

ACTIVATED CARBONS FROM END-PRODUCTS OF TREE NUT AND TREE FRUIT PRODUCTION AS SORBANTS FOR REMOVING METHYL BROMIDE IN VENTILATION EFFLUENT FOLLOWING POSTHARVEST CHAMBER FUMIGATION

Wiley A. Hall 4th and Spencer S. Walse*

¹USDA ARS San Joaquin Valley Agricultural Sciences Center, Parlier, CA, 93648, U.S.A.

Abstract

End-products of tree nuts and tree fruits grown in California, USA were evaluated for the ability to remove methyl bromide (MB) from ventilation effluent following postharvest chamber fumigation. Activated carbon sorbents from walnut and almond shells as well as peach and prune pits were prepared using different methods of pyrolysis, activation, and quenching. Each source and preparation was evaluated for yield from starting material (% *m/m*) and performance on tests where MB-containing airstreams were directed through a columnar bed of the activated carbon. We report the number of doses needed to first observe the breakthrough of MB downstream of the bed and the capacity of the activated carbon for MB (% *m/m*) based on a fractional percentage of MB mass sorbed at breakthrough relative to mass of the bed prior to testing. Activated carbons from prune pits, prepared either by steam activation or carbon dioxide activation coupled to water quenching, received the greatest number of doses prior to breakthrough and had the highest capacity, approximately 12 to 14 %, outperforming a commercially-marketed activated carbon derived from coconut shells. Experimental evidence is presented that links discrepancy in performance to the relative potential for activated carbons to preferentially sorb water vapor relative to methyl bromide.

Key Words: methyl bromide, VOC reduction

Introduction

Methyl bromide (MB), as a postharvest fumigant, is highly effective against insect and microorganism pests.^{1,2} MB is also an atmospheric source of reactive bromine gases,³ which deplete stratospheric ozone.^{4,5} Anthropogenic utilization of MB is regulated by international agreement under the Montreal Protocol. In instances where postharvest chamber fumigations are permitted, contribution(s) to ozone depletion can be minimized, or eliminated, by removing MB from the ventilation effluent. Various technologies have been used for this purpose and several are commercially-available, including those utilizing: regenerative thermal oxidizers, catalytic recuperative oxidizers, homogeneously- and heterogeneously-catalyzed Swain-Scott nucleophilic chemistries, and activated carbon sorbents.

The extent that the global agricultural community embraces these technologies is a function of the juxtaposition between capital costs, operational costs, and regulatory costs, which must be considered uniquely for each sector. Recently, the costs associated with the removal of MB from the ventilation effluent of chamber fumigations were critically evaluated for several technologies in scenarios pertinent to specialty crop agriculture in California USA.⁶ The major cost (ca. >85% of total cost) of utilizing activated carbon sorbent was associated with transportation, both the movement of sorbent to fumigation facilities and, if the MB was not destroyed following sorption, the movement of spent sorbent to hazardous waste disposal sites.

As part of a larger research project to develop more cost-effective approaches to minimizing MB emissions from agricultural operations, we expanded on the work of others⁷⁻¹⁴ by conducting experiments to determine if activated carbons produced from sources in close proximity to the fumigation chambers were technically viable. Almond shells, walnut shells, peach pits, and prune pits were selected for investigation because the respective industries conduct postharvest chamber fumigations with MB at facilities where the end-product is generated. Moreover, these industries are exploring the potential use of char, generated via the pyrolysis of end-product, for a variety of applications, including: soil amendment, carbon sequestration budgets, and as an attenuator of agrochemical runoff. We report the results of compulsory studies intended to

quantify the relative potential for the activated carbons to remove MB from an airstream that simulates the ventilation effluent from a fumigation chamber. Results are presented and discussed relative to activated carbon derived from coconut shell, the type of sorbent used in several commercial systems that remove MB from effluent during chamber ventilation.

Material and Methods

Chemicals.

A 50-lb (23 kg) cylinder of compressed MB, Meth-o-gas 100® (> 99.5% purity), was obtained from Cardinal Professional Products (Woodland, CA, USA). Respective 300-lb (136 kg) cylinders of compressed ultra high purity nitrogen (> 99.9% purity) and carbon dioxide (> 99.3% purity) gases were used for the carbon preparation and were received from the Fresno, California USA Airgas® distributor. When air was used for carbon preparation, it was supplied by a compressor that pushed air (60 psi) serially through an Altech® L21 charcoal filter and a Drierite®-filled moisture trap. Commercially-marketed activated carbon derived from coconut shell source, Westates Vocarb 48C (WEST-AC), was purchased from Siemens Industry, Inc (Alpharetta, GA, USA) and was stored at ambient conditions in an air-tight jar until use. Deionized (DI) water was produced with a Millipore Elix 10/Gradient A10 water purification system to a specification of 18 MΩ resistivity.

