

FINAL REPORT

DURATION: 99-00

WTFRC Project #:

WSU Project # 13C-4164-2119

Project title: DPA contamination of organic apples and pears

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Cooperators: David Yonge and Reid Miller

Affiliation: Center for Multiphase Environmental Research, Washington State University

Cooperator: Charles Forney

Affiliation: Agriculture and Agri-Food Canada, Nova Scotia

Cooperator: Miles McEvoy

Affiliation: WSDA Organic Program

Objectives:

The objectives for this project that began with the 1999 crop were to:

1. Determine where in the postharvest handling process fruit can be contaminated with DPA.
2. Develop commercially viable options to remove DPA from contaminated surfaces.

Significant findings:

1. Working with the 1999 crop, we determined that the application of sodium hypochlorite, even at high doses, did not remove DPA from apples. There are no commercially acceptable methods of removing even trace amounts of DPA from apple surfaces. This line of research was abandoned when we were told by WSDA that any product applied to remove DPA would have to fall within the guidelines of chemicals approved for organic production under regulations set by WSDA and USDA.
2. Packers were contacted to determine their methods of cleaning packing equipment prior to packing organic fruit. The majority pack on Monday so as to utilize the weekend to clean the equipment. Most are cleaned with pressurized hot water while some followed with chlorine dioxide foam on hard surfaces. Most packers clean the dump tank carefully and change the water. Some packers use low levels of chlorine (50 ppm) in the dump tank.
3. Researchers in Italy determined that DPA moved onto apples from bins, storage room walls and equipment. The question that remained was whether this was a serious economic risk. We contracted with Dr. Charlie Forney, who has experience in ambient air DPA monitoring, to determine the seriousness of this movement. This work is still in progress, but preliminary reports indicate that a significant concentration of DPA exists in CA rooms with no DPA-treated fruit (**DPA Contamination_Figure1.pdf**). DPA was present in large concentrations in the CO₂ scrubber utilized for rooms in the facility (**DPA Contamination_Figure2.pdf**).
4. Dr. Forney verified that DPA did off gas from treated apples and wooden bins. It appears that 2 mil polyethylene film adsorbed larger quantities than other materials. Plastic bin materials sent from Washington were held in a chamber with 10 ppm DPA and after one month there was no detectable residue.

- In 2000, an additional contract was awarded to Drs. Yonge and Reid at WSU to determine how to analyze bin material for residual DPA and its potential for off gassing once a bin had picked up DPA. After developing a method to analyze DPA contained in hard surfaces they determined that DPA does remain within wooden bin material with a higher concentration inside the bin than on the outside. Samples are being collected over time to look at decay of the DPA. The bin had held commercially treated DPA the previous season and in prior years. To date, three groups of fruit box samples have been collected for DPA analysis. The collection dates were 11/3/00, 4/12/01, and 5/24/01. Sample analysis and quantification have been completed on the 11/3/00 and 4/12/01 samples (data presented in **Table 1**) and GC/MS quantification is in progress for the 5/24/01 sample set. The data in **Table 1** summarize the findings to date. It can be seen that the concentration varies by as much as a factor of two, depending on the side of the box from which the sample was collected. DPA concentration within each side exhibited a lower variability, with an average confidence interval of approximately 1.4 mg/kg. No detectable decrease in concentration of DPA was observed over the 5-month period between sampling events.

Table 1. Plywood fruit box DPA concentration for samples collected on November 3, 2000, and April 12, 2001. Note that sides 1-4 are vertical sides of the box and side 5 is the bottom of the box. DPA concentrations are based on 64.1% extraction efficiency.

