Navarro, S. and Donahaye, E. [Eds.](1993) Proc. Int. Conf. Controlled Atmosphere and Fumigation in Grain Storages, Winnipeg, Canada, June 1992, Caspit Press Ltd., Jerusalem, pp. 503-509.

A DESCRIPTIVE MODEL FOR THE BEHAVIOUR OF PHOSPHINE WHERE VESSELS ARE DAMAGED WHILE CARRYING FUMIGATED GRAIN

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ABSTRACT

The results of toxicological hygienic control of ship atmosphere are presented. These studies were conducted during the transportation of phosphine fumigated grain aboard the Blasco and Novoship bulkers and were conducted with the cooperation of DM (France) Research Fumigation Company and Degesch America, Inc. (U.S.A.).

Phosphine ejection due to depressurization of ship holds, and the distribution of the gaseous cloud formed from such an accident was modeled. In the study on the Novoship the total surface of the "emergency" hole was 250 m^2, the volume of ejected gas was 4,000 m^3 which came from an initial fumigant concentration of 215 ppm. The parameters of the ejected gaseous cloud depended on the ship atmospheric characteristics at the moment of the "accidental" discharge. In this study the length of the cloud on the cargo deck was 70-80 m and the initial concentration of 215.0 ppm of phosphine decreased to 9.2 ppm in 16 min. In the next 8 min the concentration decreased to 2.5 ppm and 45-50 min. after the discharge phosphine was not detected on the deck.

These data have been the basis for the development of recommendations to provide safety for seamen in case of an emergency when fumigated goods are transported by ship.

INTRODUCTION

In 78 per cent of cases, the most serious accidents that occur on ships carrying fumigated cargo arise because of lack of knowledge by the crew of the "behaviour" of this type of load in situations involving damage to the vessel. Under the general heading of "damage", national and international regulations list not only explosion and fire on-board, but also spillage and dispersal of dangerous cargo and leakage from liquid or fumigated loads, (Marshall 1989). This type of situation confronts experts, users, crews, and health and safety inspection bodies with the problem of ensuring the protection of personnel when cargo that is dangerous or potentially hazardous is being carried, not only under normal conditions, but also when an accident occurs (Belobrov, 1990). In spite of the high level of sea-traffic to and from the countries that then formed the Commonwealth of Independent States (C.I.S.) (amounting to more than 30 million metric tonnes annually, there is a lack of scientific and technical knowledge concerning safety in situations involving damage to vessels carrying grain fumigated with fumigants releasing the highly toxic gas, phosphine, (Belobrov 1993). It can, therefore, be said that the constant anxiety of officers and crew in this regard is justified and is expressed in the question they put to those developing new technologies for the fumigation of grain in transit: "How will the air containing highly toxic fumigant in the hold behave if the ship is damaged -- if, for example, the hold ruptures during a ship-to-ship or ship-to-quay collision, if the hatches are ripped off or if any other similarly extreme situation should occur?" It is precisely a concern for human safety in this type of event that provides the basis for the scientific research described here.

For the first time in the history of maritime research, a team comprising representatives of the C.I.S., France, USA, and Germany, has carried out a simulation in which a very large gas cloud was vented from a hold, whose sealing had been breached. This experiment, simulating damage to a seagoing vessel, was performed *in situ* on board the "Marshal Grechko", a ship belonging to the Russian "Novoship" line carrying phosphine-fumigated grain on the transatlantic run between New Orleans and Novorossiisk.

Scope and objectives of the experiment

The objective was to study the mechanisms determining the formation of the phosphine gas cloud when vented from the hold, define the parameters determining its spread throughout the ship, evaluate the risk of life and health of those aboard, and develop concrete measures for elimination of risk by the crew for the promotion of crew safety and for initial emergency procedures.