Sorbent Preparation

Pits from two species of tree fruits, *Prunus domestica* (prunes) and *Prunus persica* (peaches), as well as shells from two species of tree nuts, *Juglans sp.* (walnuts) and *Prunus amygdalus* (almonds), were obtained as end-products of key California USA horticultural production and used as carbon sources. Sorbents from respective carbon sources were prepared, as detailed below, using different methods following the general sequence of pyrolysis, activation, and then quenching. During pyrolysis, the carbon source was heated under an inert gas atmosphere to form char, a carbonaceous derivative material with a “rudimentary porous structure” relatively void of non-carbon heteroatoms.¹⁵ A single type of carbon source served as starting material

and was loaded into a 2" X 2.25" X 22" (5.1 X 5.7 X 55.9 cm, inner diameter (ID) X outer diameter (OD) X length (L)) mullite working tube (Carbolite, MVO66325-N-18) to fill the heated-zone of a 13" (33.0 cm)- tube furnace (Thermolyne, 21100). The mass of the carbon source loaded into the working tube was measured gravimetrically. The contents of the tube were flushed with nitrogen gas at $\sim 900 \text{ mL min}^{-1}$ for 1 h with the temperature controller set to 75°C . The furnace temperature controller was increased to 700°C , which resulted in ramp rate of $\sim 25^\circ\text{C min}^{-1}$, and held isothermal for 1 h. The furnace temperature controller was increased to 800°C and the char was then "activated" to form a sorbent, as described in detail below, by introducing either carbon dioxide or steam into the tube to remove residual material, such as tars, from the pore spaces. Sorbent was "quenched" using various procedures during the return to temperature $< 50^\circ\text{C}$. When preparation was completed, the mass of the carbon sorbent was measured gravimetrically. Sorbents were ground using a hand mill equipped with tooth auger and fine plates (Lehman Mills, Quaker City Mill #1171295), sized to a 20/40 mesh with brass sieves (McMaster-Carr, 3286K14 and 3286K16), and stored at ambient conditions in an air-tight jar until use.

CO₂ Activation with Nitrogen Quenching

To activate the char, carbon dioxide was flushed through the tube furnace at $\sim 900 \text{ mL min}^{-1}$ following pyrolysis and just before the furnace temperature controller was set to 800°C . After 1 h, the carbon dioxide was replaced with nitrogen and the temperature controller was turned off to initiate a gradual decrease of the CO₂-activated nitrogen-quenched carbon (CO₂A-NQ) to $< 50^\circ\text{C}$.

Steam Activation with Nitrogen Quenching

Steam was directed through high temperature silicone rubber tubing (McMaster-Carr, 5236K871) into the char-containing tube for 1 h following pyrolysis and just before the furnace temperature controller was set to 800°C . Steam was generated by sparging nitrogen through a 1000-mL round bottom flask containing $\sim 800 \text{ mL}$ of boiling DI water. The feed rate of steam, $4.73 \pm 0.34 \text{ g min}^{-1}$, was determined by measuring the mass of water before and after the 1-h

process in triplicate trials. Quenching was as above to yield steam-activated nitrogen-quenched carbon (SA-NQ).

CO₂ Activation with Air Quenching

Following CO₂ activation, the furnace temperature controller was lowered to 300°C and air (ca. 20 to 40 RH) was directed through the furnace tube at ~900 mL min⁻¹ for 1 h. The air was then replaced with nitrogen gas and the CO₂-activated air-quenched carbon (CO₂A-AQ) was allowed to cool to < 50°C before being processed for use as described above.

CO₂ Activation with Water Quenching

Following CO₂ activation, the furnace temperature controller was lowered to 300°C and the entire contents was transferred using heat-resistant gloves to a 32oz. (946 mL)-mason jar filled with approximately 1 mL water for every 2 g raw material. The carbon - water mixture was allowed to cool to < 50°C, the water was decanted, and the CO₂-activated water-quenched carbon (CO₂A-WQ) was dried in an oven at 110°C overnight before being ground, sized, and stored for use as above.

Sorbent Testing on PACT

The PACT (Parallel Adsorbent Column Tester) apparatus, described in detail elsewhere, is an approximately 3,500 n: 1 scale model of a chamber ventilation system.¹⁶

PACT diverts a single source of flowing air (i.e., an airstream) into 7 channels. Briefly, air is pulled with an oil-free vacuum pump through 1" Tygon tubing connecting two vessels and a mixing chamber in series. The first vessel (conditioning) was filled with either water, to humidify, or silica gel, to dry, the airstream. To increase the humidity from ~25 to ~70%, silica gel was removed from the conditioning vessel and replaced with water to a depth of ~ 10 cm. The second vessel (knock-out) allowed any water droplets to fall out of the airstream and

contained a HOBO datalogger (Onset, #U10-003) to monitor temperature and %RH. Next, the airstream was combined with MB (Meth-o-gas 100® Great Lakes Chemical Corporation, >99.5% purity) as metered by a rotameter (Key Instruments, #10410_R5) before entering into a mixing chamber comprised of a 3" (ID) x 39" (L) schedule 40 poly(vinyl chloride) pipe. The MB-containing airstream was then routed through the vacuum pump; the pressure of the airstream entering and exiting the pump was monitored with respective Magnehelic gauges (Dwyer Instruments, Cat. No. 2020C). Exhaust from the pump was directed through a stainless-steel manifold with 7 channels as well as an outlet that was tuned to balance pressure. Unless otherwise noted, the total flow of MB and air into the manifold was 50 SCFH (~23,502 mL min⁻¹).

