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Numerical Simulation and Validation of Ozone Concentration Profile in Green Gram (*Vigna radiate*) Bulks

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ABSTRACT
The new fumigant ozone offers an alternative to contact insecticides such as phosphine and methyl bromide as a grain fumigant. This study was carried out to test the flow characteristics of ozone from points of release to the available concentration of ozone to kill pests at other areas along the storage bin. A mass transfer model which predicts ozone concentration as a function of time was applied along with continuity equation to simulate the ozone transfer in a storage bin. Ozone exchange rate based on grain bed thickness was taken into account and evaluated using the correlation developed during the experiment. The relative error between the experimental and predicted ozone concentration values for the entire bin geometry was less than 25.7%. Overall, the general trends of measured ozone concentration were compatible with the simulated ones.

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Ozone; Continuity Equation; Fumigation; Green Gram; Half-Life; Saturation Time; Simulation

Introduction

In India, insect occurrence is reported often in farm and godown storages. Currently, farmers and grain processors mostly rely on phosphine and methyl bromide to the control the pests in stored products. More than 45 countries discovered stored product insect pests develop a resistance against phosphine (Bell and Wilson 1995). Moreover, it has been argued to be genotoxic when exposed to fumigators (Garry et al. 1989). Use of methyl bromide is restricted due to its ozone-depleting properties (WMO 1991). Also, it is highly toxic to warm-blooded animals (Dansi, Van Velson, and Vander Heuden 1984).

Ozone is a potential alternative compound to current fumigants (Isikber and Oztekin 2009; Kells et al. 2001; Sousa et al. 2016). Ozone is attractive because it does not leave any undesirable residue in the food product (Cullen et al. 2010) and ozone can be generated on-site using ozone generator (Pandiselvam and Thirupathi 2015) at the time of use, eliminating the need to transport and store chemical containers (Mendez et al. 2003). In addition, energy input required for ozone fumigation treatment is much lower than thermal and radiation treatment (Khadre, Yousef, and Kim 2001). The U.S. FDA approved ozone as a direct food additive (FDA 2001).

Ozone-rich atmosphere in grains storage involves the transfer of ozone through grain bulks. Engineering properties of grains are estimated to design ozone-based storage bins (Pandiselvam, Thirupathi, and Mohan 2015a; Ravi and Venkatachalam 2014). The highly reactive nature of ozone causes some distinctive challenges to make the effective movement of ozone through a stored grain mass. The ozone concentration level for fumigation has to be optimized based on quality changes of grains (Pandiselvam, Sunoj, and Uma 2016b; Pandiselvam, Thirupathi, and Vennila 2016a). Its efficiency as fumigation in a grain bulk depends on whether the applied gas moves through the grain column in the given time and gives a complete morality of insects (Shunmugam et al. 2005). As concentration gradient is expected to be the major factor in ozone transfer through grain bulks, it is imperative to determine the flow characteristics and ozone concentration profile pattern through grain bulks.

Therefore, this work aims to investigate the numerical simulation and flow characteristics of ozone gas in stored green gram bulks as a function of time.

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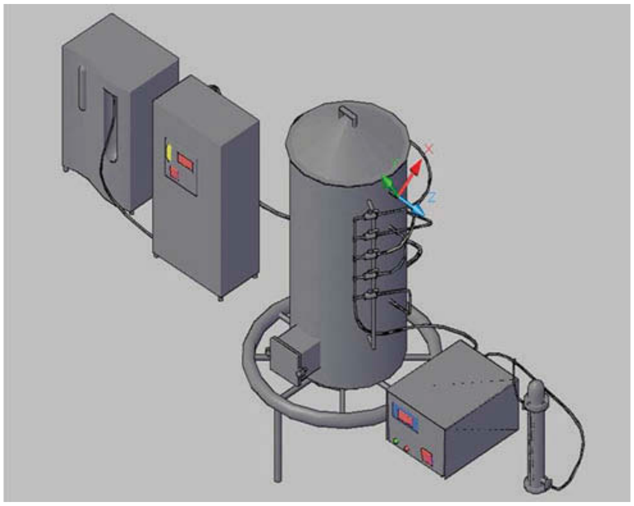

Figure 1. Schematic diagram of ozone fumigation apparatus.

