With the Standard aeration the phosphine release rate was faster in Oxford than in Fuquay-Varina (Fig. 2). The freespace concentration decreased by 78.4% in the first 30 min of aeration and decreased by 96.8% within the first hour. The unusually high reading of 13 ppm at 4 h post-aeration was double-checked and determined to be an accurate reading, but its occurrence cannot be explained.

Adequate aeration of the freespace was easily achieved within the standard 72 h aeration period (Table 1). The 0.2 ppm concentration at 22 h post-aeration was already below the maximum allowable reentry level of 0.3 ppm. The cases were also well aerated at 71 h post-aeration (0.08 ppm), but the hogsheads still retained 1.0 ppm at 95 h post-aeration. Because of their larger size, hogsheads are always slower to aerate than are cases.

Concentration changes in the Roof-Vent-Only warehouse were much slower than in the Standard warehouse in Oxford, but followed a slightly different pattern from the Roof-Vent-Only in Fuquay-Varina (Fig. 2). No decrease in freespace concentration during the first 30 min of aeration could be detected, but a relatively high loss (compared to Fuquay-Varina) of 42.9% of the phosphine at 1 h post-aeration was measured. However, the next reading increased significantly and readings for the next 2.5 h exceeded the one at 1 h post-aeration, so the true loss at 1 h post-aeration may have been less than that indicated by our reading. Because of the small total area of the openings and the effect of climatological factors such as wind and temperature on Roof-Vent-Only aerations, the actual gas losses and the measurements of those losses are expected to be more erratic than with more rapid wide-open aerations. Of the pre-aeration concentration, 31.4% remained 20 h post-aeration (2 h before fully opening the warehouse).

Adequate aeration of the freespace was easily achieved within 72 h with a 0.3 ppm

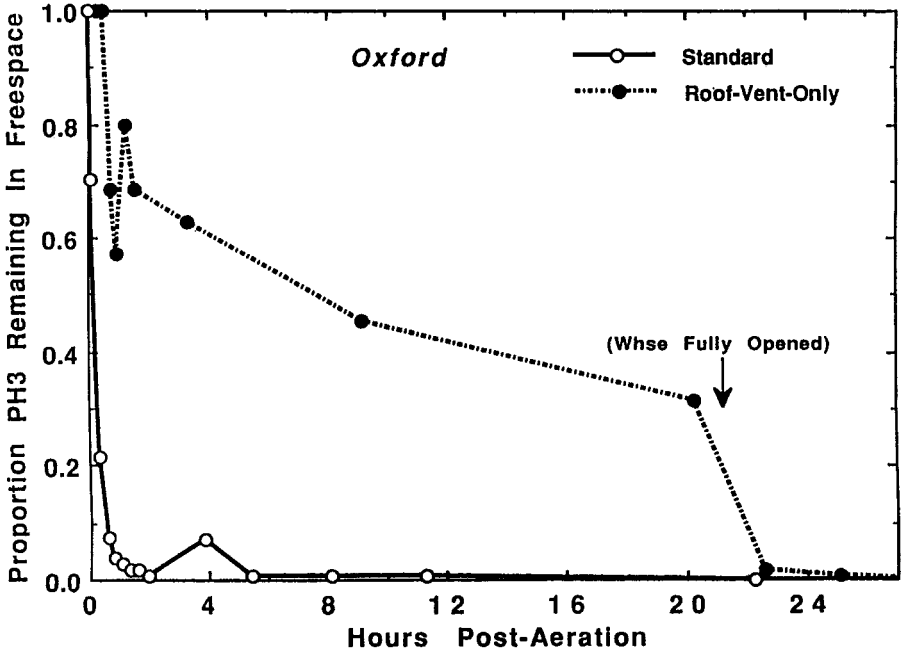

Fig. 2. Release of phosphine from two tobacco warehouses in Oxford, NC, during the first 24 h of aeration using one Standard and one modified aeration method. The modified aeration warehouse was fully opened at approximately 22 h post-aeration.

concentration at 51 h post-aeration and no detectable level at 75 h (Table 1). Cases were also well aerated with 0.08 ppm at 75 h post-aeration, but the hogsheads still retained 1.0 ppm at 98 h post-aeration.

Outside downwind concentrations. The height of the warehouses in Fuquay-Varina was 10.4 m, so phosphine concentrations were measured just outside the door, and at 5.2, 10.4, 31.2, and 52.0 m downwind from all three warehouses, except that no measurement was taken outside a door of the Roof-Vent-Only warehouse where no door was opened. Because the Standard aeration and the Door-Only aeration began >4 h apart, the wind direction relative to the warehouse orientations differed during the first 1.25 h-post-aeration when measurements were taken. Wind blew parallel to the length of the Standard warehouse, i.e., directly through one door and out the other. Wind blew perpendicular to the length of the Door-Only warehouse thereby pulling the phosphine out as much as pushing it. Again, because no door was opened on the Roof-Vent-Only warehouse the wind direction was unimportant. During the time when measurements were taken for a given warehouse, wind direction was reasonably constant, generally within a directional range of 30°.

