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Original Article

Hazardous Gases and Oxygen Depletion in a Wet Paddy Pile: An Experimental Study in a Simulating Underground Rice Mill Pit, Thailand

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Abstract: During the rice harvesting season in Thailand, large amounts of fresh paddy are sent to rice mills immediately after harvesting due to a lack of proper farm storage space. At certain levels of moisture content, rice grains may generate hazardous gases, which can replace oxygen (O_2) in the confined spaces of underground rice mill pits. This phenomenon has been observed in a fatal accident in Thailand. Our study aimed to investigate the type of gases and their air concentrations emitted from the paddy piles at different levels of moisture content and duration of piling time. Four levels of moisture content in the paddy piles were investigated, including dry paddy group (< 14% wet basis (wb)), wet paddy groups (22–24, 25–27 and 28–30%wb). Our measurements were conducted in 16 experimental concrete pits 80 × 80 cm wide by 60 cm high. Gases emitted were measured with an infrared spectrophotometer and a multi-gas detector every 12 h for 5 days throughout the experiment. The results revealed high levels of carbon dioxide (CO_2) (range 5,864–8,419 ppm) in all wet paddy groups, which gradually increased over time. The concentration of carbon monoxide (CO), methane (CH_4), nitromethane (CH_3NO_2) and nitrous oxide (N_2O) in all wet paddy groups increased with piling time and with moisture content, with ranges of 11–289; 2–8; 36–374; and 4–26 ppm, respectively. The highest levels of moisture content in the paddy piles were in the range 28–30%wb. Nitrogen dioxide (NO_2) concentrations were low in all paddy groups. The percentage of O_2 in the wet paddy groups decreased with piling time and moisture content (from 18.7% to 4.1%). This study suggested that hazardous gases could be emitted in moist paddy piles, and their concentrations could increase with increasing moisture content and piling time period.

Key words: Hazardous gases, Rice mill, Paddy, Underground pit, Moisture content

Introduction

The economy of Thailand is largely based on agriculture[1)], and at present Thailand is the world's largest rice exporter[2)]. Large rice mills play a pivotal role in the production of rice for both domestic consumption and export.

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In general, fresh paddy (rice in the husk) from the fields is sent to rice mills immediately after harvesting because of a lack of proper storage spaces at the rice fields and the need to sell paddy quickly for financial reasons[3]. There is considerable variability in moisture content and temperature of freshly harvested paddy. The moisture content of harvested paddy usually ranges between 18% and 26% wet basis (wb), but may be as high as 22% to 30%wb[4–6]. Drying is needed to reduce seed respiration and avoid the dangers of heating[6]. A paddy moisture content of about 13–14%wb is considered adequate for storage and milling[5, 6]. The basic goal of industrial rice milling is to transform unhulled paddy rice into hulled and polished white rice[7]. Several large rice mills have a bucket elevator installed partially underground to transport wet paddy to the baking machine. The paddy arriving at the mill-feed area by truck is dumped at the intake area or ground level pit, and usually left to stand for a few hours in order to reduce the moisture content to 13–14%wb. Later it is transferred directly to an underground pit through a valve and a transfer chute that is used to draw the damp paddy into the drying machine (Fig. 1). If the amount of rice deposited exceeds the loading capacity rate for transport to the baking machine, the wet paddy may be allowed to stand for one to three days near the intake area.

Environmental hazards, such as noise and dust, arising from the production process, have been described in an earlier report[8], but in 2004, a serious accident occurred when workers were found dead in an underground pit at a large rice-mill in one of the province in northeastern Thailand[9, 10]. The government report indicated that the wet paddy pile (–30%wb) was dumped and on standby for transfer to the drying step at the mill's intake area. A female worker who first entered the pit collapsed while checking for obstructions to the bucket conveyor and cleaning out residual grain and grain dust at the bottom of the pit. Other workers entered the pit in a rescue attempt but also collapsed. After the emergency rescue team with safety equipment and independent breathing apparatus arrived, the victims were immediately transported to hospital. Seven victims died at the scene while the others were unconscious. Several gases were detected which exceeded the regulation standard, including concentrations of carbon dioxide (CO_2), carbon monoxide (CO), nitromethane (CH_3NO_2), and nitrous oxide (N_2O). A government investigation concluded that it was likely that gases created due to fermentation likely displaced oxygen (O_2) from the storage or intake area pit which in turn led to asphyxiation of the workers[10].

