More than 2,000 fresh fruit fumigations have been performed in Chile using pure cylindered phosphine and the HDS System, since this patented method was developed in Chile in the year 2003.

Most of these fumigations were supervised by the Chilean agricultural authorities, SAG, together with foreign agricultural authorities.

The gas concentration was monitored continuously during each fumigation and the data were printed out for recordkeeping in order to maintain a fingerprint of each fumigation for future analysis.

At this time, two countries, Mexico and Iran, have agreed a protocol with the Chilean government in order to ask that the fruits, exported from Chile to those countries, must be fumigated with pure cylindered phosphine, using FOSFOQUIM’s patented fumigation procedure.

Fumigated fruits have been successfully exported to countries in Europe, Asia, Latin America and others. No damage to the fruits has been observed and no phosphine residues were found on fruits.

The fumigations are carried out only through FOSFOQUIM personnel because of the high quality and safety standard of this service provided by FOSFOQUIM.

The company had to invest large amounts of money in gas dispensing equipment, aeration equipment, laboratory tests, research, monitoring equipment, training and vehicles to be able to follow the demand for this novel technology. Logistic experts ensure the customers a good service, coordinated with local and foreign authorities.

Until April 2006, about 79 cooling chambers were adapted for phosphine fumigation in Chile with a total volume of 51,300 cubic meter.

This technology has converted Chile into one of the largest cylindered phosphine consumer worldwide.

At this time, efficacy of phosphine is being tested on other pest species, different than the pests were phosphine has proven to be effective. Also other types of fruits are being evaluated as for their resistance to phosphine, in order to ensure fruit quality.

A new age in phosphine fumigation started after FOSFOQUIM developed in the year 2001 the Horn Diluphos System for direct blending of phosphine with air.

Phosphine gas has been used for over 70 years as an insecticide, and it is presently the most accepted fumigant for stored products. It has a great ecological advantage; its application in pure form from cylinders does not leave harmful residues in the environment nor in treated products.

Nevertheless, because phosphine forms explosive and self flammable mixtures with air at concentrations over 18,000-ppm, it had not been possible to apply phosphine in its pure state by means of direct dilution with air, even though this would be the best way to apply the gas.

The problem then is to manage the dilution of pure phosphine with air into concentrations, below

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the limit of self-ignition, without producing ignition in the process.

Carrying out a series of different tests, Fosfoquim S.A. has managed to solve the problem by patenting a system for the safe dilution of phosphine with air.

The HORN DILUPHOS SYSTEM® (HDS) allows the blending of pure phosphine with air, to obtain a continuous flow of air mixed with phosphine at a concentration of 10,000 ppm at a rate of 19, 47 or 200 grams/minute of phosphine, depending on the model of dispensing equipment used. It is an automatic system that informs the operator on an LCD screen about the steps to follow.

Since the HDS system was developed, a lot of new tools and fumigation methods have been developed for different applications of phosphine to silos, flat storages, bunker storages, empty spaces, mills, containers and others.

Among these new fumigation technologies, FOSFOQUIM patented a method for the fumigation of fresh fruits with phosphine at low temperature and high phosphine concentrations, where the fruits are not damaged and the pests on the fruits are controlled effectively.

So far, the treatment with high dosages of methyl bromide (30-60 grams/m³) was the most used and effective fumigation method for fresh fruit, which, although quick and efficient, has a series of disadvantages, such as the known ozone depletion, residues and phytotoxicity.

The use of pure phosphine has as main advantage, compared to methyl bromide, which is the fact that it does not leave bromine residues in the fruit after treatment and that after liberated into the atmosphere, phosphine is oxidized into phosphoric acid by the action of sunlight. But not only that, phosphine has also great advantages for worker safety.

For several years, phosphine has been investigated as a fumigant for the treatment of fresh fruit and vegetables. Most of the research has shown good results as for mortality of insects. However, acceptable results were not obtained in regard to the quality of treated fruit, which had always suffered damage, change in taste, and could not be commercialized.

This observed damage had been caused by two reasons mainly:
- presence of ammonia in the phosphine that was generated through hydrolysis reaction of metal phosphides
- and, relatively high fumigation temperature, over 15 °C, at which the tests have been carried out.

Aluminum phosphide or magnesium phosphide based products have the great disadvantage that, if they are used at low temperature, they produce phosphine very slowly, which forces the application of the product at high temperature.

