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ORIGINAL ARTICLE

Fumigation Monitoring and Modeling of Hopper-Bottom Railcars Loaded with Corn Grits

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Abstract

Introduction Bulk railcars are a common method of moving commodities in the USA. Allowances are given for the practice of treating railcars with fumigates during transit because the routes are limited access and not on public roads. Recent technology has become available for monitoring phosphine gas (PH_3) fumigation on railcars which logs the phosphine concentration and temperature of the test point in the railcars.

Materials and Methods Two hopper bottom railcar shipments of corn grit were monitored for phosphine during 8-day transit from mill to processor. Several phosphine-sensing units were used in each railcar and spaced across the top layer. Mathematical modeling of the railcar fumigation was carried out using computational fluid dynamic software. Because access to lower depths in the railcar was not available, supplement experiments were performed with small columns of corn grits (2.5 m height x 0.55 m diameter) to test for phosphine at greater depths. Also, in the grain columns, bioassays of both phosphine susceptible and resistant, adult *Rhyzopertha dominica* (F.), lesser grain borer, and *Tribolium castaneum* (Herbst), red flour beetle, were included at the 0 cm, 25 cm, and 60 cm below the surface.

Results The phosphine concentrations in the railcar headspace varied with time with phosphine spiking over 1600 ppm and gradually settling to over 300 ppm at the end of the 8 days. Total gas dosage was estimated as concentration*time (CT) over the 8 days as 115,000 and 125,000 ppm*h at the top of each railcar. The supplement grain column fumigation tests found significant phosphine penetration into the column at 2 m depth with ~380 ppm after 2 days which reduced to ~260 ppm after 8 days, and all insects, at all locations, were dead after 8 days. The CFD simulation models were shown to provide estimates of the phosphine concentration and distribution which matched well with the observed data, validating the CFD approach as a useful tool.

Discussion The simulation models were shown to provide estimates of the phosphine concentration and distribution which matched well the observed data, validating the CFD approach as an efficient tool for future planning and analysis of similar fumigations.

Keywords Phosphine · Lesser grain borer · Red flour beetle · Computational fluid dynamics · Wireless sensors · Mathematical modeling

Introduction

United States (US) agriculture produced ~580 million metric tons of grains and oilseeds in 2021 and ~556 million metric tons in 2020 (USDA-NASS, 2021). These commodities were transported between locations for storage, processing, or export using trucks, railcars, and barges. Transportation by rail accounted for ~25% of total US grain transport (Association

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of American Railroads, 2021). Rail is the predominant method for long-distance transport of grain, with an average hauling distance for corn and wheat railcars being 1,129 and 1,037 miles (1,817 and 1,667 km), respectively in 2009 (Prater & Sparter, 2013). US class 1 railroads moved ~ 1,500,000 carloads of grains and oilseeds and moved ~750,000 carloads of processed-grain products in 2021. Corn had the highest rail volume moved with ~691,000 carloads while wheat had ~305,000 carloads (Association of American Railroads, 2021). Bulk grain and flour are typically shipped by rail in hopper bottom cars. These railcars have openings in the top for loading commodities and sloped floors so commodities can unload through doors in the bottom of the car. Boxcars have flat floors and are used for shipping pallets of packaged grain and grain products and typically have sliding doors on each side of the car to facilitate loading and unloading.

During storage and transportation through these supply and distribution channels, infestation by stored product insects could potentially occur. Insect infestations can lead to contamination and reduced quality and have a significant economic cost to the food industry for controlling these pests (Agrafioti et al., 2020a, b; Brabec et al., 2021). A common pest suppression method for bulk grain or packaged grain-based products is fumigation with phosphine. This fumigant is widely used in the US for the treatment of rail cars during transport because it is relatively inexpensive, easy to apply, and is considered a chemical residue–free treatment. Although phosphine can be applied directly as a gas, railcars are commonly treated with solid tablets and applied within fabric blankets or sachets that react with moisture in the air to release phosphine gas. Phosphine treatments usually require several days of confinement to provide maximized control of insects, and it is important to maintain an adequate gas concentration during the treatment period (Agrafioti et al., 2018; 2020a; Brabec et al., 2021). The duration of the treatment depends on factors such as gas concentration, temperature, and phosphine-susceptibility of the insect species. Inadequate concentration-time (CT) due to low gas concentrations or poor gas containment can lead to minimal control of the insect populations and the development of insect resistance. Resistance to phosphine is an important global issue and management of resistance is critical in maintaining phosphine as an effective post-harvest treatment (Nayak et al., 2020).

The US grain industry commonly fumigates with phosphine rail shipments during warm seasons. These treatments have two potential benefits: to eliminate any insects that might be present in the material when loaded into the cars and to prevent insects from infesting the material during transport. However, little information is available on the efficacy of these treatments, in contrast with other storage methods, such as containers and silos, where phosphine distribution and the concomitant insecticidal effect have been quantified (Agrafioti et al., 2018, 2020a, b, 2021). There is potential variation among fumigation events due to varied railcar types and their structural integrity and gas-holding ability, environmental temperatures, airflow across the railcar during movement, and duration of transport. Historically, it has not been feasible to monitor gas concentrations during railcar shipments due to the inaccessibility of the railcars during transit. Recently, wireless phosphine measurement devices have become commercially available. These electronic devices can be deployed on individual railcars and collect data on gas concentration and temperature and exposure time that would provide information on treatment effectiveness and help guide ways to improve efficacy (Agrafioti et al., 2020a; Brabec et al., 2019).