Toxic gases are known to be a hazard arising in agricultural installations. In farm silos, the most hazardous gas produced by fermentation is reported to be nitric oxide which, when combined with oxygen, produces nitrogen dioxide (NO_2) commonly referred to as "silo gas"[11]. Carbon monoxide (CO) may be produced by chemical reactions during the composting process or biodegradation of organic materials by microorganisms[12, 13]. Similarly, methane (CH_4) is also produced by the anaerobic process in an organic substrate[14, 15]. A case report published by the Fatality Assessment and Control Evaluation (FACE) program of the US National Institute for Occupational Safety and Health (NIOSH) indicated that during ensiling carbon dioxide (CO_2) is always produced[16].

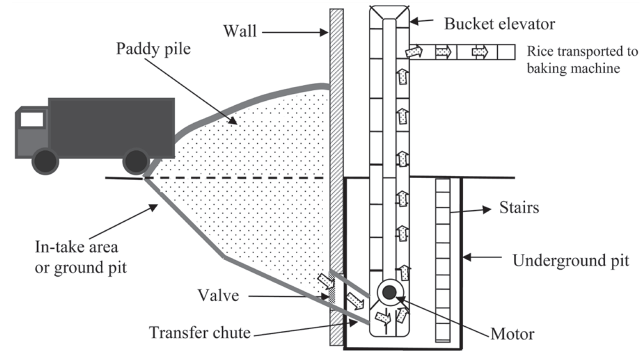

Fig. 1. Drawing of loading area and underground pit in rice mills

Asphyxiation will occur if the oxygen content of the air inside a confined space becomes too low to support life. In Thailand there are many reports of deaths in several types of confined spaces. However, the incident in one of the province in northeastern Thailand in 2004 was the first report from a rice mill, and to date in Thailand there is lack of information about this type of hazard. In this study we investigated the types and concentrations of hazardous gases generated at different moisture contents in paddy piled for varying durations of time.

Materials and Methods

Study Sample and Study Setting

This experimental study employed a repeated measures design with three replicates. The study samples were rough rice (cultivar RD 15) taken simultaneously from the same field in Pimai District, Nakorn Ratchasima Province, northeast Thailand.

Moisture content was determined by a grain moisture meter (Kett, Model Riceter L, Australia) based on the electrical resistance method and was calibrated by the Ministry of Commerce, Thailand.

Initially the fresh paddy at the loading area had a moisture content of 15–22%wb. We divided 3,040 kg of fresh paddy equally into four lots of 760 kg for use in each experiment. One lot was reduced in moisture content by open drying to <14%wb and served as the control group. The remaining three lots of 760 kg were used to form the wet paddy groups. The required amount of water to be applied to each was calculated on the basis of the initial moisture content of the paddy. Water was added by spraying onto each lot and mixed thoroughly to achieve the required three additional moisture levels of 22–24%wb, 25–27%wb and 28–30%wb.

The 760 kg fractions of paddy with four moisture content levels were then sub-divided into four equal 190 kg groups and allocated to open-topped rectangular experimental pits measuring 80 × 80 × 60 cm (Fig. 2). In the central part of each pit a horizontally perforated pipe of 40 cm in length was embedded, placed in the middle of the casing (30 cm in height) and closed off using a stopper at the outside end of the box.

