Methyl chloride (CH_3Cl) and methyl bromide (CH_3Br) emissions from economically important tropical crops

Ya-Ting Chen

ABSTRACT

Tropical rainforests have recently been confirmed to be the largest source of methyl chloride and a missing source for methyl bromide. However, very few field studies have quantified methyl halide emissions from tropical plants. This study presents the first methyl halide emission measurements from 16 tropical crop species at the University of California, Berkeley Botanical Gardens. Leaf vial experiments qualitatively identified 15 out of the 16 species as CH_3Cl emitters and 7 species as CH_3Br emitters. *Coffea arabica* was the highest emitter for both CH_3Cl and CH_3Br. In addition, bag enclosure experiments were conducted on living plants to quantitatively determine net emission fluxes from *C. arabica* as well as a previous studied species, *Angiopteris lygodiifolia*. There were strong correlations between CH_3Cl and CH_3Br emission from both *C. arabica* and *A. lygodiifolia*, suggesting that the methyl halide productions share similar biological mechanisms in these species. Temperature observations also showed that methyl halide emissions from *C. arabica* strongly depended on temperature. Using the mean net emission flux, global CH_3Cl emission by *C. arabica* was estimated to be 0.11 Tg yr^{-1}, representing approximately 7.5% of the total CH_3Cl emissions from tropical forests. Overall, the findings suggested that tropical crops make an important contribution to global terrestrial emissions of CH_3Cl, but less so for CH_3Br.

KEYWORDS

methyl halides, tropical rainforests, net emission flux, stratospheric ozone, ozone-depleting compounds

INTRODUCTION

Methyl chloride (CH_3Cl) and methyl bromide (CH_3Br) are important to the chemistry of both the troposphere and stratosphere. Having atmospheric lifetimes of 1.3-year and 0.7 years, CH_3Cl and CH_3Br can transport their halogen atoms to the stratosphere and thereby destroy ozone molecules (O_3) via radical chain reactions (Rhew, Teh, & Abel, 2007). After the Montreal Protocol restricted the production of anthropogenic ozone-depleting compounds in the 1990s, the ambient concentrations of many halogenated compounds such as chlorofluorocarbons (CFCs) have stabilized or declined (World Meteorological Organization, 2003). Therefore, because they are the most abundant natural halogen-containing compounds in the atmosphere, CH_3Cl and CH_3Br have been receiving increasing attention in determining the future of the ozone chemistry (World Meteorological Organization, 2007; Blei, Hardacre, Mills, Heal, & Heal, 2010). Current estimates show that CH_3Cl and CH_3Br contribute up to 25% of present-day ozone destruction by halogens in the stratosphere, and it is predicted that natural CH_3Cl and CH_3Br will contribute to more than 50% of the equivalent effective stratospheric chlorine by 2050 (WMO, 2007). Over the last decade, there has been a notable decrease in atmospheric levels of CH_3Br, but no clear trend for CH_3Cl (Clerbaux & Cunnold, 2007). However, because of the variety of natural sources, large uncertainty still exists in the global budgets of CH_3Cl and CH_3Br.

The high level of uncertainty in measuring CH_3Cl and CH_3Br emissions leads to an imbalance between the global sources and sinks of the methyl halides (Saito & Yokouchi, 2008). The major natural sources of CH_3Cl and CH_3Br include oceans, biomass burning, salt marshes, certain fungi and higher plants, and senescent or dead leaves (Saito & Yokouchi, 2008; Gebhardt, Colomb, Hofmann, Williams, & Lelieveld, 2008; Rhew, Chen, Teh, & Baldocchi, 2010). Oxidation by hydroxyl radicals and soil consumption are the primary removal processes for CH_3Cl and CH_3Br (Rhew, Miller, Bill, Goldstein, & Weiss, 2002; Gebhardt et al., 2008). But the current estimate of total CH_3Cl emissions from these natural sources accounts for only about half of the estimated total sinks (Saito & Yokouchi, 2006), while 30% of the estimated sources for CH_3Br are also unidentified (Rhew et al., 2010). Yokouchi et al. (2000) recently discovered tropical rainforests as the missing source for CH_3Cl. Since then, several studies have measured and confirmed high concentrations of atmospheric CH_3Cl in tropical rainforests (Yokouchi et al., 2000; Yokouchi, Ikeda, Inuzuka, & Yukawa, 2002; Yokouchi, Saito, Ishigaki, & Aramoto, 2007;

Saito, Yokouchi, Kosugi, Tani, Philip, & Okuda, 2008; Gebhardt et al., 2008; Blei et al., 2010). Three-dimensional global models suggested that the large emissions from the tropics can explain the gaps in the CH_3Cl budget (Lee-Taylor, Brasseur, & Yokouchi, 2001; Yoshida, Wang, Zeng, & Yantosca, 2004; Gebhardt et al., 2008). To balance the global CH_3Cl budget, tropical rainforests would have to emit 2.4-2.9 Tg y^{-1}, which is about 60-70% of the total source (Yokouchi et al., 2007). However, because of tropical rainforests' large geographical distribution and high biodiversity in plant species, this source's global CH_3Cl emissions remain highly uncertain (WMO, 2007). The global models also showed that the CH_3Br budget contains tropical sources (Lee-Taylor et al., 2001; Yoshida et al., 2004). Although previous studies had suggested that tropical rainforest does not contribute significantly to CH_3Br emissions, the few field measurements have not confirmed the magnitude of global CH_3Br emissions from the tropics (Gebhardt et al., 2008; Blei et al., 2010). Therefore, it is important to conduct more field measurements in the tropical rainforest ecosystem in order to increase our understanding of the atmospheric budgets of CH_3Cl and CH_3Br.

Both biogenic and abiotic mechanisms could explain the high emissions of CH_3Cl from tropical rainforests (Gebhardt et al., 2008). First, a common biotic mechanism takes place in plant cells via enzymatic transfer of a methyl group from S-adenosyl-L-methionine (SAM) to accepter chloride (Cl^-) (Saito & Yokouchi, 2006). Since this methyltransferase activity is known to depend on temperature, a positive correlation should exist between temperature and tropical plants' CH_3Cl production (Heldt, 2004; Rhew, Østergaard, Saltzman, & Yanofsky, 2003; Saito & Yokouchi, 2006). Second, plant degradation also releases CH_3Cl through abiotic chloride methylation by plant pectin, and this process accounts for the CH_3Cl emissions from leaf litter and during biomass burning (Hamilton, McRoberts, Keppler, Kalin, & Harper, 2003; Gebhardt et al., 2008). Growing in the warmer climate and decomposing easily due to higher level of moisture, tropical plants thus produce CH_3Cl during both their lifespan and decay (Saito & Yokouch, 2008). Previous studies have suggested that CH_3Cl and CH_3Br production share the same biological mechanism (Hamilton et al., 2003). It is possible that many unidentified tropical species are strong CH_3Cl and CH_3Br emitters. However, methyltransferase activity appears to be highly species dependent, and very few studies have focused on tropical plants' methyl halide emissions to provide deeper understanding of the production mechanisms (Yokouchi et al., 2007; Saito & Yokouchi, 2006; Blei et al., 2010).

