MODIFIED TOBACCO WAREHOUSE AERATIONS FOR LOWERED ACUTE EMISSIONS OF PHOSPHINE INTO SURROUNDING ENVIRONS

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Atmospheric emissions of phosphine will soon be regulated by the State of North Carolina. The proposed phosphine standard (≤ 0.1 ppm at the property boundaries) addresses not environmental contamination, but rather the health and safety of citizens in the proximity of warehouse fumigations. It is just after opening a warehouse during conventional aerations that phosphine is most rapidly vented. 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 three days, 2) a modified aeration with only roof vents open for one day and then all doors and vents open for the following two days, and 3) a second modified aeration with only one large door open for one day and then all doors and vents open for the following two days. Determined were the rates of phosphine emission from the warehouses throughout aeration, the gas concentrations downwind from the warehouse, and the adequacy of aeration in both the commodity and warehouse freespace. The modified aerations reduced the peak emission rates of phosphine by >81%, adequately aerated the warehouse freespace, and for most practical situations adequately aerated the tobacco.

Several methods are used to control the cigarette beetle, *Lasioderma serricorne* (F.), in post-harvest tobacco. Methoprene is widely used to inhibit the increase of cigarette beetle 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. Therefore, it is important to maintain the option of using phosphine while protecting people in the surrounding community from gas released during aeration.

Most tobacco warehouses were originally built well away from surrounding communities, but in many cases the community has since developed very near the warehouses. Therefore, the standard pratice of aerating tobacco warehouses by immediately opening all doors and vents can sometimes release large concentrations of phosphine toward nearby homes, yards, and streets. The gas dissipates rapidly (Fluck & 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, the North Carolina Air Pollution Control Requirements (Section 15 NCAC 2D) has been amended to regulate the emission of 93 chemicals including phosphine. The proposed phosphine standard (≤ 0.1 ppm 2 meters above the ground at the property boundaries) is meant to deal with 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, it is important to understand that 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

regulated. (Simultaneous concentration assessments by collecting samples with vacuum tubes and later analyzing with gas chromatography 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 samplies 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, RH, solar radiation, wind speed and direction, and the temperatures within the warehouse freespace and the tobacco were monitored throughout the aeration. These data will not be reported here, but are being used for modeling purposes.

Oxford test: Two test warehouses were fumigated and aerated, respectively, on August 4 and 8. One other non-test warehouse on the site was fumigated and aerated at the same time. The two test warehouses were not separate structures, but rather the middle section and one end section of a three-section building. Each warehouse had 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 were 39.0, 48.8, 8.8, and 10.4 meters, respectively. Volume of each warehouse was 18,268 m^3. The number 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 a Roof-Vents-Only aeration conducted as before with the four roof vents open for the first 24 hours and all other vents and the two end doors open for the remaining 48 hours of aeration. No Door-Only aeration was 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 we ended with one line each for the freespace, cases, and hogheads. This allowed us to measure the average concentrations of all three sites with three readings. Prior to using this approach we tested to ensure that each line was contributing 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 aerations. As in Fuquay-Varina the outside temperature, RH, solar radiation, wind speed and direction, and the temperatures within the warehouse freespace and the tobacco were monitored throughout the aeration.

RESULTS

Release of Phosphine From Warehouses and Adequacy of Aeration

Fuquay-Varina: Temperature of the tobacco was 25.0 °C and the outside daylight temperatures, when doors were kept open during aeration, averaged 26.7 °C. 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 hours until 11:00 PM of the first day, and again at ca. 1, 2, 3, and 4 days 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.

maximum concentration in the surrounding air for the entire aeration period can be minimized by a more gradual release of phosphine. The model to be used in assessing regulatory compliance ("SCREEN", Version 1.1) (Brode 1988), and similar models, directly and linearly correlate gas concentration at a distance from a warehouse to the mass of gas released from the warehouse.

Therefore, we compared two modified aeration methods with the most commonly used one (fully opened doors and vents throughout the aeration). We 1) indirectly determined the rate at which phosphine left each warehouse by subtracting the amount in the warehouse at any given time from the amount inside at a previous time, and (2) monitored the phosphine concentration downwind from each warehouse.

MATERIALS AND METHODS

Warehouses holding tobacco owned by Flue-Cured Tobacco Cooperative Stabilization Cooperation (FCSC) were selected for the testing in the summer of 1989. Two different tests were conducted, one in Fuquay-Varina, N.C. and one in Oxford, N.C..