The study was set up in a partially open building. In total, sixteen pits comprising four sets of four different levels of moisture content of the paddy were used for monitoring the emission of gases (Fig. 2 and 3). In the sets of four pits, three were monitored for CO_2, N_2O and CH_3NO_2 and the other for CO, NO_2, O_2 and CH_4 concen-

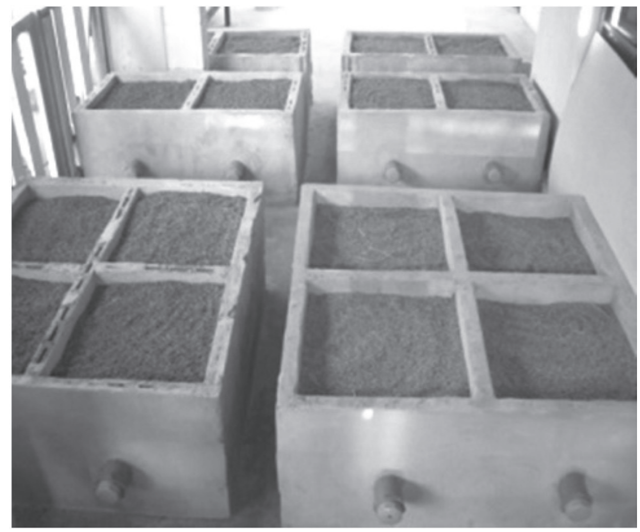

Fig. 2. Four sets of paddy pits

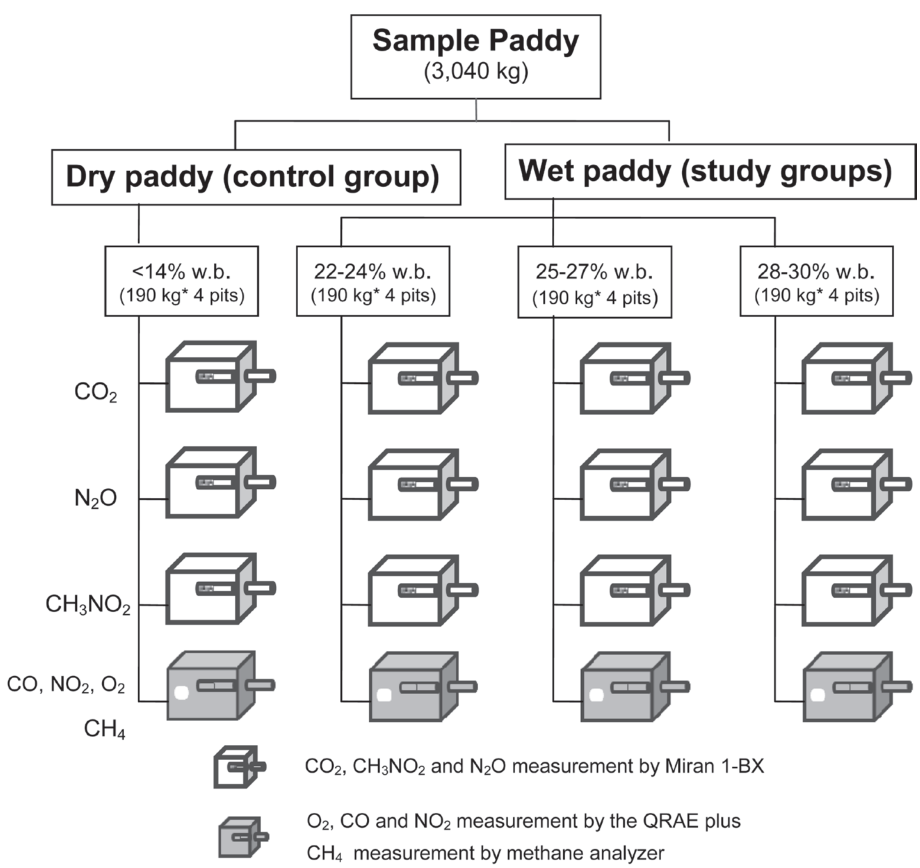

Fig. 3. Schematic of study samples in experimental pits and gas measurement

trations. The experiment was run for a period of 120 h.