Different mathematical models and computation fluid models have been developed for phosphine fumigation studies by many research groups throughout the world. Isa et al. (2016) worked with mathematical models that could predict fumigant distribution in leaky grain silos which used fan-forced fumigation. Agrafioti et al. (2020b) combined the distribution of phosphine within specific fumigated structures with insect mortality models. Also, Agrafioti et al. (2021) modeled the distribution of phosphine gas in 20 and 40 ft (6.1 and 12.2 m) metal shipping containers, illustrating the parameters that may affect gas distribution. Apart from silos and shipping containers, there are several reports for other types of storage structures, such as food processing facilities (Chayaprasert et al., 2006), bulked grains (Plumier & Maier, 2018), and bunkers (Boac et al., 2014). To the authors' knowledge, there was still inadequate information regarding modeling the distribution of phosphine in railcars. In this context, the major objective of this study is to collect fumigation data from railcars during transit in commercial applications, for which there are not many data available. In addition, a secondary objective of this work was to model a hopper bottom railcar loaded with product and estimate fumigation outcomes after 4–8 days of transit.

Materials and Methods

Hopper Bottom Railcars and Fumigation

Hopper bottom railcars were being used at a corn processing facility to ship corn grits to customers. A hopper bottom railcar has the capacity to carry over 95 tons of products. The railcars were 17.8 m long × 4.8 m height × 3.4 m wide. Each railcar is configured to have three hoppers with partitions separating each hopper. The shipments of corn grits originated from central Iowa, USA. The trip took over 8 days until the railcar reached its final destination. The weather data was retrieved by the weather service for the days and locations of the railcars during transit. The weather data was used with the phosphine distribution modeling to adjust the phosphine concentration with the varied environmental temperatures and solar radiation. A railcar was monitored in August 2019 and a second railcar was monitored in September 2019.

Each railcar was given a dose of tablets as supplied with the pre-packaged product (PHOSTOXIN®Tablet Prepac, Degesch American, Richmond, VA, USA). Each pre-pack contained three strips of tablets (Fig. 1a). Each strip held 11 tablets within a polymeric fleece fabric; thus, the residue from the reacted phosphine tablets remained packaged and later removed. All three strips are used in one railcar for a total of 33 tablets. Each tablet weighed ~3 g and released ~1 g of phosphine gas thus a total of 33 g of phosphine gas was generated. The three fabric strips were equally spaced across the top before the top hatches were closed (Fig. 1b).

Fumigation Monitoring

Monitoring railcars was accomplished using Centaur phosphine sensing electronics and software operating in data logging mode (Brabec et al., 2019). Each sensing unit is powered by a battery. The sensing units measure phosphine concentration and temperature and time. Each railcar had four sensing units deployed and spaced along the top of the railcar. However, for the second railcar, data transfer issues were encountered and only two of the units provided data from that trial. The monitoring system also requires a communication gateway/router for the sensors to transfer measurements to the internet database and software. The communications with the sensing units must be initiated after each sensing unit is turned “On” and while the sensors are within ~100 m of a communication gateway. Then, the cloud-based software can communicate with the sensors with either a computer or cell phone. Menus in the software can be accessed for setting up process details and communication frequency. Once the units are placed into the railcars and out of range of the gateway, the sensors can continue to collect in data logging mode and store over 80 data events. These sensing units were set to record data every 4 h and had the capacity to monitor fumigation for about 14 days. After the railcars reached their destination, local staff would retrieve the sensing units and turn them “Off.” Then, the units were placed in sturdy shipping cases and sent back to the US Department of Agriculture – Agricultural Research Service (USDA-ARS) lab in Manhattan, KS, USA, where the communication gateway was located. For downloading the data, the Centaur software was modified, and the communication frequency was changed from every 4 h to every 5 min. Then, the sensors were turned “On,” and the software would automatically download the stored 80 data events. A portion of data was transferred after each 5 min. Many communications cycles were required before all the stored data was retrieved to the cloud-based storage and downloaded to the local computer. The accuracy of the sensors has been successfully evaluated by Brabec et al. (2019).

Phosphine Penetration into Corn Grits

The fumigation monitoring with the electronic sensing units was limited to data at the top of the railcar. Access deeper into the corn grits was not available during the railcar fumigations. Sub-experiments were done to estimate phosphine distribution deeper using columns of corn grits stored in long tubes fabricated from three barrels (Fig. 2). These tests were conducted at USDA-ARS. The two columns were each comprised of three stacked barrels and had a total height of 2.4 m and a diameter of ~58 cm. Each column contained ~500 kg of corn grits and was filled to ~18 cm of the top. Two levels of phosphine were tried, and each treatment was repeated three times. A high level of phosphine was generated by using two phostoxin pellets (0.6 g × 2) (Degesch American, Richmond, VA, USA) which were placed at the top of the corn grits on a damp paper towel. A low level of phosphine was generated by using a single phostoxin pellet (0.6 g × 1). Two phosphine

Fig. 1 Photo of phostoxin prepack (**a**) and photo of top of railcar (**b**) with corn grits for shipment and the Centaur sensing units were placed on the top in red bags

Fig. 2 Columns of barrels used to test potential phosphine distribution deeper into the corn grits. The columns had air sampling ports located vertically at every 40 cm from the top of the corn grits

sensing units were placed on top of corn grits. Also, each column had five air sampling ports inserted into the side and space vertically every 40 cm. Phosphine concentrations were measured at the air sampling ports using a Drager X-am 5000 (Drägerwerk AG & Co. KGaA, Germany, www.draeger.com) handheld gas-meter along with the Drager Air Pump X-am 1/2/5000. The vertical air sampling ports were measured after 2, 4, 6, and 8 days of treatment. The barrels were purged with fresh air for 40 min after each trial using compressed air.