Although it is crucial to accurately estimate the contribution of tropical rainforest to global CH_3Cl and CH_3Br productions, field experiments in the past decade have only measured emissions from approximately 400 tropical plant species in Southeast Asia region. I present measurements of CH_3Cl and CH_3Br net fluxes from 16 major tropical crops that were measured for their methyl halide emissions for the first time. All these tropical crops are widely cultivated. I modified the vial method from Yokouchi et al. (2007) to conduct a survey of methyl halide-emitting plants and applied bag enclosure experiments to evaluate their emission strength. My objectives were to identify new emitters among these diverse greenhouse-grown tropical plants at the University of California, Berkeley (UCB) Botanical Garden, as well as to develop effective techniques to provide accurate measurements. By quantifying CH_3Cl and CH_3Br emissions from abundant tropical plants, my study aimed to improve the estimate of global methyl halide emissions from the tropical rainforest ecosystem.

My specific research questions are:

1) Are any of these 16 economically important tropical rainforest crops methyl halide emitters?
2) Are vial and bag enclosure experiments effective in measuring methyl halide emissions?
3) Does temperature affect CH_3Cl and CH_3Br emissions from tropical plants?
4) What are the contributions of the highest CH_3Cl and CH_3Br emitter of my study to the global methyl halide emissions?

I hypothesize that:

1) The existence of methyl halide emitters among tropical crops is species-specific because of the variation in the activity of enzyme methyltransferase across species. Also, there should be a positive correlation between CH_3Cl and CH_3Br emissions in the same species because they are likely to share the same enzymatic production pathway.
2) The vial and bag enclosure experiments are effective in detecting methyl halide emissions, but the estimates might have accuracy problems. Estimates may be over- or under-calculated by several orders of magnitude because of the

differences in the sampling environment as well as the lack of replicates for each species (I had 1 individual per species in my study).

3) Methyl halide emissions increase as the day becomes warmer because methyltransferase is temperature dependent, generating a diurnal emission pattern in which the highest emissions correspond to the hottest hours of the day.

4) If the highest emitter has significant emissions and is an abundant species, its contribution to global emissions of CH_3Cl would be large because of its wide geographical distribution and large emission rate.

METHODS

Study system

My study subjects consisted of 16 economically important tropical crop species (Table 1) in the Tropical Greenhouse at UCB Botanical Garden (37°52’29’’N, 122°14’19’’W). Globally, 14 of these species cover an area of about 66 million hectares, or 3.6% of the total tropical land surface (FAO, 2008). Since these 16 species have never been measured for their methyl halide emissions, my experiment was the first attempt to estimate their methyl halide emissions as well as their contribution to the global methyl halide budgets. I chose to study tropical crop species because their wide distributions directly depend on global anthropogenic food production, making their methyl halide emissions susceptible to human activities. To verify the effectiveness of my methods, I also examined species that were measured in previous studies: *Osmunda regalis var. spectabilis*, *Rhododendron brookeanum subsp. kinabaluense*, *Rhizophora mangle*, and *Angiopteris lygodiifolia* (Yokouchi et al., 2002; Yokouchi et al., 2007; Saito & Yokouchi, 2008), although these species are not crops.

Table 1. The economically important tropical crops in the UCB Botanical Garden evaluated in this study.

	Family	Genus and Species	Common Name
1	Arecaceae	*Cocos nucifera*	Coconut
2	Rubiaceae	*Coffea arabica*	Arabica coffee
3	Euphorbiaceae	*Acalypha hispida*	Philippines medusa / fox tail
4	Euphorbiaceae	*Hevea brasiliensis*	Rubber tree
5	Euphorbiaceae	*Manihot esculenta*	Yuca / tapioca pearls
6	Lauraceae	*Cinnamomum zeylanicum*	Cinnamon
7	Malvaceae	*Theobroma cacao*	Cocoa / chocolate
8	Piperaceae	*Piper nigrum*	Black pepper
9	Orchidaceae	*Vanilla planifolia cv. variegata*	Vanilla
10	Zingiberaceae	*Zingiber officinale*	Ginger
11	Myrtaceae	*Psidium guajava*	Guava
12	Rubiaceae	*Coffea liberica*	Kape Barako
13	Anacardiaceae	*Mangifera indica*	Mango
14	Bromelioideae	*Ananas comosus*	Pineapple
15	Sapotaceae	*Synsepalum dulcificum*	Miracle fruit
16	Araceae	*Colocasia esculenta*	Taro

Greenhouse screening of potential CH_3Cl and CH_3Br-emitting species

Data collection

To determine methyl halide emitters among the 16 tropical species, I used the improved vial method adopted from Yokouchi et al. (2007). The vial experiments were conducted from 24 September and 5 November 2010 (Table 2). I harvested fresh, mature leaves from different parts of the same plant for each species at the Tropical Greenhouse and brought the leaves back to the UCB campus laboratory within two hours. Leaf harvest occurred between 9:00 and 13:00 on the sampling dates. I carefully chose leaves that received about equal amounts of sunlight. For each tropical species, I incubated 1-4 leaves in a 40 mL screw-cap glass vial sealed with an inert Teflon sampling cap. After 15 minutes of incubation, I used a 10 mL glass syringe to collect 10 mL of headspace air sample from the vial. I repeated these steps 2 more times to obtain a total of 3 gas samples for each tropical species. The sampling and measurements for each species were conducted on the same day. All tropical plants in the study were ground plants except *T. cacao* and *R. mangle* which were grown in pots (*R. mangle* was in a separate nursery greenhouse). A

second sampling was done for *C. liberica* and *R. brookeanum subsp. kinabaluense*, and as a result they each had a total of 6 samples.

Table 2. Air temperature and measured species for the 10 sampling dates in the vial experiment. '*' indicates the second set of measurements for the species. Leaf harvest occurred between 9:00 and 13:00 on sampling dates.

Dates (2010)	Incubation location	Air Temp (°C)	Species measured in order of the day
24 Sept	Outdoor	20-22°	*R. brookeanum subsp. kinabaluense*
01 Oct	Outdoor	20-22°	*V. planifolia*
			T. cacao
13 Oct	Outdoor	25-32°	*Z. officinale*
			P. nigrum
15 Oct	Outdoor	18-26°	*A. hispida*
			C. nucifera
20 Oct	Outdoor	17-21°	*M. esculenta*
			C. zeylanicum
			H. brasiliensis
22 Oct	In lab	21-25°	*P. guajava*
			C. liberica
27 Oct	Outdoor	17-18°	*M. indica*
29 Oct	In lab	22-28°	*S. dulcificum*
			C. esculenta
			A. comosus
03 Nov	In lab	22-31°	*R. mangle*
			*C. liberica**
05 Nov	In lab	23-27°	*O. regalis var. spectabilis*
			A. lygodiifolia
			C. arabica
			*R. brookeanum subsp. kinabaluense**

I incubated harvested leaves both inside the laboratory and under the natural sunlight inconsistently (Table 2), and therefore temperature was not a well-controlled factor in the vial experiments. I conducted 33 of the 75 leaf incubations inside the laboratory by placing the leaves underneath a lamp to provide constant amount of sunlight for the harvested leaves. The air temperature inside the laboratory was measured throughout the sampling day, and ranged from 17-30° C over different incubation days. I subjected the other 42 incubations to natural sunlight by placing them on the fifth floor balcony of the Department of Geography building. The air temperature for outdoor incubations was taken from the Google Weather website and it ranged from 17-32° Celsius. On all incubation days, the length of time between leaf harvest and sample analysis ranged from 1.5-9 hr. For each species, the samples had similar biomass weights, but the average weight of the leaf samples varied between species. When I incubated the leaves inside the laboratory, I placed one control vial at least 60 cm away from the leaf samples and used it to incubate the air inside the laboratory to determine the background methyl

halide concentrations for comparison. When I incubated outdoors, I also collected an ambient air sample to determine the background methyl halide concentrations on the balcony.

