TO: John S. Sanders, Ph.D.
Environmental Program Manager II
Worker Health and Safety Branch

FROM: Harvard R. Fong, CIH
Senior Industrial Hygienist
(916) 445-4211

Michael O’Malley, MD, MPH
Medical Consultant
(916) 445-4281

Yvette Nonato, MD, DPBRM, FPARM
Research Scientist
(916) 445-2174

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SUBJECT: WORKSITE EVALUATION AND PRIORITY ILLNESS INVESTIGATION FOLLOWING A PHOSPHIDE FIRE AT A KERN COUNTY COMMODITY PROCESSING FACILITY: OBSERVATIONS AND RECOMMENDATIONS

On December 10th, 2009 a fire occurred at a pistachio processing plant in Wasco, Kern County, associated with Aluminum Phosphide fumigation. We conducted a pesticide workplace site evaluation on January 12, 2010. Information for the workplace evaluation was obtained from Carlos Ramos (the sanitation/fumigation supervisor) and from observations of the location and objects involved. Information for the illness investigation was obtained from the Kern Department of Agriculture Staff and the Worker Health and Safety (WHS) Branch Staff interviews of affected employees. Additionally, medical records (from the three (3) hospitals where affected employees were managed) were reviewed.

Background
Phosphide fumigants liberate phosphine (PH₃) gas on contact with either moisture in the environment or acid in the intestinal tract. Aluminum phosphide (AlP - Phostoxin®, Fumitoxin®, et al) is used for commodity fumigation and occasionally for rodent control. Aluminum phosphide reacts with water to form phosphine gas:

\[ \text{AlP} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + \text{PH}_3 \]

On contact with oxygen or water, phosphine has a tendency to decompose to more stable forms of phosphorous - ultimately to phosphoric acid. This may occur explosively at concentrations above 1.8%, especially when trace amounts of diphosphine are present to catalyze the reaction.
(Cotton and Wilkinson, 1972). There is a long history of safety issues associated with the application of phosphine-generating fumigants as well as with the disposal of the unspent residue.\(^1\) These include fires and/or explosions causing occasional traumatic injuries and illnesses consistent with exposure to phosphine gas. Because phosphine breaks down quickly to phosphate after absorption from the lungs, it is not usually possible to confirm poisoning with biological monitoring. Air monitoring in the workplace is often the best means of confirming exposure but in reality, air monitoring may be overlooked in responding to a fire or other emergencies associated with the use of a phosphine-generating fumigant.

Investigation
On arrival at the facility, Harvard Fong, Dr. Michael O’Malley and Martha Sanchez met with Mr. Ramos. Mr. Ramos provided copies of the company’s Fumigation Management Plan (FMP) and the Applicator’s Manual for Fumitoxin\(^\circ\) (AMF). Although the FMP appeared adequate, no information specific to a fire/explosion event was included. The closest the FMP addressed such events were a fill-in line for “Fire or combustibility issues” in the “Preliminary Planning and Preparation” and directions to instruct/notify personnel as to proper emergency response on the “Application” section. The FMP was primarily designed to ensure that employee exposure is below the permissible exposure limits (PEL). On the other hand, the AMF mentioned only a passing reference to the pyrolytic properties of Aluminum Phosphide and Phosphine in the “Precautionary Statements” and a general warning about these properties in the “Spill and Leak Procedures.” The AMF had no specific examples of potentially hazardous conditions. Information provided in the AMF allowed for a deduction that conditions in place during the event led to an uncontrolled pyrolytic incident. Without the knowledge of lower explosive limits, auto-ignition temperatures, gas evolution rates and principles of air flow and confinement, a fumigator could not have been aware of the “perfect storm” that was in place around the time of application.

An evaluation of the event site and Mr. Ramos’ explanation of the evolving situation during the event, led to a plausible explanation of the cause of the fire. As shown in Photo One, the bulk bags of pistachios associated with the fire were under black plastic films and ground-sealed with sand snakes. Photo Two shows the fumigation set up. According to Mr. Ramos, the pile under fumigation that day was four bags wide and 20 bags long, for a total of 80 bags under fumigation. Each bulk bag weighed 2,200 pounds (997 kg) and 4 ft. x 4 ft. x 5.5 ft. in dimension (88 cubic feet or 2.5 cubic meters). The total volume under fumigation was 200 cubic meters or \(2 \times 10^5\) liters. The bags were elevated from the ground by wooden pallets.