Insect Bioassays

Two species of insects were used in this study, *Tribolium castaneum* (Herbst), red flour beetle (Coleoptera: Tenebrionidae), and *Rhyzopertha dominica* (F.), lesser grain borer (Coleoptera: Bostrichidae). For each insect species, two different strains were used, a phosphine resistant and a phosphine susceptible. For *R. dominica*, 4-to-8-week-old adults of a susceptible (laboratory strain maintained in culture > 30 years at the USDA-ARS in Manhattan, KS, USA) and phosphine-resistant (field strain collect in Enid, OK, USA in 2009) strains were used. For *T. castaneum*, 2-to-5-week-old adults of a susceptible (laboratory strain maintained in culture for > 30 years at the USDA-ARS in Manhattan, KS, USA) and a phosphine-resistant (field strain collected in Enid, OK, USA, in 2009) strains were used. *Rhyzopertha dominica* was reared on organic wheat and *T. castaneum* was reared on organic whole wheat flour and brewer's yeast in a 95:5 ratio respectively. Susceptible strains were reared in a Percival incubator (Perry, IA, USA) at 27°C and 65% relative humidity (r.h.) in continuous darkness and resistant strains were rear in a separate walk-in environmental chamber (Percival Scientific, Inc. Model CTH-811, Perry, IA, USA) at 27°C and 65% r.h. in continuous darkness.

All beetles used in experiments were collected and placed into plastic bioassay tubes (10 cm long and 1.2 cm inner diameter) with the ends sealed with corks and a nylon string to facilitate extraction from the corn grits. Ten 0.5-mm holes and four 1.0-mm holes were drilled into each tube to facilitate gas penetration. In each tube, 20 individuals of a given species and strain, were added with ~250 mg of respective diet approximately 24 h prior to testing. There were three tubes per treatment barrel for each insect species and strain combination or 12 tubes total per barrel per treatment. The bioassay tubes were inserted into the corn grits at one of three locations using a push-rod. The first location was the top of the corn grits at a depth of 2 cm from the top. The second location was 25 cm, and the third location was 60 cm from the top. There was one set of four tubes, which included each insect species and strain combination, which was used for the control bioassay and for each trial. The tubes were inserted 2 cm into the corn grit and located in an untreated barrel.

After each fumigation trial, the tubes were collected and taken into the laboratory and observed under a stereo microscope for the number of beetles alive, affected, or dead. Affected adults are those on their backs and unable to right themselves, uncoordinated walking, legs, and antennae twitching, or limited responses when gently prodded with a fine-tip brush (Scheff et al. 2019). Alive adults were fully mobile and dead adults did not respond to gentle probing by a fine-tip brush. After initial observations were taken, adults were transferred to a filter paper-lined arena, along with the diet from the bioassay tubes and placed into an environmental chamber at 27°C and 65% r.h. in complete darkness. Adults were observed 24 h post fumigation for the number of alive, affected, and dead adults. Means and standard errors (SE) were calculated for the percentage of live, affected, and dead adults after fumigations.

Modeling of Railcar Fumigation

Modeling of the railcar was accomplished using the computational fluid dynamic (CFD) model developed by Centaur Analytics, Inc. CFD is a branch of fluid mechanics that uses numerical analysis and data structures to predict and analyze fluid flows, temperature, heat, and mass transfer events. Recent studies published by Agrafioti et al. (2021) and Agrafioti et al. (2020a) presented a CFD model that was appropriate for phosphine fumigations and validated its performance in treated silos and shipping containers. Detailed descriptions of the model equations for air velocity, temperature, phosphine concentration, phosphine sorption, and their implementation in porous media were presented. The model (as described in detail in Agrafioti et al., 2020a) requires different inputs for each grain type. Specifically for the simulation of corn grits, the porosity and tortuosity values were 0.4 and 1.5, respectively. The sorption coefficients were set to F=0.18, K_{bind}=0.03414, and $S_{\mathrm{sorp}}K_{\mathrm{f}}$=0.0075. Also, the phosphine concentrations were used to estimate the mortality of stored-product insects based on an earlier developed insect indicator function (Collins et al., 2005, Agrafioti et al., 2020b). For the present work, the first railcar was studied using the CFD methodology (Fig. 3), aiming to validate the accuracy of the model with railcar sensor data and analyze the fumigation process in greater detail.

Boundary Conditions

For improved simulation predictions, the weather/ambient conditions during the transit of the first railcar were considered as boundary conditions to the CFD model. An implementation of the boundary conditions to the model is described in Agrafioti et al. (2020b). In Fig. 4, the time series of ambient temperature, wind velocity, and solar radiation are presented which were used as part of inputs for the railcar fumigation simulation.

Meshing

To solve the transport equations of the model, a discretizing procedure (meshing) of the complicated railcar geometrical (Fig. 5) was performed. For this study, the mesh used was structured, and all cells were designed as hexahedra, thus ensuring better modeling accuracy. Furthermore, the mesh resolution was increased near the walls to properly capture large gradients. The total number of grid cells was ~ 410,000. The average grid cell represented ~500 cc of volume within the railcar (4.8 m height × 3.4 m width × 17.8 m long).

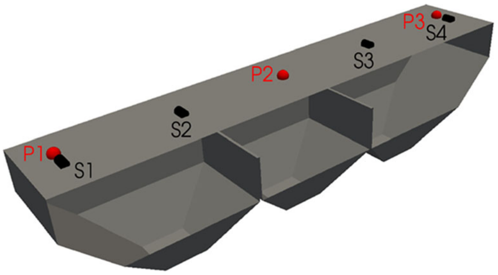


Fig. 3 The three-dimensional model of the hopper car considered in this work. The rail car had three hoppers divided by two partitions (bulkheads). Black cylinders depict the location and the names of the wireless phosphine sensors whereas the position of the phosphine tablets is shown in red spheres

Phosphine Gas Release

To account for the phosphine gas release in the simulation model, the reaction of the aluminum phosphide tablets was a non-linear model (Fig. 6). The phosphine gas model is inserted in the computational domain as a source term in the respective mass transport equations. The tablets are modeled as completely reacted after 4 d with 90% of the gas produced after 2.5 days. This does not show temperature variations and effects.

