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MOVEMENT OF PHOSPHINE GAS IN UPRIGHT CONCRETE ELEVATORS

C. REED

Department of Grain Science and Industry, Kansas State University, Manhattan, KS 66506 USA [e-mail: carlgs@ksu.edu]

ABSTRACT

Phosphine monitors with electrochemical cells and data-loggers were used to describe movement of phosphine gas escaping from fumigated grain in upright concrete grain bins. The monitors were placed in ground and below ground enclosed areas, outside the elevator, and at bin-top locations to characterize phosphine concentrations. A monitor suspended from the bin roof recorded the fumigant concentration in the air inside the bin and above the grain. Data were taken at each location at 15-minute intervals during 23 separate fumigation events at 15 grain elevators in Kansas, USA. The predominant direction of gas movement was upward through the fumigated grain. In several cases, phosphine concentration in the grain headspace increased and decreased daily, reaching its maximum at mid-morning and its minimum at late evening. The pattern was consistent with the theory that chimney effects produce a generally upward airflow through the grain, with the rate of air movement influenced by the temperature differential between the grain and the ambient air. Enclosed areas at the bin-top level or above were more likely to contain phosphine concentrations greater than 0.3 ppm than were enclosed areas at ground or below ground levels. Significant wind effects were observed in several cases.

INTRODUCTION

In the hard red winter wheat areas of the U.S., wheat often is fumigated with phosphine (PH_3) fumigant as it is moved from one bin to another. Most upright, concrete, elevator bins have several unsealed openings at or near the roof level, 30 to 45 m above the ground. These include the grain fill port and man-holes which often are located inside an enclosed worker area, ventilation ports in the outside wall immediately under the roof overhang, and ventilation ports in the bin wall connecting one bin to another (intervents). In addition, many bin roofs are equipped with aeration or extraction fans. At the ground-level or subterranean parts of the bin, small openings around the slide valve as well as aeration ducts allow exchange of gases with outside air. Some or all of these openings are routinely left unsealed during grain fumigations.

Typically the fumigated grain is considerably warmer than the ambient temperature at some time during the fumigation. This is because warm grain is much more likely to be infested than cold grain and because in North America, most grain fumigant is applied to summer-harvested crops such as winter wheat, which are harvested hot and are typically fumigated in the fall or winter. In tall upright bins of warm grain surrounded by cool ambient air, chimney effects greatly influence the movement of fumigant gases (Banks, 1990). Strong winds are common on the great plains of North America, where the majority of the summer-harvested grain is produced. Strong winds also contribute to air currents within the grain mass in upright grain stores (Mulhearn *et al.,* 1976).

This paper examines how weather conditions combine with physical features of upright concrete bins to influence the movement of PH_3 liberated from aluminum phosphide fumigants. The movement of gas within the mass of stored grain and within the elevator affects both the probability of a successful fumigation and worker exposure to the fumigant.

MATERIALS AND METHODS

Gas monitors (Pac-III, National Draeger, Inc., Pittsburg, PA) equipped with electrochemical cells sensitive to hydrides were placed at various locations in grain elevators prior to grain fumigations. The elevators were located in Kansas within the area 95 to 100° W and 38 to 40° N. The gas monitors had data-recording capabilities and were programmed to record at 15-minute intervals. They were calibrated to zero immediately prior to each use. Monitors with low-level sensors (0–20 ppm), placed in worker areas, were calibrated with certified gas immediately prior to each use. Monitors with high-level (0–500 ppm) sensors, placed inside the fumigated bin, were factory-calibrated as required.

A monitor was placed directly over the fill port of the bin in head-houses or galleries. This monitor usually was suspended about head-high (1.5 m above the floor) against the gallery wall. Other bin-top, inside locations included distributor floors or a second location in a head-house or gallery, if the mechanical fumigant dispenser was located there. A monitor was placed outside at the bin-top level and suspended about 0.6 m above the roof. A monitor was suspended about 1.5 m above the floor from the slide valve wheel at the discharge spout beneath the fumigated bin. At some elevators, the mechanical fumigant dispenser was installed in the tunnel or head-house basement. In such cases, a monitor was placed near the device, about 1.5 m above the floor. At some elevators, monitors were placed outside the elevator to detect PH_3 escaping from the fumigated bin. A monitor was suspended from the roof of the fumigated bin at distances from 0.5 to 1.5 m below the roof. The distances to the grain surface depended on side-to-side location and degree of bin filling and ranged from 0.5 to 3 m.

