Proactive Best Available Control Technology Analysis

District BACT Guideline 5.2.12

Phosphine Fumigation of Nuts, Dried Fruit, Grain, and Beans

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I. Introduction

The objective of this project is to proactively update the Best Available Control Technology (BACT) guideline 5.2.12, which covers phosphine fumigation of nuts, dried fruit, grain, and beans. This guideline was last updated on January 23, 2013.

This proactive update is necessary to incorporate the most stringent emission control standards that have been achieved in practice. Furthermore, the proactive update to this BACT guideline will bring consistency in implementing the BACT standard throughout the regional offices of the District for new and modified phosphine fumigation of nuts, dried fruit, grain and beans triggering BACT. The discussion in this document will be limited to the following items:

- Source of emissions
- Top-Down BACT Analysis for each pollutant
- Recommendation

II. Source of emissions

This BACT determination applies to the phosphine fumigation of nuts, dried fruit, grain and beans.

For all of the agricultural commodities - nuts, dried fruit, grain and beans - there are several common methods of fumigating with phosphine. Not all of these methods are used for every commodity. However, for any given method, the procedures are the same regardless of the commodity being fumigated.

The most common form of phosphine fumigant is a solid product that is sold either in tablet or powder form under the trade name Phostoxin® or under several other generic names. This product is formulated with 55% aluminum phosphide (AlP) and 45% ammonium carbamate (NH_2COONH_4). For the purposes of this evaluation, this product will referred to generically as aluminum phosphide. Aluminum phosphide reacts with moisture in the atmosphere to form phosphine gas, aluminum hydroxide, ammonia and carbon dioxide. Aluminum hydroxide is an inert solid, and carbon dioxide is not considered a Hazardous Air Pollutant (HAP). Thus, both are not a concern for air pollution. However, phosphine gas is a HAP and, as indicated below, ammonia is an affected pollutant.

Section 2 of District Rule 2201 states the following:

> "This rule shall apply to all new stationary sources and all modifications to existing stationary sources which are subject to the District permit requirements and after construction emit or may emit one or more affected pollutant."

Per Section 3 of Rule 2201, an affected pollutant is defined as, “Those pollutants for which an Ambient Air Quality Standard has been established by the EPA or by the California Air Resources Board, (ARB), and the precursors to such pollutants, and those pollutants regulated by the EPA under the Federal Clean Air Act or by the ARB under the Health and Safety Code including, but not limited to, VOC, NO_x, SO_x, PM10, CO, and those pollutants which the EPA, after due process, or the ARB or the APCO, after public hearing, determine may have a significant adverse effect on the environment, the public health, or the public welfare.”

The California Air Resources Board (ARB) has established an acute toxic reference exposure level for ammonia. Therefore, the ARB has determined that ammonia may have a significant adverse effect on the environment, the public health, or the public welfare. Based on this determination, ammonia is considered to be an affected pollutant. Therefore, sources that emit ammonia are subject to the requirements of District Rule 2201.

The balanced chemical equations for this reaction are listed below:

Phostoxin reacts with moisture in the air to produce Phosphine or Hydrogen Phosphide, PH_3:

$AlP + 3H_2O \Rightarrow Al(OH)_3 + PH_3$; 1 mole AlP yields 1 mole PH_3

Ammonium carbamate releases ammonia and carbon dioxide as follows:

$NH_2COONH_4 \Rightarrow 2NH_3 + CO_2$; 1 mole NH_2COONH_4 yields 2 moles ammonia

Phosphine is also available in gaseous form in pressurized cylinders. Gaseous phosphine is available in two forms. It can be purchased as a mixture of phosphine gas and carbon dioxide that is sold under the trade name Eco2Fume®. Eco2Fume® is comprised of 1.8-2.2% (by weight) phosphine and 97.8-98.2% (by weight) carbon dioxide. Alternatively, it can be purchased as a pure gas under the trade name VAPORPH$_3$OS. Pure phosphine has a lower flammable limit, in air, of 1.8% by volume, and as a result, it must be blended with air when used. This means that VAPORPH$_3$OS® must be used in conjunction with special blending equipment. Because there is no ammonium carbamate (NH_2COONH_4) in either of these products, the use of these products results in zero ammonia emissions.

<u>Stacked bins:</u>

This process involves loading the commodity into bins then stacking the bins and covering the entire stack with gas tight tarps. The tarps are weighed down around the perimeter to seal them to the ground. If aluminum phosphide is used, a predetermined number of tablets are placed in paper bags or metal pans and placed among the stacks. If gaseous phosphine is used, a tube or “wand” which passes under the tarp is placed among the stacks. After the tarps are sealed, the end of the tube that is sticking out of the tarp is connected to the gas cylinders and the gas is introduced into the stacks.