Measurement of Gases

Measurements were made at the start of the experiment and at twelve hour intervals up to 120 h. Concentrations of CO_2, N_2O and CH_3NO_2 were determined with the Miran 1-BX (Foxboro, USA) based on an infra-red gas detector analyzer. The instrument was set at a flow rate of 2.5 L/min. For each measurement of gas, the pipe was opened and air was drawn from the central part of each pit through the PVC pipe, via a teflon pipe fitted with a particulate filter, and then into the gas detector. Measurements were made on gas drawn over a period of approximately three minutes.

The concentrations of CO, O_2, and NO_2 were measured with the QRAE multi-gas detector (RAE Systems, USA) based on an electrochemical sensor. The equipment was set up at a flow rate of 0.25 L/min and the response time was 20 s. Gases were measured for two minutes to ensure a steady state reading.

The concentration of CH_4 was measured by collecting samples with the $PCXR_4$ air sampling pump (SKC, USA) at a flow rate of 1 L/min into a 5 liters SKC Tedlar sample bag, and then analyzed by the methane analyzer APHA-370 (Horiba, Japan).

Results

Gas Concentrations in Paddy Piled at Four Levels of Moisture Content

The setting of the experimental pits was monitored for ambient temperature which ranged between 21.4° and 30.7 °C and relative humidity which ranged between 60.2% and 87.4%.

The mean concentration of CO_2 from start to the end of the experiment (120 h) ranged from 8.7–30.6 ppm in the < 14%wb group, to 5864–7529 ppm in the 22–24%wb group, to 7578–8130 ppm in the 25–27%wb group, and to 7525–8419 ppm in the 28–30%wb group. The results indicate elevated initial concentrations of CO_2 in all wet paddy groups but not the control (<14%wb) with some further increase during the course of the experiment (Fig. 4).

The increase in the concentrations of CO over the period of the experiment was positively associated with the moisture content levels. The mean concentration of CO during the experiment ranged from 0–1 ppm in the <14%wb group, to 12–23 ppm in the 22–24%wb group, to 16–38 ppm in the 25–27%wb group, and to 18–59 ppm in the 28–30%wb group. The CO concentration remained low in the <14%wb group but a rapid increase in CO was observed in the first 12–24 hours in the two high moisture groups with concentrations of 227 ppm (25–27%wb) and 289 ppm (28–30%wb). This was followed by a gradual decrease to a constant level at 72 h after piling the paddy.

Low levels of CH_4 were found in all groups during the experiments ranging from 1.9–2.0 ppm (<14%wb), to 1.9–2.2 ppm (22–24%wb), to 4.2–7.4 ppm (25–27%wb), and to 5.8–8.1 ppm (28–30%wb). The highest concentration was 8.1 ppm in the highest moisture paddy group (28–30%wb).

The mean concentration of CH_3NO_2 increased with increasing moisture content, ranging from 1.5–14.1 ppm (<14%wb), to 36.3–100.3 ppm (22–24%wb),to 42.6–146 ppm (25–27%wb), and 56.3–201.7 ppm in the 28–30%wb. In the <14%wb group, CH_3NO_2 levels were found to be low throughout the experiment, but in the higher moisture content groups. CH_3NO_2 levels peaked at 374 ppm, and then gradually decreased.

The mean concentration of NO_2 increased with increasing moisture content of the paddy ranging from 0.1–0.2 ppm (<14%wb), to 4.3–5.7 ppm (22–24%wb), to 4.7–10.1 ppm (25–27%wb), and 8.4–12 ppm in the highest moisture group (28–30%wb). The lowest N_2O concentration was found in the <14%wb group throughout the experiment. In the wet paddy groups, the lowest concentration of N_2O was observed at the initial stage and the highest peak after 48–60 hours, at 26 ppm in the 28–30%wb group, and then gradually decreased.

NO_2 was not detected either in the <14%wb group or in the other groups and was only found at concentrations which did not exceeded 1 ppm throughout the experiment.