Materials and methods

Sample preparation

Green gram (CO 8) was procured from the local market in Thanjavur of Tamil Nadu, India. The moisture content of the green gram was determined by oven method (AOAC 1995).

Fumigation apparatus

Fumigation apparatus consists of an oxygen concentrator, ozone generator, pilot scale storage bin, ozone analyzer and ozone destructor (Figure 1).

Oxygen concentrator

In the ozone generation process, oxygen obtained from the oxygen concentrator (Model—Oz-Air HG5, Oxygen flowrate—5 Lpm maximum; Power consumption—750 watts; Oxygen pressure—20–100 PSIG) was used as input.

Ozone generator

Ozone gas was produced by the ozone generator (Material-stainless steel; Power consumption-350 Watts; Size of ozone generator-600 × 500 × 300 mm; Output-5 g h^{-1}) developed by the Oz-Air private limited (www.oz-air.com), Noida, India.

Pilot-scale storage bin

To reduce the influence of the surroundings on the ozone gas transfer process, a closed bin was used. A pilot scale storage bin was connected with an ozone generator to distribute the gaseous ozone evenly throughout a grain mass. The bin was made up of food-grade stainless steel (SS 304) at 1.5-m height and 0.6-m diameter. It was designed in such a way that the grains can be loaded at the top and unloading can be done at the bottom. Ozone gas was passed at the bottom of the storage bin. To measure the ozone concentration in the storage bin, five concentration ports were placed. Each level of the concentration port has been fitted with a brass ball valve and connected with T and L-bend, with the help of 10-mm diameter polyurethane hose pipe. Each of the valves was directly connected to the ozone analyzer. The ozone concentration can be measured at each port by turning on the valves. Gas leakage was prevented with the help of gasket provided at the loading and unloading part of the storage bin. The bin consists of the plenum chamber at the bottom. The holes in the plenum chamber are made of 2-mm diameter, which helps to distribute the ozone gas uniformly throughout the bin.

Ozone analyzer

A dual beam photometer (UV 254 nm) was used for measuring the ozone concentration in the storage bin. The ozone concentration is displayed either in ppm, % wt/wt or g/Nm^3 on a 16-character alphanumeric display. It was recorded in ppm at every 5-min interval.

Ozone destructor

The thermal ozone destructor (Material: SS 316 Grade, Size: 150D × 500 L (mm) Power consumption: 800 Watts, Insulating material: Glass wool; Temperature: 200° C) connected with ozone analyzer to convert the ozone into oxygen. It was switched on 15 min in advance to achieve the stability. The temperature of operation could be set on the controller. The left over ozone gas is passed to the destructor, due to high temperature the ozone was destructed to oxygen.

Numerical modeling

Concentration profile and flow characteristics of ozone in the stored green gram bulks cannot be considered as constant during fumigation because it is the function of ozone concentration, time and bed thickness. Transfer of ozone between the green grams depends mainly on the differential partial pressure of the gas. The availability of ozone in the storage bin depends on the bed thickness and grain bulk ecosystem. An inclusion of bed thickness as a dependent property and reasonable boundary conditions in the model description makes the equations nonlinear. Therefore, the solution for this equation must be performed by numerical methods.

Hence, a one-dimensional numerical model by applying the principle of the law of conservation along with continuity equation was used to assess the concentration profile and flow characteristics of ozone in the stored green gram bulks. Cylindrical coordinates were selected for the equation development. The first law of thermodynamics is used for developing conservation equation for fluid flow in the packed element at any time (Geankoplis 2003).

The following assumptions were considered for the numerical simulation:

a) green gram are considered as uniform in size, shape, continuous mass and free flowing; b) stored green gram bulks consist of smaller size grains compared to the bed dimension; c) void fraction/porosity of the grains are uniform throughout the bed; d) all the stored grains have the same physical, mechanical and aerodynamical properties in any direction of bed; e) frictional forces of grains are negligible during fluidization; f) grains are linearly distributed in ozone entrainment zone and are picked by air uniformly; g) effect of broken, foreign materials and bed compaction are not considered in mathematical model; and, h) ozone diffusion takes place in the vertical (Z axis) axis of the storage bin in unsteady steady-state condition.