Prior to each experiment, six (of seven) stainless-steel columns were loaded with sorbent material to a 11.4-cm bed depth, the ends of each column were capped with circular 40-mesh stainless steel strainer cloth (1/8" OD), all columns were placed in the working tube (*vide infra*), and the furnace temperature controller was set to 300°C with a nitrogen gas flow of ~900 mL min⁻¹ for 2 h. The 7th column contained no sorbent. After the heating period, all columns were stored in an air-tight jar containing ~5 g drierite® until being fitted onto the 7-channeled manifold of the PACT apparatus. SPME fiber assemblies, with the fibers retracted into the fiber guide for time-weighted averaging (TWA) sampling with $z = 10$ mm,¹⁶ were inserted into the sampling ports and all airflows were metered as described above.

To simulate chamber effluent consistent with ventilation of a postharvest MB fumigation,^{7,8,16} [MB] in the airstream of the PACT apparatus was temporally modulated from the start of a dose at $t = 0$: 16,210 ppmv for 3 min, 4,870 ppmv for 13 min, and 0 ppmv for the remaining 14 min (30 min total). For a single test, dosing was repeated serially ($Dose_n$, where $n = 1, 2, 3, \dots$ etc.) at ~60 min intervals. After each dose, the mass of the MB cylinder was gravimetrically measured. Additionally, each column was gravimetrically measured and each SPME fiber was removed for analysis of MB with gas chromatography (GC) coupled to flame-ionization detection (FID) (*vide infra*). A "breakthrough" threshold was reached when [MB] exiting a column exceeded 500 ppmv (~13 mg escaping the column over the 30 min dosing period).⁷ If

breakthrough (BT) was observed on the same column for two consecutive doses, the column was replaced with an empty column. Dosing continued until all columns containing sorbent were removed from the PACT apparatus.

The capacity of an activated carbon sorbent to sorb MB was calculated as the percentage of the total mass of MB sorbed ($m_{MB,sorbed}$) by the column over consecutive doses, including the first dose where BT was observed ($Dose_n$, where $n = 1, 2, 3, 4, \dots, 1st\ BT$), relative to the mass of carbon sorbent measured just before testing, m_{AC} , in the form:

$$\% Capacity_{MB} = m_{MB,sorbed} / m_{AC} * 100\% \quad (1)$$

where $m_{MB,sorbed}$ is calculated by

$$m_{MB,sorbed} = m_{entering} - m_{exiting} \quad (2)$$

and $m_{entering}$ is the total mass of MB entering the column containing no carbon sorbent (e.g., column attached to the 7th channel of manifold) and $m_{exiting}$ is the total mass of MB exiting a carbon containing-column as calculated by:

$$m_{entering} = \sum_{Dose_1}^{Dose_{BT}} [MB]_{TWA} * 0.224 LPM * 30 min \quad (3)$$

or

$$m_{exiting} = \sum_{Dose_1}^{Dose_{BT}} [MB]_{TWA} * 0.224 LPM * 30 min \quad (4)$$

where, $[MB]_{TWA}$ is the time-weighted average [MB] in $mg\ L^{-1}$ (*vide infra*), 0.224 LPM ($L\ min^{-1}$) is the flow rate through the column, and 30 min is the duration of a dose.

SPME Methodology / Gas Chromatography

The use of SPME fibers in concert with TWA sampling to quantify an analyte has been rigorously discussed in general context.¹⁷⁻²⁰ In addition, the use of SPME-based TWA sampling to quantify MB in airstreams of the PACT apparatus as well as ventilation effluent for postharvest chamber fumigations, has been described and intrinsic advantages discussed relative to other available approaches.¹⁶ Previous work supports calculations of $[MB]_{TWA}$ in the form:

$$[MB]_{TWA} = \frac{m}{SR * t} \quad (5)$$

Where m is the mass of MB sorbed onto the fiber over the span of time, t , that the fiber assembly is exposed to the PACT airstream and SR is the translational rate of MB diffusion, which has been experimentally determined to be $1.416 * 10^{-4} \text{ cm}^3 \text{ s}^{-1}$.¹⁶

After a dose, each carboxen / PDMS Stable Flex SPME fiber assembly (#57335-U, Sigma-Aldrich (Milwaukee, WI) was removed from the sampling ports of the PACT apparatus and the fiber guide was buried into a septum (#6514, Grace, Deerfield, IL). Just prior to GC-FID analysis, the fiber guide was removed from the septum, the SPME fiber assembly was loaded into a SPME fiber holder (#57330-U, Sigma-Aldrich), the fiber guide was injected 2" into the inlet, and the fiber was desorbed for 1 min. An Agilent 6890 GC was used with a split-splitless inlet at 250 °C, a 100:1 split ratio, and a 0.75 mm ID SPME injection sleeve inlet liner (#2-6375,05, Sigma-Aldrich, Bellefonte, PA). The analytical column was a 30 m (L) x 250 µm (ID) DB-5 with 0.25 µm film thickness and was held isothermally at 150 °C for 3 min and 1.8 mL min⁻¹ He carrier flow. The FID was at 275 °C with respective flows of 30 mL min⁻¹ H₂, 400 mL min⁻¹ air, and 30 mL min⁻¹ N₂ make-up. Retention time was used for chemical verification of MB. A previously described approach was used to calibrate FID detector response relative to PACT airstreams metered to ~11,000 and 2500 ppmv over exposure (i.e., sampling) times of 0.75, 1.5, 3.0, 6.0, 10, and 15 min, which encompass $[MB]_{TWA}$'s ranging from ~60 to 6000 ppmv when $t = 30 \text{ min}$.¹⁶