Monitors were left in place for 5 to 8 days. Preferably, they were placed shortly before the grain to be monitored was fumigated as it was moved to the bin in and around which the monitors were located. The fumigant application was accomplished by elevator employees, and application techniques varied. Data were transferred from the monitors to a computer using Dräger software (Dräger GasVision 4.0). They were graphed and analyzed visually and analyzed by correlation, means, or general liner models procedures, if required.

Air temperature, grain temperature, and the wind speed and direction were recorded during the fumigation sessions. A remote data-logger to which the various environmental sensors were connected was placed outside the gallery near the edge of the flat roof of the fumigated bin. Air temperature and wind data were recorded hourly. Grain temperatures were taken from elevator records or with a sensor connected to the data-logger.

RESULTS AND DISCUSSION

Direction of phosphine movement in the grain mass

Data collected from the sensors in air spaces in and around the fumigated bin provided indirect evidence of fumigant movement within the grain mass. Evidence of the direction and rate of phosphine gas movement within the grain mass is obtained from Fig. 1. In this example all of the fumigant was applied to the grain in the bottom half of the bin. After about 40 h, PH_3 gas began to concentrate in the bin headspace. As the shortest distance between the grain surface and the part of the mass to which fumigant was applied was about 15 m, the gas must have moved upwards at the rate of at least 0.3 m/h after it generated from the fumigant formulation. During this time the mean ambient temperature was 8ºC and that of the grain was 24ºC.

A second indication that the predominant direction of PH_3 gas is upwards through the grain mass is seen in Table 1. In enclosed areas adjacent to fumigated bins, the concentration of PH_3 in the air was consistently and significantly ($p<0.01$) greater above the bin than below it. This is consistent with more constant PH_3 leakage from the fumigated grain into above-bin than below-bin areas of the elevator.

TABLE 1
Percent of all phosphine readings by concentration range in above-bin and below-bin enclosed areas of elevators during grain fumigation

Location	Phosphine Concentration Range		
	0 ppm	0.01 – 1.0 ppm	> 1.0 ppm
Above the bin[a]	27.2	55.3	17.5
Below the bin[b]	71.9	26.1	2.0

[a] Above-bin locations included bin-deck floors of head-houses and galleries, and distributor floors
[b] Below-bin locations included tunnels, staircases, and ladder shafts

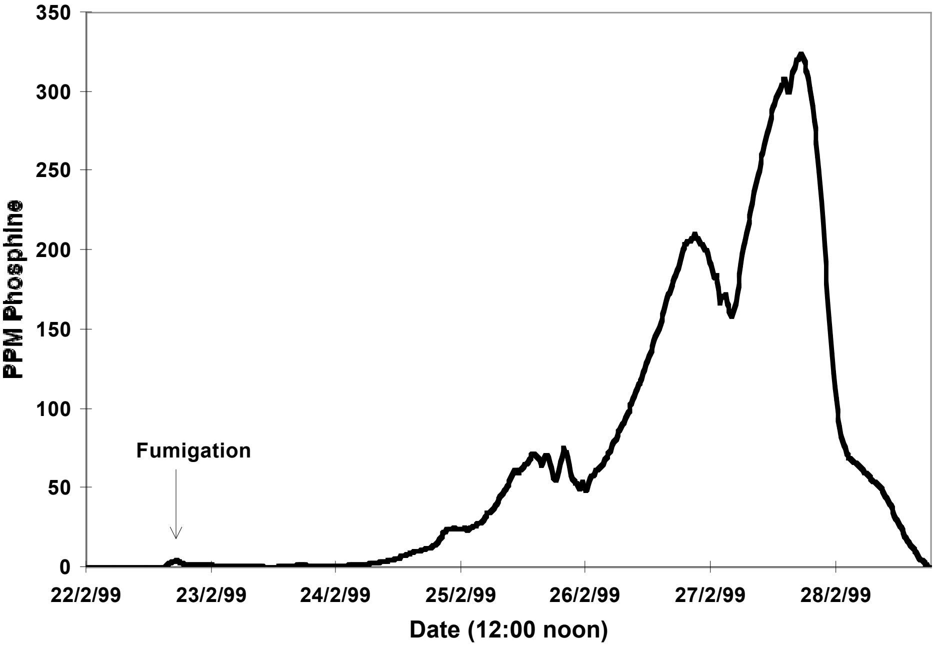

Fig. 1. Phosphine concentrations in the headspace of a bin 39 m tall, 11.2 m diameter when grain was fumigated early 2/23/99 by applying the fumigant only to grain in the bottom half of the bin.

