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# Coastal salt marshes as global methyl halide sources from determinations of intrinsic production by marsh plants

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[1]   Emissions of $CH_3Cl$, $CH_3Br$ and $CH_3I$ were measured biweekly for 12- to 24-month periods between March 2002 and March 2005 from monospecific stands of four dominant southern California coastal salt marsh plants. These measurements revealed large inherent differences between species and more detailed patterns of seasonal production than previously reported. Marsh plants displayed intrinsic abilities to produce methyl halides. Salt marsh plants produced 92% of $CH_3Cl$ and 90% of $CH_3Br$ emitted and only 41% of the emitted $CH_3I$. Unvegetated areas emitted 7.9% of $CH_3Cl$, 9.9% $CH_3Br$, and 59% of the emitted $CH_3I$. The accuracy of the estimated methyl halide emissions from a coastal marsh and probably other ecosystems can be dramatically improved with increasing the number of species being measured and including emission from barren (mudflats and soil) areas. Estimates of global salt marsh emissions based on vegetated and barren area are 130, 21, 5.5 (mg m$^{-2}$ yr$^{-1}$) for $CH_3Cl$, $CH_3Br$, and $CH_3I$, respectively, or 1.2, 3.9, and 0.8% of total global fluxes of these gases.

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## 1.   Introduction

[2]   Methyl chloride ($CH_3Cl$), methyl bromide ($CH_3Br$) and methyl iodide ($CH_3I$) are chemically important atmospheric constituents. They are also significant vectors of halogen transport (especially for bromine and iodine) from the terrestrial and marine environment to the atmosphere. Accurate knowledge of $CH_3Br$ and $CH_3Cl$ sources is particularly needed because their relatively long residence times allow them to reach the lower stratosphere where halogen radicals produced from their photodissociation and OH attack catalytically destroy ozone. Despite its short residence time, $CH_3I$ can contribute to stratospheric ozone destruction [*Solomon et al.*, 1994], strongly affect tropospheric chemistry, especially of the marine boundary layer, and indirectly promote marine aerosol and cloud condensation nuclei formation [*Davis et al.*, 1996; *Carpenter et al.*, 1999; *O'Dowd et al.*, 2002].

[3]   Methyl halides ($CH_3X$) are naturally produced by photoautotrophs and certain fungi. The major mechanism of biosynthesis is enzymatic [*Wuosmaa and Hager*, 1990], although an additional abiotic mechanism in leaf litter has

been proposed [*Hamilton et al.*, 2003]. The relative environmental importance of higher plant methyl halide emissions, especially from marshes [*Varner et al.*, 1999; *Rhew et al.*, 2000; *Cox et al.*, 2004], agriculture [*Redeker et al.*, 2000] and tropical plants [*Yokouchi et al.*, 2002] has only recently been appreciated. Vegetation from temperate coastal salt marsh plants was estimated to produce 10% of the global source strength for the two gases $CH_3Cl$ and $CH_3Br$ [*Rhew et al.*, 2000].

## 2.   Materials and Methods

### 2.1.   Location and Plant Species

[4]   The location for this study was Upper Newport Bay, California, near the old salt dike (33°38.75N, 117°52.94W; Figure 1). Four halophytic species *Spartina foliosa* (Cordgrass), *Salicornia virginica* (Pickleweed), *Batis maritima* (Saltwort) and *Frankenia grandifolia* (Alkali Heath) were chosen based on their known ability to produce methyl halides [*Rhew et al.*, 2000] and their dominance in southern California coastal salt marshes.