The percentage of oxygen in the <14%wb group remained constant at 20.9% whereas the decline in oxygen in the other groups was strongly associated with increases in the moisture content levels. In the 22–24%wb group, the levels of O_2 during the experiment (120 h) gradually decreased from 18% to 15%. In the highest moisture paddy groups (25–27%wb and the 28–30%wb), we found a rapid decrease in oxygen from 18% to 9% and from 18% to 4%, respectively.

Discussions

This study aimed to study the type and concentrations of gases arising from various levels of wet paddy piled on standby for the purpose of reducing the moisture content to 13–14%wb. We demonstrated that paddy should be

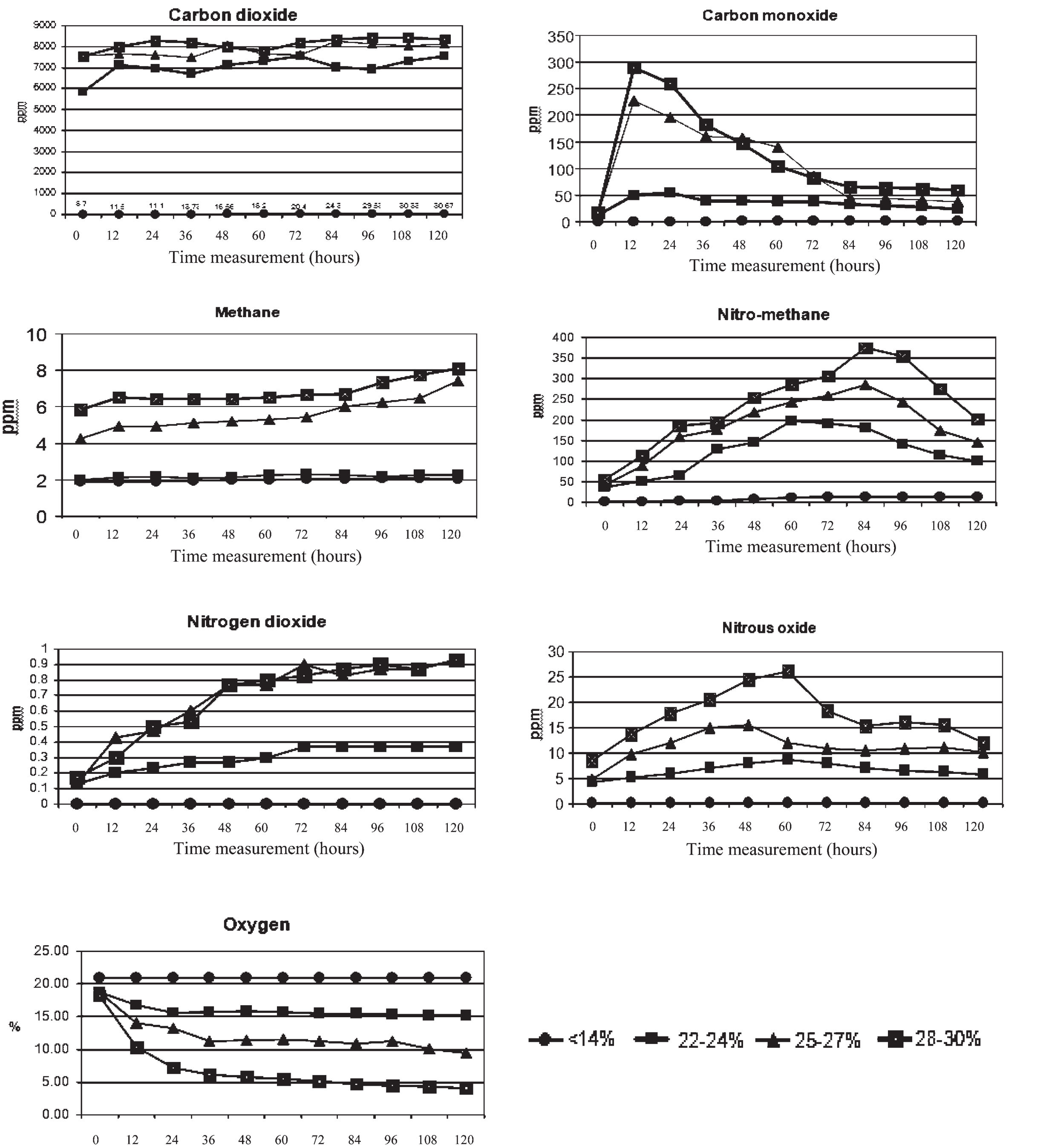

Fig. 4. The mean concentration of various gases over time at different moisture content of piled paddy

dried to this level of moisture content to enable safe storage by reducing respiration and preventing mold or fungi growth[5, 17].