The transport of ozone into intergranular air in the grain column describing by partial differential equation is given as

$$\frac{\partial c}{\partial t} = D_e\left(\frac{\partial^2 c}{\partial z^2}\right) - \mathrm{V}_z\left(\frac{\partial c}{\partial z}\right)$$

where,

c = concentration of ozone, ppm,
t = time, s,
D_e = diffusivity, m/s,
V_z = velocity of ozone in 'z' direction.

Solution for numerical model

Experiments were conducted to measure the ozone concentration profile in the stored green gram bulks at 31 ± 2 °C. The ozone concentration was measured at every 5-min interval from each port. After summarizing experimental results, the numerical differentiation equation with associated initial and boundary conditions was linearized into the algebraic equation using finite element method. A MATLAB code was written to solve an algebraic equation. The relative error between the predicted and measured ozone concentrations was calculated.

Results and discussion

The moisture content of the green gram taken for the study was 10.86 ± 0.07 (%) (d.b.). Two important parameters for ozone flow through the green gram bulks were the porosity and bulk density of the sample; known to be 0.38 and 723 kg m^{-3}, respectively.

Simulated ozone concentration in green gram over the entire bin geometry is presented in Figure 2. Ozone concentration shows a significant decrease from 502 to 180 ppm at around 0.6 m distance regions from the ozone injection point (perforated floor). Fully perforated floor would create parallel ozone flow streamline and lower the risk of non-ozonation zones in the grain bulks at the bottom of the bin. However, the higher grain mass configuration in the present case had resulted in the nonflow paths at grain surface. Such non-uniformity in ozone flow patterns within the grain bed can lower the efficiency of the fumigation process. The non-uniformity of ozone distribution may be due to the variations in concentration gradient between such regions and regions away from the floor, which creates high and low ozone concentration

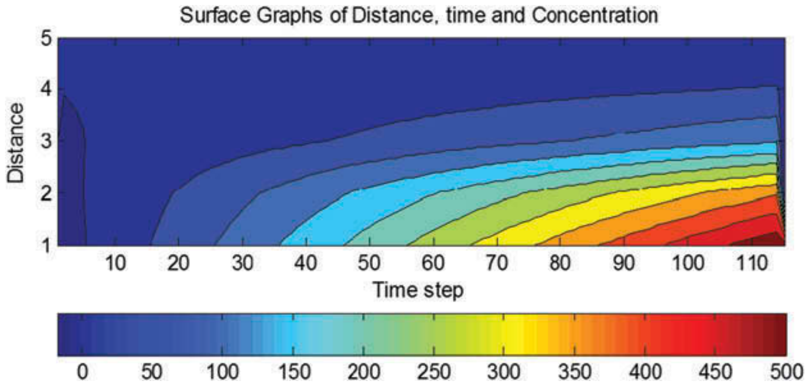

Figure 2. Simulated ozone concentration as a function of time in green gram bulks.

zones within the grain bulks. A linear airflow distribution may be achieved using two or more diffusion channel or ozone injection points, which may provide favorable results in higher bed thickness (Xu et al. 2002). However, such multichannel ozone release systems may cause difficulties in cleaning and maintenance.

Figure 2 shows that ozone gas highly diffuses in the lateral direction as compared to the vertical direction. This may be due to the resistance of grains to ozone flow is higher in the vertical direction because of the kernel orientation and flow paths varies with the direction (Jayas, Sokhansanj, and Moysey 1987). In practical situations, when the bin is filled with green gram, the ovoid shaped green gram kernels lie with the major axes horizontal, thus possibly providing more resistance to ozone flow in the vertical direction. Similar results recorded for the upward flow of CO_2 was lower for horizontal kernel orientation than for vertical kernel orientation for barley and wheat (Shunmugam et al. 2005). Also, the density of ozone, (2.14 kg m^{-3}) at standard temperature and pressure is 1.5 times greater than the density of air (1.43 kg m-$^{-3}$). The density difference may result in mass flow in addition to molecular diffusion; hence, the rate of movement of ozone in the downward direction would be greater than upward movement of ozone, against the force of gravity.