MATERIALS AND METHODS

To solve the problems involved, the team used techniques employed in meteorological surveys, health and safety inspections, and chemical assays, combined with methods for mathematical modelling of the formation of the risk situation around Holds 3 and 1, as described by the irrational equation $Y = A + B/\sqrt{x} + C/x$; (Y is the concentration of PH_3, A,B,C are coefficients of the equation, x is the time after opening the hold). This allowed the prediction of the time during which dangerous levels of fumigant would be present. With the goal of improving the monitoring accuracy of the contaminated atmosphere, a multi-location sampling procedure was instituted using gas/liquid chromatographic analysis. This allowed the sampling of dozens of air samples in one or two minutes. In order to determine phosphine concentration values, a TSVET type chromatography assay device of USSR origin was used, plus a Dräger gas multi analyser (from Germany), in conjunction with a set of phosphine detection tubes. To monitor the atmosphere without need for human intervention in areas to which access was difficult, the team implemented for the first time a new "BAEGES" model of individual chemical dosimeter developed by Dräger. These analysers were attached to the ship's structure. Their readings were recorded 30 min to 1 hr from the time of initial exposure.

With the consent of the Ship Master, Hold 3 was selected as the test hold. Hold 3 was fumigated by Research Fumigation Corp., USA. Hold 1 served as a reference for comparison . It was loaded with grain fumigated using technology based on the "Phyto-Explo" apparatus and developed by the private French company "Desinsectisation Moderne". It was identical to the test hold with the exception of the air/gas volume, that was smaller by 290 m^3. The basic characteristics of the holds are shown in Table 1.

The difference between the French and American methods of fumigation was not taken into account.

The test was carried out in calm weather with some wind. Ambient air temperature around the ship was +20.3°C and humidity was 63%. Starboard wind speed was in the range of 2.7-4.1 m/sec .

Phosphine (PH_3) was monitored throughout the test period according to a predetermined location schedule (Fig. 1) including all major sampling points on the main deck and main vessel superstructure. Samples were taken at 2 min intervals.

The beginning of the experiment was defined as the time at which the hatches were opened. The opening procedure took 2 min and 18 sec. Sampling was carried out by a special team comprising 7 persons.

Table 1: Basic characteristics of the holds used in the study.

	Hold # 3	Hold # 1
Gas/air volume	4,000 m^3	3,710 m^3
Gas/air temperature	+23.2 ^{o}C	+23.8^{o}C
Phosphine level	302 mg/m^3 (215 ppm)	252 mg/m^3 (178 ppm)
Area of hold breach simulated by opening the hatches	260 m^2	260 m^2
Distance to main vessel superstructure	200 m	226 m