Before the leaf incubations, I conducted blank tests to evaluate the reliability of the vial method. When vials with ambient air were sealed and placed under natural light condition, CH_3Cl and CH_3Br concentrations in the vials showed no significant change over 2.5 hours. Therefore, the tests showed that the clean vials do not emit or uptake CH_3Cl and CH_3Br, and the vials were leak-proof. When ambient air samples incubated inside the vials were injected into the GC/MS at different gas volumes (5 mL, 10 mL, 15 mL, and 20 mL), the analysis also showed a linear relationship between the methyl halide concentrations and the volume injected. This demonstrated that the GC/MS should be able to measure gas concentrations from 10 mL of air sample.

Bag enclosure method

Data collection

Based on the results from the greenhouse screening, I conducted bag enclosure experiments on *C. arabica* to determine its methyl halide emission patterns because it was the highest CH_3Cl and CH_3Br emitter among the 16 species. To ensure that my bag enclosure method was capable of measuring CH_3Cl emission, I also examined *A. lygodifolia* which is a known CH_3Cl emitter (Yokouchi et al., 2007). The measurements were performed from January 2011 to March 2011 at the Tropical House. I enclosed multiple branches of a plant with a self-constructed 50 L-Teflon bag and extracted the air sample within with pre-evacuated stainless steel gas canisters logarithmically at 30, 60 and 120 minutes following leaf enclosure. In order to understand the effect of diurnal pattern on plants' methyl halide emissions, I measured the species during the morning (9:00-12:00) and the afternoon (12:00-15:00) to establish a daytime emission pattern. Thus, I took air samples at around these 6 different times of a day: 10:30, 11:00, 12:00, 13:30, 14:00, and 15:00. 2 individuals of *C. arabica* were measured; 2 one-day experiments (morning and afternoon measurements) were conducted on the first individual while the 2 half-day experiments (morning or afternoon measurement) were conducted on the second individual. 3 one-day experiments were conducted on 1 individual of *A. lygodiifolia*.

Throughout the experiments, air temperature and pressure were recorded using a barometer. I also harvested the enclosed leaves and dried them over 2 days at 65 °C to obtain the dry leaf weight.

Before sampling the plants, I conducted 3 leakage tests on the Teflon bag and found the average leakage rate to be -3.061 parts per trillion (ppt) per minute, which is a relatively small value. Therefore, the Teflon bag was reasonably leak-tight and should be effective in containing gas emissions from tree leaves.

Correlations

To determine the correlation between CH_3Cl and CH_3Br emissions from the tropical species, and the correlation between temperature and methyl halide emissions, I conducted regression and correlation analysis on Microsoft Excel.

Air analysis

To determine whether CH_3Cl or CH_3Br were emitted, the vial air samples were measured once by gas chromatography/mass spectrometry (Agilent 6890N/5973 GC/MS) with a custom inlet system that measures low volume air samples. The air canister samples from the bag enclosure experiments were measured twice by GC/MS. The gas samples were compared against a natural air working standard (561 ppt CH_3Cl and 9.4 ppt CH_3Br on the SIO-2005 scale). Details of the cryotrapping and sample inlet system, chromatographic separation, mass spectrometer settings, and calibration methods are described in Khan, Rhew, Whelan, Zhou, & Deverel (2011).

Flux calculation

Net fluxes were calculated using the following equation:

$$\text{Netflux}(\text{nmol}g^{-1}\text{d}^{-1}) = \frac{m \times n \times (1440\text{min/day}) \times (1000\text{nmol/pmol})}{\text{w (g)}} \qquad \text{(Eqn. 1)}$$

where *m* (ppt/min) represents the slope of the linear least squares fit to the measured dry air mole fractions versus time; *n* represents the number of moles of air in the chamber; and w (g) represents the weights of dry leaf (M. A. H. Khan, pers. comm.., April 27, 2011). Net flux errors were calculated by propagating the standard error on the slope with the uncertainties (volume, temperature and pressure) associated with *n*.

Positive slopes represented net emission, while negative slopes represented net uptake. Net uptake rates were converted to the first order uptake rates k (min^{-1}) by plotting the natural log of the concentration versus time and subsequently normalized by multiplying the rate constants with seasonally averaged background concentrations in Northern Hemisphere air between 1998-2001 (10.4 ppt for CH_3Br and 535.7 ppt for CH_3Cl [Simmonds et al., 2004]). This normalized net uptake rate was substituted for *m* in Eqn. 1 to yield the normalized net uptake flux. Unless otherwise specified, fluxes are reported in nanomoles per gram dry leaf weight per day (nmol g^{-1} d^{-1}). For clarity, this study reports net consumption rates as negative values, while net production rates are reported as positive values.

Global Emission Extrapolation

Using data on global distribution of *C. arabica* (FAO, 2008), I extrapolated its estimated global methyl halide emissions by simply multiplying *C. arabica*'s methyl halide net flux rate (nmol g^{-1} h^{-1}) with the weight of global biomass harvested (g). I calculated the weight of global biomass harvested (GBH) using the following equation:

$$GBH = W \times NL \times NT \times A, \qquad \text{(Eqn. 2)}$$

where *W* is the average weight of dry leaf measured from *C. arabica*'s leaf samples in my study (≈ 0.1602 gram), *NL* is the average number of leaves on each mature *C. arabica* plant (I assumed 2,000 leaves per tree), *NT* is the average number of plants per square meter area (I assumed 1 tree per m^2), and *A* is the global area of *C. arabica* harvested in 2008 (97.5 billion m^2 [FAO, 2008]). After several unit conversions, I obtained the final global methyl halide emissions in the unit of grams per year (g yr^{-1}).

RESULTS

Greenhouse screening of potential CH_3Cl and CH_3Br-emitting species

CH_3Cl emission

Using the vial method, I found that all the tropical crops except *H. brasiliensis* had positive net CH_3Cl emission flux (Table 3). Although *H. brasiliensis* showed an average uptake of CH_3Cl (-0.005 ± 0.013 nmol g^{-1} d^{-1}), 1 of the 3 samples for this species emitted CH_3Cl at a rate of 0.0094 ± 0.006 nmol g^{-1} d^{-1}. The highest emitter among the 16 tropical crops was *C. arabica* with a mean emission rate of 17.999 ± 4.556 nmol g^{-1} d^{-1}. The weakest emitter was *C. nucifera* with a mean emission rate of 0.014 ± 0.008 nmol g^{-1} d^{-1}. The mean CH_3Cl emission rate from all tropical crops was 1.754 ± 4.50 nmol g^{-1} d^{-1}. Only 2 of the 3 species in the Euphorbiaceae family (*A. hispida* and *M. esculenta*) were CH_3Cl emitters. On the other hand, the 2 species from the Rubiacea family, both in the *Coffea* genus (*C. arabica* and *C. liberica*), were CH_3Cl emitters. Species belonging to a family that is known to contain CH_3Cl emitters were all found to be CH_3Cl emitters (Table 3). On the other hand, *C. esculenta* emitted CH_3Cl even though the Araceae family is known to contain only non-emitters.