Bins with Plastic Liners:

This process involves loading the commodity into bins that have been lined with plastic bin liners which are essentially large plastic bags. If aluminum phosphide is used, a predetermined number of tablets are placed in a small paper envelope which is set on top of the commodity in the bin, then the plastic bin liner is gathered up and sealed using a zip tie and tape. If gaseous phosphine is used, a tube or "wand" is held over the stack so that the bin liner can be drawn up around it. The phosphine gas is introduced into the bag then the wand is removed and the liner is sealed with a zip tie and tape.

Palletized Stacks:

This process involves placing a plastic bin liner on top of a pallet. Finished product is then placed on the pallet and the bin liner is draw up over the stack of finished product. If aluminum phosphide is used, a predetermined number of tablets are placed in a small paper envelope which is set on top of the product stack, then the plastic bin liner is gathered up and sealed using a zip tie and tape. If gaseous phosphine is used, the bin liner is drawn up over the stack of finished product and sealed. A tube or "wand" is then used to puncture the bag and phosphine gas is introduced into the bag. The wand is then removed and the hole in the liner is sealed with a tape.

Fumigation Chambers:

This process involves loading the commodity into plastic bins which are in turn loaded into an airtight fumigation chamber. If aluminum phosphide is used, a predetermined number of tablets are placed in paper bags or metal pans and placed among the bins. The chamber door is then closed and sealed. If gaseous phosphine is used, the doors are closed and sealed and a tube or "wand" is inserted through an opening. The phosphine gas is introduced into the chamber, then the wand is removed and the opening is sealed. Circulation fans are then used to distribute the phosphine evenly throughout the chamber.

Warehouses:

The process for warehouse fumigation is similar to that used in fumigation chambers. The primary difference is that a fumigation chamber is specifically designed for fumigation where a warehouse is not. Warehouses are typically much larger than fumigation chambers and are not typically designed to be airtight. As a result, extra effort to seal a warehouse has to be taken prior to fumigation. Once the warehouse has been sealed the procedures are essentially the same.

Storage Silos:

For commodities that are stored in silos, if aluminum phosphide is used, a predetermined number of tablets are placed in a paper bag or metal pan and placed in the silo, then all access doors and vents are sealed. If gaseous phosphine is used, all access doors and vents are sealed and a tube or “wand” is inserted through an opening. The phosphine gas in introduced into the silo, then the wand is removed and the opening is sealed.

Stockpiles of Field Run In-Hull Almonds:

This type of fumigation is specific to almonds only. Field run in-hull almonds are almonds that have been harvested but have not yet been processed.

During the season, almonds are received from the field and are unloaded, arranged in stockpiles, tarped and fumigated in stockpile yards to protect the product from the weather and deterioration. The stockpiles are located in large yards that cover many acres. The almond industry produces over 1.3 billion pounds of almonds, which equates to 5.2 billion pounds of field delivered product before processing. It is imperative that grower lots and varieties are kept separate and thus field run in-hull almonds requires a very large, spread out stockpile area at industry operations.

Because the storage area is so large, and product is not in close proximity to the huller building, access to power, scales to weigh out dispensing of the product and other tools needed to apply gaseous phosphine are not reasonably accessible. In addition, the fumigation chemical is toxic, and moving cylinders of phosphine across a large storage yard that commonly becomes rough and uneven is not safe or appropriate. The parties who represent the manufacturer of this product strongly discourage the use of Eco2Fume®in this type of application for safety reasons.

Furthermore, scales and dispensing equipment are calibrated and can easily fall out of proper adjustment/calibration when jostled around in movement from location to location. Uneven or even unintentional excessive exposures or applications could then occur. Therefore, phosphine fumigation of tarped stacks of field run in-hull almonds is accomplished through solid fumigant.

III. Top-Down BACT Analysis

Per District Policy APR 1905, Risk Management Policy for Permitting New and Modified Sources, the District must evaluate health risk from new and modified sources, with the following requirements:

A. In order to control emissions of hazardous air pollutants to the maximum level achievable, applicants must apply Toxic Best Available Control Technology (T-BACT) to each new and modified emissions units with:

   1. A greater than de minimis increase in cancer risk; or

   (A de minimis increase in cancer risk is an increase in risk of one per million, as determined by a health risk assessment.)