Diurnal patterns

In seven of twenty-four recorded fumigation sessions, a definite diurnal pattern of fumigant concentration and dissipation was observed in the headspace of the bin. Fig. 2 demonstrates this diurnal pattern in cool wheat (16°C). This case was chosen because the diurnal pattern is so clearly observed, without wind effects. It is untypical in that the headspace concentration response lagged 14-18 h behind the ambient temperature changes. In many cases, the apparent response to ambient temperature was almost immediate. In four sessions, significant correlation coefficients were calculated between ambient temperature and headspace PH_3 concentration, with negative r^2's ranging from 0.41 to 0.57. Lag times ranged from 0 to 18 h. The diurnal "mountain-peak" pattern, observed here in the headspace, was demonstrated at the grain surface by Reed and Worman (1993) and at various places within the grain mass by Williams *et al.* (1996).

Wind effects

Based on the conclusions of Mulhearn *et al.* (1976), strong wind passing over the tall upright grain bins will contribute to upward-moving air currents in the grain. This would tend to draw phosphine out of the grain mass into the headspace. However, wind velocity was often negatively correlated with headspace PH_3 concentration. A highly significant correlation coefficient ($p<0.01$) was calculated between wind speed and PH_3 concentrations in three data sets. The r^2's were -0.62, -0.58, and -0.54. In a fourth case, the r^2 of –0.2 was determined to be significantly greater than zero ($p<0.05$). Apparently air entering and exiting the headspace through intervents (from a contiguous bin), outside vents, or aeration ducts produced cross-currents that removed PH_3 from the headspace faster than it moved out of the grain.

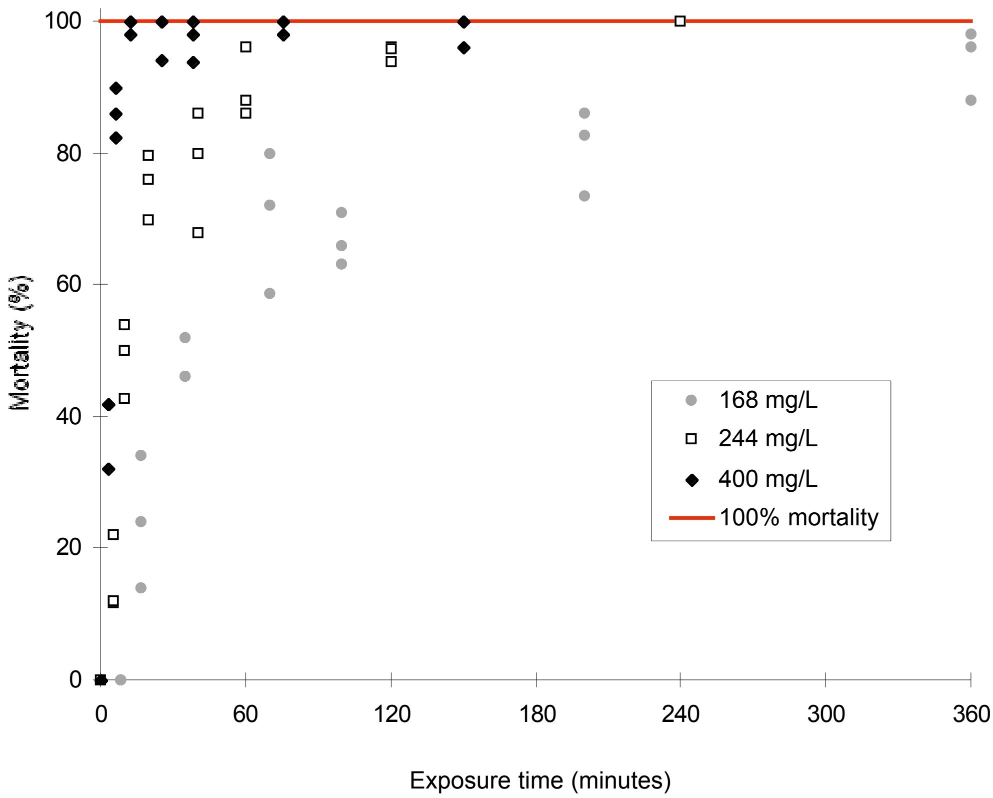

Fig. 2. Phosphine concentrations in the headspace of a bin and ambient temperature during a fumigation.

