Methyl bromide adsorption on activated carbon to control emissions from commodity fumigations

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Abstract

A process to control emissions of methyl bromide (MB) into the atmosphere following the fumigation of commodities has been developed. The process consists of adsorbing the MB in the vent-stream from a fumigation process onto activated carbon (carbon). Research was undertaken to observe the effects of (1) temperature, (2) relative humidity (r.h.), (3) the concentration of MB in the vent-stream, and (4) carbon type on the amount of MB that could be adsorbed (loaded) on the activated carbon. Temperature had the most effect on the loading, followed by r.h., for a given type of carbon. The loading decreased as temperature and r.h. increased. For a given temperature and r.h., the loading varied significantly for different carbon types. These differences were consistent with the type of pore structures of the carbons, which in turn is determined by the raw materials and by the activation procedures used during the carbon manufacturing process. Temperatures in the carbon column rose in response to the adsorption of MB. By monitoring the temperatures, the adsorption zone could be followed throughout the column from the inlet at the start of an adsorption run to column exhaustion, or breakthrough at the end of the trial. Breakthrough was reached when the MB concentration in the column exhaust stream reached 500 ppm (2 mg/l) MB. Relative humidity of the vent-stream was less critical than first anticipated because of the heating of the column. The temperature increase due to the heat of adsorption lowered the r.h. at the adsorption zone which led to the increased adsorption capacity normally associated with low humidities. Published by Elsevier Science Ltd.

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1. Introduction

With the finding that methyl bromide (MB) is an atmospheric ozone depletor, there has been increased pressure from the agricultural community to modify the application technology for MB so that it might still be used without being emitted into the atmosphere. The loss of this agricultural chemical in the state of California alone would result in an estimated loss of 241 million dollars in imports and exports (Anon., 1996). Much pressure has been brought to either convince other countries to adopt the provisions of the US Clean Air Act (CAA) which calls for banning MB in the year 2001, or to amend the CAA to provide for certain uses of MB. If the CAA is amended, it will probably be with the proviso that emissions can be controlled to acceptable levels. With this in mind, the USDA-ARS (Agricultural Research Service) has been looking into ways to trap, recycle, incinerate or chemically destroy MB following fumigation but prior to being emitted into the atmosphere. Several review articles have extolled the virtues of using activated carbon and other materials as sorbent materials to remove volatile organic compounds (VOCs) and other compounds from air and water streams
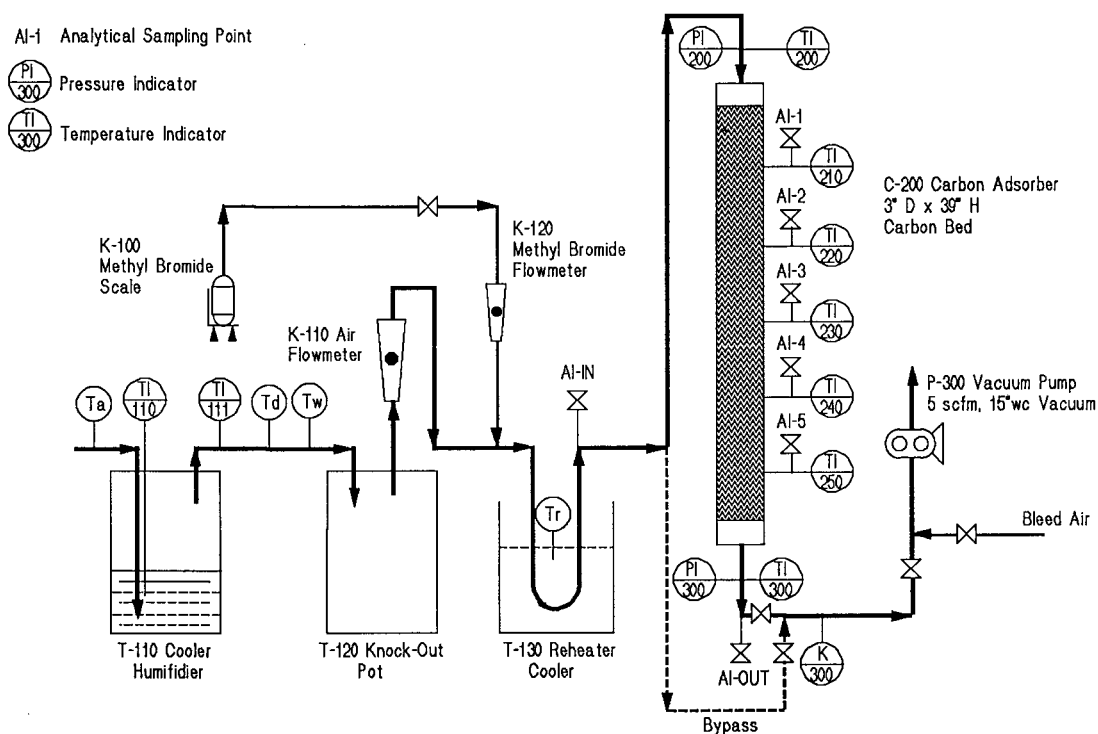