Side of box (sample collection 11/3/00)	DPA (mg/kg)	Confidence interval (mg/kg) ($\alpha = 0.05$)
1	19.3	± 2.96
2	14.9	± 2.93
3	12.6	± 3.29
4	11.4	± 1.94
5	10.9	± 3.36
Overall Average	13.8	± 3.0
Side of box (sample collection 4/12/01)		
1	21.0	± 6.7
3	33.0	± 0.5

- In addition, Dr. Yonge exposed organic apples (Pippin) to DPA contaminated bin wood under conditions similar to full scale storage operations (97% N₂, 2% O₂, and 1% CO₂ atmosphere and 4°C). Two organic apples were placed in a 1-gallon zip lock bag with two 2.5-inch fruit box wood disks. The apples were not allowed to touch the wood. The bag was then purged with the gas mixture described above. The gas purge was repeated once per week and apples were tested at an exposure time of one, two, and three weeks. DPA quantification for the apple exposure samples is in progress. Apple samples are currently being analyzed at the GC/MS center. The resulting data will be shared at the postharvest meeting in July.
- Percent DPA recovery using the extraction procedure developed was estimated by spiking blended plywood (plywood purchased from a local hardware store) with a known mass of DPA (in acetone), allowing the acetone to evaporate and proceeding with the acetonitrile extraction procedure. This evaluation resulted in a 64.1% $\pm 0.8\%$ extraction efficiency, or recovery, of DPA. More recent extraction efficiency tests on the fruit box plywood indicate

significantly lower extraction efficiency and higher variability than with the purchased plywood. For example, the fruit box extraction efficiency tests yielded an average percent recovery of 41% \pm 18%. The cause of the lower percent recovery and higher variability is unknown at this time.

3. Research in labs of Drs. Yonge and Forney is continuing, and additional information should be available for dissemination at the Postharvest Conference of 2002.

Results and discussion:

1. DPA contamination is a constant danger in both storage and packing since the chemical is volatile and will be held on wood, hard surfaces and equipment. It will penetrate wooden bin material more than plastic material.
2. It appears that it will be difficult to develop an easy method of assaying the concentration of DPA within bin material that would relate to the risk of DPA contamination of apples.
3. Prevention of DPA contamination requires the use of new or previously untreated bins and storage in rooms cleaned of DPA residue that are plumbed so that air flow will not be mixed with rooms with treated fruit.
4. Packing equipment should be carefully cleaned prior to running non-treated fruit.

Budget:

The total amount awarded for this project was \$34,180 in 1999.

Project duration: 1999-2000

Current year: 2000

Funding allocation:

Dr. Kupferman for experiments to remove DPA from apples - \$20,180.

Drs. Yonge and Reid for experiments on developing a method to determine the amount of DPA within bin material - \$10,000.

Dr. Forney for the movement of DPA within storage rooms and in the atmosphere - \$4,000 with matching funds from the Canadian government.

No additional funds are being requested for this project at this time. Research by Drs. Yonge, Reid and Forney is continuing throughout this crop year.

Figure 1. DPA in storage room air (Fomey).

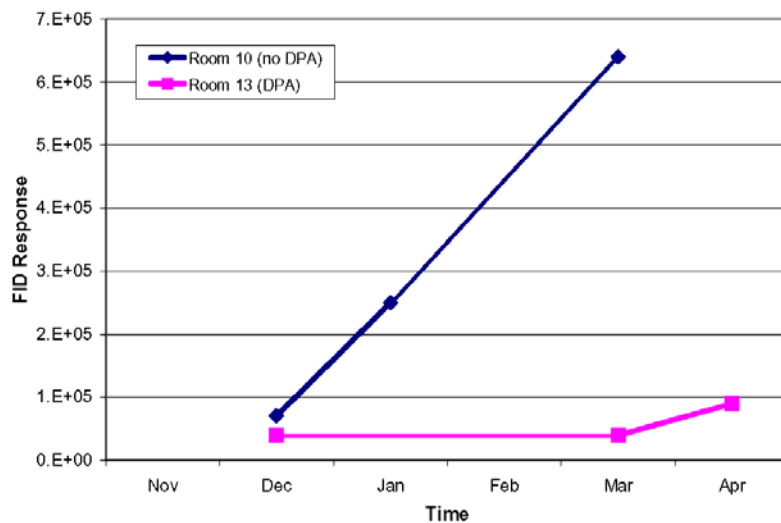


Figure 2. Volatiles released from scrubbers (Fomey).