Phosphine movement in enclosed elevator areas and outside the elevator

Air currents also assist the movement of PH_3 that escapes the bin and enters worker areas. Figure 3 demonstrates this movement in the reclaim tunnel of a country elevator. The pattern of PH_3 concentrations recorded at the fumigated bin was reflected in the readings of a monitor 35 m distant in the same tunnel. The mean elapsed time between five clearly visible events was 2 h with a standard deviation of 0.5 h. Thus the PH_3 moved along the tunnel at the rate of about 0.3 m/min.

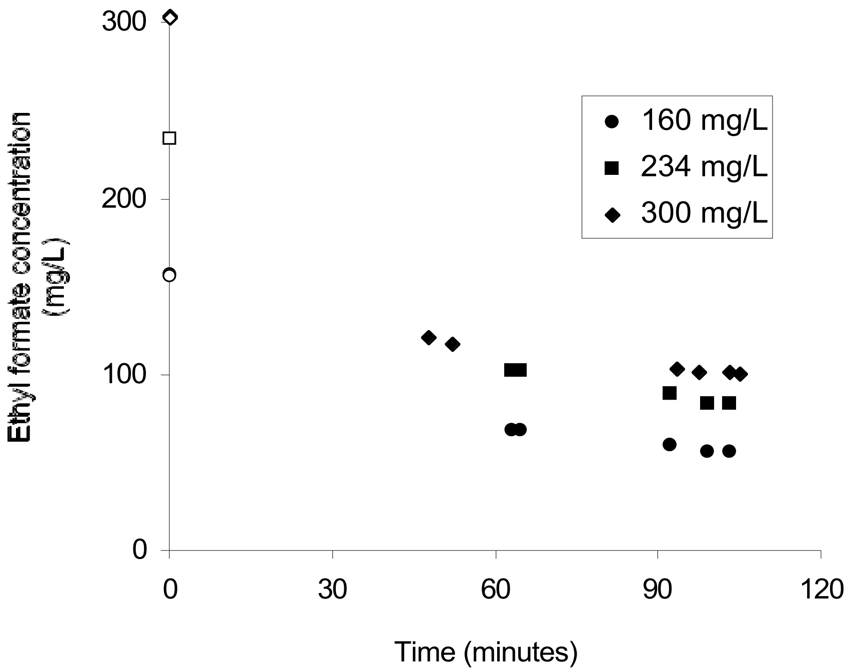

Fig. 3. Phosphine concentration in the reclaim tunnel of a country elevator near the fumigated bin, and 35 m distant.

Outside the elevator, PH_3 escaping from the fumigated grain appeared to become diluted so rapidly as to be virtually undetectable even close to the structure. Of 6,577 concentrations recorded at ground-level locations outside the elevators during fumigations, 69 were greater than zero, and the majority of these were so low as to be within the probable error range of the instrument. None approached 0.3 ppm.

REFERENCES

Banks, H.J. (1990) Behaviour of gases in grain storages. In: *Fumigation and Controlled Atmosphere Storage of Grain: Proc. Int. Conf.* (Edited by Champ, B.R., Highley, E., and Banks, H.J.) Singapore, 14-18 Feb. 1989 96-107.

Mulhearn, P.J., Banks, H.J., Finnigan, J.J., and Annis, P.C. (1976) Wind forces and their influence on gas loss from grain storage structures. *J. stored Prod. Res.,* **12,** 129-142.

Reed, C. and Worman, F. (1993) Quality maintenance and marketing of wheat stored on farms and in elevators in Kansas: description, techniques, and innovations. Bulletin 660, Kansas Agricultural Experiment Station, Manhattan pp 55.

Williams, P, Nickson, P.J., Braby, M.F. and Henderson, A.P. (1996) Phosphine fumigations of wheat in 2500 m^3 steel bins without recirculation facilities. *J. stored Prod. Res.,* **32,** 153-162.