Fuquay-Varina test: Three test warehouses were fumigated and aerated, respectively, on June 15 and 19. Seven other non-test warehouses on the site were fumigated and aerated at the same time. The three test warehouses were separate structures with no common walls. Each warehouse had 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, were 38.1, 58.5, 8.8, and 10.4 meters for warehouses #22 and #23, and 38.1, 58.5, 7.9, and 9.4 meters for warehouse #15. Volume of the warehouses were 21,407 m^3 for warehouses #22 and #23 and 19,484 m^3 for warehouse #15. The number 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 warehouses 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 remained open throughout the 3-day aeration period. Warehouse #15 (=Door-Only) was aerated by opening only one of the large end doors for the first 24 hours and then opening all vents and the other end door for the remaining 48 hours of aeration. Warehouse #22 (=Roof-Vents-Only) was aerated by opening the four roof vents for the first 24 hours and then opening all other vents and the two end doors for the remaining 48 hours 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 at night which was normal procedure for aeration of those warehouses

During aeration phosphine concentrations were monitored both inside each warehouse, to assess the rate at which it was exiting the warehouse, and downwind from the warehouse to assess concentrations that would be subject to regulation. Polyethelene 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® tubes. Four of the sampling sites were in the warehouse freespace, and were1) either *high* (4.9 m above the floor) or *low* (1.8 m above the floor), and 2) either *centered* (1 m from the center alley) or *off-centered* (9 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 at 3 m above the floor. One case and hogshead site was located ca. 17 m in from the front door and 2 m from the center alley, and another case and hogshead site was located ca. 37 m in from the front door and 6 m from the center alley.

Outside downwind concentrations were measured with Drager tubes held in the middle of the airstream at 3 m above groundlevel, the height at which concentrations are to be

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. This demonstrated the initial rapid release of phosphine during standard aeration that must be addressed in complying with regulatory standards. Adequate aeration of the freespace was achieved within the standard 72 h aeration period (Table I). The <0.1 ppm was well below 0.3 ppm which is the maximum allowable reentry level. The cases were also well aerated at 72 h post-aeration. However, the hogsheads still retained 2.2 ppm, meaning they could not be moved in marketing channels without further aeration.

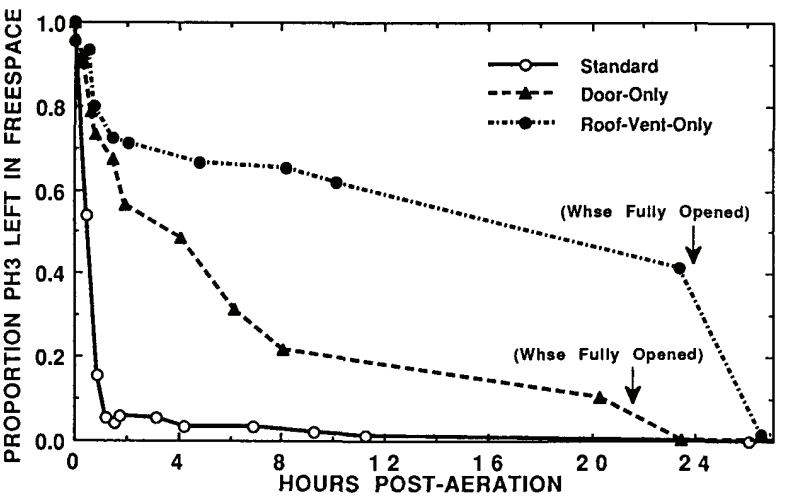

Fig. 1. Phosphine loss from warehouses in Fuquay-Varina, NC

Table I. Concentration (PPM±SE) of phosphine inside the Fuquay-Varina warehouses' freespace (n = 4), cases (n = 2), and hogsheads (n = 2) at selected times to illustrate the adequacy of aeration. The maximum concentration allowed for re-entry without supplemental breathing apparatus is 0.3 ppm.

		Sampling site		
Type aeration	Hrs post-aeration	Freespace	Case	Hogshead
Standard	26	0.15 ± 0.05	24.0 ± 14.0	67.5 ± 12.5
	49	<0.1	0.65 ± 0.35	9.00 ± 1.00
	75	<0.1	<0.1	2.15 ± 0.15
	98	<0.1	<0.1	0.65 ± 0.15
Door-Only	23‡	1.00 ± 0.24	21.0 ± 11.0	63.5 ± 13.5
	43	0.23 ± 0.09	6.75 ± 5.25	17.5 ± 2.50
	68	<0.1	0.15 ± 0.05	6.00 ± 3.00
	92	<0.1	<0.1	1.30 ± 0.80
Roof-Vent-Only	27‡	5.75 ± 0.48	95.0 ± 15.0	190. ± 0.00
	46	1.13 ± 0.46	14.0 ± 1.00	47.5 ± 7.50
	72	<0.1	0.80 ± 0.00	13.5 ± 1.50
	95	<0.1	0.25 ± 0.05	3.50 ± 0.50

‡ Warehouse had been fully opened for ca. 2.5 h at this time.

Until completely opened at ca. 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% was still left at ca. 24 h post-aeration just before fully opening 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 hour, respectively. Because the greatest rush 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 sharper slope than the Door-Only curve, the maximum reduction in the problem of regulatory compliance should be even greater than 79% with the Door-Only 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 the first 30 min of aeration and only 11.0% was released in the first hour. Of the pre-aeration concentration, 41.5% was still left at ca. 24 h post-aeration just before fully opening 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.