CH_3Br emission

Of the 16 species examined, 7 were found to emit CH_3Br while the others were found to consume CH_3Br (Table 3). *C. liberica* showed neither uptake or emission of CH_3Br in all of its 6 samples. The highest CH_3Br emitter was *C. arabica* with a mean emission rate of 0.348 ± 0.115 nmol g^{-1} d^{-1}. The weakest emitter was *A. comosus* with a mean emission rate of 0.001 ± 0.001 nmol g^{-1} d^{-1}. The 3 species from the Euphorbiaceae family all consumed CH_3Br at similar rates. The mean CH_3Br emission rate from all tropical crops was 0.029 ± 0.087 nmol g^{-1} d^{-1}, which is about 60 times smaller than the mean CH_3Cl emission rate.

Table 3. Summary of net CH_3Cl and CH_3Br fluxes from 20 tropical plants in the Tropical House.

Family	Species	CH_3Cl (nmol g^{-1} dry wt d^{-1})		CH_3Br (nmol g^{-1} dry wt d^{-1})	
		mean	sd	mean	sd

Anacardiaceae	*M. indica*	0.033	0.015	-0.001	0.001
Araceae[b]	*C. esculenta*	0.260	0.110	0.001	0.003
Arecaceae	*C. nucifera*	0.014	0.008	-0.005	0.002
Bromelioideae	*A. comosus*	0.125	0.114	0.001	0.001
Ericaceae[a]	*R.*[a] *brookeanum subsp. kinabaluense* (6)	4.950	5.895	0.007	0.007
Euphorbiaceae[c]	*A. hispida*	0.027	0.094	-0.006	0.004
Euphorbiaceae[c]	*H. brasiliensis*	-0.005	0.013	-0.002	0.001
Euphorbiaceae[c]	*M. esculenta*	0.114	0.013	-0.002	0.0002
Lauraceae[a]	*C. zeylanicum*	0.125	0.080	0.004	0.005
Malvaceae	*T. cacao*	0.023	0.039	<-0.0001	0.001
Marattiaceae[a]	***A. lygodiifolia***[a]	0.874	1.669	-0.001	0.005
Myrtaceae[a]	*P. guajava*	0.500	0.042	0.019	0.004
Orchidaceae	*V. planifoia*	4.174	6.980	0.059	0.100
Osmundaceae[a]	*O.*[a] *regalis var. spectabilis*	144.857	125.857	0.343	0.209
Piperaceae	*P. nigrum*	0.696	0.371	<-0.0001	0.002
Rhizophoraceae[a]	***R. mangle***[c]	0.157	0.021	<-0.0001	0.0004
Rubiaceae[a]	*C. arabica*	17.999	4.556	0.348	0.115
Rubiaceae[a]	*C. liberica* (6)	0.239	0.174	0	0
Sapotaceae	*S. dulcificum*	3.232	1.295	0.060	0.031
Zingiberaceae[a]	*Z. officinale*	0.507	0.183	-0.004	0.003

[a]The family, genus, or species is known to contain methyl chloride emitters.
[b]The family, genus, or species is known to contain non-emitters.
[c]The family, genus, or species is known to contain both emitters and non-emitters.
Bolded name shows that this particular species has been measured for methyl chloride emission before. 3 emission measurements were conducted for each species using the vial experiment, unless otherwise noted in the parenthesis.

CH_3Cl emission from previously measured plants

The 4 previously measured genus and species were all found to emit CH_3Cl at relatively higher level than the 16 tropical crops (Table 3). Among all 20 tropical species, *O. regalis var. spectabilis* was the highest CH_3Cl emitter with a mean emission rate of 144.857 ± 125.857 nmol g^{-1} d^{-1}. *R. brookeanum subsp. kinabaluense* ranked right below *C. arabica* as the third highest emitter, with a mean emission rate of 4.950 ± 5.895 nmol g^{-1} d^{-1}. Both *A. lygodiifolia* and *R. mangle* emitted CH_3Cl at similar rates as the 16 tropical crops (0.874 ± 1.669 nmol g^{-1} d^{-1} and 0.157 ± 0.021 nmol g^{-1} d^{-1} respectively). The average emission rate from *O. regalis var. spectabilis, R. brookeanum subsp. kinabaluense, A. lygodiifolia* and *R. mangle* was about 37.71 ± 71.46 nmol g^{-1} d^{-1}, which is about 22 times higher than the average CH_3Cl emission rate of all 16 tropical crops.

Variability in the vial experiment

I observed considerable variability in emission rates obtained by the vial experiment (Figure 1). Fluxes varied widely between and within the species, with the CH_3Cl emission rates ranging from 0.04 to 12.23 nmol g^{-1} d^{-1} (by *V. planifolia*). When I repeated the sampling for a few species on two different days (*R. brookeanum subsp. kinabaluenes and C. liberica*), I also found that newer samples had distinctively different emission rates than the previous samples, such as a difference of 168 times in the CH_3Cl emission rate for *R. brookeanum subsp. kinabaluense* (Table 4). *C. liberica* had the same CH_3Br emission rate for all of its samples (0 nmol g^{-1} d^{-1}).

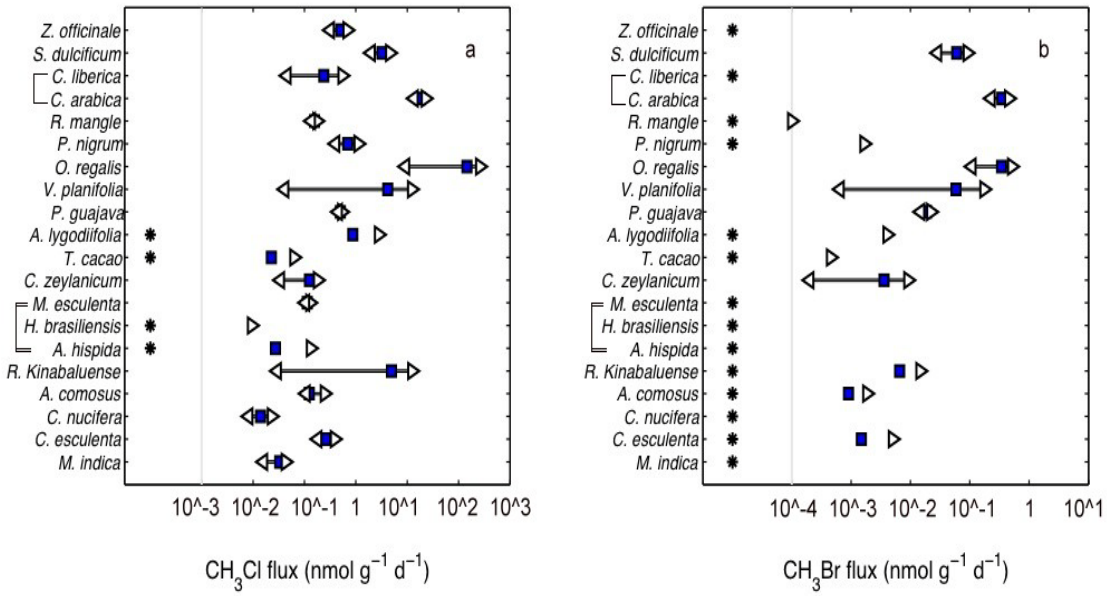

Figure 1. Results of the vial experiment, showing the minimal, maximal, and mean net emission fluxes of CH_3Cl (a) and CH_3Br (b) from 20 tropical plants in the Tropical House at UCB Botanical Garden. Blue squares represent average net flux measurements. Right arrows represent the maximum net flux rate and left arrows represent the minimum. The vertical grey lines at x = 10^{-3} in plot 'a' and at x = 10^{-4} in plot 'b' represent the lowest positive net flux measurement for the methyl halide emissions. (*) to the left of the vertical grey line indicates that the species has negative or zero net flux rates for any of the minimum, mean, and maximum net flux rate, but no actual value is assigned to these negative net flux rates on the plots. Horizontal line is drawn to connect the symbols when the minimum, average, and maximum net flux rates are all positive. A species with only negative or zero net flux measurements has no symbols except the (*) to the left of the grey line. Species surrounded by the thin bracket belong to the same genus, and species surrounded by the thicker bracket belong to the same family but not genus. Note that the species are arranged by their family names in alphabetical order. Also note that *C. liberica* and *R. brookeanum subsp. kinabaluense* had 6 measurements while all other species had 3 measurements.