Another, and major problem, is that these metal phosphides always produce ammonia as a by-product and ammonia is known to be very phytotoxic.

The reactions involved in ammonia generation are following:

\[ \text{NH}_2\text{CO}_2\text{NH}_4 \rightarrow 2\text{NH}_3 + \text{CO}_2 \]
\[ \text{AlN} + 2\text{H}_2\text{O} \rightarrow \text{AlOOH} + \text{NH}_3 \]
\[ \text{Mg}_3\text{N}_2 + 6\text{H}_2\text{O} \rightarrow 3\text{Mg(OH)}_2 + 2\text{NH}_3 \]

For these two reasons, damage to the fruit it is always expected when using metal phosphides.

But on the other hand, because of the pyrophoric characteristics of the product, until the HORN DILUPHOS SYSTEM® was developed, it was not possible to apply pure cylindered phosphine for fumigations.

Now, using the HORN DILUPHOS SYSTEM®, it has been possible to carry out fresh fruit fumigation with pure phosphine free from ammonia, at low temperature and with high gas concentrations, with the surprising discovery that the quality of the fruit is not damaged and that it is possible to eliminate the main pests from fruits, without detecting phosphine residues in the fruits after some hours or days of aeration.

More than 2,000 fresh fruits fumigations have been performed in Chile using pure cylindered phosphine and the HDS System, since this patented method was developed in Chile in the year 2003. More than 1,500 fruit fumigations were done in the year 2006 until July.

Fumigated fruits have been successfully exported to countries in Europe, Asia, Latin
America and others. No damage to the fruits has been observed and no phosphine residues were found on fruits.

In this fresh fruit fumigation method, pure phosphine free from ammonia is used at low temperature for the control of pests. The gas is applied in fumigation chambers, cooling chambers or controlled atmosphere chambers.

It was determined that this can be done successfully, if the fumigation is carried out at a temperature between −1.5 and 6 °C with a concentration of pure phosphine free from ammonia, between 1,000 and 2,000 ppm in a sealed enclosure, with an exposure time between 24 and 72 hours, depending on the pest.

It was discovered that when lowering the temperature, it is possible to carry out the fumigation with a very high concentration of phosphine with no damage to the fruit, since at that temperature, the metabolic activity of fruit is slowed down. This high concentration compensates the low activity of the insects at low temperature, controlling the pests.

Some small off-taste of fumigated fruit was observed following the fumigation, but this disappeared after 1 or 6 days of storage at low temperature.

The main condition to avoid damage to the fruit during the fumigation period is to maintain the temperature low, not warming up the fruits.

The fruit is preferably treated at the cold storage temperature of each specie. For example, for apples, grapes, kiwis and berries, pears, nectarines, peaches, etc the treatment with temperature from −1.5 to 2 °C is preferable. In the case of other fruits like avocados, citrus fruit, mangos, it is preferable to treat them at their corresponding cold storage temperature.

The best way to do the treatment with phosphine is to fumigate the fruit directly in the cooling chambers, where the fruit is stored after the selection process, and leaving the cooling system working during the whole fumigation period.

The cooling chambers are modified for the fumigation process, installing one phosphine-air-mixture injection pipe, that blows the gas into the chamber near the fans of the cooling system in order to get a fast distribution of the gas inside the chamber, and a suction pipe, that sucks the air from inside the chamber but far away from the injection point.

The air from inside the chamber is recirculated through the Horn Diluphos System (HDS), where the phosphine is added to the air flow. In this procedure, no increase of pressure is generated inside the enclosure to be fumigated.

The size of phosphine dispensing equipment used for the standard fumigation procedures in Chile is such, that the time required for fumigation is less than, or close to, one hour. Fumigating with the HDS 800 (the largest available model) it takes 50 minutes to apply the gas to the largest fruit fumigation chambers in Chile with 4,800 cubic meters, using a dose of 2.1 g/cubic meter for the Mexican-Chilean fumigation protocol.

Additionally, aeration systems are installed in the chambers, which allows for the aeration of chambers, depending on the size of the blowers, in less than 90 minutes.

Most of these fumigations done in Chile are supervised by the Chilean agricultural authorities, SAG, together with foreign agricultural authorities.

At this time, two countries, Mexico and Iran, have agreed a protocol with the Chilean government in order to ask that the fruits, exported from Chile to those countries, must be fumigated with pure cylindered phosphine, using FOSFOQUIM’s patented fumigation procedure.