Photo One: Bulk bags covered by film.

Photo Two: Example of fumigated bag stack.

Photo Three: Tray placement location and tray assembly
Photo Four: Wooden pallets with space underneath for fumigation trays.

At the end of each film-covered (tarped) pile, a tray assembly (See Photo Three) containing Aluminum Phosphide was slid into the gap in the pallet where forklift forks would be inserted to lift the load (see Photo Four). Note the minimal clearance from the ground to the bottom of the tray. This configuration contributed to, but was not the only condition for the pyrolytic event that ensued.

Each tray was loaded with 1 pound (453 grams) of Aluminum Phosphide pellets. This was approximately 750 pellets of the Fumitoxin® formulation. For a 7,040 cubic feet of commodity under fumigation (88 cubic feet/bag x 80 bags), the pellet dosage was approximately 213 pellets per 1,000 cubic feet, well within the listed “Dosage Range” of the AMF (150 to 450 pellets per 1,000 cubic feet).

During the fumigation, a rainstorm arrived in the area. The fumigation was located next to the downspout from the roof of an adjacent warehouse (Photo Five). The soil and angle iron shown in the photo had apparently been placed there to divert water from the downspout away from the fumigation pile. On December 10th, however, the increased volume of rain water allowed pooling around the fumigation pile and for water to seep under the tarp. This seepage was directly in line with the trays of Aluminum Phosphide under the end pallet.
Once a large quantity of water was introduced under the tarp, a cascade of events most likely occurred:

Water that pooled under the trays raised the local relative humidity in the airspaces to much higher than normal levels. This hastened the conversion rate of Aluminum Phosphide. According to the Genium Material Safety Data Sheet (MSDS, 2006), Phosphine is one of the relatively few compounds which are described as "endothermic" i.e. heat is absorbed into the compound, rather than released from it. Majority of endothermic compounds are thermodynamically unstable and may decompose explosively under various circumstances (i.e., open flame, auto ignition, a spark, etc.)

In this incident, as Aluminum Phosphide absorbed heat in the confined airspace under the pallets, Phosphine (an unstable material), was generated. The auto-ignition temperature of phosphine has been reported as 38° C (100° F). The lower explosive limit (LEL, also known as the lower flammability limit) for phosphine gas is 1.78% by volume. Under normal conditions, simple gas diffusion along the pallets would have been sufficient to maintain concentrations under the LEL. The accelerated conversion to Phosphine may have allowed for a localized concentration equal to or greater than the LEL in the confined spaces within the pallet.

Ultimately, local conditions (temperature and gas concentration) turned critical, igniting the Phosphine gas, which in turn caused combustion of the cardboard sheets that covered the wooden pallets, and other nearby flammable materials (see Photos Six and Seven).
Workers near the tarped pistachio pile noted smoke. Although the workers were untrained in the proper emergency response, they attempted to douse the incipient fire with water.

The Fumitoxin® label states: 
*Classified by UL, Inc. as to fire hazard only when used specifically as directed in the instructions on this container, and supplemental labeling. FUMITOXIN® is noncombustible, but exposure to moist air or water releases flammable and toxic phosphine gas. Spontaneous ignition may result if contacted by water, acids or chemicals.*

The Genium MSDS is even more explicit: 
**Extinguishing Media:** Dry chemical powder. Dry agent. Dry sand. Carbon dioxide. Do not use water.

By the time workers realized that dousing with water was not working, staff trained in proper emergency response and procedures had arrived and began using Ammonium Phosphate-based, dry-chemical fire extinguishers. Fifteen (15) fire extinguishers were used, ultimately controlling and extinguishing the fire.