   2. A greater than de minimis increase in non-cancer risk;

   (A de minimis increase in non-cancer risk is an increase in the hazard index of one, as determined by a health risk assessment.)

B. New sources or modification projects shall not result in a significant increase in cancer risk, except as provided in Section IX of APR 1905 (Discretionary Approval). A significant increase in cancer risk is an increase in the Maximum Excess Cancer Risk of at least 20 per million as determined by a health risk assessment.

C. New sources or modification projects shall not result in a significant increase in non-cancer risk, except as provided in Section IX of APR 1905 (Discretionary Approval). A significant increase in non-cancer risk is an increase in the hazard index of at least one as determined by a health risk assessment.

Since phosphine (chemical abstract number: 7803-51-2) is a HAP, the District must evaluate the chronic risk for phosphine emissions, when scenario A.2 above occurs as a result of the health risk assessment.

BACT analysis

Step 1 - Identify All Possible Control Technologies

The following BACT clearinghouse references were reviewed to determine whether any phosphine fumigation of nuts, dried fruit, grain and beans operations have been required to employ NH_3 and phosphine controls:

- EPA RACT/BACT/LAER clearinghouse
- CARB BACT clearinghouse
- South Coast AQMD (SCAQMD) BACT clearinghouse
- Bay Area AQMD (BAAQMD) BACT clearinghouse
- Sacramento Metro AQMD (SMAQMD) BACT clearinghouse

- San Diego AQMD (SDAQMD) BACT clearinghouse
- San Joaquin Valley APCD (SJVAPCD) BACT clearinghouse

Also, the following Air Districts' Rules and Regulations were reviewed to determine what NH_3 and phosphine emission limits are currently imposed on phosphine fumigation of nuts, dried fruit, grain, and beans operations:

- South Coast AQMD
- Bay Area AQMD
- Sacramento Metro AQMD
- San Diego AQMD
- SJVAPCD

Finally, the District also conducted a survey of permit limits phosphine fumigation of nuts, dried fruit, grain, and beans operations located in the SJVAPCD. The purpose of the survey was to determine what NH_3 and phosphine emission control standards are currently achieved in practice.

A. Survey of BACT Guidelines:

The EPA RACT/BACT/LAER clearinghouse does not include general guidelines, only determinations made by individual agencies. The clearinghouse was searched for phosphine fumigation of nuts, dried fruit, grain, and beans operations, but none were found.

The CARB BACT clearinghouse did not contain any guidelines for phosphine fumigation of nuts, dried fruit, grain, and beans operations.

The SCAQMD LAER/BACT clearinghouse for non-major polluting facilities and for major polluting facilities was searched for phosphine fumigation of nuts, dried fruit, grain, and beans operations but none were found.

The BAAQMD BACT clearinghouse was searched for phosphine fumigation of nuts, dried fruit, grain, and beans operations, but none were found.

The SMAQMD clearinghouse was searched for phosphine fumigation of nuts, dried fruit, grain, and beans operations, but none were found.

The SDAQMD clearinghouse was searched for phosphine fumigation of nuts, dried fruit, grain, and beans operations, but none were found.

The SJVAPCD clearinghouse has one BACT guideline for phosphine fumigation of nuts, dried fruit, grain, and beans operations. The requirements are shown in the table below:

Guideline	Pollutant	Achieved in Practice or in the SIP	Technologically Feasible	Alternate Basic Equipment
5.2.12	Ammonia (NH_3)	Stacked Bins, Bins with Plastic Liners, Palletized Stacks, Shipping Containers, Fumigation Chambers, Warehouses, Storage Silos and Stockpiles: use of aluminum phosphide based solid fumigant and/or phosphine cylinder gas and fumigated inside gas tight tarps, gas tight bin liners or a gas tight enclosure	Ammonia Scrubber (98% control)	*Use of phosphine gas or a mixture of phosphine gas and carbon dioxide from pressurized cylinders
	Phosphine (T-BACT)		Carbon Absorption or Equivalent (95% control)	

*Note that the Alternate Basic Equipment listed here is already listed as Achieved in Practice (AIP). Therefore, the AIP control technology taken from this guideline will be listed as follows: "Stacked Bins, Bins with Plastic Liners, Palletized Stacks, Shipping Containers, Fumigation Chambers, Warehouses, Storage Silos and Stockpiles: use of 1. aluminum phosphide based solid fumigant fumigated inside gas tight tarps, gas tight bin liners or a gas tight enclosure; and/or 2. phosphine gas or a mixture of phosphine gas and carbon dioxide from pressurized cylinders, fumigated inside gas tight tarps, gas tight bin liners or a gas tight enclosure."