In the case of the Mexican Protocol, the fruits are fumigated with phosphine after packing the fruits in the processing facilities before shipment, and then a number of boxes are inspected by the Chilean or Mexican agricultural authorities. If no live insects are found, and the concentration curve of the monitor shows that the concentration was always higher than a certain limit, the fumigated lot is approved for export. If one live insect is found, the export of the fumigated lot is rejected. During this first season 2005-2006 of the Mexican-Chilean Protocol, no live insects were found during inspection of exported fruits by the Chilean agricultural authorities SAG or
the Mexican agricultural authorities.

In the case of Iran, the Chilean authorities have to check if the fruits were exposed to enough gas for enough time. If the fumigation was successful, which means that there was always a high gas concentration and the exposure time is longer than the limit, the fruits are released for export. If concentration or time were lower than required, the export of the fumigated lot is rejected.

The protocols agreed between the Chilean Government and the Mexican Government, and Iranian Government, establish exactly the conditions that apply for each protocol, regarding exposure time, temperature, concentration and others.

For all the phosphine fruit fumigations done in Chile, the gas concentration is monitored continuously and the data are stored electronically and printed out for recordkeeping in order to maintain a fingerprint of each fumigation for future analysis.

For this purpose, infrared monitors are used which are able to store the data and allow after fumigation to download the data to a computer.

The fumigations are carried out only through FOSFOQUIM personnel because of the high quality and safety standard of this service provided by FOSFOQUIM.

FOSFOQUIM trains its fumigators for several months in the use of the Horn Diluphos System, the handling of pure phosphine and the fruit fumigation technique, and only the fumigators that approve different written tests are allowed to start using the HDS units, first under supervision of an expert fumigator. Only after certification that the operator is well trained, the new fumigator can be made responsible for a fumigation procedure.

The company had to invest large amounts of money in gas dispensing equipment, aeration equipment, laboratory tests, research, monitoring equipment, training and vehicles to be able to follow the demand for this novel technology.

The number of fumigations increased considerably after starting with the two intergovernmental protocols with Mexico and Iran.

Logistic experts ensure the customers a good service, coordinated with local and foreign authorities.

Until April 2006, about 79 cooling chambers were adapted for phosphine fumigation in Chile with a total volume of 51,300 cubic meter of fruit fumigation chambers.

This technology has converted Chile into one of the largest cycled phosphine consumers worldwide.

In order to provide a good service, reducing the time required for gas injection, FOSFOQUIM developed in the time between 2001 and 2005, three models of phosphine blending devices.

The largest model developed in the year 2005, HDS 800, is able to apply 200 grams of phosphine per minute, which permits distributing the gas in the largest available cooling chambers in about one hour.

Also large grain warehouses are being fumigated with this new model of HDS unit, where in some cases, 300,000 tons of grain are fumigated in only a couple of hours, achieving an even gas distribution in less than 24 hours.

Until July 2006, more than 2,000 kg of phosphine were applied to fruits in Chile and more than 800,000 cubic meter of fruit fumigation chambers were fumigated with hydrogen phosphide in about 2,000 fumigations.

With this new tool in quarantine and pre-shipment fumigation, several actors in the industry and regulatory organizations are investigating the application of phosphine to different pests and fruits or vegetables.

At the same time, new phosphine monitoring technologies are being developed. Since it is of real importance to know exactly to which concentrations the fruits are exposed during fumigation, FOSFOQUIM is improving the available monitoring technologies, in order to ensure an effective method to control fumigation and thus also the pests.

New studies are being made in Chile by the fruit export association for other pests; in Argentina agricultural research centers are investigating the effect of phosphine on the Mediterranean fruit...
fly; in Chile and Germany, different studies are being made for residue analysis of phosphine in different type of fruits; Fruit export companies in Chile are researching for new markets, where fruits fumigated with phosphine, and thus free of pests, can be exported to; and different organizations are asking for this technology in, countries where it is still not available.

At this time, efficacy of phosphine is being tested on other pest species, different than the pests were phosphine has proven to be effective. Also other type of fruits are being evaluated as for their resistance to phosphine, in order to ensure fruit quality.

Until now it has been demonstrated that it is possible to control the main pests of the fruit, such as the mealybugs, *Pseudococcus spp*; apple moth, *Cydia pomonella*; eulia, *Proeulia spp*; fruit tree weevil, *Naupactus xanthographus*; mediterranean fruit fly, *Ceratitis capitata*; fruit fly, *Bactrocera spp*, *Anastrepha spp*; and *Thrips spp*.