The Door-Only and Roof-Vent-Only aerations provided adequate aeration of the freespace within 72 h (Table I). Neither adequately aerated either the cases or hogsheads within the same period, and the Roof-Vent-Only commodities were the slowest to aerate. 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, should be 24 h.

Oxford: Temperature of the tobacco was 27.8 ^{o}C. 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 hogheads so that variance in the concentrations was not measured.

The Standard aeration released phosphine even faster 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 strangely high reading of 13 ppm at 4 h post-aeration w double-checked and determined to be an accurate, but unexplainable reading.
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 72 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). We were unable to detect any decrease in freespace concentration for the first 30 min of aeration, but measured a relatively high loss (compared to Fuquay-Varina) of 42.9% of the phosphine by 1 h post-aeration. 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 indicated by our reading. Because of the small total area of openings and the great effect of such factors as wind and temperature on Roof-Vent-Only aerations, the actual gas losses as well as 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% was left at 20 h post-aeration just before fully opening the warehouse.

Adequate aeration of the freespace was easily achieved within 72 h with a 0.3 ppm concentration at 51 h post-aeration and no detectable level at 68 h. 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 warehouses were opened several hours 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.

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 II). The concentrations tended to diminish with increasing distance, but less so with 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 none 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. It is important to remember that seven other warehouse were aerated on this site at this same time, thus contributing to the concentrations that we measured. We could not assess the contribution that these warehouse made.

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

		Sampling site (No. warehouse heights downwind)				
Type aeration	Hours post-aeration	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.

DISCUSSION AND CONCLUSIONS

It is important that we maintain the option of fumigating a wide variety of commodities such as tobacco, grain, and peanuts, with phosphine. It is also important that the fumigations be done in a safe manner that complies with regulatory standards. In testing several solutions to this problem we monitored the decrease in freespace concentrations, but monitored commodity concentrations only to determine if aeration was adequate within an acceptable perioid. Phosphine in the early stages of aeration moves much too slowly into the freespace to contribute significantly to what is released to the outside.

Both the tested modifications minimized the peak phosphine concentration which the public would be exposed to and which would be subject to regulation. They also adequately aerated the warehouse freespace, and with an additional day of aeration should aerate the commodity at least as well as the standard aeration. This slight delay in aeration of 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.

Which modification is best suited for meeting the stated objectives is open to interperetation. The Roof-Vent-Only reduced the initial release of phosphine by >81% and the Door-Only reduced it by >79%. The difference between 81% and 79% is small, but these were 30 min post-aeration readings. The model used to determine compliance will consider smaller time frames, such as the first 15 min post-aeration, where differences are probably greater. A distinct advantage of the Door-Only aeration was that at 24 h, just before fully opening all the doors and vents, it retained only 10.6% of its pre-aeration concentration while the Roof-Vent-Only warehouse still held 41.5%. This means that when fully opened the Roof-Vent-Only still retained 41.5% of the problems associated with a Standard aeration. 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 get into a warehouse as soon as possible often prohibits this option.

Downwind concentrations of phosphine demonstrated that close to the warehouse a large problem exists but that concentrations are rapidly diluted with distance from the warehouse. Warehouses are located in various places, with some opening directly onto city streets and others being hundreds of meters from public areas. Therefore, managers of warehouses located close to the public may need to modify aerations, suspend use of those warehouses, or cease fumigating with phosphine.

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LA MODIFICATION DE L'AERATION DES MAGASINS DE STOCKAGE AFIN D'ABAISSER LA CONCENTRATION DES EMISSIONS DE PHOSPHINE DANS L'ATMOSPHERE ENVIRONNANTE

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RESUME

L'émission de phosphine, ainsi que celle d'environ 1.500 autres produits chimiques, est sur le point d'être réglementée par l'état de Caroline du nord (Etats-Unis). La norme de phosphine proposée (0,1 ppm à la zone limitrophe de la propriété) ne concerne pas tellement la contamination de l'environnement mais plutôt la santé et la sécurité des citoyens vivant à côté des magasins de stockage. C'est parce que la phosphine est évacuée d'un seul coup après l'ouverture du magasin pour permettre l'aération de ce dernier et que la concentration s'élève aussitôt dans les environs immédiats, que la législation a voulu rendre cette émission plus uniforme. Ainsi, on a examiné trois types d'aération pour ces magasins : 1) une aération standard, toutes les portes et évents restant ouverts pendant trois jours, 2) une aération modifiée comprenant des évents d'aération en toiture ouverts pendant deux jours et, enfin, 3) une deuxième modification comprenant une seule et large porte maintenue ouverte pendant un jour, les autres portes et évents étant alors ouverts pendant les deux autres jours. On a mesuré les taux d'émission de phosphine depuis l'intérieur du magasin jusqu'aux orifices d'aération, les concentrations en gaz stagnant dans le magasin et la possibilité d'aérer à la fois l'intérieur du magasin et des dépendances. Ces modifications ont entraîné une réduction de 80 % des pics du taux d'émission de phosphine. Des autres résultats sont discutés.