Results

Railcar Monitoring Data

The top layers of the corn grits were monitored for over 8 days. Both hopper-bottom railcars held phosphine gas at the top for the entire eight days (Fig. 7). In one railcar, the phosphine was generated early and during days 1–3. For the other railcar, the phosphine generation was delayed a bit and had more generation during the middle of the cycle. Both railcars had spikes of phosphine generation which reached over 1600 ppm. By the end of the trip, the phosphine concentration had decreased to around 200–300 ppm. The concentration and time data were combined to calculate total C*T values for the entire exposure period. The averaged C*T values were 115,000 ppm*h for the top layer of the first railcar and 125,500 ppm*hr for the second railcar. Brabec et al. (2021) found C*T values over 50,000 ppm*h would kill both susceptible and resistant lesser grain borers in bioassays in wheat. The C*T values in these hopper bottom railcars were significantly higher. However, a measurement at the top of the commodity does not necessarily equal the phosphine concentration within the bulk commodity. Brabec et al. (2019) found during a fumigation event with a 3.7-m-deep bin of wheat, the top of the bin had over 2000 ppm of phosphine while the middle of the bin had only 4 ppm after 36 h. Gas distribution within the railcar was only by natural convection air currents as produced by varied daily environmental conditions and movement of the car. There were no fans involved for moving the air through corn grits to help distribute more uniformly the phosphine gas.

Phosphine Penetration Test Results

The railcars had phosphine measurements taken at the top of the corn grit. For estimating the phosphine penetration in the bulk, supplemental experiments were performed that recorded gas concentration at depths up to 2 m below the surface. Phosphine gas was detected at a lower depth even after 2 days of treatment. As seen in Fig. 8a, although the phosphine at the top of the corn grits was over 1200 ppm, the phosphine in the

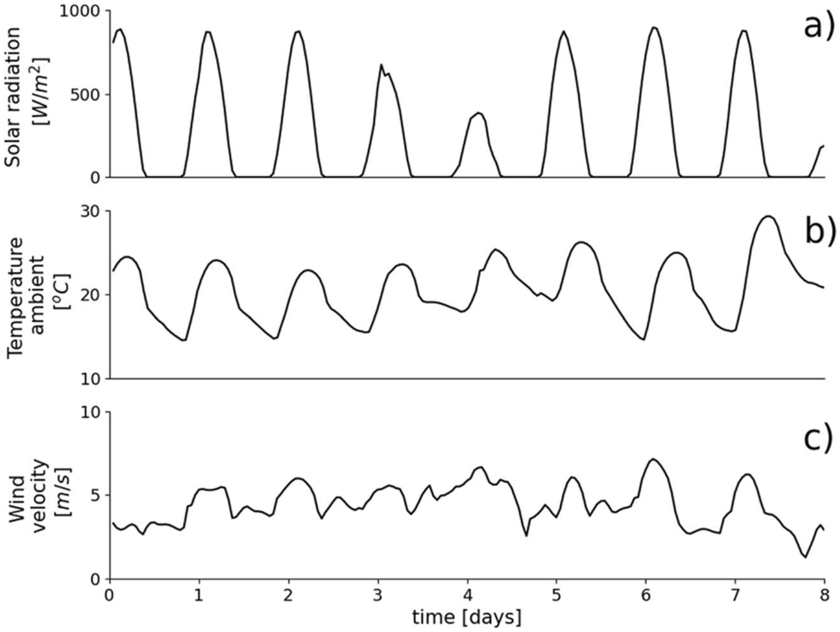


Fig. 4 Time variation of ambient conditions for the CFD model: **a** solar radiation, **b** ambient air temperature, and **c** wind velocity

corn grit was a gradient from ~600 ppm at 25 cm down to ~350p pm at 2 m. After 4 days, the gas concentration in the bulk was level at ~380 ppm for the high treatment and ~180 ppm for the low treatment. Then after 8 days, the phosphine concentration was about a level at 300 ppm for the high treatment verse ~120 ppm for the low treatment at 2 m depth. A rough estimate of the total phosphine concentration*time (C*T) was ~28,000 ppm*h and ~14,000 ppm*h for the high- and low-dosage treatments at 2 m, respectively. These levels of dosages are strong and fatal for most adult stored product insects. For this particular grain product, the corn was ground through roller mills which would kill the internal insects in the bulk. Also, the material is being moved and handled with conveyors and elevator legs which would also disrupt any insect activities. It is assumed the corn grit did not contain any live insects during loading. So, the main concern would be the potential migration of insects into the railcar or potentially infested residue although the railcars were dry-cleaned prior to loading. The railcars are 4.8 m tall which include some clearance at the bottom and above the tracks and some settling of the corn grits at the top during transit. If the clearance above the rails is ~1 m and the corn grits settled ~1 m, then the bulk would end up being ~3 m deep. There was a similarity in the phosphine concentration measurements at the five test points including 25-, 70-, 110-, 145-, and 200-cm-deep locations. Our assumption would be that the remaining corn grits below our lowest test point would be near the value of our lowest test point.