Summary of BACT Guidelines:

Based on the above information, the current achieved in practice BACT emissions limitation for phosphine fumigation of nuts, dried fruit, grain and beans operations would be:

NH_3:

- Stacked Bins, Bins with Plastic Liners, Palletized Stacks, Shipping Containers, Fumigation Chambers, Warehouses, Storage Silos and Stockpiles: use of 1. aluminum phosphide based solid fumigant fumigated inside gas tight tarps, gas tight bin liners or a gas tight enclosure; and/or 2. phosphine gas or a mixture of phosphine gas and carbon dioxide from pressurized cylinders, fumigated inside gas tight tarps, gas tight bin liners or a gas tight enclosure. (Achieved in Practice)

- Ammonia Scrubber with 98% control (Technologically Feasible)

- Use of phosphine gas or a mixture of phosphine gas and carbon dioxide from pressurized cylinders (Alternate Basic Equipment)

Phosphine (T-BACT):

- Carbon Absorption or Equivalent (95% control) (Technologically Feasible)

B. Survey of Permit Requirements:

In order to evaluate what NH_3 and phosphine controls are currently being achieved by phosphine fumigation operations of nuts, dried fruit, grain and beans permitted in the SJVAPCD, all permitted sources within the District were searched for phosphine fumigation operations.

The SJVAPCD currently has 122 active PTO for phosphine fumigation operations of nuts, dried fruit, grain and beans.

The most common requirements on the permits within the SJVAPCD are as follows:

NH_3:

- Stacked Bins, Bins with Plastic Liners, Palletized Stacks, Shipping Containers, Fumigation Chambers, Warehouses, Storage Silos and Stockpiles: use of 1. aluminum phosphide based solid fumigant fumigated inside gas tight tarps, gas tight bin liners or a gas tight enclosure; and/or 2. phosphine gas or a mixture of phosphine gas and carbon dioxide from pressurized cylinders, fumigated inside gas tight tarps, gas tight bin liners or a gas tight enclosure

- Minimization of the use of fumigant

Phosphine (T-BACT):

- None listed

Summary of Permit Requirements to Establish the Achieved in Practice BACT Standard:

Based on the above information, the current most stringent achieved in practice BACT emissions limitation for phosphine fumigation of nuts, dried fruit, grain, and beans operations would be:

NH_3: Stacked Bins, Bins with Plastic Liners, Palletized Stacks, Shipping Containers, Fumigation Chambers, Warehouses, Storage Silos and Stockpiles: use of 1. aluminum phosphide based solid fumigant fumigated inside gas tight tarps, gas tight bin liners or a gas tight enclosure; and/or 2. phosphine gas or a mixture of phosphine gas and carbon dioxide from pressurized cylinders, fumigated inside gas tight tarps, gas tight bin liners or a gas tight enclosure

Phosphine: None listed

Step 2 - Eliminate Technologically Infeasible Options

There are no technologically infeasible options listed in Step 1. All of the emission control options under consideration are based on either current BACT requirements, current rule requirements, or actual source test data. Therefore, no further discussion is required.

Step 3 - Rank Remaining Control Technologies by Control effectiveness

The following control technologies have been identified and are ranked based on stringency:

NH_3:

1. Stacked Bins, Bins with Plastic Liners, Palletized Stacks, Shipping Containers, Fumigation Chambers, Warehouses, Storage Silos and Stockpiles: use phosphine gas or a mixture of phosphine gas and carbon dioxide from pressurized cylinders, fumigated inside gas tight tarps, gas tight bin liners or a gas tight enclosure. (100% control) – Achieved in Practice[1]

2. Ammonia Scrubber (98% control) – Technologically Feasible[2]

3. Stacked Bins, Bins with Plastic Liners, Palletized Stacks, Shipping Containers, Fumigation Chambers, Warehouses, Storage Silos and Stockpiles: use of aluminum phosphide based solid fumigant fumigated inside gas tight tarps, gas tight bin liners or a gas tight enclosure. – Achieved in Practice

4. Minimization of use of fumigant – Achieved in Practice

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[1] The two Achieved in Practice control technologies originally proposed by the SJVAPCD District BACT Guideline 5.2.12 have been separated based on control efficiency, since phosphine gas eliminates ammonia emissions entirely, whereas aluminum phosphide based solid fumigants do not. However, it will be noted that aluminum phosphide based solid fumigants can be used in place of phosphine gas to satisfy BACT if it is demonstrated that it is infeasible for a facility to obtain or use phosphine gas pressurized cylinders.