The decrease in ozone concentration values was observed with increasing bed thickness (Figure 3). Ozone saturation time in green gram increased with an increase in bed thickness followed the polynomial trend. The ozone is a strong oxidizing agent. Fumigation of grains using ozone, initially it reacts with grain surface because of the organic nature of the stored material and a high surface contact area of the grains (Hansen, Hansen, and Jensen 2013), afterward diffuse the internal layer (Churmasov, Rezchikov, and Gavrilova 2002). In all our experiments, at the start of the fumigation progress, ozone gas was consumed soon after it entered the storage bin, similar to maize (Santos et al. 2007), wheat (Hardin et al. 2010), paddy (Pandiselvam, Thirupathi, and Anandakumar 2015b) and rice (Ravi, Venkatachalam, and Rajamani 2015). As the fumigation progressed, the rate of gaseous ozone consumption decreased resulting in ozone penetrating deeper into the grain bulks (Hardin et al. 2010). It indicates that ozone flowed freely through the grain with little degradation once the molecular sites responsible for ozone decomposition became saturated (Mendez et al. 2003; Pandiselvam, Thirupathi, and Anandakumar 2015b). However, with an increase in grain bed thickness, the lines take a nonparabolic shape, which indicates an increase in grain bed thickness, the parallel ozone flow paths begin to change to nonparallel lines. Thus, an increase in bed thickness fastens the adsorption of ozone by the green gram.

Storage bins filled with more grain mass are at the risk of poor distribution of ozone. Experimental investigations carried out with paddy (Pandiselvam, Thirupathi, and Anandakumar 2015b) and rice (Ravi, Venkatachalam, and Rajamani 2015) grains also showed that ozone absorption in the grain layer is influenced by grain mound height (absorption is higher in the lower layers of the grains mound). This confirms the results of the present study. Previously published data shows that ozone concentration decreases faster if microflora present on grain surface (Wang et al. 2010). Allen, Wu, and Doan (2003) stated that the higher is the mycological contamination, lower the ozone diffusion into the grain mass.

Figure 4 shows that ozone concentration increases with increase in time. Ozone movement inside the pore space between the grains not only depends on diffusion because mass flow also occurred due to continuous generation by ozone generator. The time required to reach the desired concentration is based on flowrate, initial concentration and ozone delivery pattern. The initial movement of ozone through the grain was obstructed by a phenomenon described as the ozone demand of the medium (Kim, Yousef, and Chism 1999).

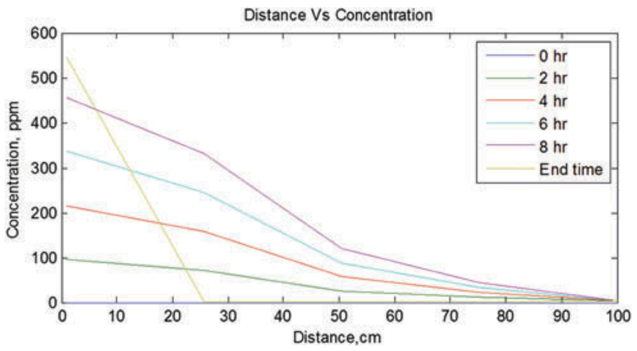

Figure 3. Residual concentration of ozone as a function of bed distance at different fumigation time.

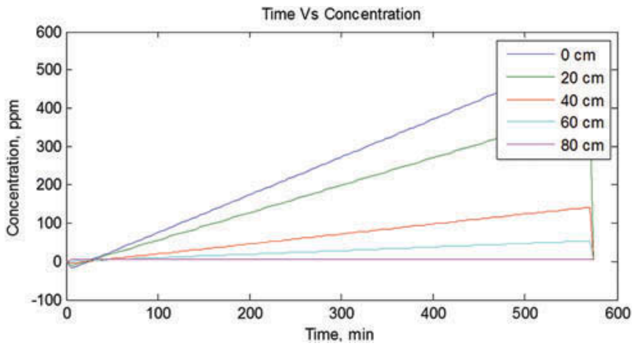

Figure 4. Residual concentration of ozone as a function of time.