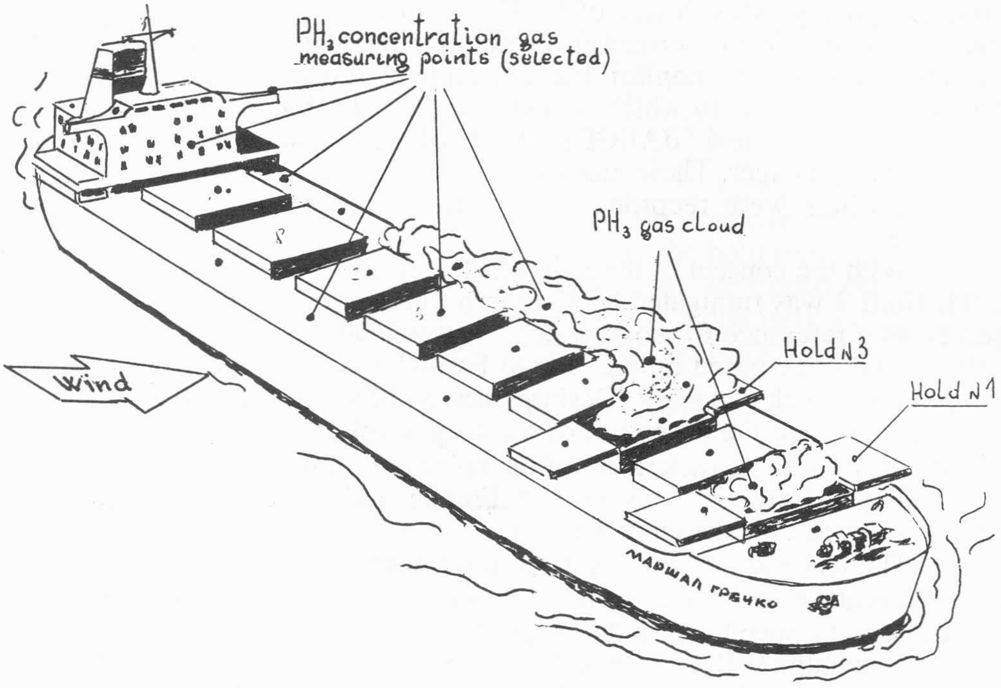

Fig. 1: Position of PH_3 concentration measurement points on-board, and position of fumigant gas-cloud spreading on to main deck.

RESULTS AND DISCUSSION

Data provided by a detailed study of air currents on the main deck show that the extreme complexity of the aerodynamic characteristics of the area around Hold 1 and Hold 3. With a cross wind, the air currents were distributed as follows:

Laminar airflow - on the windward side of the loading deck, over the hold hatches and in the space between the hatch coamings;
Turbulent airflow - on the loading deck and near the leeward side of the holds;
Laminar/turbulent airflow- on the leeward side of the main deck, the forecastle, and the main superstructure.

We were not able to confirm the existence of the "lift-off" airflow effect on the side into the wind. Detailed study of the aerodynamic characteristics of the locations where damage could occur shows that the speed at which the fumigant disperses, the time needed to control the risk-creating situation on board, the parameters of the spread of the gas cloud, and the severity of any contamination of work and accommodation areas, are all dependent on prevailing atmospheric conditions and air currents.

The above mentioned description is confirmed by contamination and chemical assays for phosphine concentrations carried out during the period of the trial. Fig. 2 shows that one minute after the hatches were opened on Hold 3, fumigant concentration values within the hold had dropped from 301.3 ± 12.6 to 103.8 ± 8.4 ppm. Two minutes later, the PH_3 level had dropped to 77.2 ± 2.6 ppm, and after 10 min the PH_3 concentration in the hold atmosphere had decreased by a factor of almost 15. It should be stressed, however, that in spite of the drop in fumigant levels in the holds during the first 10 min following initiation of the "accident", concentration values over the last 20 min dropped more slowly, leading to continuing risk from the toxic effects of the pesticide.

Values read throughout the period of the test at the selected locations on the loading deck indicate that the air/gas cloud covered an area of 923 m^2 and was borne by prevailing air flow toward the starboard side of the vessel and spread over the lee side of the loading deck to a maximum depth of 3 m (hold height) and over a distance of 80-90 m. Given this, it can be said that the highest phosphine values putting the crew at most risk were located for the longest period in the vicinity of the "damaged" hold and Holds 4 and 5, that were next in line down the ship (42.77 ± 8.7, 23.1 ± 1.8, and 12.6 ± 2.2 ppm). The total time during which lethal concentrations were present was 16 min. Dangerous values existed for 24 min, and harmful concentrations for 42 min. One hour later, the presence of phosphine was virtually undetectable.

During this simulation of damage to Hold 1 the volume of the gas cloud was 300 m^3. The risk situation following the opening of the hatches lasted less than 5 min, at which point the phosphine levels had dropped by a factor of more than 250 - a result confirmed by the diagram illustrated in Fig. 2.

Systematic monitoring of phosphine values on the opposite side of the ship, on the poop deck and aft deck, as well as in living and working areas of the main superstructure, did not indicate any phosphine presence. This suggests the desirability of a safety zone of 30 m between the vent location (i.e., hold blow-out) of the toxic agents and the main vessel superstructure.