Fig. 1. The design of the bench-scale adsorber used to determine the loading of methyl bromide on various activated carbons under various conditions. "T1-" markings denote places where temperatures were taken; "Al-" denotes where gas grab samples were removed and analyzed by GLC; "Pl-" denotes where pressure readings were taken to provide flow rate data; and "k-" markings denote where flows were determined. The numbers in the circles just denote the position where the sample took place and are arbitrary.

(Paramele et al., 1979; Goldhaar and Graham, 1991; Graham, 1992; Knaebel, 1995). In 1995, the Horticultural Crops Research Laboratory which is a part of ARS, entered into a Cooperative Research and Development Agreement with GFK Consulting Ltd (San Clemente, CA) to research the potential use of activated carbon to capture MB following a fumigation and to transport the trapped MB to a central treatment facility where the MB would be desorbed and disposed of in an environmentally sound manner. Here we present the results of the first phase of that research, namely an analysis of the adsorption of MB on activated carbon under different conditions.

2. Materials and methods

Three types of carbon were obtained from three companies specializing in the use and sale of activated carbon. Carbon from American Norit Co. Inc. (Atlanta, GA) consisted of peat-derived extruded pellets (4 mm) of carbon designated R1540 and had an apparent density of 490–580 kg/m^3. Carbon from Calgon Carbon Corp. (Pittsburgh, PA) was a granular (4 × 10 mesh) bituminous-derived carbon designated BPL 4 × 10 and had a minimum apparent density of 470 kg/m^3. Carbon from Westates Carbon Products and Services of Wheelabrator Clean Air Systems (Los Angeles, CA) designated as CC 601 was a granular (4 × 8 mesh) coconut shell-derived carbon with an apparent density of 465 kg/m^3.

Adsorption experiments were carried out in an apparatus designed at the Fresno laboratory and designated as C-200, the bench-scale carbon adsorption column (BSAC) made of schedule 40, pvc pipe shown in Fig. 1. The C-200 BSAC was modeled after ventilation conditions used with a 2040 m^3 (72,000 ft^3) tarpaulin fumigation chamber located at the port facility of San Diego. In that facility, at the end of a fumigation, fresh air is admitted around the periphery of the chamber and the contents are evacuated at a rate of 280 m^3/min (10,000 ft^3/min). After 30 min of ventilation time, the MB concentration in the chamber is reduced to less than 5% of its original value with a ventilation rate of 1 air exchange every 7 min.