Ozone is highly reactive due to electron configuration of the molecule. Hence, ozone movement through the grain layer is restricted. Choi et al. (2002), Santos et al. (2007) and (Pandiselvam, Thirupathi, and Anandakumar 2015b) confirmed that gaseous ozone followed first-order kinetics as it flowed through glass beads, maize, and paddy, respectively. This interaction of one ozone molecules into other ozone molecules results in a breakdown of ozone to oxygen and thus also a reduction in ozone concentration (McClurkin and Maier 2010). At ambient condition, the half-life of ozone is 20–40 min (Kells et al. 2001). The shortest half-life of ozone was observed for the higher grain mass (Ravi, Venkatachalam, and Rajamani 2015). The half-life of ozone is 5.57 and 6.78 min for maize and rice grains at a moisture content of 12.8 and 14.2%, respectively (Ravi, Venkatachalam, and Rajamani 2015; Santos et al. 2007). This is mainly due to an interaction of the ozone gas to the grains, even after the saturation phase. Therefore, it is difficult to maintain steady state ozone concentrations in the interstices of the material to ensure uniform treatment to all the material in a storage container.

From Figure 5, it was observed that the regression line follows a diagonal pattern. It shows that the predicted concentration has higher accuracy. The relative error between the experimental and predicted values for the entire bin geometry ranged from 0.06% (9 h) and 25.7% (1 h) (Table 1). At sampling time 2 h and above, the predicted ozone concentrations were close to the measured values. Ozone was detected on the outside of the storage bin within 2 h of release confirming that gas leaked from ozone measuring valves. Gas leakage was rectified by silica paste. The amount of ozone lost through the bin in this experiment, however, did not affect the overall success of the fumigation, but may help explain why lower concentrations of ozone were recorded at the first and second hour of the fumigation.

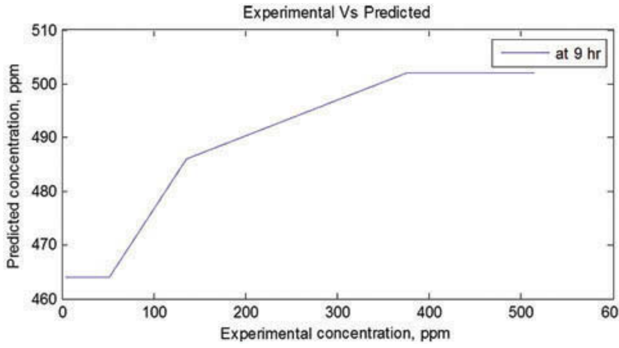

Figure 5. Comparison between measured and predicted ozone concentrations.

Table 1. Relative error between experimental and predicted values of ozone concentration.

	Ozone concentration, ppm		
Time, h	Experimental	Predicted	Relative error, %
1	26	35	25.7
2	87	94	7.4
3	156	152	2.4
4	221	210	4.9
5	282	268	4.9
6	336	326	2.7
7	402	385	4.3
8	464	443	4.6
9	502	501	0.06

The relative error values of 25% of the present model are of the same order than those reported by Jayas and Jeyamkodan (2002) and Rennie and Tavoularis (2009) for CO_2 measurement, who also pointed out that such error does not reduce the usefulness of mathematical models for developing guidelines for grain handling. Despite all the considerations accounting for the validation of the model, it can be concluded that the general trends of the measured ozone concentrations were compatible with the simulated ones.

Conclusion

The rate of ozone transfer was calculated with the correlation to bed thickness. An increase in bed thickness generally decreased the ozone penetration. Higher diffusion in the downward direction of the storage bin resulted in a density of ozone. A significant difference in ozone concentrations was observed between 0.2–0.6-m bed thicknesses. A better agreement with the measured level of ozone gas concentration was obtained for 9-h exposure time, being a relative error about 0.06%. From the bulk flow studies, improper ozone flow zone can be detected using the simulation model. This information is relevant to assist in the design of an ozone-based storage bin as a tool for predicting the efficiency of ozone fumigation.

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References

Allen, B., J. N. Wu, and H. Doan. 2003. “Inactivation of Fungi Associated with Barley Grain by Gaseous Ozone.” *Journal of Environmental Science and Health Part B-Pesticides, Food Contaminants and Agricultural Waste* 38:617–30.

Association of Official Analytical Chemists (AOAC). 1995. *Official Methods of Analysis*, 98–9. Washington, DC: AOAC.