Our findings showed that carbon dioxide concentrations increased with piling time and moisture content. The results are consistent with an earlier study which found that the respiration rate of rice increases with increasing moisture content[18]. They may be explained by the fact that the respiration processes of grain normally involve both aerobic and anaerobic processes[19]. In aerobic respiration, living cells present in the paddy use oxygen and produce water, heat and CO_2 but in addition, yeast produces ethyl alcohol and CO_2 anaerobically[20]. Other processes also generate CO_2; for example, in an experimental study CO_2 was detected as a result of a reaction between N_2O and CO[21].

Carbon monoxide production has been demonstrated by chemical reactions during the process of composting organic materials by microorganisms in experiments in which rice was used as the organic material[12, 13]. Fungi as *Aspergillus* spp. are in the most common microorganisms found in stored grain, at various sites in rice mills[22, 23] and in wheat stored in a silo[24]. These microorganisms might also play an important role in producing CO. This explanation is supported by Hellebrand *et al*[25] who reported that CO evolved during the composting of grass waste, peaked after a few days and then declined. The phenomenon of an immediate peak in CO followed by a sharp decline a few hours later, may be explained by one or more of the following mechanisms: 1) CO was hydrolyzed by phototrophic bacteria with water, producing H_2 and CO_2[26]; 2) grain temperature increased in piled paddy over several days[27] this might have initiated H_2O decomposition to H_2 and O_2 so that O_2 could then combine with CO resulting in a sharp decrease in CO[28]; and 3) CO may be used in the reaction between N_2O and CO[21] resulting in decreased CO and higher concentrations of CO_2.

Methane can be produced by either the anaerobic process or fermentation of an organic substrate[15]. Earlier studies reporting the presence of CH_4 were based on the decomposition of organic matter during cultivation of rice paddies[14]. In our experiments, however, the concentrations of CH_4 were very low.

We found another CH_4 related gas in our experimental pits, CH_3NO_2, which is generated from de-nitrification of methane[29, 30] and usually manufactured in the laboratory using an acid mist of methane and nitric acid at 450–500°C[29, 30]. It can also be produced from a nitriding agent comprising an oxygenated nitrogen compound, such as nitric acid and nitrogen dioxide (NO_2), either alone or in a mixture with a carbon compound[30]. In this study, we found oxygenated nitrogen compounds N_2O and NO_2 in our pits. The production of carbon compounds including ethanol, acetic acid or acetaldehyde, might also occur in the pits because the process of anaerobic fermentation of rice could produce ethanol[20]. A northeast Thai study[27] found the grain temperature of piled paddy at 29% wb to be between 60 to 80 °C within 40 h, which did not meet CH_3NO_2 generating conditions and the levels of CH_4 available for conversion to CH_3NO_2 was low. So the presence of CH_3NO_2 cannot be adequately explained but we suggest it is associated with the observation of low CH_4, N_2O and NO_2 concentrations.

The low concentrations of NO_2 in our analyses contrast with other reports. High levels of NO_2 were reported in hay and grain silos after six days of storage[31], and in maize and grass silage production after 2 to 3 days in silos[16]. The low level of NO_2 found in our study may be due to the consumption of NO_2 together with CH_4 to generate CH_3NO_2.