Bioassay Results at Three Depths

For these experiments, which included high and low phosphine levels and three replications, 112 bioassays were observed with 72 of the bioassays exposed to phosphine gas. Among all insect species and strains and all bioassay depths, there was 100% mortality for those treated with phosphine gas for the 8-day trials. In contrast, there was no control mortality in the untreated barrel for the susceptible and resistant *T. castaneum* adults. The average mortality of the control phosphine-susceptible *R. dominica* strain was less than 4%

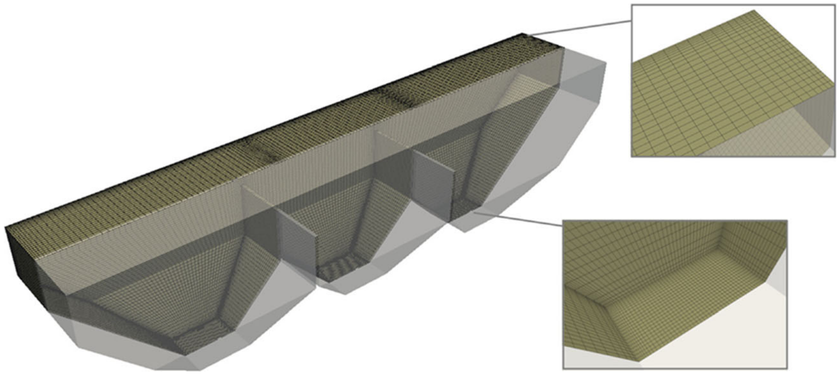


Fig. 5 The mesh used for the simulation of the rail car. The mesh resolution is increased near the walls. The slice view reveals the two partitions and their respective mesh

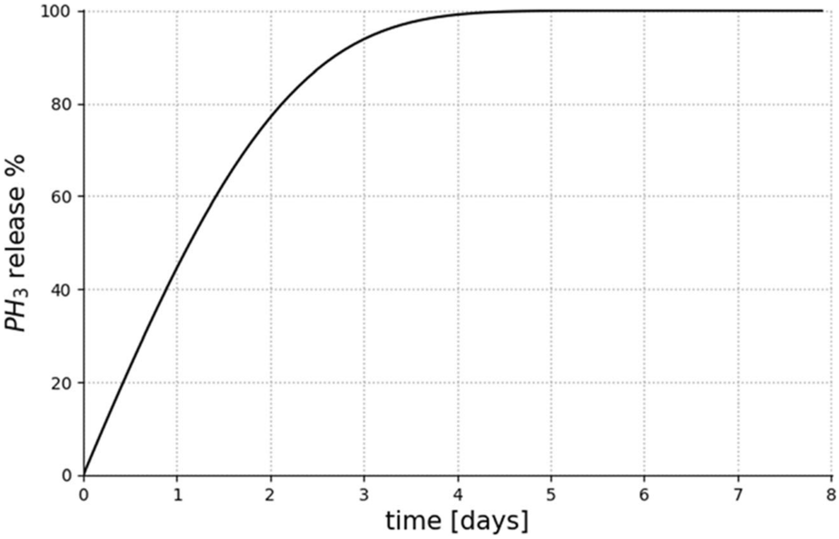


Fig. 6 Time evolution of the aluminum phosphide tablets releasing phosphine gas (as a percentage of the total quantity available). Data provided by Detia Degesch GmbH. *Note*: PH_3 is the chemical compound syntax for phosphine

and the control phosphine-resistant strain was less than 9% among the fumigation trials.

A subsequent trial was conducted which included control bioassays in each column and all locations, but no phosphine gas was introduced into the columns. Among all locations and in both columns, the average mortality of control *T. castaneum* susceptible and resistant beetles was less than 1%. The average mortality of phosphine-resistant *R. dominica* was less than 2% among all locations and barrels. However, the average mortality of phosphine-susceptible *R. dominica* adults was 60.8 ± 18.3 % among all locations column A. It should be noted that in column B, there was no mortality of the phosphine-susceptible control *R. dominica.* In the earlier trial, column A was treated with a high dose of phosphine while column B was treated with a low dose. After the 8-day trial, the columns were vented for over 40 min, and 24 h later, the columns were vented a second time for another 10 min. Potentially, some small amount of residual phosphine might have been degassed from the corn grits. This degassed phosphine would have been higher in column A. As a result, there was some mortality of the control phosphine-susceptible *R. dominica*.

Railcar Fumigation Modeling

Model Comparison with Wireless Sensor Data

The simulation process yielded the progress of phosphine concentration for the entire fumigation treatment as well as predictions of insect mortality. To ensure the accuracy of the model in predicting the phosphine concentration, a comparison is made between railcar sensor data and the CFD model