Results and Discussion

Quantifying Sorbed MB: SPME versus Gravimetric Methodology

In addition to measuring $m_{entering}$ via TWA sampling of a column containing no sorbent, the mass of MB lost from the cylinder was tracked to provide an analogous estimate, $m_{entering-grav.}$, in the form:

$$m_{entering-grav} = (m_{cyl-f} - m_{cyl-i}) * \frac{flow_{PACT}}{flow_{column}} \quad (6)$$

where m_{cyl-f} and m_{cyl-i} are respectively the final and initial mass of the cylinder and $flow_{PACT}$ and $flow_{column}$ are respectively the total PACT flow into the manifold ($\sim 23,502 \text{ mL min}^{-1}$) and an individual column ($\sim 224 \text{ mL min}^{-1}$).

Figure 1 shows the relationship between the quantification of MB across eight serial doses ($Dose_n$, where $n = 1, 2, 3, \dots, 8$) of the PACT apparatus using gravimetric- versus SPME-based methodologies. Note the agreement between the slope of the line obtained from a least-squares analysis ($m = 0.75$) and the average ratio, 0.737 ± 0.055 (ave. \pm stdev., $\bar{x} \pm s$, $n = 8$), of MB concentrations measured by SPME methodology, $m_{entering}$, relative to gravimetric methodology, $m_{entering-grav.}$. We have interpreted this difference to be a result of MB losses to the system forward of the SPME sampling ports. This result identifies that SPME measurements and $m_{entering}$ should be used, whenever possible, to quantify MB in airstreams of the PACT apparatus. Additionally, this result supports the conclusion that MB loss due to system was consistent across trials and that experiments involving the PACT apparatus be conducted in facilities with sufficient ventilation (e.g., fume hoods) to minimize MB inhalation exposure to individuals conducting the tests.

Commercially-sourced Activated Carbon Sorbent “Benchmark”

WEST-AC, derived from coconut shell, served as a commercially-marketed “benchmark” of comparison for the various preparations of activated carbon sorbents from tree fruit pits and tree nut shells. WEST-AC, randomly selected from one of four different commercial batches, was loaded into two columns of the PACT apparatus and nine replicate tests were conducted to evaluate, as measures of performance, the capacity for MB (%) and the number of doses needed to first observe BT. One-way ANOVAs were not significant (Capacity: $F_{(17, 0.006)} = 2.273$; $P = 0.1215$, BT: $F_{(17, 0.004)} = 2.531$; $P = 0.1562$), indicating the overall average capacity, $10.9 \pm 1.8\%$ ($\bar{x} \pm s$), as well as the average number of doses applied before BT, 7 ± 1 ($\bar{x} \pm s$), could be used to estimate the performance of WEST-AC irrespective of the batch.

Tree Fruit Pit and Tree Nut Shell Activated Carbon Sorbents

The average yields across all preparations and sources of activated carbon sorbent, ranged from 7 to 31% (w/w) and were estimated as the fractional percentage of the mass after quenching relative to the mass of starting material loaded into the working tube prior to pyrolysis (Figure 2). A one-way ANOVA was significant ($F_{(15, 0.0476)} = 5.262$; $P = 0.015$), indicating that the overall average yield across all preparations and carbon sources, $22 \pm 6\%$ ($\bar{x} \pm rsd$), was not an accurate indicator of all yields. Means comparison testing only showed significant difference between yields for CO2A-WQ and SA-NQ preparations, independent of source carbon type (Tukey-Kramer HSD, $\alpha = 0.05$). The yield of activated carbon sorbent prepared by SA-NQ from almond shells was $< 10\%$, far below any other preparations, suggesting an unlikely prospect of its commercial use to remove MB in ventilation effluent from postharvest chamber fumigations.

The performance of each type of preparation and source on the PACT tests, expressed as both the number of doses needed to first observe BT (Figure 3A) as well as the corresponding capacity for MB (%) (Figure 3B), were evaluated relative to results for WEST-AC. Activated carbons from prune pits prepared by CO2A-WQ as well as SA-NQ resulted in the greatest number of doses needed to first observe BT, ~ 7.5 , and the highest corresponding capacity, ~ 12 to 14%. CO2A-AQ and CO2A-NQ preparations of activated carbon from prune pits as well as all

preparations of activated carbons from peach pits and walnut shells reached BT in ~3 to 6 doses and had capacities ranging from 4 to 7 %. Regardless of preparation, activated carbons derived from almond shells performed relatively worse, as is clearly demonstrated by fewer number of doses needed to first observe BT.