[2] For individual projects, operations without a stack will include a technologically feasible cost analysis to determine the cost of enclosing the operation. However, it should be noted that this control technology is technologically infeasible for infield operations, as it is infeasible to enclose such an operation.

Phosphine:

1. Carbon Adsorption or equivalent (95% control) – Technologically Feasible

Step 4 - Cost Effectiveness Analysis

This is a proactive determination that is not part of a permitting action. Therefore, a cost effective analysis is not necessary.

Step 5 - Select BACT

The following NH_3 emission control standard has been determined to be achieved in practice. This established performance standard is recommended as the Achieved in Practice requirement.

NH_3: Stacked Bins, Bins with Plastic Liners, Palletized Stacks, Shipping Containers, Fumigation Chambers, Warehouses, Storage Silos and Stockpiles: use of phosphine gas or a mixture of phosphine gas and carbon dioxide from pressurized cylinders, fumigated inside gas tight tarps, gas tight bin liners or a gas tight enclosure.[3]

No phosphine emission control standards were found to be achieved in practice. The following performance standard is recommended as the Technologically Feasible requirement for T-BACT.

Phosphine: Adsorption or equivalent (95% control) –Technologically Feasible for T-BACT

IV. Recommendation

Upon approval, adopt the proposed draft BACT guideline in Appendix A into the District's BACT Clearinghouse.

Appendices

Appendix A: Proposed Draft BACT Guideline 5.2.12
Appendix B: Current BACT Guideline 5.2.12 (1/23/13)

[3] If it is suitably demonstrated that it is infeasible for a facility to obtain or use phosphine gas pressurized cylinders, aluminum phosphide based solid fumigants can be used in place of phosphine gas to satisfy BACT.

Appendix A
Proposed Draft BACT Guideline 5.2.12

San Joaquin Valley
Unified Air Pollution Control District

Best Available Control Technology (BACT) Guideline 5.2.12

Emissions Unit: Phosphine fumigation of nuts, dried fruit, grain, and beans
Industry Type: Agricultural products
Equipment Rating: All

Pollutant	Achieved in Practice or contained in SIP	Technologically Feasible	Alternate Basic Equipment
Ammonia (NH3)	Stacked Bins, Bins with Plastic Liners, Palletized Stacks, Shipping Containers, Fumigation Chambers, Warehouses, Storage Silos and Stockpiles: phosphine gas or a mixture of phosphine gas and carbon dioxide from pressurized cylinders, fumigated inside gas tight tarps, gas tight bin liners or a gas tight enclosure[4]	Ammonia Scrubber (98% control) (not applicable to infield operations)	
Phosphine (T-BACT)		Carbon Absorption or Equivalent (95% control)	

BACT is the most stringent control technique for the emissions unit and class of source. Control techniques that are not achieved in practice or contained in a state implementation plan must be cost effective as well as feasible. Economic analysis to demonstrate cost effectiveness is required for all determinations that are not achieved in practice or contained in an EPA approved State Implementation Plan.

[4] If it is suitably demonstrated that it is infeasible for a facility to obtain or use phosphine gas pressurized cylinders, aluminum phosphide based solid fumigants can be used in place of phosphine gas to satisfy BACT.

Appendix B
Current BACT Guideline 5.2.12 (1/23/13)

San Joaquin Valley
Unified Air Pollution Control District

Best Available Control Technology (BACT) Guideline 5.2.12

Emissions Unit: Phosphine fumigation of nuts, dried fruit, grain, and beans
Industry Type: Agricultural products
Equipment Rating: All
Last Update: 1/23/2013

Pollutant	Achieved in Practice or contained in SIP	Technologically Feasible	Alternate Basic Equipment
Ammonia (NH_3)	Stacked Bins, Bins with Plastic Liners, Palletized Stacks, Shipping Containers, Fumigation Chambers, Warehouses, Storage Silos and Stockpiles: use of aluminum phosphide based solid fumigant and/or phosphine cylinder gas and fumigated inside gas tight tarps, gas tight bin liners or a gas tight enclosure	Ammonia Scrubber (98% control)	Use of phosphine gas or a mixture of phosphine gas and carbon dioxide from pressurized cylinders
Phosphine (T-BACT)		Carbon Absorption or Equivalent (95% control)	

BACT is the most stringent control technique for the emissions unit and class of source. Control techniques that are not achieved in practice or contained in a state implementation plan must be cost effective as well as feasible. Economic analysis to demonstrate cost effectiveness is required for all determinations that are not achieved in practice or contained in an EPA approved State Implementation Plan.