The BSAC was designed to treat approximately 1/3500 of this flow, or 83.4 l/min (2.9 ft^3/min), for a long enough time to allow the chamber concentration to drop to 5% of its original value (i.e., 30 min). The column, C-200, had a diameter of 7.6 cm (3 in), a height of 99 cm (39 in) and it held approximately 2.3 kg (5.0 lb) of clean carbon. Absolute humidity of the inlet air stream was adjusted in T-110 (aluminum 15-l pressure cooker) by vigorously bubbling air through temperature-controlled water. T-120 (also an identical pressure cooker as T-110) served to disengage and eliminate any entrained water droplets from the air stream. Following the humidity adjustment, MB gas (99.9%) from a commercial pressure cylinder was introduced, though a 4.8 mm (0.20 in) i.d. polyethylene tube into the 2.0 cm i.d. pvc pipe carrying the humidified stream, to achieve an initial concentration of 64 mg/l (16,000 ppm) (v/v) which is a level which might be encountered at the end of a fumigation. The concentration was gradually reduced to 500 ppm over a period of 30 min to simulate what actually happens during the aeration of a fumigation. A total of 38.5 g MB was added during the 30 min period. The average concentration for the 30 min period was approximately 15 mg/l (3800 ppm). We assumed perfect back mixing during the ventilation period when we calculated the concentration profile. The instantaneous MB flow rate was controlled based on the indications

of a Matheson Instruments model FM 1050 rotameter (K-120) (Matheson Instruments, Montgomeryville, PA) calibrated for MB and on the weight of MB lost from the cylinder placed on a Mettler (Mettler Instrument Corp., Hightstown, NJ) Top-loading Balance model P10N denoted as K-110 in Fig. 1.

Following introduction of the MB into the air stream, the mixture was further heated or cooled in a Precision model 25 Water Bath (Precision Scientific Inc., Chicago, IL) (T-130) to achieve the desired column inlet temperature and r.h. The MB-laden stream was then carried to the carbon column in 2.54 cm i.d. pvc pipe. Target inlet temperatures of 8, 15, 25, or $35 \pm 3°C$ were used along with relative humidities of 50, 75, or $95 \pm 5\%$. Temperatures were automatically recorded in the carbon column at positions marked "TI–110, 111,...250, 300" in Fig. 1. A PC software program from Iotech Inc. (Cleveland, OH) called TempBook/66 Data Acquisition System linked to type "T" thermocouples was used to record all temperatures except those at "Ta, Td, Tw, and Tr" which were taken manually with thermometers. Temperatures in T-110 and T-130 were manually adjusted throughout each run to maintain the desired temperature and relative humidity in the air stream as monitored by thermometers Td and Tw (dry bulb and wet bulb, respectively). Pressures in the system were measured using simple U-tube manometers filled with water. A typical inlet pressure was −33 mm (−15 in.) of water. A typical pressure drop across the column was 19 mm (7.5 in.) of water. Stream flow through the column was verified by an Eclipse-Dungs Control model VBS-327 (Eclipse-Dungs
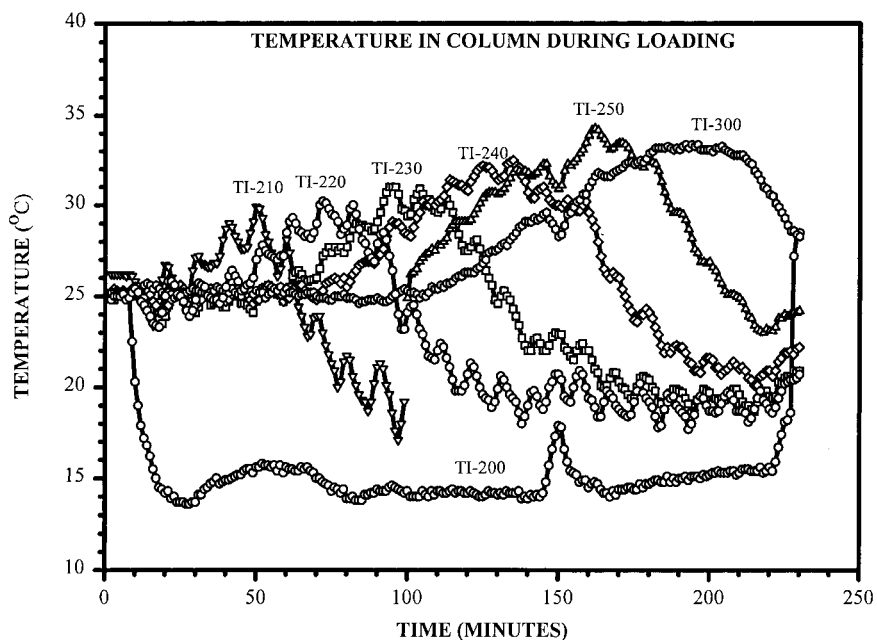

Fig. 2. Temperatures in the carbon column during a typical loading experiment. "Tl-" designations refer to positions shown in Fig. 1. At 145 min, the column temperature (T-200) rose due to changing of the ice in the pre-cooler.