In an attempt to correlate the performance of activated carbon derived from peach pits, prune pits, almond shells, and walnut shells to the type of carbon source, data was analyzed to indirectly probe the competitive sorption of water vapor and its potential influence on the sorption of MB. Results from PACT testing of preparations were grouped by type of carbon source and the grand mean of the mass of MB (and water) sorbed by a particular column at BT based on gravimetric measurement was normalized relative to that detected by SPME-based TWA sampling, $m_{MB,sorbed}$ (Figure 4). Given the finding from previous PACT studies¹⁶ that MB quantification with SPME-based TWA sampling is unaffected across a range of ~ 20 to 80% RH, a likely explanation for the discrepancy in performance was the preferential sorption of water vapor by carbon source types. It is critical to note that activated carbons derived from prune pits had the lowest ratio (of water sorbed relative to MB sorbed) and those derived from almond shells had the highest ratio. A one-way ANOVA was significant ($F_{(14, 0.835)}=3.983$; $P = 0.038$), indicating that the overall average ratio across carbon sources, $1.45 \pm 0.2\%$ ($\bar{x} \pm sd$), was not a representative estimate for each carbon source. Subsequent means comparison testing only showed significant difference between prune- and almond- derived activated carbon sorbents (Tukey-Kramer HSD, $\alpha = 0.05$).

The interpretation that the performance of activated carbon derived from almond shells, peach pits, prune pits, and walnut shells was related to the source-specific competitive sorption of water vapor was further supported by an experiment conducted with WEST-AC. The relative humidity in the PACT system was increased from ~25 to ~70%, WEST-AC was loaded into five columns, and eight tests were conducted that evaluated, as above, the grand mean of the mass of MB sorbed by a particular column based on gravimetric measurement normalized relative to that detected by SPME-based TWA sampling, $m_{MB,sorbed}$ (see Figure 4). The ratio resulting from

the PACT testing at ~70% RH was significantly higher at the 99% confidence interval than that obtained with ~20% RH (T-test: $t_{21} = 2.0796$, $P > |t| = 0.0003$).

It is interesting to note the selectivity of each activated carbon source for water vapor as related to the MB removal from the airstreams of the PACT apparatus. Data suggests that the two preparations of activated carbon from prune pits that used water vapor for either activation, SA-NQ, or quenching, CO2A-WQ, imparted a surface modification that decreased the potential for competitive sorption and ultimately resulted in more MB removal from the airstream per mass of activated carbon sorbent. Future studies will focus on scaling, from gram- to kilogram-scale, the production of prune pit-derived activated carbon prepared by SA-NQ and CO2A-WQ. If the preparation is effectively scaled, as assayed by performance on the PACT apparatus, the logical extension would be to conduct confirmatory trials to quantify MB removal from ventilation effluent following a commercial postharvest chamber fumigation.

Notes

Mention of trade names or commercial products in this publication is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the U.S. Department of Agriculture. USDA is an equal opportunity provider and employer.

Acknowledgments

This research was funded by the USDA-Agricultural Research Service as well as the USDA-Foreign Agricultural Service and the California Dried Plum Board under the Technical Assistance for Specialty Crops program, agreement # 2010-19.

References

- (1) Johnson, J. A.; Walse, S. S.; Gerik, J. S. *Outlook Pest Manag.* **2012**, *23*, 53-58.
- (2) Bell, C. H.; Price, N.; Chakrabarti, B. *The Methyl Bromide Issue*; John Wiley and Sons: Hoboken, NJ, 1997.
- (3) Lary, D. J. Gas phase atmospheric bromine photochemistry. *J Geophys. Res.-Atmos.* **1996**, *101*, 1505-1516.
- (4) Solomon, S. Progress towards a quantitative understanding of Antarctic ozone depletion. *Nature* **1990**, *347*, 347-354.
- (5) Yung, Y. L.; Pinto, J. P.; Watson, R. T.; Sander, S. P. *J. Atmos. Sci.* **1980**, *37*, 339-353.
- (6) Thompson, J. in: Proceedings of Annual International Research Conference on Methyl Bromide Alternatives and Emissions Reductions, San Diego, CA, USA, 2013; URL (<http://www.mbao.org/2013/Proceedings/51ThompsonJ.pdf>)(accessed October 2014) pp. 1-2.
- (7) Leesch, J. G.; Knapp, G. F.; Mackey, B. E. Methyl bromide adsorption on activated carbon to control emissions from commodity fumigations. *J. Stored Prod. Res.* **2000**, *36*, 65-74.
- (8) Synder, J.D.; Leesch, J.G. Methyl bromide recovery on activated carbon with repeated adsorption and electrothermal regeneration. *Ind. Eng. Chem. Res.* **2001**, *40*, 2925-2933.
- (9) Knapp, G.F. in: Proceedings of Annual International Research Conference on Methyl Bromide Alternatives and Emissions Reductions, San Diego, CA, USA, 1995; URL (<http://www.mbao.org/1995airc/002.pdf>)(accessed October 2014)
- (10) Gan, J.; Yates, S.R. Recapturing and decomposing methyl bromide in fumigation effluents. *J. Haz. Mat.* **1998**, *57*, 249-258.
- (11) Gañán, J.; González, J.F.; González-García, C.M.; Ramiro, A.; Sabio, E.; Román, S. Carbon dioxide-activated carbons from almond tree pruning: Preparation and characterization. *Appl. Surf. Sci.* **2006**, *252*, 5993-5998.
- (12) Heschel, W.; Klose, E. On the suitability of agricultural by-products for the manufacture of granular activated carbon. *Fuel*, **1995**, *74*, 1786-1791.
- (13) Kazemipour, M.; Ansari, M.; Tajrobehkar, S.; Majdzadeh, M.; Kermani, H.R. Removal of lead, cadmium, zinc, and copper from industrial wastewater by carbon developed from walnut, hazelnut, almond, pistachio shell, and apricot stone. *J. Haz. Mat.* **2008**, *150*, 322-327.
- (14) Klassen, T.K.; Ledbetter, C.A.; Uchimiya, M.; Lima, I.M. Activated biochar removes 100% dibromochloropropane from field well water. *Environ. Chem. Lett.* **2013**, *11*(3), 271-275.
- (15) Rodríguez-Reinoso, F. In *Encyclopedia of Materials: Science and Technology* (Second Edition); Editors-in-Chief: , K. H. J. B., Robert, W. C., Merton, C. F., Bernard, I., Edward, J. K., Subhash, M., Patrick, V., Eds.; Elsevier: Oxford, **2001**, p 22-34.
- (16) Hall, W. A.; Bellamy, D. E.; Walse, S. S. Solid-Phase Microextraction for the Quantification of Methyl Bromide in Ventilation Effluent from Postharvest Chamber Fumigations. *J. Ag. Food Chem.* **2013**, (submitted).