Workers in the vicinity of the fire were likely exposed not only to Phosphine but also to Phosphorus Oxides (PO₃) and combustion products from burnt plastic films, bags and cardboards. Most likely, these workers were also exposed to the extinguisher agent, unreacted Aluminum Phosphide and spent material (primarily, Aluminum Hydroxides).
Medical Findings
The Kern County Department of Agriculture investigation indicated that ten (10) employees of the pistachio processing company had medical evaluations following the December 10, 2009 accident; nine (9) were available for interview by WHS staff on Tuesday January 12, 2010. The remaining employee left employment with the plant prior to the WHS visit and could not be reached. Information on this employee was available from the initial interview by Kern County Department of Agriculture staff. Medical records on two (2) cases were available from information collected by Kern Department of Agriculture staff. Medical records for seven (7) additional cases were made available to the WHS staff by the California Department of Public Health, Occupational Health Branch.

The extent of medical evaluation varied according to the judgment of individual treating providers. One Bakersfield hospital performed bronchoscopy on all three (3) of the patients seen there, and found abnormalities in each. The seven (7) patients examined at two (2) other hospitals did not have bronchoscopies. There were also minor variations in the use of x-rays and pulse oximetry, and the supportive treatment administered to individual patients.

The case summaries below integrate information from emergency room and hospital admission records, interviews conducted by Kern County Department of Agriculture staff on December 10 and December 11, 2009, and interviews by WHS staff on January 12, 2010.

A summary of the findings for individual workers is shown below:

Case # 2010-291, a 25 year-old forklift driver assisted in trying to extinguish the fire. When evaluated in the emergency room at Hospital A, he reported symptoms of nausea, vomiting, chest tightness, wheezing, and shortness of breath exacerbated by coughing. At a subsequent interview, he described additional symptoms including tremor, abdominal pain and sleepiness. Physical examination showed elevated blood pressure (162/93mmHg), rapid heart rate (112 beats per minute), and a rapid respiratory rate (28 cycles per minute). Additional exam findings included diaphoresis (sweating), pharyngeal erythema (redness in the throat), decreased breath sounds at the bases of the lungs and mild rhonchi (abnormal breath sounds).

Blood gases showed a normal O₂ saturation (97%) and a borderline low level of bicarbonate (22 mEq/L). His ECG (electrocardiogram) demonstrated a variable heart rate (61-96 beats per minute), with occasional paired premature ventricular contractions (PVCs). He had a normal chest x-ray, but the bronchoscopy performed prior to discharge showed acute airway inflammation, with no evidence of pulmonary edema.

Case # 2010-292, a 24 year-old forklift driver, employed by a labor contractor, had worked 4-5 months at the plant. He assisted in putting out the fire. On subsequent interview, he mentioned

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2 Hospital A – Bakersfield Heart Hospital, Hospital B – Mercy Hospital in Bakersfield, Hospital C – Delano Regional Medical Center

3 WHS interview 1/12/2010
that there was a strong “ugly” odor present at the time. In the ER, he reported that he had breathed fire extinguishing agent as well as fumes from the fire.

In the ER at Hospital B, he complained of headache, sore throat, intractable nausea, vomiting, mild shortness of breath, and body aches. His blood pressure was slightly elevated (141/69) and he had a normal chest x-ray.

He was treated with morphine and ketorolac for pain, as well metoclopramide for nausea. He was admitted for observation because of concern about his exposure to phosphine. He was discharged on December 11 without any medications, but noted on subsequent interview\(^3\) that he had a headache for 4 days afterwards.

**Case #2010-293** provided no information on job title, age, or details of exposure. When Kern County Agricultural Commissioner (CAC) investigators interviewed him at an emergency room on December 10, 2009, he reported dizziness and nausea. He signed himself out of the emergency room against medical advice, and was no longer employed at the pistachio processing company when WHS staff came to interview workers on January 12, 2010.

**Case # 2010-294**, age 20, a forklift driver, worked at the processing plant 6 months before the fire, and was employed by a labor contractor. He saw sparks and smoke coming from the covered tarp, accompanied by a smell that resembled “maiz” (corn), and used the extinguisher to put the fire out. He estimated that his total exposure time was about 15 or 20 minutes.

In the emergency room at Hospital C, he reported having nausea, neck pain, chest pain, shortness of breath, and irritation of the eyes and upper respiratory tract. He had slight elevation of temperature (100.2°F), slightly elevated blood pressure (146/91 mm Hg), and conjunctival congestion. His arterial blood gases showed a borderline elevation of pH (7.43), lower than expected PaCO2 (25 mm Hg), an elevated PaO2 (151 mm Hg, while receiving 1.5 L O\(_2\)/minute by nasal cannula). His chest x-ray was normal except for hyper-inflated lungs. He was observed for 24 hours, and then released from the hospital. At the time of the January 12, 2010 follow-up interview, he reported that he felt some symptoms intermittently since being released from the hospital.