Controls, Inc., Rockford, IL) venturi tube (K-300) placed between the column and the pump and attached to a Dwyer model 246 incline manometer (Dwyer Instruments Inc., Michigan City, IN). Gas grab samples were collected at points labeled "AI-IN, AI-1,…AI-5, AI-OUT". These samples were taken using B-D Yale Model 2304 glass syringes equipped with a shutoff value (Becton–Dickinson & Co., Franklin Lakes, NJ).

Since adsorption of MB on activated carbon is an exothermic reaction, we used the temperatures at the various thermocouple locations in the column to determine the progress of the adsorption front. The average temperature at a given location increased as long as the adsorption occurred upstream (i.e., the adsorption front was upstream of the location of the thermocouple). Once the adsorption front passed the location of the thermocouple, the temperature started to decrease towards the column inlet temperature (Fig. 2). The adsorption front at any given location coincided approximately with the peak average temperature at the location. The column inlet and outlet static pressures were monitored to determine the pressure drop for the various types of carbon, and for the various operating conditions. These procedures also served to verify the overall integrity of the system, since major leaks, such as an open sample connection, would be easily detected by abnormal pressure readings. The air flow was measured with a Dwyer model RMC-104 (Dwyer Instruments Inc., Michigan City, IN) rotameter (K-110) preceding the column and using the Eclipse-Dungs venturi tube (K-300), previously described, following the column to assure that no leakage was occurring. Grab samples of gas were analyzed on a Hewlett Packard Gas Chromatograph Model 5840 (Wilmington, DE) equipped with a flame ionization detector and a heated gas injection loop of 1.0 cc volume. Conditions for the gas chromatograph were as follows: column was a GS-Q Megabore (30 m × 0.53 mm) held at a temperature of 100°C, inlet temperature was 150°C, FID detector temperature was 275°C; helium flow through the column was 20 cc/min, while flows to the FID detector were hydrogen at 30 cc/min, and air at 250 cc/min. These grab gas samples showed the progress of the adsorption front through the column as well as verifying the breakthrough of the MB at the bottom of the column. Breakthrough was defined as the time when MB concentration at the outlet reached 500 ppm (2 mg/l).

The main tool for measuring the breakthrough at the outlet of the column was an on-line MTI Portable Gas Chromatograph model P100 (Hewlett–Packard, Wilmington, DE) equipped with a thermal conductivity detector. This chromatograph monitored the outlet stream every 3 min for the presence of MB. The MTI operated in conjunction with an IBM (White Plains, NY) Thinkpad® laptop computer with a 486 Intel chip. Conditions for the MTI gas chromatograph are as follows: column temperature 120°C, detector temperature was uncontrolled, gain was set to high, injection time 20 s, and inject time was 200 ms, helium flow through the 8-m PoroPlot Q column was set at a head pressure of 2.1 kg/cm^2 (30 psi).

Driving the whole system by generating a vacuum at the end of the column was a Gast Model R5325A-2 rotary vane pump (Gast Manufacturing Corp., Benton Harbor, MI) capable of pulling the required volume of air/fumigant mixture through the column bed. The pump exhausted directly into a laboratory hood. The entire system, from the preconditioning portion at T-110 to pump (P-300) ran under negative pressure during the testing periods. Working under vacuum was important for the safe operation of the experiments, since any leak would result in room air flowing into the system without MB escaping into the room.