- (17) Ouyang, G.; Chen, Y.; Setkova, L.; Pawliszyn, J., Calibration of solid-phase microextraction for quantitative analysis by gas chromatography *J. Chromatogr. A.* **2005**, *1097*, 9-16.
- (18) Ouyang, G.; Pawliszyn, J. SPME in environmental analysis. *Anal. Bioanal. Chem.* **2006**, *386*, 1059-1073.
- (19) Ouyang, G.; Pawliszyn, J. A critical review in calibration methods for solid-phase microextraction. *Anal. Chim. Acta.* **2008**, *627*, 184-197.
- (20) Koziel, J.; Jia, M.; Khaled, A.; Noah, J.; Pawliszyn, J. Field air analysis with SPME device. *Anal. Chim. Acta.* **1999**, *400*, 153-162.

Listing of Figures

Figure 1. The relationship between the quantification of methyl bromide (MB) across eight serial doses to the PACT apparatus ($Dose_n$, where $n = 1, 2, 3, \dots, 8$) using gravimetric measurement ($m_{\text{entering-grav.}}$) of MB loss from the source cylinder versus SPME-based TWA sampling of a column containing no sorbent (m_{entering}).

Figure 2. The yields ($n = 4$, bar height = \bar{x} , error bars = $\pm s$) of each type of preparation (CO_2 -activated air-quenched (CO2A-AQ), CO_2 -activated nitrogen-quenched (CO2A-NQ), steam-activated nitrogen-quenched (SA-NQ), and CO_2 -activated water-quenched (CO2A-WQ)) for each source of activated carbon sorbent (almond shell, peach pit, prune pit, and walnut shell) were estimated as a percentage of the mass of material after quenching relative to the mass of starting material loaded into the tube furnace prior to pyrolysis.

Figure 3. The number of doses needed to first observe breakthrough (A) and the capacity (%) to sorb methyl bromide (B) were used as measures of sorbent performance and evaluated for each type of preparation (CO_2 -activated air-quenched (CO2A-AQ), CO_2 -activated (CO2A-NQ), steam-activated (SA-NQ), and CO_2 -activated water-quenched (CO2A-WQ)) and each source of activated carbon (almond shell, peach pit, prune pit, and walnut shell), where bar height = \bar{x} and error bars = $\pm s$. Commercially-marketed activated carbon, Westates Vocarb 48C (WEST-AC) served as a benchmark of comparison with results shown \pm 95% confidence intervals (dashed red lines).

Figure 4. Results from PACT testing of all activated carbon preparations were grouped by type of carbon source. The grand mean of the mass of methyl bromide (MB) (and water) sorbed by a particular column based on gravimetric measurement was normalized relative to that detected by SPME-based TWA sampling, $m_{\text{MB,sorbed}}$. Results suggest the discrepancy between the ability of carbon source types to sorb MB was related to the source-specific competitive sorption of water vapor.