**Case # 2010-295**, a 38 year-old maintenance mechanic, helped remove the tarp from the burning pallets and also used an extinguisher to help put out the fire. In the emergency room at Hospital B, he reported sore throat, headache, nausea and vomiting. In a separate interview the same day with Kern CAC staff, he reported additional symptoms including chest pain, and eye irritation. CPCS advised extended observation and he was held overnight.

He was discharged on December 11, 2009, but had chest pain the following day that required re-evaluation at the Hospital B emergency room. At that emergency room visit, he had slight elevation of blood pressure, but otherwise normal vital signs, normal O\(_2\) saturation, normal physical findings, and a clear chest x-ray.
He had a CT scan December 22, 2009 that showed no evidence of restrictive lung disease or pulmonary fibrosis. However, he reported still having mild chest pain and a burning sensation in his chest at the January 12, 2010 interview.

He sought follow-up care for physical and anxiety-related symptoms that caused him to miss work intermittently through December, 2010. He had 3 separate Pulmonary Function Tests (PFTs), on May 14, 2010, October 18, 2010 and November 30, 2010 that did not meet American Thoracic Society (ATS) standards for acceptability and repeatability. The Pulmonary Function Studies showed decreased lung volumes, indicating possible restrictive lung disease.

**Case # 2010-296**, the 20 year-old was the initial responder to the fire. He reported sore throat, a runny nose, chest tightness and shortness of breath exacerbated by coughing, as well as nausea and vomiting when evaluated in the emergency room at Hospital A. He had a low-grade fever (99.5°F), slightly elevated blood pressure (151/83 mm Hg) and was observed to be anxious, pale and diaphoretic. Examination showed conjunctival and pharyngeal erythema (eye and throat redness), nasal swelling, and rhonchi (abnormal breath sounds) in the lungs. Arterial blood gases were normal on room air. His chest x-ray was normal. His electrocardiogram showed some minor abnormalities, probably unrelated to the exposure. On the advice of CPCS, he was observed overnight in the hospital and received supportive treatment for nasal congestion and nausea. Intravenous steroids, inhaled steroids, bronchodilators and antibiotics were prescribed for his respiratory problems. He had a bronchoscopy December 11, 2009 that showed marked erythema in the left upper lobe airways, with evidence of tracheobronchitis (airway inflammation).

**Case # 2010-297**, a 34 year-old maintenance worker, initially learned about the fire over a plant radio. He reported that he tried to calm down the other plant workers who were attempting to extinguish the fire and said that he observed a cloud of “smog” at the scene of the fire. In the emergency room at Hospital C, he reported burning of the eyes (described as blurry vision in a subsequent interview), nausea and vomiting. Pulse oximetry showed an oxygen saturation of 95%, but he did not have persistent respiratory difficulty. A subsequent arterial blood gas, on 2 liters/minute of oxygen, showed 99% saturation. His chest x-ray was reported as normal. He was admitted to the hospital for observation overnight and discharged on December 11, 2009. He reported subsequently that he felt fine when he got out of the hospital.

**Case # 2010-298**, a 20 year-old maintenance worker and assistant mechanic also learned about the fire over a plant radio. He cut the tarp covering a burning pallet and then used a forklift to move the pallet. In the emergency room at Hospital C, he reported difficulty breathing, headache, eyes burning, nausea, vomiting, feeling weak, chest congestion, burning lungs, and sore throat. (In a subsequent interview, he also reported experiencing dizziness.)

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4 A non-calcified left upper lung granule, was noted, but no findings likely related to the exposure. Specifically, there was no CT evidence of interstitial lung disease.

5 While in triage, O₂ saturation ranged from O₂ sat 95% to 97%. Respiration was listed as 16-17 cpm. 2-4L/min of oxygen was given. Chest was non-tender. Breath sounds and chest x-ray were normal.
He had an elevated respiratory rate (22 cycles per minute), conjunctival congestion and erythema. Examination of the lungs demonstrated rhonchi (abnormal breath sounds) and wheezing. He had a slightly elevated white blood cell count, normal arterial blood gases on room air, and a normal chest x-ray. He was admitted for overnight observation and received supportive treatment that included supplemental oxygen and “aerosol treatment.”