Table 4. Emission rates for repeated vial experiments.

Species Name	Sampling date (2010)	Net CH_3Cl flux (nmol g^{-1} d^{-1})	Net CH_3Br net flux (nmol g^{-1} d^{-1})
R. subsp. kinabaluense	24 Sept	0.0586 ± 0.0335	0.0003 ± 0.0005
	05 Nov	9.8411 ± 3.8846	0.0128 ± 0.0015
C. liberica	22 Oct	0.3438 ± 0.1829	0 ± 0
	03 Nov	0.1335 ± 0.0928	0 ± 0

Bag enclosure experiment

I chose to conduct bag enclosure experiment on *C. arabica* and *A. lygodiifolia.* *C. arabica's* CH_3Cl and CH_3Br emissions both increased over the time of day (Figures 2a, 2b). There were positive net CH_3Cl flux and positive net CH_3Br flux during each bag enclosure for *C. arabica*, and the net fluxes from the second bag enclosure of the day was always higher than those of the first. For two sampling dates, only one bag enclosure was conducted and there were positive net CH_3Cl flux and positive net CH_3Br flux for each measurement. However, the afternoon emission rate on March 2 was relatively smaller than all other measurements. On average, *C. arabica*'s net CH_3Br flux was about 20 times smaller than its net CH_3Cl flux. The highest CH_3Cl flux rate measured was 26.577 ± 0.204 nmol g^{-1} d^{-1}, and the corresponding CH_3Br flux rate, 0.282 ± 0.005 nmol g^{-1} d^{-1}, was also the highest for CH_3Br emission. The higher emission rate always occurred during the second bag enclosure of the day, which took place between 12:00 and 14:00 when the air temperature peaked. There were strong and statistically significant correlations between temperature and the net methyl halide fluxes from *C. arabica,* with a R^2 value of 0.896 ($p = 0.0004$) for CH_3Cl emission and a R^2 value of 0.917 ($p = 0.0002$) for CH_3Br emission (Figure 3).

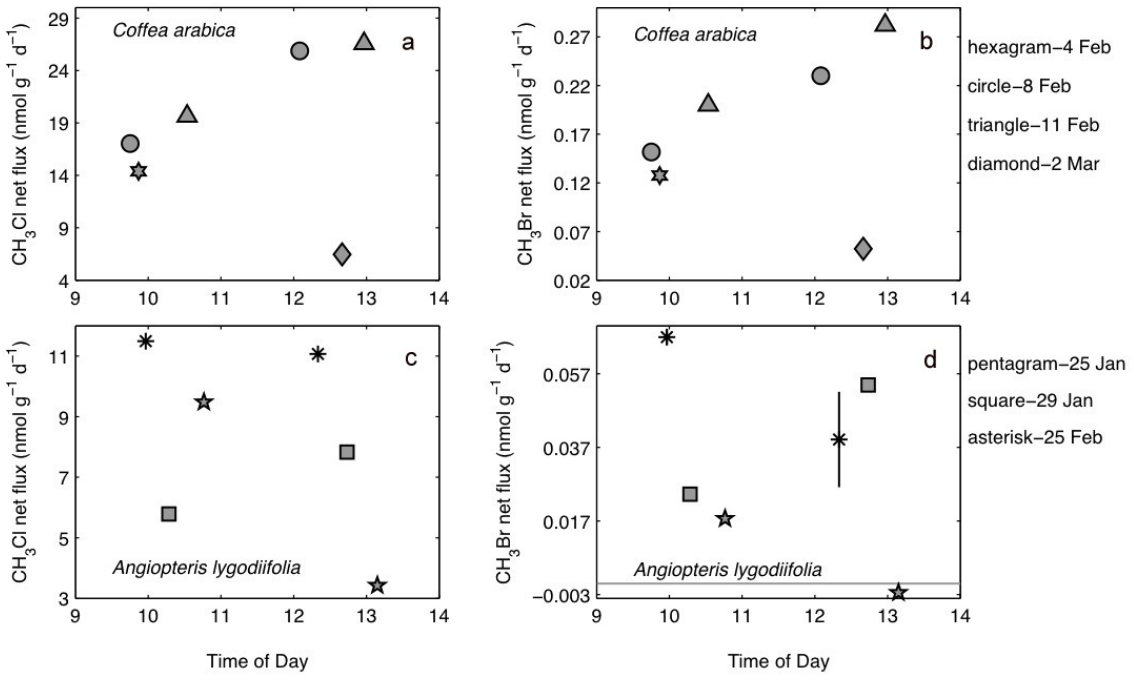

Figure 2. Results of the bag enclosure experiment, showing emission rates of CH_3Cl and CH_3Br from *C. arabica* (a and b) and *A. lygodiifolia* (c and d) over the time of day in the Tropical House at UCB Botanical Garden. Methyl halide flux measurements were conducted over 4 sampling dates for *C. arabica* and 3 sampling dates *for A. lygodiifolia*. In plots 'a' and 'b', hexagon represents February 4, circles represent February 8, triangles represent February 11, and diamond represents March 2, 2011. In plots 'c' and 'd', pentagram represents January 25, squares represent January 29, and asterisks represent February 25. The horizontal grey line in plot 'd' indicates zero CH_3Br net flux. Morning and afternoon measurements were conducted consecutively in all sampling dates except for February 4 and March 2, in which only the morning or afternoon measurement was conducted. The morning measurements took place between 9:00 and 12:00 while the afternoon measurements were conducted between 12:00 and 14:00. Standard deviations are indicated by the lines above and below the symbols.

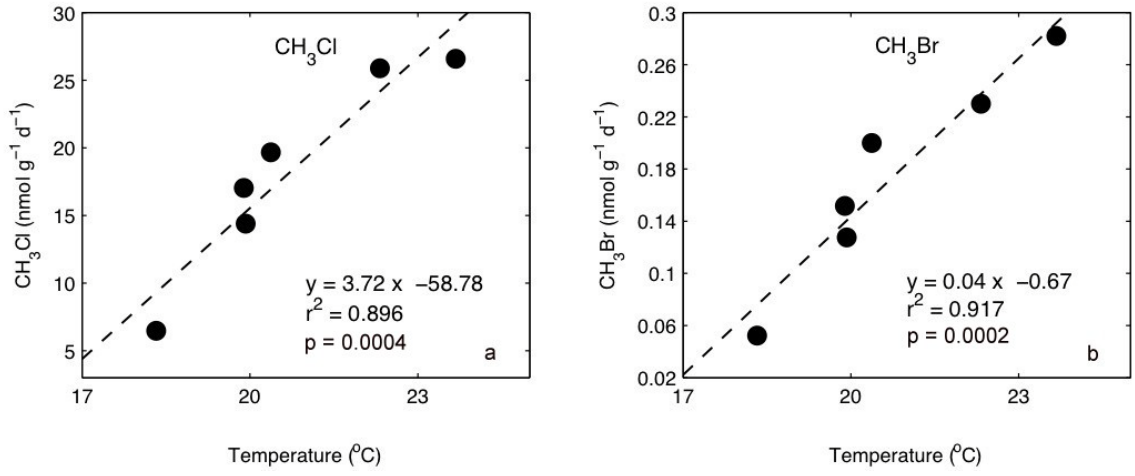

Figure 3. Correlations between temperature and methyl halide emissions from *C. arabica*. The correlation calculation included all bag enclosure measurements (n = 6) for *C. arabica*. (a) shows CH_3Cl emissions; (b) shows CH_3Br emissions.