Bell, C. H., and S. M. Wilson. 1995. "Phosphine Tolerance and Resistance in *Trogoderma Granarium* Everts (Coleoptera: Dermestidae)." *Journal of Stored Products Research* 31:199–205. doi:10.1016/0022-474X(95)00012-V.

Choi, H., H. Lim, J. Kim, T. Hwang, and J. Kang. 2002. "Transport Characteristics of Gas Phase Ozone in Unsaturated Porous Media for In-Situ Chemical Oxidation." *Journal of Contaminant Hydrology* 57:81–98. doi:10.1016/S0169-7722(01)00219-4.

Churmasov, A. V., V. G. Rezchikov, and A. A. Gavrilova. 2002. "A Mathematical Model of Plant Reaction to the Action of Ozone." *Dostizhenija Nauki I Tehniki APK* 11:12–15.

Cullen, P. J., V. P. Valdramidis, B. K. Tiwari, S. Patil, P. Bourke, and C. P. O'Donnell. 2010. "Ozone Processing for Food Preservation: An Overview on Fruit Juice Treatments." *Ozone: Science and Engineering* 32:166–79. doi:10.1080/01919511003785361.

Dansi, L., F. L. Van Velson, and C. A. Vander Heuden. 1984. "Methyl Bromide: Carcinogenic Effects in the Rat Forestomach." *Toxicology Applied Pharmacology* 72:262–71. doi:10.1016/0041-008X(84)90311-9.

FDA, United States Food and Drug Administration. Rules and Regulations. 2001. "Part 173-Secondary Direct Food Additives Permitted in Food for Human Consumption (21 CFR Part 173 Authority: 21 USC. 321, 342, 348)." *Federal Register* 66:123.

Garry, V. F., J. Griffith, T. J. Danzl, R. L. Nelson, E. B. Whoston, L. A. Krueger, and J. Cervenka. 1989. "Human Genotoxicity: Pesticide Applicators and Phosphine." *Science* 246:251–5.

Geankoplis, C. J. 2003. *Transport Processes and Separation Process Principles*. Upper Saddle River, NJ: Prentice-Hall.

Hansen, L. S., P. Hansen, and K.-M. V. Jensen. 2013. "Effect of Gaseous Ozone for Control of Stored Product Pests at Low and High Temperature." *Journal of Stored Products Research* 54:59–63. doi:10.1016/j.jspr.2013.05.003.

Hardin, J. A., C. L. Jones, E. L. Bonjour, R. T. Noyes, R. L. Beeby, D. A. Eltiste, and S. Decker. 2010. "Ozone Fumigation of Stored Grain; Closed-Loop Recirculation and the Rate of Ozone Consumption." *Journal of Stored Products Research* 46:149–54. doi:10.1016/j.jspr.2010.03.002.

Isikber, A. A., and S. Oztekin. 2009. "Comparison of Susceptibility of Two Stored-Product Insects, *Ephestia Kuehniella* Zeller and *Tribolium Confusum* Du Val to Gaseous Ozone." *Journal of Stored Products Research* 45:159–64. doi:10.1016/j.jspr.2008.12.003.

Jayas, D. S., and S. Jeyamkodan. 2002. "Modified Atmosphere Storage of Grains, Metas, Fruits and Vegetables." *Biosystems Engineering* 82:235–51. doi:10.1006/bioe.2002.0080.

Jayas, D. S., S. Sokhansanj, and E. B. Moysey. 1987. "The Effect of Airflow Direction on the Resistance of Canola (Rapeseed) to Airflow." *Canadian Agricultural Engineering* 29:189–92.

Kells, S. A., L. J. Mason, D. E. Maier, and C. P. Woloshuk. 2001. "Efficacy and Fumigation Characteristics of Ozone in Stored Maize." *Journal of Stored Products Research* 37:371–82. doi:10.1016/S0022-474X(00)00040-0.

Khadre, M. A., A. E. Yousef, and J.-G. Kim. 2001. "Microbiological Aspects of Ozone Applications in Food: A Review." *Journal of Food Science* 66:1242–52. doi:10.1111/jfds.2001.66.issue-9.

Kim, J.-G., A. E. Yousef, and G. W. Chism. 1999. "Use of Ozone to Inactivate Microorganisms on Lettuce." *Journal of Food Safety* 19:17–34. doi:10.1111/jfs.1999.19.issue-1.