The majority of the "trials" consisted of operating the column with repetitive 30 min

"ventilation periods" (runs) until breakthrough was observed at the outlet of the column. These "runs" varied in number depending of when the carbon became saturated and breakthrough was observed. During each 30 min period, the column was normally charged with 38.5 g of MB in 2500 l (88 ft^3) air. The runs continued until the column outlet concentration reached 500 ppm MB (2 mg/l). The carbon was weighed at the beginning and end of each trial. The weight gain was due to the adsorbed MB plus water that was either adsorbed or desorbed during the trial. Most of the trials were carried out during the winter months. We noticed an increase of moisture of the clean carbon between its initial arrival during the summer of 1995 and the winter of 1995–96. During the winter, Fresno usually experiences weeks of cold with high relative humidity and this winter was no exception. The clean carbon merely adsorbed water from its surroundings since it was stored in "208-l" fiberboard drums which are permeable to moisture. The amount of water either in clean carbon or loaded carbon was determined by the standard xylene method (ASTM method D-2867-83, reapproved 1988; Anon., 1988).

Several trials were made at a higher average MB concentration to determine the possible effects of concentration on the sorption. The amount of MB introduced was changed to 28.5 g in each run during a trial, but the time of introduction was 10 min instead of 30 min as in the previous trials. This produced an average concentration of 8440 ppm MB. Data obtained from the trials were analyzed statistically using the General Linear Models Procedure of SAS (SAS, 1989). Design of the experiments was derived from designs of non-replicated experiments discussed by Cockran and Cox (1957) and Milliken and Johnson (1989).
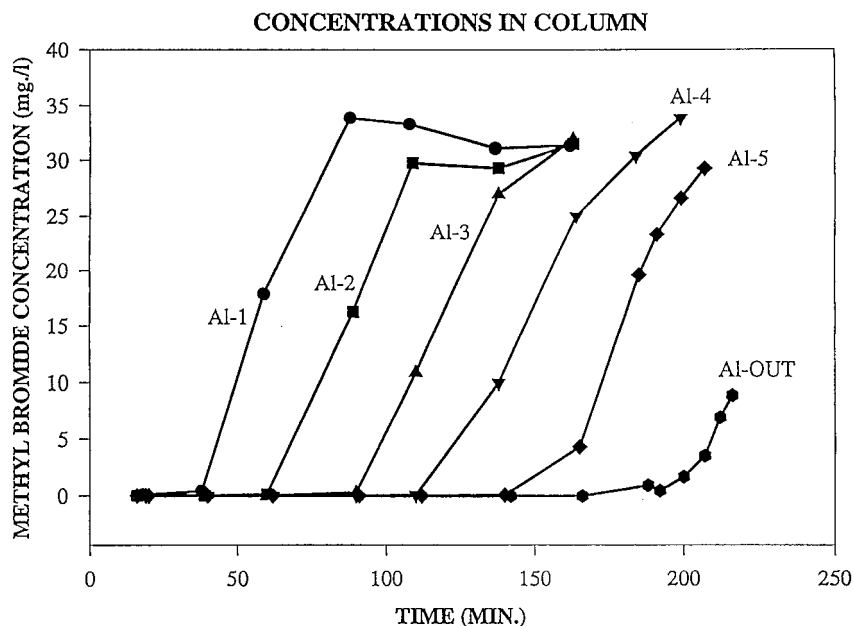

Fig. 3. Concentrations in the carbon column during a typical adsorption experiment. "Al-" designations refer to position shown in Fig. 1. The breakthrough curve is shown as "Al-OUT".

3. Results and discussion

Adsorption of MB by activated carbon for a given trial could easily be followed by observing the temperatures along the axis of the carbon column. Fig. 2 shows the temperature profile for one of the typical higher concentration (8440 ppm) trials (10 min introduction time). The gas inlet (TI-200) temperature for this run was held at 15°C. At 15 min into the trial, the MB-laden gas was introduced. The temperature did not rise immediately because the thermocouple is located a few centimeters below the upper surface of the carbon. The temperature at TI-210 peaked after 50 min and before it peaked, the temperature at TI-220 was already rising. Each successive thermocouple peaked at approximately 20 min intervals until the bottom position is the warmest, indicating that breakthrough of the MB was imminent. The variations of temperature at each position during the trial followed the 10 min addition intervals used for this example. Temperatures were highest when the concentration was high at the beginning of each run and dropped off as the concentration decreased over the 10 min interval. The same peaking and fluctuation of the temperatures at each position occurred in the lower concentration trials when the MB additions were made over a 30 min period. A similar pattern of temperature variation within the column was observed at 3800 ppm concentration. Fig. 3 shows the appearance of interstitial MB from the same locations used for the thermocouples. The MB in the interstitial space showed up after the temperature peaked at each location. As the carbon became loaded at each position, the MB in the