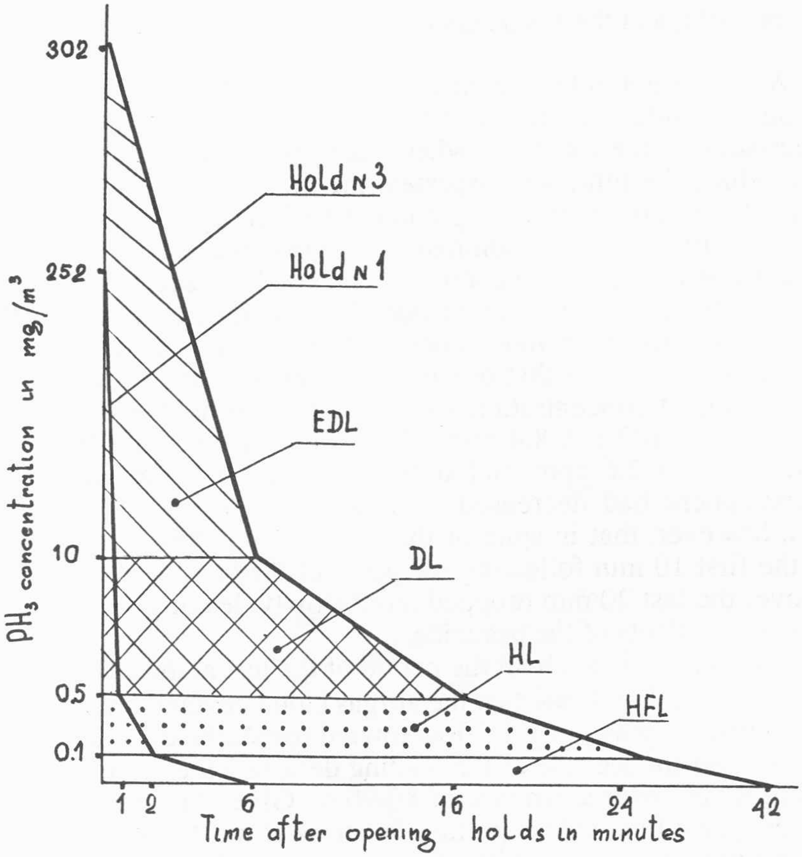

Fig. 2: Changes in PH3 concentrations of fumigant gas-cloud after opening of holds 1 and 3.

EDL - extremely dangerous levels
DL - dangerous levels
HL - harmful levels
HFL - harmless levels

CONCLUSIONS

1. The development of a risk situation involving a breach in the integrity of a hold containing extremely toxic gas (PH_3) is linked directly to the speed

and direction of air flow, the time taken for the hold to rupture, the area of the breach, and the volume of the fumigated headspace contained in the hold.

2. Data obtained in this trial do not allow us to confirm the hypothesis maintaining that the gas cloud is "lifted off" on the side of the vessel into the wind, which, were this to occur, would eliminate any risk to the health and safety of the crew.
3. Where damage involving a breach in the sealing of a hold containing large volumes of fumigant gases is sustained, the real level of risk to the vessel's crew increases the shorter the distance between the main vessel superstructure and the hold involved.
4. Data obtained in this trial enabled us to develop a number of preventive recommendations to enable ship's officers to get emergency situations under control, to forecast emergency situations with a high degree of certainty, and to improve the safety levels and effectiveness of emergency and repair work. All these will contribute to promoting the safety and well-being of all personnel on board.

REFERENCES

Belobrov, E.P. (1990) Medical and technical measures on safety in transport of grain treated with phosphine. Proceedings of the All-Union Conference, Moscow. pp. 209-210 (In Russian).

Belobrov, E.P. Vacquer, B. and Zakladnoy, G. (1993) Modern technologies for grain fumigation during sea-shipping. 2nd Int. Symposium on Maritime Health. Antwerpen. p. 51.

Marshall, V.C. (1989) Major chemical hazards. Ellis Harwood Ltd., New-York, NY. pp. 112-123.