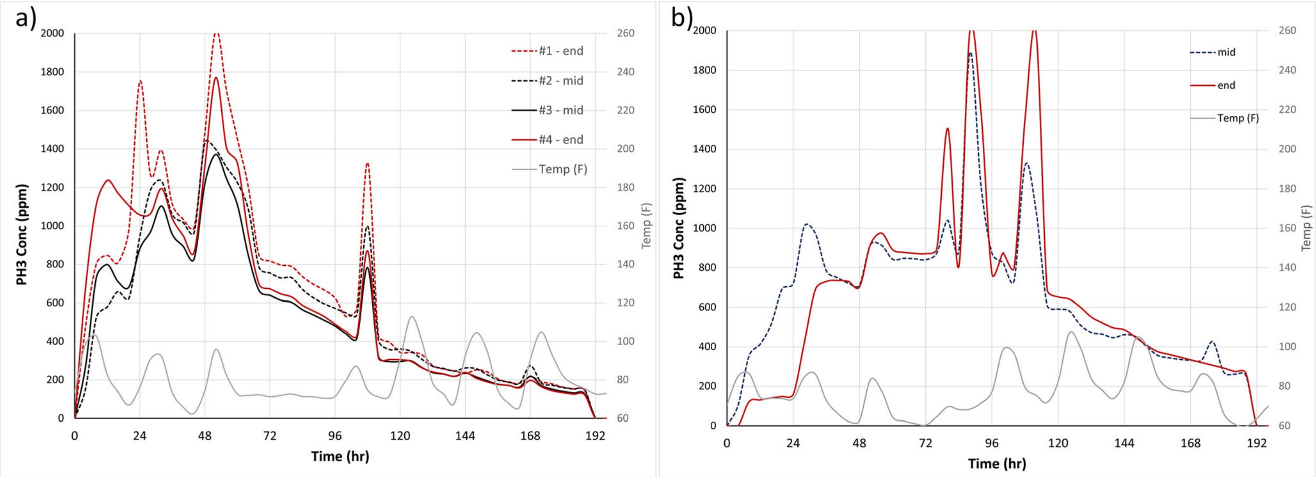


Fig. 7 **a**, **b** Fumigation monitoring data from two hopper-bottom railcars. These hopper-bottom railcars were monitored during the summer of 2019. The railcar/chart on the left had four phosphine sensing units; #1-end, #2-mid, #3-mid, and #4-end. The railcar/chart on the right had two phosphine sensing units; one in the middle and one at the end. Previously, Fig. 3 displayed the approximate location of the sensors. Temperature data was overlaid at the bottom of each chart (gray line) showing daily temperature variations

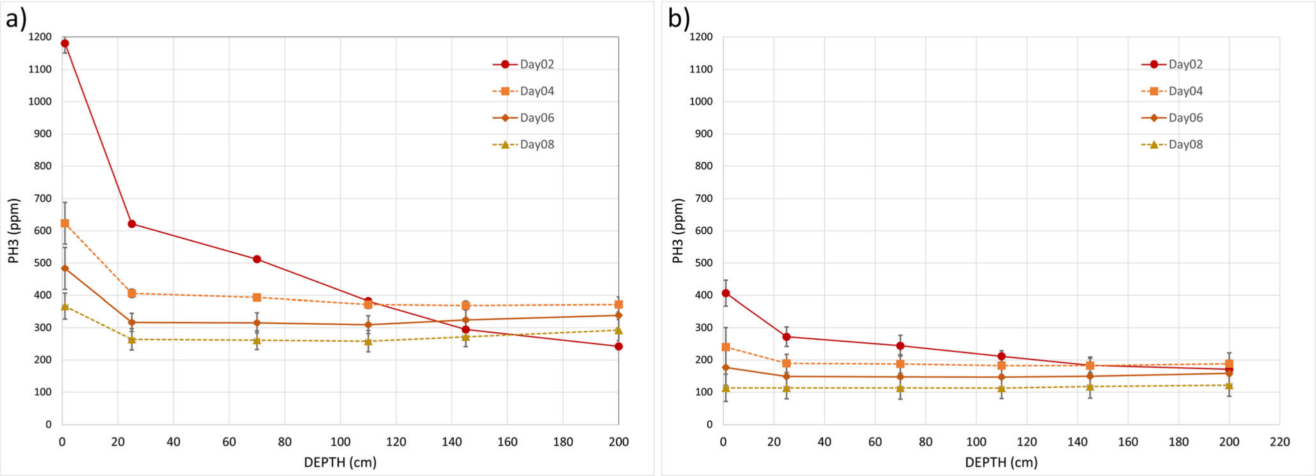


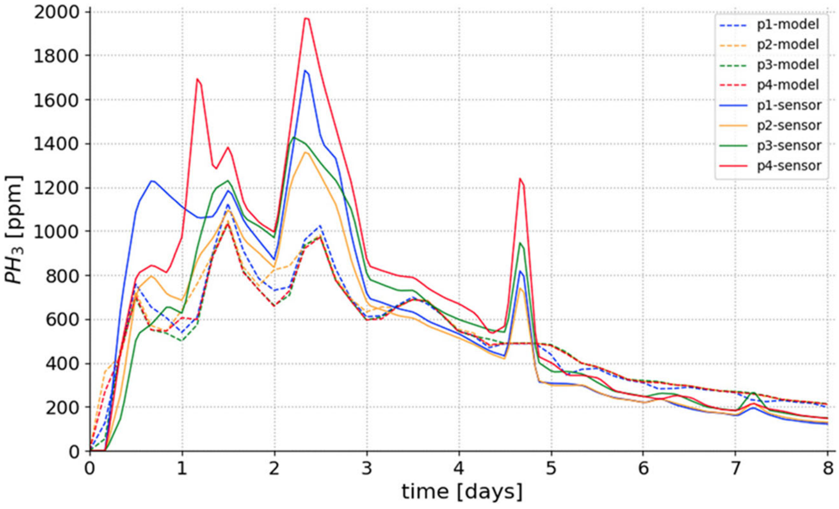
Fig. 8 a, **b** Phosphine concentrations were measured during supplemental experiments and in columns of corn grits. Each column had six air sampling points space vertically every 40cm. The left figure was the high phosphine treatment. The right figure was the low phosphine treatment. The individual lines represent phosphine concentration data taken after 2, 4, 6, and 8 days of treatments

