METHYL BROMIDE RECOVERY

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This summer, we completed a series of tests of the MBECp (Methyl Bromide Emission Control process) with the 100 cfm "Portable Adsorber" (PAD). This pilot unit treated 100 cfm of the aeration stream being exhausted for methyl bromide removal. In two cases, the entire aeration stream was treated by passing through the pilot unit. The tests were carried out under the Cooperative Research and Development Agreement (CRADA) between USDA-ARS, Great Lakes and GFK Consulting at the ports of San Pedro, CA; Newark, NJ; Philadelphia, PA and Wilmington, DE and at the processing plant of Well•Pict in Watsonville, CA. The various Packers/Shippers, the Commercial Fumigators, USDA-APHIS, Cal-EPA Department of Pesticide Regulations and the California Department of Food and Agriculture all offered their full support and assistance for our work and its goals, and we want to express our sincere appreciation to the individuals and agencies that helped.

The MBECp is designed to capture methyl bromide (MB) during the end-of-treatment venting from commodity fumigations. The ventilation air, instead of discharging directly to the atmosphere, passes through a deep bed of coconut-based activated carbon, until the MB concentration is reduced to 500 ppm (2 oz/1000 cft, 2 mg/l). The spent carbon will eventually be treated by Great Lakes to recover the bromine content of the captured MB and to regenerate the carbon for recycling back to the fumigation sites.

We performed six tests in all. They were for the commodities and locations listed below:

1. Strawberries, Watsonville CA, PPQ, Hong Kong Export
2. Kiwis, San Pedro CA, PPQ, Chile Import
3. Brassware, Newark NJ, PPQ, India Import
4. Botanicals, Newark NJ, non-PPQ
5. Lemons, Philadelphia PA, PPQ, Costa Rica Import
6. Yams, Wilmington DE, PPQ, Costa Rica Import

With approval from APHIS and from the fumigators, we performed a complete cleanup of the ventilation air with the PAD for two of the tests. Data from the first test (Watsonville Strawberries) is not included in the analysis due to GC problems. The ventilation rate was very high (<5 min to reach 500 ppm), which precluded the use of a suddenly balky GC.

Our tests demonstrated that the MBECp makes <u>substantial</u> MB reductions feasible and practical, from commodity fumigations. Achieved or achievable recoveries of MB as a function of MB charged are shown in the following table:

	Durables & Perishables	Perishables only	Durables only
Avg MB captured, % of charge	80%	70%	86%
Range	61% - 89%	61% - 83%	80% - 89%

The maximum <u>concentration</u> reduction in the ventilation air is even more substantial. MB concentrations at the start of the ventilation period ranged from 7,000 to 12,000 ppm. When the MBECp is in use to capture MB, the maximum concentration discharged to the environment will be 500 ppm. The amount of methyl bromide entering the environment is thus reduced by 60-90%. Equally important, the maximum MB mass emission rate is reduced by 93-96% through the efficacy of the MBECp. These reductions provide reduced environmental concentration in the vicinity of the fumigation site, aiding in compliance with local regulations.

A further reduction in emission rates can be achieved by the appropriate specification of the minimum <u>initial</u> ventilation rates. Some of the ventilation rates specified in the PPQ Treatment Manual for small fumigations appear high, especially when we compare them to ventilation rates used for large systems. We recognize the importance of reducing MB concentration quickly at the end of treatment, but we must point out that the MBECp equipment size and cost increases with the ventilation rate. The preliminary MBECp sizing is based on San Diego's 72,000 cft "Grid" fumigations. San Diego's ventilation rate was 10,000 cfm, for an + 7:1 V/F (<u>V</u>olume of enclosure/ventilation <u>F</u>low rate = vent ratio). A vent ratio, applied to <u>any</u> well-mixed chamber, provides the same concentration reduction with time, regardless of size. The table below shows concentrations vs ventilation time for a 3,500 cft chamber with 500 cfm ventilation rate, and an initial concentration of 12,000 ppm:

Ventilation time, min	MB concentration ppm
0	12,000
10	2,876
20	
	689
30	165

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Fig 1 shows the actual data from one of the PAD test runs with a 11,200 cft chamber. The PAD treated a 100 cfm slipstream, and the actual ventilation rate was unknown. The best fit of the actual data (squares) with the theoretical model (solid line) was obtained with 1000 cfm ventilation rate - for a vent ratio of 11:1. The solid line with crosses shows the concentration decay with the proposed PAD 7:1 vent ratio.

Fig 2 shows the actual data from a 3,100 cft ventilation, where 100% of the ventilation air was treated by the PAD at 100 cfm. The PAD was used until the MB concentration dropped to 1,500 ppm. This occurred Apr. 75 min after the start of the vent cycle, and was done because of time restraints. Otherwise the PAD would have been used down to 500 ppm. At 75 min, the fumigator's high capacity vent fans were started, and the residual concentration dropped rapidly. Integration of the ventilation curve shows that Apr. 9 lbs of MB were vented when the concentration reached 500 ppm. This represents 82% of the 11 lb MB charged, and it is the amount that will be captured by the MBECp. Fig 2 also demonstrates the validity of our model: With a known chamber volume (3,100 cft), and a known ventilation rate (100 cfm), there is virtually no difference between the predicted MB concentrations and the measured MB concentrations over a 1 hr ventilation time span. The predicted values equal the actual values. If any two variables are know, such as chamber volume and concentration vs time, the ventilation rate can be estimated. Or, if flow and concentration vs time are known, the chamber volume can be estimated.

Observations during the various fumigation tests indicate that for most of them, intensive mixing during the ventilation cycle is imperative for reducing the MB concentration as fast as possible, and to use the least amount of air possible. The former is important to protect the commodity; the latter to minimize the cost of MB capture. Unless the ventilation can be modeled as a "plug-flow" system - where clean air sweeps a relatively small cross section tunnel by virtually displacing the contaminated air, a "CSTR" (continuously stirred reactor) is the most logical model to calculate concentration decay. This model was used in Figs 1 & 2. The "CSTR" model calculates concentration A at time t, from a starting concentration A_0 at t = 0 as follows:

$$A = A_o * \exp(-t*F/V)$$

where F = ventilation rate in cfm, V = chamber volume in cft, and t = ventilation time in min.