Emission rates from *A. lygodiifolia* did not show a consistent pattern over the time of day (Figure 2c, 2d). On 2 of the 3 sampling dates (January 25 and February 25, 2011), the afternoon's emission rate was lower than the morning's. On the first sampling date (January 25), the second bag enclosure measured a CH_3Cl emission rate of 3.423 ± 0.015 nmol g^{-1} d^{-1}, which is less than half of the emission rate from the first bag enclosure of the day (9.477 ± 0.057 nmol g^{-1} d^{-1}). On the third sampling date (February 25), the second bag enclosure's flux rate (11.069 ± 0.026 nmol g^{-1} d^{-1}) was only slightly lower than that of the first (11.494 ± 0.029 nmol g^{-1} d^{-1}), which was also the highest emission rate measured for *A. lygodiifolia*. The measurements from the second sampling date (January 29) showed a vivid increase in the emission rate over the time of day, going from 5.784 ± 0.021 nmol g^{-1} d^{-1} in the morning to 7.830 ± 0.041 nmol g^{-1} d^{-1} in the afternoon. There were negative slopes for the linear regressions between temperature and the emission rates of methyl halides from *A. lygodiifolia.*

Correlation between methyl halide emissions

There were a moderate correlation between the methyl halide emissions from *A. lygodiifolia (*R^2 = 0.541; p = 0.0376) and a very strong correlation between those from *C. arabica (*R^2 = 0.962; p = 0.0001) (Figure 4).

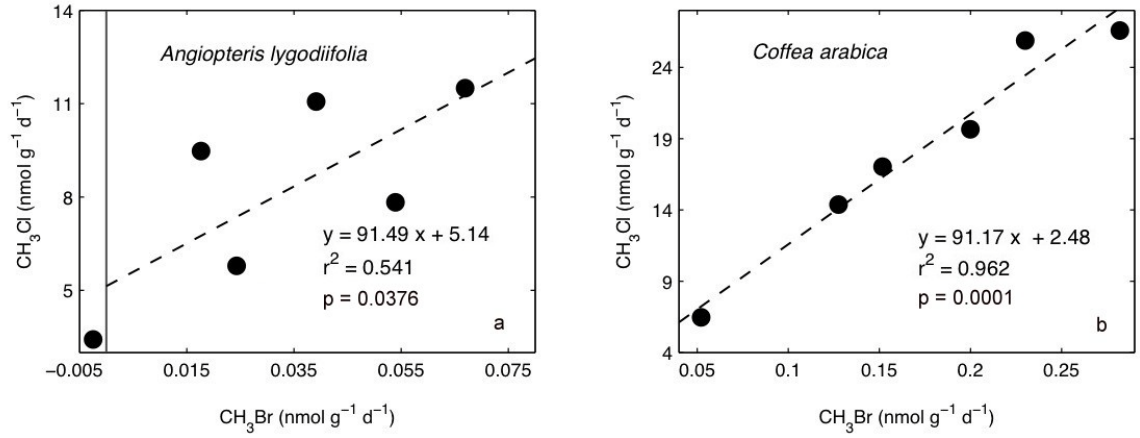

Figure 4. Correlations between CH_3Cl and CH_3Br emissions for *A. lygodiifolia* (a) and *C. arabica* (b). The correlation calculations included all bag enclosure measurements (*n* = 6) for each species.

Global emission extrapolation

Based on the *C. arabica*'s emission results from my study (mean CH_3Cl emission rate: 0.0385 ± 0.0158 μg g^{-1} hr^{-1}; mean CH_3Br emission rate: 0.688 ± 0.321 ng g^{-1} hr^{-1}), I estimated that that global *C. arabica* plantations emit about 0.01 ± 0.004 Tg CH_3Cl and 0.19 ± 0.09 Tg CH_3Br annually.

DISCUSSION

The magnitude of known atmospheric methyl halide sinks is much greater than known methyl halide sources (Cox et al., 2005). Therefore, in order to balance the global methyl halide budget, identifying the remaining unknown methyl halide sources has been a crucial ongoing task. By improving the quantification of global emission rates of ozone-depleting gases, we also gain insight into the ozone depletion cycle. My study aimed to assess the effectiveness of two emission measurement techniques, the vial and the bag enclosure experiments, as well as to provide methyl halide emission data from tropical species, which have recently been discovered to be the largest biogenic source of CH_3Cl (Yokouchi et al., 2000; Yokouchi et al., 2007; Gebhardt et al., 2008). Although tropical rainforests are not a significant source for CH_3Br, studying CH_3Br emission from these tropical species shows positive correlation between CH_3Cl and CH_3Br emission, which suggests that CH_3Cl and CH_3Br synthesis share similar biotic mechanisms in certain tropical plants (Saito & Yokouchi, 2006). Furthermore, in the tropical regions, tropical crops' distribution and growth are tightly bound to human activities. Therefore, investigating CH_3Cl emission by tropical crops provides a better assessment of the human impact on ozone depletion.

Identification of CH_3Cl and CH_3Br emitting plants in the Tropical Greenhouse

CH_3Cl emission

This study represents the first screening of 16 economically important tropical crop species for their methyl halide emissions. All tropical crops except *H. brasiliensis* emitted

CH_3Cl in the vial experiment. By converting the unit of my emission results to μg g^{-1} h^{-1}. I obtained an average of 0.004 μg g^{-1} h^{-1} for all 16 tropical crops, which was about 10 times smaller than the average emission rate in the previous greenhouse and field measurements in the tropics (Yokouchi et al., 2002; Yokouchi et al., 2007; Saito & Yokouchi, 2006; Saito et al., 2008; Blei et al., 2010). Assuming the vial experiment effectively measured the emission rate, the difference between my measurements and previous studies could be caused by the difference in study location. In contrast to all the previous greenhouse and field studies conducted in the tropical region, UCB Botanical Garden resides in a higher latitude with cooler climate (37°52'29''N, 122°14'19''W). Thus, the colder climate might have contributed to lower emission rates from the tropical plants because of the temperature dependency in plant's methyl halide productions (Hamilton et al., 2003). The difference in the vial incubation time might have also been a factor (15 minutes in my study versus 4-8 days in Yokouchi et al. [2007]). In the experiment conducted by Yokouchi et al. (2007), CH_3Cl concentration in the vials showed linear increase for a few days under constant natural light condition. Thus, my average emission rate could have been higher if I had incubated the leaves longer. However, it was not plausible to incubate the leaves for more than a day because my study aimed to measure emission from freshly harvested leaves, which should release the same amount of CH_3Cl as intact, live plants. Older or dead leaves might release CH_3Cl at a lower rate because of physical stress and decay (Blei et al., 2010).