Table 1
Methyl bromide load on 3 different types of activated carbon under various humidity and temperature conditions. Moisture on the carbon both before and after the adsorption are given for some of the loading experiments

Type of carbon	Average (ppm)	Inlet temperature (°C)	Relative humidity (%)	Load (%)	Pre-treat water (%)	Post-treat water (%)
Calgon	3800	15	50	12.5		2.4
	3800	15	100	10.6	1.6	2.0
	3800	15	50	13.4		0.9
	3800	25	50	10.5		0.8
	3800	25	75	7.3		3.5
	3800	25	100	7.5		3.1
Westates	3800	8	75	18.3		1.8
	3800	15	50	15.8	5.4	2.6
	3800	15	100	13.6		4.0
	3800	25	50	10.5	6.0	3.9
	3800	25	100	8.8	0.7	5.6
Norit	3800	15	50	12.5		1.4
	3800	15	100	6.4	2.4	3.6
	3800	35	50	5.5		3.2
Calgon	8440	8	75	18.3		0.6
Westates	8440	15	50	22.6		1.0
Norit	8440	8	75	12.6		3.2
	8440	35	50	8.2		1.8

interstitial spaces at that position increased until it reached the average concentration of each run; in this instance approximately 30–35 mg/l (8400 ppm).

Adsorption capacities under various conditions are shown as %LOAD (g MB/100 g carbon) in Table 1. The adsorption capacity was influenced by all of the variables tested: carbon type, MB concentration, temperature and relative humidity.

The first observation made was that Norit carbon, which is derived from peat, consistently had the lowest capacity. The highest capacity for MB was exhibited by Westates carbon, which is derived from coconut shells. The different capacities are probably due to the different raw materials used for each carbon as well as the differences in the activation processes used to produce each of the final products. The source and activation processes used determine the pore size and structure of the final products. Activated carbon is used for the sorption of many products in different applications: the removal of high molecular weight dyes from the textile industry, the cleanup of chlorinated solvents from contaminated ground water and the adsorption of low molecular pollutants from water and air streams (Goldhaar and Graham, 1991). It is the pore structure which makes a given carbon more or less suitable for a given application. Peat and bituminous coal-based carbons have a significant amount of their pore volume in macropores (>500 angstroms (10^{-10} m) in diameter) and in mesopores (20–500 angstroms (10^{-10} m) in diameter. Coconut shell carbons have a majority of their pore volume in micropores (<20 angstroms (10^{-10} m) in diameter). Large molecules, such as pigments, are preferentially adsorbed in macro- and mesospores while smaller molecules such as MB are more effectively adsorbed in micropores. This specificity explains the high capacity of the Westates carbon, which has the highest amount of micropores of the three carbons tested (Graham, 1992).

As expected, the adsorption capacity of the carbon was higher in every case when the concentration average was higher (i.e., 3800 ppm in a 30 minute run compared with 8440 ppm in a 10 min run). As statistical analysis showed, based on the average concentration of 3400 ppm, the temperature and the humidity were both significant ($P \leqslant 0.05$), but there was no significant interaction between temperature and humidity or carbon type ($P > 0.05$) on the loading of MB on the carbon. By comparing the experiments at any relative humidity, one can see that as the temperature is decreased from 35 to 8°C, the capacity of each carbon increased. Likewise, as the relative humidity was increased for a given inlet temperature, the adsorption capacity decreased. As the relative humidity approaches 100%, water starts to condense in the pores and occupies space that would normally be available for organic molecule adsorption. The capacity for the organic molecules is, therefore, reduced. Table 1 shows the results of the moisture test for the carbons both before (% pre-treat water) and after (% post-treat water) several of the trials. At 50% r.h., the carbons lost water in each of the two trials tested for water. Conversely, at 100% r.h., the carbons gained water in each of the three trials tested.