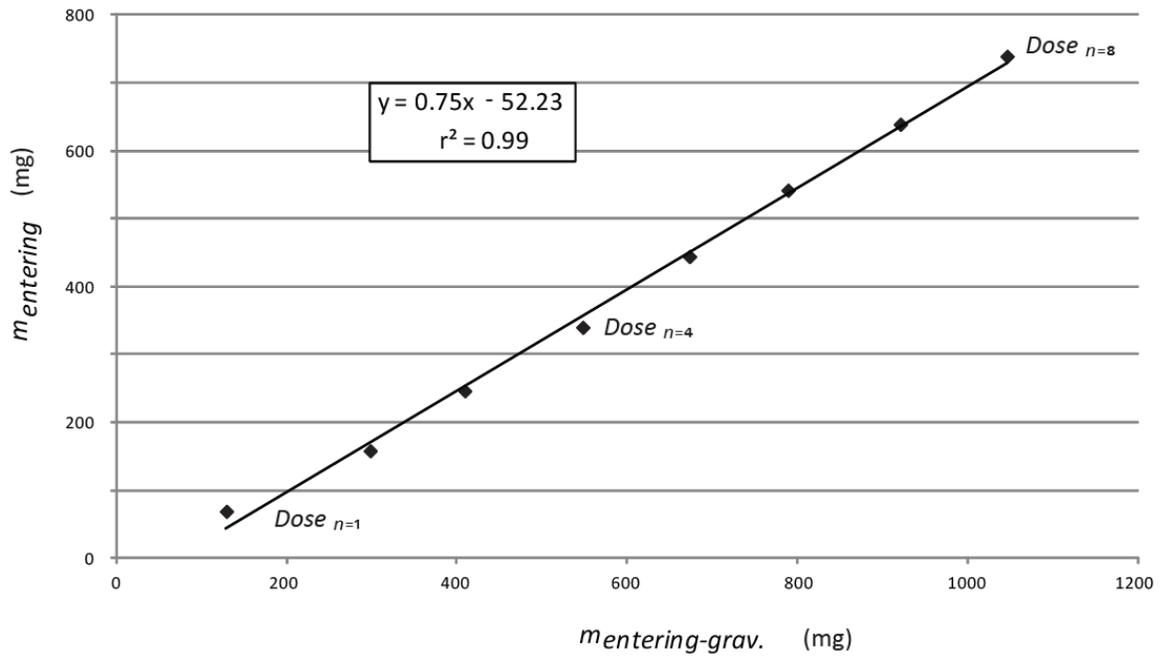


Figure 1. The relationship between the quantification of methyl bromide (MB) across eight serial doses to the PACT apparatus ($Dose_n$, where $n = 1, 2, 3, \dots, 8$) using gravimetric measurement ($m_{entering-grav.}$) of MB loss from the source cylinder versus SPME-based TWA sampling of a column containing no sorbent ($m_{entering}$).

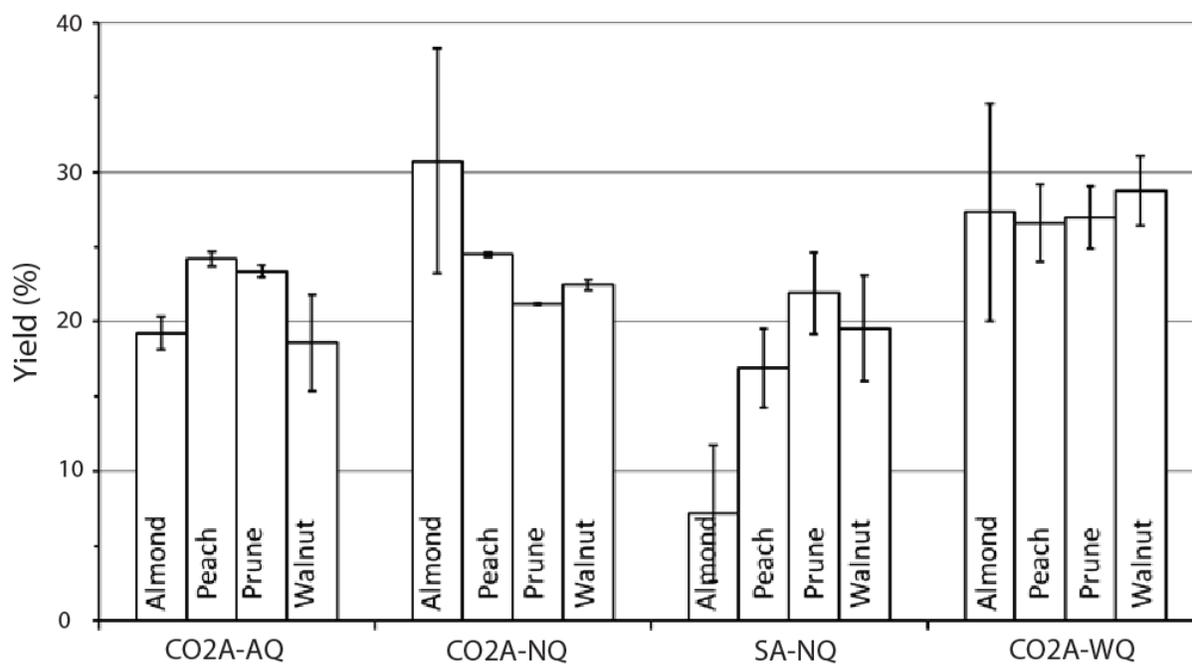


Figure 2. The yields ($n = 4$, bar height = \bar{x} , error bars = $\pm s$) of each type of preparation (CO_2 -activated air-quenched (CO2A-AQ), CO_2 -activated nitrogen-quenched (CO2A-NQ), steam-activated nitrogen-quenched (SA-NQ), and CO_2 -activated water-quenched (CO2A-WQ)) for each source of activated carbon sorbent (almond shell, peach pit, prune pit, and walnut shell) were estimated as a percentage of the mass of material after quenching relative to the mass of starting material loaded into the tube furnace prior to pyrolysis.