McClurkin, J. D., and D. E. Maier. 2010. "Half-Life Time of Ozone as a Function of Air Conditions and Movement." 10th International Working Conference on Stored Product Protection, Portugal, 381–5.

Mendez, F., D. E. Maier, L. J. Mason, and C. P. Woloshuk. 2003. "Penetration of Ozone into Columns of Stored Grains and Effects on Chemical Composition and Processing Performance." *Journal of Stored Products Research* 39:33–44. doi:10.1016/S0022-474X(02)00015-2.

Pandiselvam, R., S. Sunoj, and D. Uma. 2016b. "Development of Multivariate Regression Model for Quantification of Proximate Content in Vigna Radiata Using Fourier Transform–NIR Spectroscopy." *Poljoprivredna Tehnika* 41 (2):61–70.

Pandiselvam, R., and V. Thirupathi. 2015. "Reaction Kinetics of Ozone Gas in Green Gram (*Vigna Radiate*)." *Ozone: Science & Engineering* 37:309–15. doi:10.1080/01919512.2014.984158.

Pandiselvam, R., V. Thirupathi, and S. Anandakumar. 2015b. "Reaction Kinetics of Ozone Gas in Paddy Grains." *Journal of Food Process Engineering* 38:594–600. doi:10.1111/jfpe.2015.38.issue-6.

Pandiselvam, R., V. Thirupathi, and S. Mohan. 2015a. "Engineering Properties of Rice." *Poljoprivredna Tehnika* 40:69–78.

Pandiselvam, R., V. Thirupathi, and P. Vennila. 2016a. "Fourier Transform–Near Infrared Spectroscopy for Rapid and Nondestructive Measurement of Amylose Content of Paddy." *Poljoprivredna Tehnika* 41 (2):93–100.

Ravi, P., and T. Venkatachalam. 2014. "Important Engineering Properties of Paddy." *Poljoprivredna Tehnika* 39:73–83.

Ravi, P., T. Venkatachalam, and M. Rajamani. 2015. "Decay Rate Kinetics of Ozone Gas in Rice Grains." *Ozone: Science and Engineering* 37:450–5. doi:10.1080/01919512.2015.1040912.

Rennie, T. J., and S. Tavoularis. 2009. "Perforation-Mediated Modified Atmosphere Packaging. Part II. Implementation and Numerical Solution of a Mathematical Model." *Postharvest Biology Technology* 51:10–20. doi:10.1016/j.postharvbio.2008.06.012.

Santos, J. E., M. A. Martins, L. R. A. Faroni, M. P. Andrade, and M. C. S. Carvalho. 2007. "Ozonization Process: Saturation Time, Decomposition Kinetics and Quality of Maize Grains (Zea Mays L.)". IOA Conference and Exhibition, Valencia, Spain, October, 29–31.

Shunmugam, G., D. S. Jayas, N. D. G. White, and W. E. Muira. 2005. "Diffusion of Carbon Dioxide through Grain Bulks." *Journal of Stored Products Research* 41:131–44. doi:10.1016/j.jspr.2003.09.005.

Sousa, A. H., L. R. D. A. Faroni, M. A. G. Pimentel, G. N. Silva, and R. N. C. Guedes. 2016. "Ozone Toxicity to Sitophilus Zeamais (Coleoptera: Curculionidae) Populations under Selection Pressure from Ozone." *Journal of Stored Products Research* 65:1–5. doi:10.1016/j.jspr.2015.11.001.

Wang, S., H. Liu, J. Lin, and Y. Cao. 2010. “Can Ozone Fumigation Effectively Reduce Aflatoxin B_1 and Other Mycotoxins Contamination on Stored Grain?” *Julius Kuhn Archiv* 425:582–8.

World Meteorological Organization (WMO). 1991. *Scientific Assessment of Ozone Depletion: 25, World Meteorological Organization of the United Nations*. Geneva, Switzerland: Secretariat of the World Meteorological Organization.

Xu, S., D. S. Jayas, N. D. G. White, and W. E. Muir. 2002. “Momentum-Diffusive Model for Gas Transfer in Granular Media.” *Journal of Stored Products Research* 38:455–62. doi:10.1016/S0022-474X(01)00048-0.