As the relative humidity approaches 100%, the adsorption capacity of activated carbon decreases sharply. The decrease in capacity at 100% r.h. that we found was much less than expected. The reason for this is that the relative humidity of the air in contact with the carbon is lowered as soon as the adsorption begins because of the heat liberated by the adsorption reaction. At the inlet concentrations used for these trials, sufficient heat was liberated to unsaturate the gas to a level below the critical 100% r.h. region.

From the linear regression analysis performed by the General Linear Models Procedure of

SAS (SAS, 1989) of the data for the 3 carbons used, 3 equations resulted, which explain the dependence of loading of MB on the carbons as a function of temperature and relative humidity ($r^2 = 0.85$):

Carbon Type	Equation describing loading
N (Peat-derived)	Load (%) = 19.5–0.258 (Temp., °C) −0.075 (r.h., %)
C (Bituminous-derived)	Load (%) = 25.7–0.483 (Temp., °C) −0.075 (r.h., %)
W (Coconut-derived)	Load (%) = 30.7–0.567 (Temp., °C) −0.075 (r.h., %)

In undertaking these experiments, it was hoped to find a suitable way to trap the MB from an effluent stream resulting from the aeration of a fumigation. We did the experiments over a wide range of temperatures and relative humidity because commodities undergoing fumigation can be either dry or wet, and be stored under ambient or refrigerated conditions. Durable commodities such as grain and nuts do little to increase the relative humidity over the period of a fumigation, while perishable commodities such as peaches and plums may increase the relative humidity of the fumigant/air mixture during the fumigation period. However, refrigerated commodities, such as imported grapes, if fumigated when the surrounding air is warm and humid, will result in a fumigant/air mixture in the chamber of 100% r.h. The cold commodity acts like a "condenser".

From the research we have conducted, it appears that although higher temperatures and humidities reduce the adsorption capacity, at least the carbons derived from coconut shells and coal adsorb sufficient quantities of MB to provide a practical method for minimizing emissions to the atmosphere for commodity fumigations. For large chambers such as those used in San Diego and Long Beach, a transportable adsorber measuring $6.1 \times 2.4 \times 2.4$ m ($20 \times 8 \times 8$ ft) loaded with 8600 kg (19,000 lb) carbon would suffice to adsorb MB from several fumigations. Assuming a conservative 10% loading capacity for the carbon (10 g MB/100 g carbon), and a 2039 m^3 (72,000 ft^3) fumigation chamber that uses 130.8 kg of MB to achieve a dosage of 64 g/m^3 (64 oz/1000 ft^3), each adsorber would be sufficient for at least 7 fumigations. This assumes that 95% of the MB charged into the chamber is adsorbed by the carbon. In reality, some MB is sorbed by the commodity during fumigation and only the amount desorbed by the commodity during the aeration phase of the fumigation would be recovered by the carbon. Once the MB is loaded on the carbon, the carbon will be transported to a reclamation site where the carbon will be desorbed with an appropriate hot gas such as air, nitrogen, or steam. This process will desorb both MB and volatiles collected from the commodity. The clean carbon is then ready to be reused at another fumigation site. MB desorbed during the reactivation process will be thermally oxidized to hydrobromic acid and recovered in a convenient form for reuse in the manufacture of brominated chemicals, including MB.

Further experiments will be conducted to verify the ability of the carbon to be recycled through the process described and the effect that recycling of the carbon has on its adsorptive capacity for MB. We are planning a series of tests where volatiles from commodity will be sorbed coincidently with MB on the carbon and the effect of the volatiles on the capacity of

the carbon will be determined. The sorption/desorption of volatiles and/or MB over many cycles will give a good indication of the reusability of the carbon.

This process offers a procedure which does not interfere with established fumigation schedules used for quarantine purposes. There is no need for concern about the effect of adsorbed commodity volatiles on subsequent fumigations, since there is no attempt to recycle the MB directly in fumigations following the one from which it was adsorbed. There is also no need for concern about the disposal of secondary hazardous wastes, because 100% of the trapped MB and adsorbed commodity volatiles are thermally destroyed during the bromine recovery process.

Acknowledgements

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