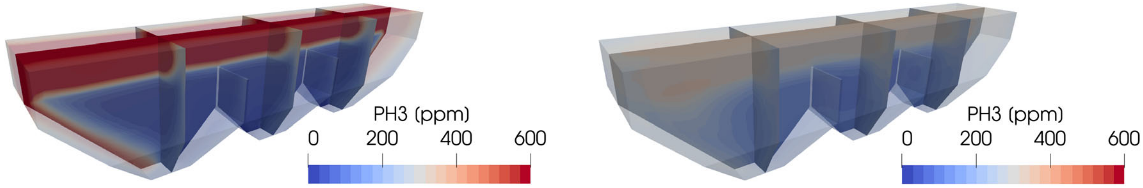
for the respective sensor positions (Fig. 9). Sensor data shows that the phosphine concentration had similar values for all positions, due to their position in the headspace. The four sensors across the top and in head space good gas retention and distribution. The general trend of railcar sensor data shows that the concentration is rapidly increasing in the first 24 h, reaching maximum values after 2.5 days. This was followed with decaying concentrations through the 8th day. In addition, there were three local maxima which we attributed to the diurnal variation of weather temperature and solar radiations. Even the peak phosphine events were determined, since the computational model considered variations from the ambient solar and air temperatures. There was some discrepancy seen with the amplitudes between the CFD model and railcar sensor data. For instance, after 1.5 and 2.5 days, the model estimated maximum phosphine peaks at ~1000ppm. The sensors measured concentration peaks at the same time point, but the measured concentrations were higher: ~1200 and ~1500ppm. After 3 days of treatment, the model and the sensor data were more closely aligned. To quantify these discrepancies, the median absolute error was determined over the 8 days and was equal to ~89 ppm.

Phosphine Concentration Predictions within the Corn Grits

Based on the results of the previous section, the overall performance of the CFD model was considered satisfactory, ensuring the validity of the phosphine concentration predictions for the entire container space as the ones presented in Fig. 10. These models present the spatial distribution of phosphine concentration in a three-dimensional view (top) and lateral cross-section views (bottom) at the end of the second and sixth day respectively. Early, the phosphine is concentrated in the headspace of the railcar, while later, the phosphine is more evenly distributed throughout the commodity. Nonetheless, there is some non-uniformity in the lower regions of the rail

Fig. 9 Phosphine concentration (ppm) comparison of railcar sensor data (solid lines) vs. CFD simulation predictions (dashed lines) at 4 positions inside the hopper car





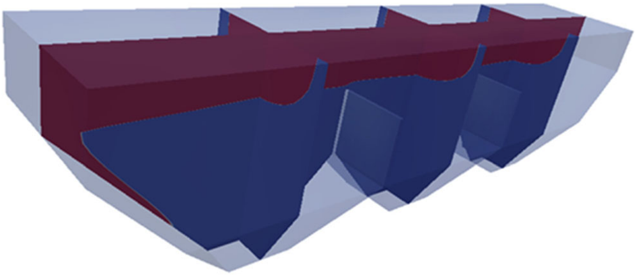
(a) phosphine after 2-days (b) phosphine after 6-days

Fig. 10 Estimated phosphine concentration profiles after 2 days (**a**) and 6 days (**b**). Three-dimensional models of mid-sections of the railcar. The concentration levels can be interpreted with the color legend video link: https://youtu.be/b0p20S9zbxg

car, particularly between the side walls and the core of the corn grits. This effect may be attributed to the air movements caused by the temperature differences between the ambient and grain. These air movements increase the penetration of the phosphine gas near the side walls of the railcar.

Predictions for Insect Mortality

Since the model can provide the spatial profile of the phosphine concentration throughout the fumigation process, the insect mortality (*R. dominica* and the sawtoothed grain beetle, *Oryzaephilus surinamensis* (L.) (Coleoptera: Silvanidae)) can be predicted based on the model described in Agrafioti et al. (2020a). Although there were no bioassays inside the railcar to compare with, the insect mortality model has been validated in similar fumigation processes before (e.g., silo fumigations, Agrafioti et al., 2020a) and shipping containers (Agrafioti et al., 2021). Figure 11 presents insect mortality profiles at the end of the fumigation process. On top, a three-dimensional view (with transparency) is presented, whereas, at the bottom, a three-dimensional view with cross-sections is visible. The red color indicates zones with 99.9% insect (*R. dominica*) mortality. According to Fig. 11, the areas near the top of the railcar reached lethal levels but this is not the case for the lower areas. Specifically, the phosphine concentration was not sufficient to control the insects at the lower core of the corn grit. An exception lies near the outer layers where the model predicted that phosphine had penetrated deeper (due to the intergranular air movements, caused by the diurnal temperature differences between the corn grits and the ambient).



(c) 99% mortality after 8-days

Fig. 11 99% mortality profiles for both adult insects and eggs at the end of the fumigation process. Three-dimensional model of railcar mid-sections for insect mortality. Red color indicates zones with 99% insect mortality for both adults and eggs. Eggs are more difficult to kill. The blue zone represents the potential survival of eggs

Discussion

To our knowledge, this is the first study in which the distribution of phosphine in hopper bottom railcars has been monitored and modeled. Based on the current results, we saw that monitoring railcars with remote sensors are a valuable tool for evaluating the variety of fumigation practices during transit. This monitoring process is currently dependent on railcar staff to carefully retrieve and ship sensing units back to the research laboratory for downloading the data. The monitoring data confirmed extremely high levels of phosphine in the headspace for over 4 days, as the concentrations obtained here can be considered sufficient to kill all insect life stages (Agrafioti et al., 2020a, b). From the supplemental testing with columns of corn grits, phosphine penetrated the ground corn over 2 m, and, as above, infestation at this layer is unlikely to occur right after the termination of the fumigation, and any future infestations depend on the sanitation conditions at the receiving facility.