### 2.2.   Incubation Conditions

[5]   Methyl halide emissive flux was determined by enclosing a single plant species in an incubation chamber and periodically withdrawing a gas sample into a valved preevacuated canister or lockable syringe. The bottom was sealed by the surrounding mud and soil (>0.5 cm deep). Different sized chambers were used to accommodate the different sized plants. The smallest was a 4L modified glass beaker (14 cm ID) with sampling port, thermometer port and an internal battery powered fan. The sampling port contained a 20-cm-long stainless steel tube (1/16 inch OD,

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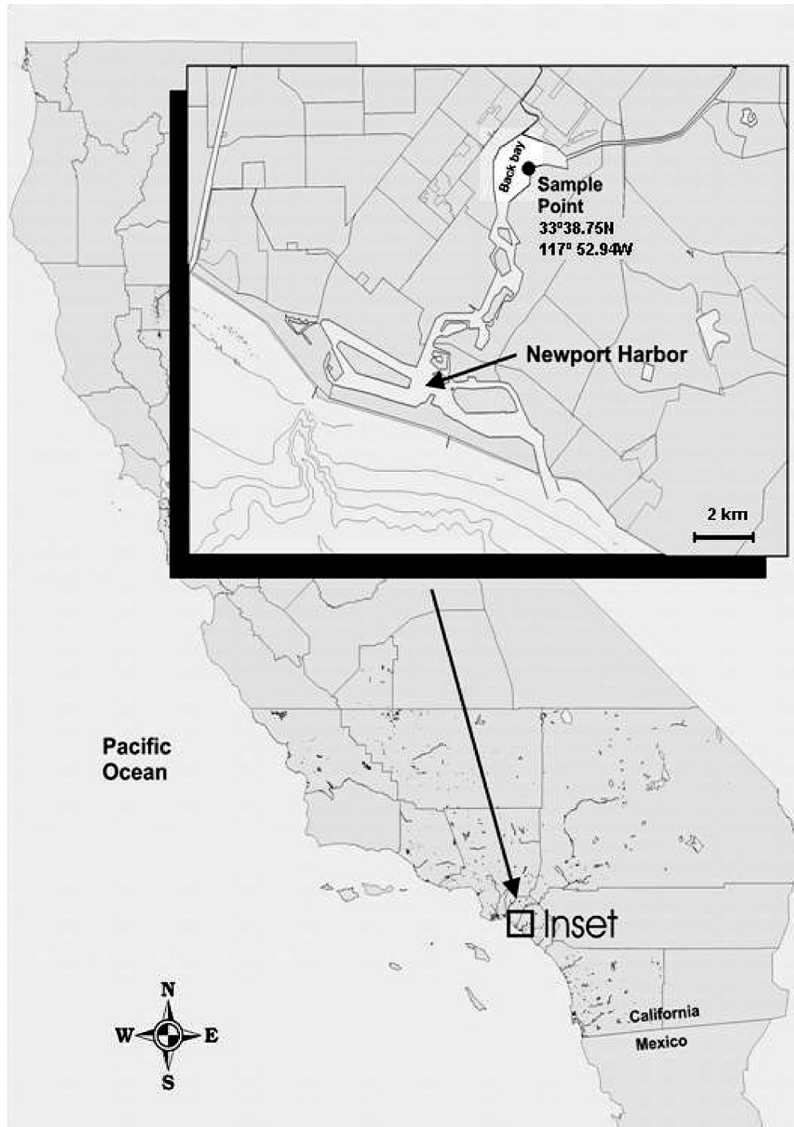[5]Now at National Academy of Sciences, Washington, D. C., USA.

**Figure 1.** Map of the sampling point located in Newport Back Bay, California (33°38.75N, 117°52.94W).

dead volume, 0.1 mL) which extended into the center of the chamber. The portion extending outside the chamber had a glass sleeve with septum for withdrawing a 30-mL gas sample into a syringe. The larger chambers were made of stackable sections of polycarbonate tubes (29.5 cm ID, 30 cm height) with polyethylene connectors, mounted on a permanent polyvinyl chloride chamber bases (15 cm height) to yield sealed chambers volumes of 24–90 L [*Redeker et al.*, 2000]. These large chambers had a sealed lid containing two ports, one for sampling and the other for a thermometer. The sampling line was a 30-cm-long stainless steel (1/4 inch OD, <5 mL dead volume) tube extending in to the center of the chamber with an Ultra-Torr® fitting for sampling with the attachment of a 500-mL stainless steel canister. These chambers did not inherently emit or absorb significant amounts of methyl halides [see *Redeker et. al.*, 2000, note 8]. Control incubations were performed similarly by positioning the same type of chamber over unvegetated areas close to, and at the same elevation as, the other chamber avoiding all aerial plant material. The green algae *Enteromorpha* sp., at times present on marsh mudflats, was avoided as a *Spartina* control site.