**Case # 2010-299**, a 51 year-old maintenance worker who had worked at the plant for 10 years, learned about the fire on the plant radio and decided to help put it out. In the emergency room at Hospital A, he reported shortness of breath, nausea, vomiting, chest pain and discomfort, and sore throat. (At a subsequent interview, he reported that he smelled the gas from fire, but did not have symptoms, and he went to hospital for evaluation only). He had a slightly elevated blood pressure (153/98 mm Hg), and a slightly rapid respiratory rate (22 cycles per minute). Examination revealed diaphoresis (sweating), pharyngeal erythema (redness from apparent irritation of the throat), decreased breath sounds at the lung bases, and rhonchi (abnormal breath sounds). The white blood cell count was slightly elevated and the arterial blood gases showed slightly low PaO2 (76 mm Hg) and an O2 saturation of 96%. Minor abnormalities of the electrocardiogram were identified, but it was unclear whether or not these were related to his exposure. His chest x-ray was initially interpreted as showing infiltrates by the emergency room staff, but was reported as normal by radiology.

Emergency staff felt his symptoms may have been related to a preexisting upper respiratory infection, but nonetheless admitted him for observation after receiving information about his exposure from CPCS. He was treated for “inhalation injury” with systemic steroids, and medications for nausea and pain. He had a bronchoscopy prior to discharge that showed tracheobronchitis with marked erythema and easy friability. A biopsy done during bronchoscopy showed benign pulmonary tissue with occasional anthracotic pigment deposits with no evidence of granuloma or malignancy.

**Case # 2010-300**, a 28 year-old supervisor, with 7 years of experience at the plant, used an extinguisher to try to put out the fire. In the emergency room at Hospital B, he complained of nausea, headache, vomiting and sore throat. (He complained of dryness in the chest and throat to Kern County Agricultural Commissioner interviewers. He also reported blurry vision in the follow-up interview). Upon arrival at the hospital, his O2 saturation was 94%, despite being on supplemental oxygen. His blood pressure was slightly elevated (141/92 mm Hg), as was his white blood cell count. His chest x-ray in the emergency room was clear. Although he appeared stable clinically, he was admitted for observation because of concerns about his exposure raised by CPCS staff.

Although a repeat chest x-ray a few hours after admission showed a right lower lobe infiltrate, his O2 saturation rose to 100%. He was discharged on December 11, 2009. He was re-evaluated in the Mercy ER on December 12, 2009 because of chest pain, but his O2 saturation remained at 100% and a chest x-ray was clear.

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6 The examination in the Medical Unit noted “few rhonchi and no rales.” He was given an “aerosol treatment because of an obvious wheezing”
On January 12, 2010, he reported that he still intermittently experienced burning in the chest, and anxiety. He was subsequently seen in an occupational clinic on February 6, 2010 for headaches, visual changes, and paresthesias - all new since the incident. He was evaluated for a possible acute cerebrovascular accident (stroke), which was ruled out on a computed tomography (CT) scan. He was re-evaluated February 7, 2010 in the emergency room and treated for a vascular (migraine) headache. CPCS was contacted and felt that his symptoms were not related to his prior exposure.

Summary of Medical information

The medical findings were consistent with exposure to phosphine gas although it is possible some symptoms were attributable to other factors, including possible exposure to fire extinguisher chemicals or combustion by-products. Seven (7) of the ten (10) workers had respiratory distress, indicated by chest pain or shortness of breath, an elevated respiratory rate or oxygen saturation below 96% (Case numbers: 2010-291, 2010-295, 2010-296, 2010-297, 2010-298, 2010-299, 2010-300). Two (2) additional cases had short-term respiratory symptoms (Case numbers: 2010-292, 2010-294).

No confirmed cases of pulmonary edema were identified, but one worker had a transient infiltrate (an indication of possible pneumonia or fluid on the lung) on a chest x-ray. Bronchoscopy carried out in three (3) cases seen at Hospital A showed airway inflammation. Three (3) workers (Case numbers: 2009-294, 2009-295, 2009-300) reported persistent symptoms they associated with the December 10, 2009 fire, more than a month after the exposure.