Other pests that are being studied for their control with phosphine are the false Chilean mite, *Brevipalpus chilensis*; and the European red mite, *Pannonichus ulmi*.

The fruits that have been successfully fumigated, without showing any damage are: nectarines, plums, apricots, cherries, avocados, grapes, oranges, tangerines, lemons, clementines, apples, pears, and others.

Also vegetables, like lettuce, artichokes, asparagus, onions and garlic have been fumigated with phosphine without suffering any damage. Especially on lettuce, excellent control of trips was obtained, and in some species, even a longer shelf life was obtained if compared to non fumigated lettuces.

New test are being made on pomegranate, *Punica granatum* L. The preliminary tests have shown good results in pest control, and the quality of the fruits was not affected by the exposure to phosphine high concentrations of phosphine. This fruit is of interest for the fruit exporters since, although only small amounts of this fruit are sold, the value of the pomegranate is high.

Also persimmon fruits have been tested for their resistance to phosphine. An excellent control of mealy bugs, *Pseudococcus viburni*, was obtained and the fruits have not suffered any damage either. Quality, taste, smell, texture and color were not affected by pure hydrogen phosphine.

As conclusion it can be mentioned that the advantages of fumigating fresh fruit with pure phosphine using the HORN DILUPHOS SYSTEM® are great. Following some of the advantages:


- No changes in taste, smell, texture, color or shelf life of the fruit, if fumigation has been conducted at low temperature. This is mainly because it is possible to fumigate at low temperature with the cooling system running (Figure 1).

- It is not necessary to heat fruits up before fumigation. Therefore, the shelf life of the fruits is extended.

- There are no residues after fumigation on the fruits and no product residues that have to be deactivated and disposed after fumigation.

- Cylindred phosphine does not produce ammonia and it is, therefore, not phytotoxic.

- The fumigation can be done in the same cooling chambers where the fruit is stored prior to shipment.

- There is no need to fumigate at the port of arrival, since the fumigation can be done at the processing plant before shipping.

- The fruit can be delivered immediately upon arrival at the port since the fruit is already fumigated and inspected, increasing capacity of the ports to receive fruits, or giving other ports, that do not have fumigation facilities, an option to deliver fruits to other parts of the receiving countries.

- This fumigation technique has no environmental problems, since only hydrogen
phosphide is applied, which is readily deactivated by sunlight upon release into the atmosphere. Therefore there is no damage to the ozone layer, as it occurs with other fumigants used for fruit fumigation.

- The fumigation is operator friendlier than methyl bromide. The gas concentration can be monitored exactly with different electronic devices in order to ensure minimum exposure of fumigators and plant workers to the gas.
- Gas injection even in the largest fruit fumigation cool houses takes less than one hour and aeration systems are installed in order to allow aerating chambers in less than 90 minutes.
- As the method permits applying the gas from outside the facility, the gas concentration can be changed at any time during the fumigation.
- The gas can be applied to a totally sealed structure without increasing the pressure, if the gas from the cylinders is mixed with air taken from the inside of the structure to be fumigated.

- The HORN DILUPHO SYSTEM® allows stopping gas dispensing at any time during gas injection (Figures 2, 3, 4, 5 and 6).
- Unlike from what had always been thought, there are no corrosion problems on the cooling equipment if ammonia cooling systems are used.

These advantages are opening, only a short time after this technology started to be used, completely new fields of research for universities and research centers, new markets and possibilities to fruit exporters, access to better quality fruits to the customers, access to new type of fruits that could not be exported before because of pests, and most important, a real alternative for humankind to methyl bromide for quarantine and pre shipment fumigation without harming the ozone layer.

**Figure 1.** Cooling chamber adapted for phosphine fruit fumigation Curicó, Chile.
Figure 2. Fumigation Van. The van is equipped with one HDS unit, spare phosphine cylinders and spare nitrogen cylinders.

Figure 3. Inside of fumigation van equipped with one HDS unit, spare phosphine cylinders and spare nitrogen cylinders, phosphine monitors, hoses for gas distribution, and tools.
Figure 4. Part of Fosfoquim’s fumigation group and fleet.

Figure 5. Aeration vehicle equipped with a blower able to aerate chambers up to 1,000 cubic meter in less than one hour.

Figure 6. HDS 800 connected to a fruit fumigation chamber.