Denitrification is the main biological process, which produces N_2O[32, 33]. Most denitrifying bacteria catalyze the reduction of nitrate (NO_3^-) to nitrogen N_2 and produce N_2O as a byproduct under aerobic conditions[34]. In general, nitrate (NO_3^-) can be found from different sources of ground and underground water, waste water, drinking water and foods[35]. So, the rise of N_2O may be due to contamination by nitrate which was also found in the rice[35] and with the denitrification process. A Japanese investigation[36] found that *Pseudomonas stutzeri* strain V1 produced N_2O during the fourth day and *Pseudomonas stutzeri* strain F1 produced little N_2O during the second day and less throughout the incubation period under aerobic conditions. However N_2O in the wet paddy groups gradually decreased and became stable after 60 to 84 h of the experiment indicating that the bacteria reduced N_2O to N_2[32, 37] and consistent with our finding that all of the moist paddy groups produced nitrogen gas. Moreover, the depletion of oxygen in the culture would enhance the reduction of N_2O to N_2[36] consistent with the decreased concentrations of N_2O at the end of our experiment.

Dillahunty *et al*[18], demonstrated that O_2 decreases with increased moisture content and the aerobic respiration process. This could occur in rice paddy because of the conversion of O_2 to water, heat and CO_2[19]. The O_2 used in the process of denitrifying bacteria is consumed in the formation of nitrous oxide and nitrogen dioxide. Additionally, the increased grain temperature in wet paddy[27] would promote the conversion of CO and O_2 to CO_2[21, 28]. However, the oxygen level in piled wet paddy decreased from 20% to 4% vol/vol by about 100,000–160,000 ppm. In contrast, all increases in gas concentrations in this study were rather low. We found water vapor in the pit pipe, possibly due to the elevated relative humidity within the pit which was sufficient to cause condensation within the pipe leading to increases in water vapor concentration.

Conclusions

We investigated the types and concentrations of hazardous gases from piled paddy at different levels of moisture content and at different periods of piling time. Our results strongly indicate that moist paddy could generate hazardous gas including CO_2, CO, CH_4, CH_3NO_2,

N_2O and be associated with a low level of O_2. It was also clearly demonstrated that these substances increase with increasing moisture content and with longer piling time. The detection of N_2O is consistent with its production by denitrifying bacteria. Paddy contains microorganisms (yeast, fungi, bacteria), which can produce CO by chemical reactions during composting. The concentrations of methane, nitromethane, nitrogen dioxide were low but the low oxygen concentration points to its consumption in the aerobic respiration process of grain and by denitrifying bacteria, which convert O_2 into water, heat, CO_2, N_2O, N_2O. It is evident that under certain conditions an oxygen deficient atmosphere could be the most important hazard leading to deaths in underground pit. When wet paddy is piled, the production of heavier gases would lead to both oxygen consumption and displacement. Working in confined spaces, such as the underground pits of a rice mill, is a high risk because gases can migrate via the valve or the hole between the ground pit and the underground pit (Fig. 1). The paddy with the highest moisture content (>30%wb) could generate the highest concentration of hazardous gases and cause low concentrations of oxygen, increasing the risk of asphyxiation of workers. This experimental study demonstrates the higher the moisture content of piled wet paddy and the longer the piling time, the greater the build up of hazardous gases. The findings suggest that the moisture content of paddy must be monitored, especially, when it is likely to be >30%wb. Fail-safe procedures should be established in order to prevent further fatalities. Rice mill managers should be adequately briefed, and prepared to install warning systems and purpose-designed ventilation together with the implementation of worker training.

Recommendations

It is evident that an oxygen deficient atmosphere could be one of the most important hazards leading to fatalities in underground pits where paddy is piled at the ground pit to reduce moisture content.

In order to adopt a precautionary approach and protect workers in mill pits:

1. Rice mill managers should be made aware that gases in the paddy pile could disperse through underground pits replacing oxygen within the pit.

2. Rice mill industries must strictly prescribe the process used for decreasing moisture content. The paddy at the highest moisture content should first be forced-warm-air dried.

3. If the paddy is moist, the duration of piling should be limited to 2 days.

4. All factories with an underground pit must follow the confined-space entry work permit system.

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