Prevention of Phospine-related Illness

The fire and subsequent worker exposures that occurred in this case were entirely preventable. Although the safety hazards of phosphine-generating fumigants have been known for a considerable time period, several potential problems were ignored in the lead-up to the fire that occurred on December 10, 2009:

1. The outdoor location of the fumigation stack was adjacent to a building downspout;
2. Once the fire began, initial responders included untrained plant personnel, who attempted to put out the fire with H2O-based extinguishers and temporarily made the fire worse;
3. There were no warning signs posted. Title 3 CCR 6782(c) requires posting for fumigations in enclosed spaces, visibly posted, 24 hours before the actual application. Bilingual warning signs are required.[60] Although not technically required for commodities fumigated outdoors, warning signs would be a helpful adjunct to increased training. A suggested sign

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7 Patient complained of tingling in both arms lasting for about 10 minutes, occurring twice weekly. On exam, there were decreases in his upper arm reflexes and slight decrease of sensation from the right should to the right fingertips.
with the simple message stating that phosphine fumigants react adversely with water is shown in Figures 2a. Figure 2b is a sample fumigation “DANGER-NO ENTRY” poster.

It is likely that no workers would have become ill if they had refrained from trying to extinguish the fire and simply called for assistance. Workers developed short-term respiratory distress that required emergency evaluation, most received only supportive care and had uncomplicated courses of hospital care. Bronchoscopies performed on three (3) workers showed significant airway inflammation.

Other preventive measures that could have been exercised to prevent the likelihood of such incident include:

(1) Fumigation should only be conducted by personnel trained in the proper, label-directed application methods of Aluminum Phosphide that meet regulatory requirements;

(2) All workers involved in the processing of produce should be adequately trained on how to handle emergencies involving the fumigation process;

(3) Fumigation of produce should be conducted in a manner that allows protection from sudden changes in weather and environmental elements;

(4) All employees shall be notified of an upcoming application, ahead of schedule;

Alternative control methods that could be used prior to the drying stage of the processing operations include:

(1) Use of the 98% CO$_2$, 2% phosphine formulation. This is also a promising means of preventing fires associated with the use of phosphide fumigants. Nevertheless, precaution is necessary in the use of the new formulation illustrated by the 41 cases associated with its use in California since 2004 (see discussion above).  

(2) Use of sealed chambers. Filling the chamber with nitrogen or carbon dioxide depletes oxygen.  

(3) Storing commodities in refrigerated storage, but this may not be economically feasible for nuts and other dried commodities.  

(4) Use of less toxic chemical such as hydroprene, methoprene, pyriproxyfen, pyrethrin and synthetic pyrethroid insecticides, for application with industrial fogging equipment.  

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(5) Treating appropriate warehouse spaces with the relatively volatile organophosphate compound, DDVP. The 7.8% formulation used for this purpose is labeled as a Category I pesticide, and is much more toxic than foggers containing insect growth regulators and pyrethrin/pyrethroid insecticides. 

Figure 2a. SAMPLE WARNING POSTER FOR ALUMINUM PHOSPHIDE

IN CASE OF FIRE

DO NOT use water

Phosphine gas can react violently to air and water

Aluminum Phosphide produces toxic gas

ALERT SUPERVISOR

EN CASO DE INCENDIO

NO USE

Puede reaccionar con agua o aire con violencia

Fosfuro de Aluminio puede producir un gas tóxico-Fosfina

Pida ayuda de su supervisor

Figure 2b. FUMIGATION WARNING POSTER

DANGER FUMIGATION
¡PELIGRO FUMIGACIÓN!

DO NOT ENTER
NO ENTRE

Fumigant: Aluminum Phosphide
Fumigant: Fosfuro de Aluminio

Date/Time of Fumigation: December X, 20XX, 8:00 a.m.
Fecha/Hora de Fumigación: Diciembre X, 20XX, 8:00 a.m.

Permittee-Operator/Permissionario-Operador: Juan de la Cruz
123 Main Street, Merced, CA 95348
Tel: (209) 123-4567