Viability of the vial experiment

On the other hand, the vial experiment might have provided inaccurate emission estimates because it was susceptible to a wide range of factors. Temperature, sunlight exposure, and the time between leave harvest and emission analysis were not controlled consistently. CH_3Cl net flux emission varied widely from 1 to 3 orders of magnitude within many species. *V. planifolia* had the widest range in its CH_3Cl net flux emission (0.04 to 12.23 nmol g^{-1} d^{-1}). *R. brookeanum subsp. kinabaluense* also had an 168 times higher CH_3Cl emission rate on the second sampling date than the results on the first sampling date. Such large variability in emission rates suggested that the vial experiment did not provide consistent or accurate measurements. Although the observation of variable emission rates within the same species

corresponded to the previous field measurements in Malaysia tropical forests (Saito et al., 2008; Blei et al., 2010), the results still demonstrated the challenge in controlling all factors to make the vial experiment a viable method.

CH_3Br emission

In contrast to CH_3Cl emission, not all tropical crops emitted CH_3Br. The average of net flux emission was 0.06 ng g^{-1} h^{-1}, and 8 out of the 16 species showed uptake of CH_3Br at very low rates. The weakest CH_3Br emitting species identified in the previous study had a net flux of 0.1 ng g^{-1} h^{-1}, which is slightly higher than the average net flux in my study (Blei et al., 2010). Blei et al. (2010), the first group to conduct flux measurements of CH_3Br in situ in tropical rainforest, observed an average rate of 0.4 ng g^{-1} h^{-1} for CH_3Br emission from 18 different species in lowland Malaysian tropical rainforest. Saito & Yokouchi (2006) was the only other group to measure CH_3Br emission rates from tropical plants, and they observed much higher CH_3Br emission rates from *Cyathea podophylla* (20 ng g^{-1} h^{-1}) and *Cyathea lepifera* (16 ng g^{-1} h^{-1}). Thus, similar to my CH_3Cl emission results, my average CH_3Br emission rate was about 7 times smaller than other studies.

Choosing species for bag enclosure experiment

Most of the previous studies arbitrarily considered any CH_3Cl emission rate above 0.01 μg g^{-1} h^{-1} to be significant emission (Yokouchi et al., 2007; Saito & Yokouchi, 2008; Saito et al., 2008). Therefore, using the same emission threshold, I found that *C. arabica* was the only significant CH_3Cl emitter with a emission rate of 0.04 μg g^{-1} h^{-1}. In addition, *C. arabica* was also the highest emitter for CH_3Br. Such correlation suggested that CH_3Cl and CH_3Br synthesis might share similar biological pathways in *C. arabica* (Saito & Yokouchi, 2006). I chose to conduct bag enclosure experiment on *C. arabica* because it was the highest emitter for both methyl halides and therefore it was easier to observe any change in the atmospheric concentrations of methyl halides in the 50 L Teflon bag. Furthermore, nearly 75-80% of the world's coffee comes from *C. arabica* (Griffin, 2006). If *C. arabica* is determined to be a very

strong methyl halide emitter, *C. arabica* would have significant influence on the methyl halide budgets because of its wide distribution and economic importance.

CH_3Cl emission from previously measured plants

The positive emission results from *O. regalis var. spectabilis, R. brookeanum subsp. kinabaluense,* and *A. lygodifolia* also agreed with previous field studies (Yokouchi et al., 2007; Blei at al., 2010). Osmundaceae, Ericaceae, and Marattiaceae families are known to contain strong CH_3Cl-emitters (Table 2). Both *O. regalis var. spectabilis* and *R. brookeanum subsp. kinabaluense* were shown in this study for the first time to be CH_3Cl-emitting plants. *A. lygodiifolia* (Marattiaceae) has been measured several times to be a significant emitter (e.g., emission rate greater than 0.01 μg g^{-1} h^{-1}; Yokouchi et al., 2007; Yokouchi et al., 2006; Blei et al., 2010). *A. lygodiifolia* was the 8th highest emitter in this study (mean net emission flux: 0.875 ± 1.669 nmol g^{-1} d^{-1}), and its emission rate was 111.46 times lower than the results from previous studies. *O. regalis var. spectabilis* and *R. brookeanum subsp. kinabaluense* also had lower emission rates than the other species in the same genus (10 times and 3.7 times lower respectively) (Yokouchi et al., 2007). Although these 3 species had lower emission rates than their counterparts in the other studies, the presence of CH_3Cl emissions suggested that my vial experiment was effective as a screening method for emitters, but not effective to accurately assess the magnitude of emissions.

On the other hand, *R. mangle* (Rhizophoraceae) has also been measured several times for CH_3Cl emission, but two previous studies gave opposite results. Yokouchi et al. (2007) found *R. mangle* to be a non-emitter using the vial measurement, while Manley, Wang, Walser, & Cicerone (2007) observed *R. mangle* as a weak emitter for both CH_3Cl and CH_3Br using the chamber incubation method. In my study, *R. mangle* was the 12th highest CH_3Cl emitter among the 20 tropical species. The CH_3Cl emission from *R. mangle* was inconsistent with the observations by Yokouchi et al. (2007) but similar to that of Manley et al. (2007). Comparing my testing environment to that of the two studies, I found that Yokouchi et al. (2007) measured a ground plant in the rainforest while both Manley et al. (2007) and I conducted measurements on *R. mangle* that grew in artificial environments, such as in a pot and in water-sealed chamber.

Thus, assuming my vial experiment is effective, the emission result from *R. mangle* suggested that a plant's growing environment could potentially affect its methyl halide emissions.

Family, genus, and species-dependency of CH_3Cl emission from tropical plants

My study showed that the two species from the Euphorbiaceae family, *A. hispida* and *M. esculenta*, were both weak CH_3Cl-emitters (mean emission rates were 0.06 ± 0.19 ng g^{-1} h^{-1} and 0.24 ± 0.03 ng g^{-1} h^{-1} respectively), while the other species in the same family, *H. brasiliensis*, showed weak uptake of CH_3Cl. This agreed with previous studies that found the Euphorbiaceae family contains both CH_3Cl emitters and non-emitters. Since species belonged to a family that is known to contain CH_3Cl emitters were all found to emit CH_3Cl, the results suggested that CH_3Cl emission could be family-dependent for many species. At the same time, Yokouchi et al. (2007) also proposed that CH_3Cl emission was a common character at genus level. The high emission from *O. regalis var. spectabilis* and *R. brookeanum subsp. kinabuluense* supported that species in the same genus share similar CH_3Cl emission character, particularly in genus *Osmunda* and *Rhododendron*. However, I found that two species within the same genus, *C. arabica* and *C. liberica*, had distinctively different emission rates (mean emission rates were 37.86 ± 9.58 ng g^{-1} h^{-1} and 0.50 ± 0.37 ng g^{-1} h^{-1} respectively). Thus, my results also suggested that species in the same genus do not necessarily have similar CH_3Cl emission pattern, and this agreed with previous studies that found CH_3Cl emission in the tropics to be highly species dependent (Blei et al., 2010; Saito et al., 2008).