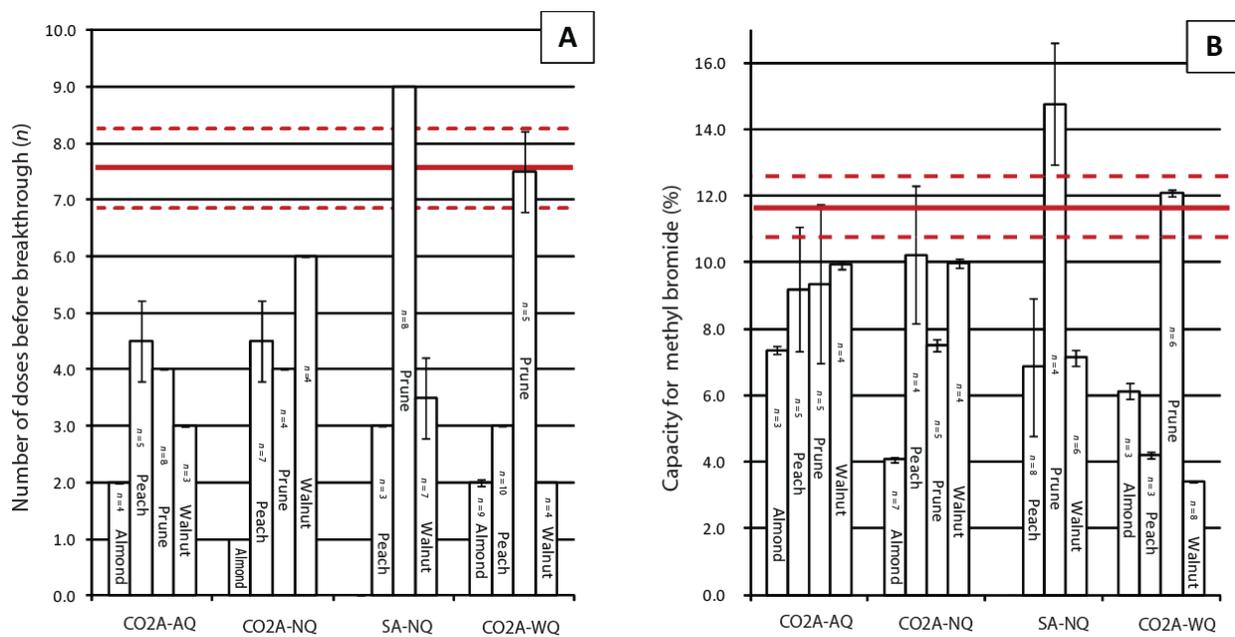


Figure 3. The number of doses needed to first observe breakthrough (A) and the capacity (%) to sorb methyl bromide (B) were used as measures of sorbent performance and evaluated for each type of preparation (CO₂-activated air-quenched (CO2A-AQ), CO₂-activated (CO2A-NQ), steam-activated (SA-NQ), and CO₂-activated water-quenched (CO2A-WQ)) and each source of activated carbon (almond shell, peach pit, prune pit, and walnut shell), where bar height = \bar{x} and error bars = $\pm s$. Commercially-marketed activated carbon, Westates Vocabr 48C (WEST-AC) served as a benchmark of comparison with results shown \pm 95% confidence intervals (dashed red lines).

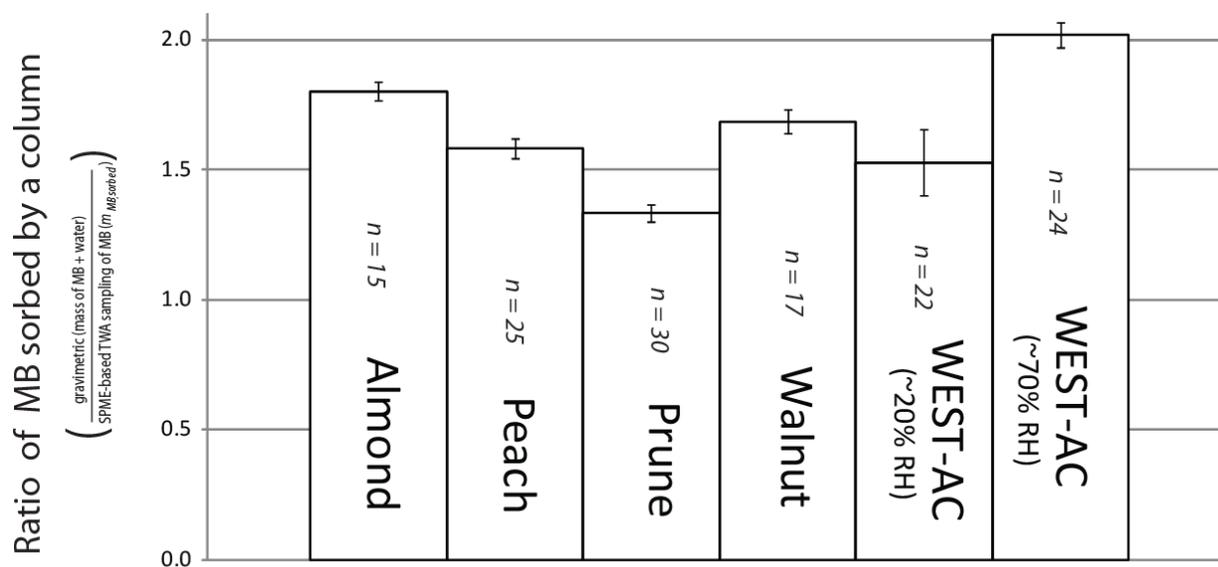


Figure 4. Results from PACT testing of all activated carbon preparations were grouped by type of carbon source. The grand mean of the mass of methyl bromide (MB) (and water) sorbed by a particular column based on gravimetric measurement was normalized relative to that detected by SPME-based TWA sampling, $m_{MB,sorbed}$. Results suggest the discrepancy between the ability of carbon source types to sorb MB was related to the source-specific competitive sorption of water vapor.