[6] Permanent chamber bases were used for *Spartina* and *Salicornia* incubations because bimonthly removal of *Spartina foliosa* was destructive to the habitat and because the woody basal and migrating stems of *Salicornia virginica* made it difficult for the glass chamber to form a seal in the soil without damaging the plants. No biomass was harvested from within the permanent bases after incubations. Control incubations used chambers without permanent bases. We began our study of *Spartina* by placing the chamber base over new shoots on the immediate edge of a pure stand. After 2 years, at the end of our measurements, the chamber base was well inside the *Spartina* bed, >3 m from the growing edge. Independent of the *Salicornia* incubations using the larger chambers, nine additional incubations of

*Salicornia* were performed using the small glass chamber followed by tissue harvesting to determine biomass specific production rates. Small glass chambers were used for *Batis* and *Frankenia* incubations. After the incubation period, all aerial *Batis* and *Frankenia* biomass, including woody biomass, was harvested for fresh weight determinations.

[7] All incubations were performed between 0930 and 1400 local time, at a period of low tide. Weather conditions and air temperatures were recorded. Incubation sampling duration and frequency ranged from 5 to 15 min at 1- to 5-min intervals depending on the plant species and chamber used.

### 2.3. Methyl Halide Analysis

[8] Analysis was performed as described by *Redeker et al.* [2000] using gas chromatography. A known amount (by pressure) of chamber air sample was preconcentrated in a glass-bead-packed stainless steel loop at 77 K. It was then directly injected onto a 50 m × 0.53 mm Poraplot-Q column (Chrompack) and detected by electron-capture (Hewlett Packard 5890 Series II). Standards in $N_2$ (9.68 ppb $CH_3Br$ and 479 ppb $CH_3Cl$; 25.4 ppb $CH_3I$) from Scott Specialty Gases were injected at low pressures to create a linear calibration curve with a range of absolute amounts bracketing sample amounts.

### 2.4. Halide Extraction and Analysis

[9] Halide analysis was intermittently performed on tissue harvested throughout the study period. The chambered *Batis* and *Frankenia* tissue harvested for biomass determination was so analyzed. *Spartina* and *Salicornia* tissue immediately adjacent to the permanent chamber base was used for halide analysis. Tissue samples were weighed, rinsed in deionized water to remove any external salts and dried to constant weight at 55°C. The dried tissue was weighed, milled into a fine powder (40-μm mesh) and stored in a capped glass vial under desiccation. Solid content of tissue (% dwt) was calculated.

[10] Halides were extracted from the milled plant tissue by adding the powder (0.5 g) to 50 mL of boiling deionized water in a 150-mL flask for 10 min. Boiled tissue was then vacuum filtered and the filtrate collected and stored frozen until halide analysis. The extraction procedure was repeated 5 times on the same sample to ensure complete halide removal from the tissue. Greater than 98% $Cl^-$, 97% $Br^-$, and 99% $I^-$ was removed from the tissue after three sequential extractions and the three-step extraction procedure became the standard method. Values were not corrected for the 1 to 3% loss. The halide concentration in each extract was determined using a specific ion meter/autotitrator in conjunction with the appropriate halide electrode using Gran's known addition method [*Redeker and Cicerone*, 2004; *Gran*, 1952]. This method allowed for the measurement of halides near their limit of detection: $5 \times 10^{-5}$ M $Cl^-$; $5 \times 10^{-6}$ M $Br^-$; and $5 \times 10^{-8}$ M $I^-$ (Thermo Orion specifications) and minimized the interfering effects of other ions and compounds. Following the autotitration the calculated initial concentration reported in mM was converted to tissue halide content as percent dry weight. The mean standard check for accuracy (with precision as

%S.D.) of the analysis was 98% for $Cl^-$ (5.7%), 88% for $Br^-$ (11%) and 95% for $I^-$ (8.0% [*Ralph and Manley*, 2006]).