Bag enclosure experiment

I found a trend of increasing methyl halide emissions in both *A. lygodiifolia* and *C. arabica* throughout the 5-hr measurement period. On two sampling dates for *C. arabica*, only one bag enclosure measurement was conducted and therefore these results merely demonstrated that *C. arabica* is a consistent methyl halide emitter in both the morning and the afternoon. The relatively small emission rate in the afternoon of March 2 could be explained by the lowest temperature (18.3 °C) that was recorded for *C. arabica* sampling (see the lowest point in Figure 3a). The strong, positive correlations between the temperature and methyl halide net flux

emissions from *C. arabica* provided evidence for the temperature dependency of the methyltransferase activity (Hamilton et al., 2003; Saito & Yokouchi, 2006; Saini et al., 1995). Although the greenhouse was meant to maintain a constant temperature throughout the day, the sunlight exposure still increased the temperature inside the Teflon bag. Therefore, the increase of 1-2° C in the air temperature during the enclosure period could have enhanced the methyltransferase activity within the plant leaves.

I chose to conduct bag enclosure experiment on *A. lygodiifolia* because this species has previously been measured 3 times in different seasons (Yokouchi et al., 2002; Yokouchi et al., 2007; Saito & Yokouchi, 2008). In my study, I found that methyl halide emissions from *A. lygodiifolia* decreased from morning to afternoon in 2 of the 3 sampling dates (January 25 and February 25, 2011). Bad sampling flasks for sampling in the afternoon of January 25 might have contributed to this unexpected reduction in methyl halide emissions. The two flux rate measurements obtained on February 25 were almost the same (0.024 μg g^{-1} h^{-1} and 0.023 μg g^{-1} h^{-1}) and therefore did not suggest significant decline in emission. However, there were negative slopes for the linear regression between the temperature and methyl halide emissions for *A. lygodiifolia*, suggesting that *A. lygodiifolia*'s methyl halide emissions are not temperature dependent. In addition, the emission rates obtained from the bag experiment were about 10.7 times smaller than the results from previous studies (Yokouchi et al., 2002; Saito & Yokouchi, 2008). Comparing the results of the vial and the bag enclosure experiments suggested that the bag enclosure method is much more accurate in quantitatively measuring CH_3Cl emissions.

For both *A. lygodiifolia* and *C. arabica*, there were moderate and strong correlations between CH_3Cl and CH_3Br emission (R^2 = 0.54 and p = 0.0376; R^2 = 0.96 and p = 0.0001 respectively). The low p-values indicated that these correlations are statistically significant, especially for *C. arabica*. These correlations suggested that CH_3Cl and CH_3Br productions share similar biological mechanism (Saito & Yokouchi, 2006).

Global extrapolation of methyl halide emissions

The annual global CH_3Cl emission from *C. arabica* was extrapolated to be 0.01 ± 0.004 Tg CH_3Cl. However, using the bag enclosure experiments, I found that *A. lygodiifolia's* CH_3Cl emission rates were roughly 10.7 times smaller than previous measurements (Yokouchi et al.,

2002; Saito & Yokouchi, 2008). If I assumed that my bag enclosure experiment is effective in measuring CH_3Cl emissions but could only detect emission rates that are 10.7 times smaller than the actual estimates, then it is plausible that *C. arabica's* emission rates in my study were also underestimated by 10.7 times. Therefore, I multiplied the extrapolated number with 10.7 to obtain 0.11 ± 0.05 Tg CH_3Cl as the resulting annual CH_3Cl emission from *C. arabica*. This corresponds to approximately 7.5% of the total tropical rainforest emissions (about 1.5 Tg; [Gebhardt et al., 2008]) and 2.6% of the total source (about 4.4 Tg; [WMO, 2007]), suggesting that *C. arabica* is non-negligible source of atmospheric CH_3Cl . However, this is still possibly an underestimate because the global area harvested (part of the global extrapolation calculation) excludes the area from which, although sown or planted, there was no harvest due to damage or failure. Also, I assumed that there are only 2,000 leaves per square meter, but the real *C. arabica* planations might have much higher density. In addition, I measured a young *C. arabica* plant (3-year-old) in my study while the average economic age of *C. arabica* plants in the fields is 30-40 years old (Duke, 1996). The older trees might emit more CH_3Cl because of their well-established metabolism. Therefore, *C. arabica*'s global CH_3Cl emissions could be higher than estimated.

I also estimated that global *C. arabica* plantations emit roughly 0.19 ± 0.09 Tg CH_3Br annually. However, since none of the species in my study have been measured for their CH_3Br emissions before, it is not certain whether the *C. arabica*'s CH_3Br emission rates were an overestimate or an underestimate. Three-dimensional models have proposed that tropical vegetations are the additional source of CH_3Br and emit approximately 45.6 Gg yr^{-1} (Warwick, Pyle, & Shallcross, 2006; Gebhardt et al., 2008), but this estimate contains large uncertainty because of limited CH_3Br emission measurements in the tropics. Nevertheless, if this estimate were accurate, *C. arabica*'s annual CH_3Br emission represents approximately 0.41% of the total CH_3Br emission from the tropical forests, suggesting that *C. arabica* is not a significant source of atmospheric CH_3Br.

Broader implications

In sharp contrast to the bag enclosure method, the vial experiment could only provide qualitative measurements with much lower precision and high variability. The inconsistency in

the vial measurements strongly suggested that using the vial experiment emission rates to extrapolate global CH_3Cl emission is susceptible to a large amount of errors. Hence, researchers should avoid using results from the vial experiment to provide global estimates, and should instead use the vial method to screen potential emitters.

Since these tropical crops are widely distributed and cultivated, their CH_3Cl emissions are significant to the global CH_3Cl production. Therefore, along with the naturally grown tropical rainforest species, tropical crops should also be taken into account in future estimates of global CH_3Cl emission. Because of tropical crops' economic importance, we should also be aware that the global CH_3Cl production is highly susceptible to human activities. Furthermore, if many tropical crops are potentially significant CH_3Cl emitters like *C. arabica*, the environmental cost of these tropical crops would be re-defined to not only include deforestation, but also ozone depletion.

Limitations

Although my research sought to improve the experimental method in Yokouchi et al. (2007) by taking CH_3Cl measurement on freshly harvested leaves instead of old harvested leaves, both of the greenhouse screening and bag enclosure experiments had many uncontrolled factors that interfered with accurate measurements of CH_3Cl emission. Variable factors including temperature, sunlight exposure, time after harvesting, water content of the leaves (Hamilton et al., 2003), and limited number of trees for experimenting all prevented me from obtaining consistent measurements or determining the most influential factors in affecting CH_3Cl emission. Although the bag enclosure experiment suggested that CH_3Cl emission was dependent on temperature, the exposure to solar radiation could also be a significant factor. Nevertheless, the bag enclosure experiment was still successful in capturing a clear diurnal emission pattern from the plants.

Future research

To continue this pioneering research on tropical plants' emission of methyl chloride, this experiment should be replicated on more than one individual plant specimen. To further

investigate methyl halide production from *C. arabica*, researchers could grow coffee trees inside the laboratory in order to control extraneous variables. Researchers could manipulate soil moisture, nutrients levels, water content, halide ion concentrations, and air temperature to determine methyl halide production's dependency on different factors. To determine if *C. arabica* in other environments also emits methyl halides, it would be necessary to measure naturally grown trees in the tropics and especially in the crop fields. Furthermore, there are many more tropical crops in the world and most of them could also be potential emitters. Identification of more tropical crops for CH_3Cl emission would not only improve the estimation of global CH_3Cl production, but also allow us to understand the extent of anthropogenic impact on CH_3Cl emission.

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