Concentrations outside the doors of both the Standard and the Door-Only warehouses greatly exceeded the pending property boundary limit of 0.1 ppm (Table 2). The concentrations tended to diminish with increasing distance, but less so in the

case of the Standard warehouse. Concentrations frequently and greatly exceeded 0.1 ppm at 5.2, 10.4, and 31.2 m, and were once too high at 51.0 m. In contrast, downwind from the Door-Only warehouse the concentration was marginally too high only once at 31.2 m and never at 52.0 m. Concentrations downwind of the Roof-Vent-Only warehouse were monitored for 1 h, but no concentration levels were detectable at any time or distance (<0.01 ppm), except that 0.01 ppm was detected once 31.2 m downwind at 5 min post-aeration. Seven other warehouses were aerated on this site at this same time, thus contributing to the concentrations that were measured. The contribution that these warehouses made could not be quantified.

Discussion

It is important to maintain the option of fumigating a wide variety of commodities such as tobacco, grain, and peanuts, with phosphine. The fumigations must also be conducted in a safe manner that complies with regulatory standards. In testing several solutions to this problem, the decrease in freespace concentration was monitored to indirectly estimate the relative phosphine emission rates from warehouses undergoing standard and modified aerations. Commodity concentrations were monitored to determine if aeration was adequate within an acceptable period. Phosphine in the

Table 2. Concentration (ppm) of phosphine downwind from the Fuquay-Varina warehouses* measured with Drager tubes at 2 meters above the ground. The North Carolina limit at the property boundary is 0.1 ppm. Warehouse height = 10.4 m

Type aeration	Hours post-aeration	Sampling site (No. warehouse heights downwind)				
		Door	0.5	1.0	3.0	5.0
Standard	0.05	20.0	0.05	—	—	—
	0.10	—	—	0.00	—	—
	0.20	—	—	—	0.60	—
	0.30	11.0	3.00	1.00	—	0.03
	0.50	20.0	1.00	0.01	0.70	0.40
	0.77	17.0	—	—	0.10	0.03
	1.00	2.5	0.10	0.30	0.30	0.03
	1.25	—	—	—	0.10	0.02
Door-Only	0.02	—	0.50	—	0.09	—
	0.15	20.0	—	0.00	—	0.00
	0.35	7.0	0.10	0.10	0.13	0.00
	0.58	7.0	0.10	0.20	0.02	0.00
	0.81	15.0	0.08	—	0.00	0.00

* No phosphine could be detected downwind of the Roof-Vent-Only warehouse except for one 0.01 ppm reading.

early stages of aeration moves much too slowly from hogsheads and cases into the freespace to contribute significantly to what is released to the outside.

Both aeration modifications minimized the peak phosphine concentration to which the public would be exposed and which would be subject to regulation. The modifications also adequately aerated the warehouse freespace, and, with an additional day of aeration, would be expected to aerate the commodity at least as well as the standard aeration. This slight delay in aeration of the commodity does not prevent the entry of personnel into the warehouse, and is a problem only if the commodity must be immediately moved from the premises.

The modification that best meets the stated objectives is open to interpretation. At 30 min post-aeration the Roof-Vent-Only reduced the initial release of phosphine by >81% and the Door-Only reduced it by >79%. The model used to determine compliance will consider smaller time frames, such as the first 15 min post-aeration, where differences are probably greater. Also, the Roof-Vent-Only has the advantage of releasing phosphine higher into the air where it can disperse before reaching ground level.

A distinct advantage of the Door-Only aeration over the Roof-Vent-Only aeration was that at 24 h, just before fully opening all the doors and vents, the former retained only 10.6% of its pre-aeration concentration, whereas the latter still held 41.5%. This 41.5% was rapidly released, as in a Standard aeration, when the Roof-Vent-Only warehouse was fully opened. One solution to this problem is to maintain the Roof-Vent-Only modification for an additional day which would theoretically leave only 17.2% ($41.5\%^2$) remaining when the warehouse is finally fully opened. The need to gain access to a warehouse as soon as possible often prohibits this option.

Downwind concentrations of phosphine demonstrated that just after initiation of aeration a large concentration of phosphine can exist close to the warehouse, but that concentrations are rapidly diluted with distance from the warehouse. Warehouses are located in various places, with some close to public areas. Therefore, managers of warehouses located near the public may need to modify aerations or suspend use of those warehouse.

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