## 3. Results

[11] All emission rates reported are net rates (plant chamber minus control) unless otherwise indicated. The two-point averaged net emission rates normalized to the marsh area enclosed by the chamber, from sampling twice a month are shown in Figures 2a through 2d for *S. foliosa*, *S. virginica*, *F. grandifolia*, and *B. maritime*, respectively. The average ambient monthly temperature at Newport Harbor was obtained from NCDC-NOAA (Climate-Radar Data Inventories, 2005, available at http://www4.ncdc.noaa.gov/cgi-win/wwcgi.dll?wwDI~StnSrch~StnID~10500018). The insolation was taken from the data set provided by Michael Goulden (UCI) from the San Joaquin Freshwater Marsh (University of California–Natural Reserve System), approximately 6 km NNE from the site along San Diego Creek. Biomass normalized net emission rates are shown for *F. grandifolia* and *B. maritima* (Figure 3). The emission values for $CH_3Br$ and $CH_3I$ shown in Figures 2 and 3 have been scaled up by appropriate factors to allow all graphs to fit on the same vertical scale. For instance, in Figure 2a, the actual measured $CH_3Br$ and $CH_3I$ fluxes from *Spartina* have been multiplied by factors of 4 and 2, respectively, to give the plotted values.

[12] We analyzed the data by determining the linear correlation coefficients between monthly emission rates and monthly mean temperature, and monthly insolation. (Fitting the data to several nonlinear regression models such as exponential and rectangular hyperbola, yielded poorer correlations.) In no instances did the same effector correlate equally with emissions of all three methyl halides from a given plant. Only weak correlations (r < 0.7) were observed, except for the correlation of $CH_3I$ emission to temperature by *Spartina* (r = 0.83) and *Batis* (biomass-based; r = 0.75). Mean monthly insolation was most often more highly correlated to emissions than mean monthly temperature. Mean monthly temperature changes, however, rarely exceeded 10°C and were usually not highly correlated with methyl halide emissions. In most instances, either temperature or insolation, for the month in which the emissions were measured, displayed the highest levels of correlation. Occasionally, it was the previous month's temperature or insolation that more closely correlated with emissions. Only at shifts of −1 month was r sometimes greater than r when no shift was applied. A shift in the emission data to one month previous insolation resulted in an increased correlation for $CH_3Br$ produced by *Batis* and *Spartina* only (r = 0.7 for both). *Salicornia* emissions were poorly correlated with monthly mean temperature and insolation (r < 0.36).