Theoretically, total control of all potential life stages of phosphine-resistant species, including eggs, would not have been achieved with the fumigation process nor would the product be protected after the railcar has been vented with fresh air. Our CFD/insect model illustrates that after 6 days the phosphine concentrations have reduced and there are increased chances of insect survival or infestation even at the top layer of the grain bulk. Prior studies with this model in rectangular containers indicated that phosphine concentrations can be high, yet survival was likely to occur in some locations, even when the container is empty and phosphine spreads more rapidly within the fumigated area (Agrafioti et al. 2020a, b, 2021). Prior models have shown that phosphine concentration can be reduced at the back side of the container or at the centrally located internal part of the commodity, e.g. in pallets (Agrafioti et al., 2020a, Agrafioti et al., 2021). In applications in various types of structures, Agrafioti et al. (2020b) found that insect mortality was proportional to phosphine concentrations and exposure and there were cases where insect survival was notably high, especially in large structures, such as horizontal warehouses and silos, where leaks are increased and the duration of the fumigation is short.

It is well established that the abiotic conditions, such as temperature and relative humidity, play critical roles in phosphine generation from dry chemical products which also affect insect mortality (Agrafioti et al., 2020b; Athanassiou & Arthur, 2018; Kaloudis et al., 2018). Athanassiou et al. (2016) revealed diurnal fluctuations in local temperatures affected phosphine concentration in containers, suggesting that there are local warm or cool spots within the container on which phosphine concentration varies remarkably. This was demonstrated by our railcar data as well, following a similar pattern. The CFD model tracked these diurnal variations in the gas concentration; however, the model slightly under-estimated the sensor gas concentration data. We have also illustrated that there were considerable variations among locations, which in many of the cases tested exceeded 200 ppm for a brief period, while certain sensors “spiked” more than others possibly in response to varied phosphine tablet reactions and gas generation. The phosphine gas generation and movement are dynamic and gas concentrations change within locations and even within the same day. This causes variations in insect mortality, leading to underdosed areas that may create resistant insect populations (Agrafioti et al., 2020b). The diurnal variations in phosphine concentrations, as a result of the variations in abiotic conditions, may also play an important role in insect survival in specific locations, since it is likely that phosphine concentration may not be sufficient for a critical period of time.

The supplemental data from the columns of corn grits in the barrels illustrated the variations in phosphine concentrations within the bulk corn grits over time. The adult insect bioassays from these supplemental trials did not result in any insect survival. Both susceptible and phosphine-resistant strains were totally (100 %) controlled by the concentrations achieved within the corn grits and at depths of up to 60 cm. The higher concentrations in these tests were like those seen during the railcar monitoring. Regarding insect resistance to phosphine, a series of laboratory bioassays and commercial fumigations have shown that if fumigations are carried out with the proper concentration-exposure combination, both resistant and susceptible insect populations can be easily controlled (Aulicky et al. 2015; Brabec et al., 2019; Agrafioti et al. 2019, 2020a, b; Sakka and Athanassiou 2021). Still, in large grain bulks, survival may occur in underdosed “nests” due to the uneven gas distribution (Agrafioti et al., 2020a, b). In this context, wireless phosphine sensors constitute a valuable tool to detect these “nests” early enough.

Based on the above and on previous studies, best management practices in using phosphine, especially in terms of achieving appropriate concentrations and exposure periods, should be carefully addressed in resistance management protocols. In other words, insect survival in commercial fumigations may be mostly due to inadequate CT treatments applied to the containers or space, rather than from the occurrence of resistant insect species, as has been previously shown in commercial fumigations in different facilities (Agrafioti et al., 2020b). Also, regarding the insects in the untreated barrels of the supplemental test, even control insects may result in some amount of insect mortality, which can be attributed to increased stress, rather than the occurrence of resistance. On the other hand, when the fumigation conditions are marginal to achieve sufficient insect mortality, e.g. the concentrations are too low or the exposure period is too short, then the differences among susceptible and resistant insect populations can be much more diverse. For instance, in fumigation in a commercial mill in the Czech Republic, Aulicky et al. (2015) found higher survival rates in a field population of *Tribolium confususm* Jacquelin du Val, confused flour beetle (Coleoptera: Tenebrionidae), in comparison with a laboratory population, due to the short insect exposure and insufficient phosphine concentration. Higher concentrations cannot alleviate this phenomenon, unless they are combined with a sufficient exposure interval, as longer treatment times may alleviate the adverse effects from dissimilar distribution (Agrafioti et al., 2019, 2021; Lampiri et al., 2020, 2021).

This study had only a couple of hopper bottom railcars which both displayed good gas-holding abilities. In general, gas-holding can be easily compromised with small defects to seals or other structural issues. In general, any leakage will significantly reduce the potential effectiveness of gas fumigations. However, there are ways to maintain phosphine at high levels and for a longer period of time, such as the recirculation system (Agrafioti et al., 2020a, b; Noyes et al., 1999) or with systems that add additional phosphine periodically (Agrafioti et al., 2018). In bulk silo systems, it was found that the placement of some of the fumigation tablets at the lower half of the grain bulk achieved a more uniform gas distribution, particularly when the grain temperature was lower than that of the surrounding air, which forced phosphine to remain within the bulk for a longer period of time (Flinn & Reed, 2008). We estimate that the effect of wind velocity in moving railcars should be considered a potential limiting factor. The same holds in the case of stationary fumigations, as it has been shown that, when stormy weather moves over grain bins, fumigants can be depleted rapidly and thus suddenly reducing the exposure (Brabec et al., 2019). Finally, the results of the present study clearly show that the CFD fumigation model was successfully validated with hopper bottom railcars and that CFD modeling can provide the inferences necessary to plan a judicious fumigation strategy in in-transit grain fumigations, taking the aforementioned factors into account.

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Statements and Declaration

The authors declare no competing interests.

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