[13] The dramatic increase in biomass normalized $CH_3Cl$ and $CH_3Br$ emission by *Frankenia* was correlated with flowering (Figure 3a). Flowering in *Batis* corresponded to a striking increase in biomass normalized $CH_3I$ emission and a secondary spike in $CH_3Br$ emission (Figure 3b). Area normalized emissions of $CH_3Cl$ and $CH_3Br$ from *Spartina* site correspond to this flowering pattern (Figure 2a; 19 and 21 flowers maximum for 2003 and 2004, respectively).
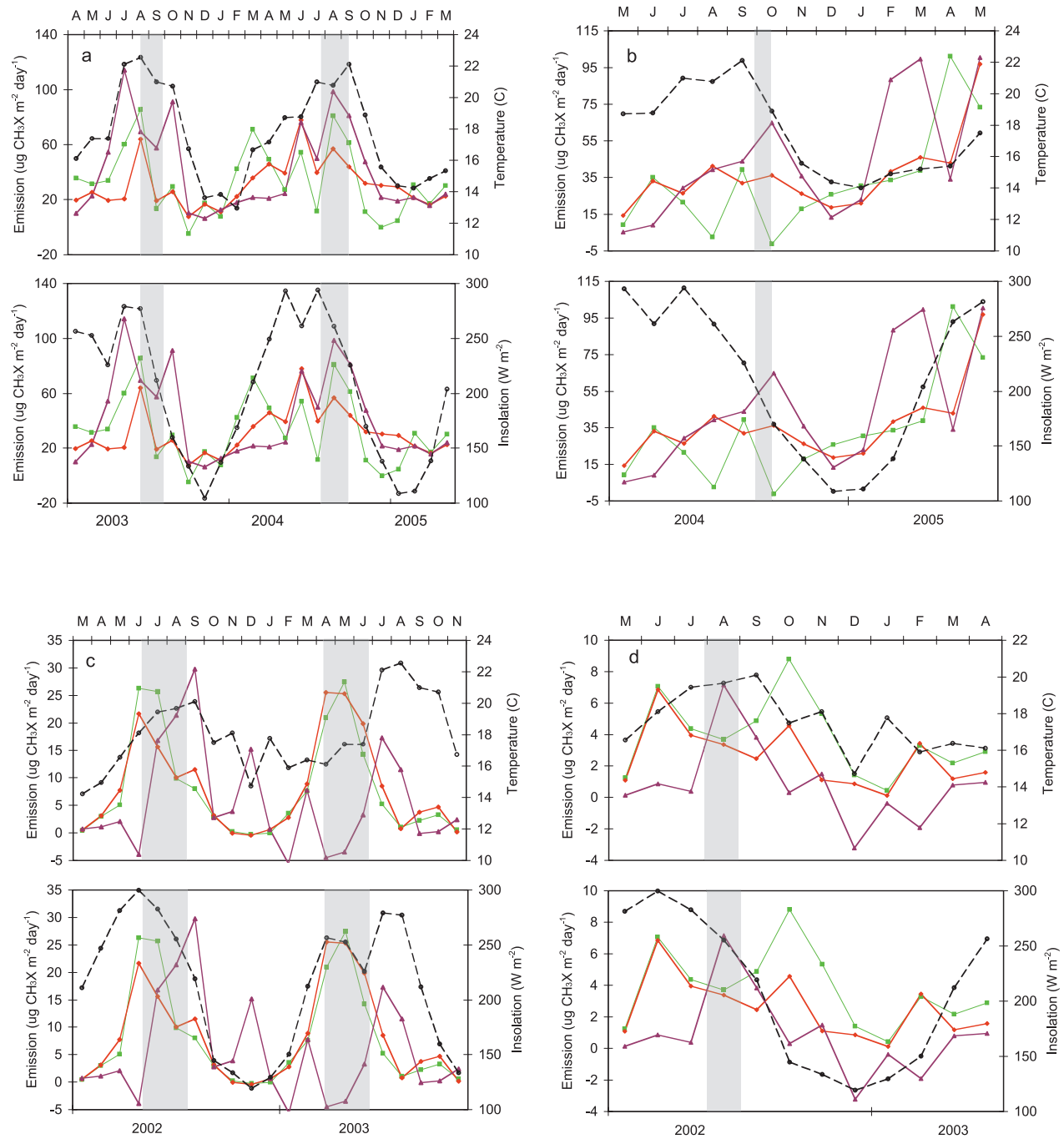
**Figure 2.** Methyl halide emissions ($\mu g \ m^{-2} \ d^{-1}$; $CH_3Cl$, green squares; $CH_3Br$, red diamonds; $CH_3I$, purple triangles) from plant species with corresponding monthly mean temperature and insolation (solid circles). Emissions of $CH_3Cl$ are shown on the $y$ axis. Actual values for $CH_3Br$ and $CH_3I$ emissions can be determined by dividing graphed values by the factor indicated below: (a) *Spartina*, April 2003 to March 2005 ($CH_3Br \div 4$, $CH_3I \div 2$); (b) *Salicornia*, May 2004 to May 2005 ($CH_3Br \div 4$, $CH_3I \div 8$); (c) *Frankenia*, March 2002 to November 2003 ($CH_3Br \div 8$, $CH_3I \div 80$); and (d) *Batis*, May 2002 to April 2003 ($CH_3Br \div 4$, $CH_3I \div 20$). Shaded rectangles indicate flowering period.
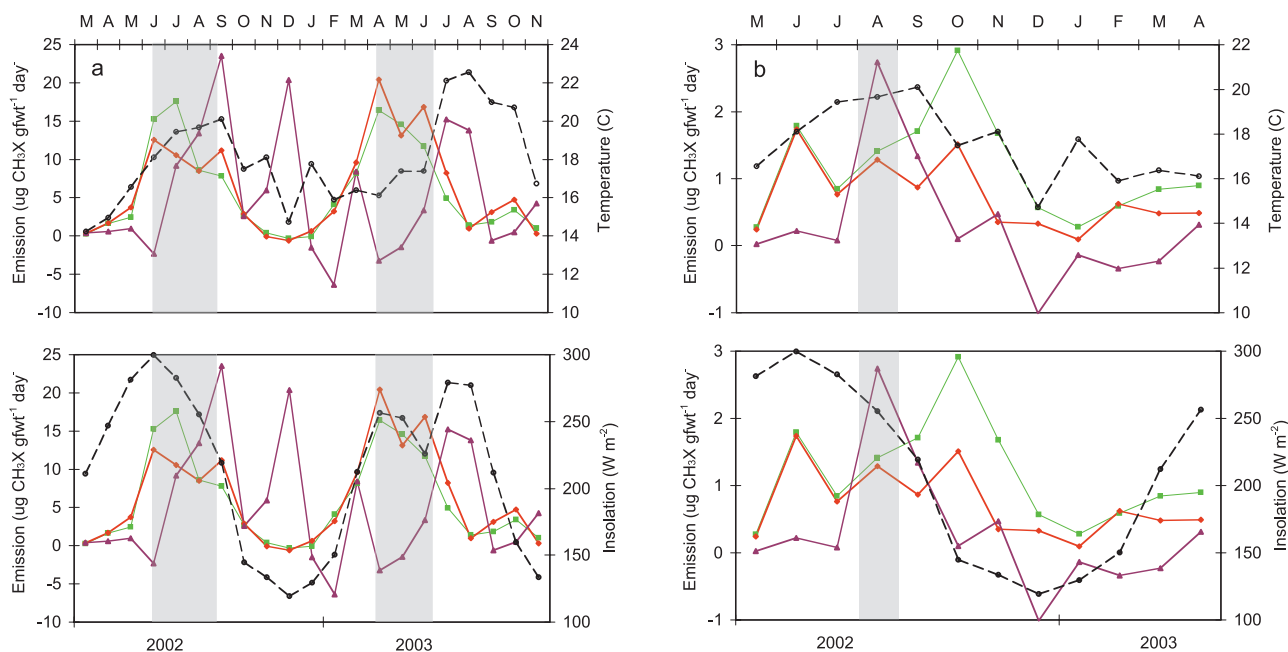
**Figure 3.** Biomass (grams fresh weight) normalized methyl halide emissions ($\mu$g gfwt$^{-1}$ d$^{-1}$; $CH_3Cl$, green squares; $CH_3Br$, red diamonds; $CH_3I$, purple triangles) and corresponding monthly mean temperature and insolation (solid circles). Emissions of $CH_3Cl$ are shown on the $y$ axis. Actual values for $CH_3Br$ and $CH_3I$ emissions can be determined by dividing graphed values by the factor indicated below: (a) *Frankenia*, March 2002 to November 2003 ($CH_3Br \div 8$, $CH_3I \div 80$) and (b) *Batis*, May 2002 to April 2003 ($CH_3Br \div 4$, $CH_3I \div 20$). Shaded rectangles indicate flowering period.

*Salicornia* flowering corresponded with a peak in $CH_3I$ emissions (Figure 2b).

[14] Initial chamber temperature and average chamber temperature during the incubation period were weakly or not correlated to emissions for all three methyl halides for all plants. *Spartina* $CH_3Br$ and $CH_3I$ emissions during non-flowering periods were poorly correlated to average chamber temperature (r = 0.5 and 0.3, respectively), however, $CH_3Cl$ emissions were weakly correlated (n = 30; r = 0.70). Because flowering appeared to be an important determinant for certain methyl halide emissions, the emission data for each plant during the flowering period were correlated to average chamber temperature. In most instances the correlation was extremely weak (r < 0.4). Average chamber temperature was moderately correlated with emissions during flowering for (1) $CH_3I$ emissions by *Spartina* during 2003 (n = 8; r = −0.71), (2) $CH_3Br$ emissions by *Salicornia* (n = 8; r = −0.71) and (3) $CH_3Cl$ emissions by *Frankenia* during 2003 (n = 8, r = +0.69). However, $CH_3I$ emissions by *Spartina* during the flowering period of 2004 and $CH_3Cl$ emissions by *Frankenia* during the flowering period of 2002 were not correlated with average chamber temperature. Methyl halide emissions by *Spartina* (located low in the marsh) and *Frankenia* (located in mid and high marsh) were not correlated with height of last high tide, time since last high tide or tidal strength (height of last high tide ÷ time since last high tide; r < 0.05).

[15] Annual emissions of $CH_3Cl$ and $CH_3Br$ from the soil and mud (control incubations) were smaller than their emissions from the plant by approximately an order of magnitude (Table 1). Methyl iodide emissions from *Spartina* and *Salicornia* and their controls were similarly related. The area surrounding *Spartina* (mud) and *Salicornia* (soil/mud) produced low levels of $CH_3I$ throughout the year with peak emissions in the late summer. The emission of $CH_3I$ from the soil where *Batis* and *Frankenia* were located was greater than or equal to plant emissions and peaked in late summer. Net consumption of $CH_3I$ by soil or mud rarely occurred, whereas consumption of the other two gases occurred more frequently, primarily in the winter.

[16] Annual plant methyl halide emission rates normalized to grams fresh weight and dry weight (gfwt and gdwt, respectively) are shown in Table 2 for these four species. The succulent plants (i.e., *Batis* and *Salicornia*) have very high water content compared to nonsucculent plants (*Spartina* and *Frankenia*), therefore, a more accurate comparison of their intrinsic methyl halide emission rates is revealed when expressed per gram dry wt. Annual biomass normalized methyl halide emission rates for *Batis* and *Frankenia* are the mean of all direct measurements. The annual biomass-normalized methyl halide emission rates for *Salicornia* and *Spartina* were indirectly determined because the plants were not harvested. The yearly mean *Salicornia* biomass density of 750 gdwt m$^{-2}$, determined at Mugu Lagoon (Ventura County, California [*Boyer et al.*, 2001]), and the yearly mean *Spartina* biomass density of 171 gdwt m$^{-2}$, determined from the Tijuana Estuary (San Diego County, California [*Zedler and Nordby*, 1986]), were therefore used. Biomass normalized emissions (n = 9) from *Salicornia* were also directly measured using the small glass chamber followed by harvesting. The

**Table 1.** Annual $CH_3X$ Emissions From Salt Marsh Plants and Controls[a]

| Species | Spartina | | Salicornia | | Batis | | Frankenia | |
|---|---|---|---|---|---|---|---|---|
| | Plant | Control | Plant | Control | Plant | Control | Plant | Control |
| $CH_3Cl$ mg m$^{-2}$ yr$^{-1}$ | 12 | 1.6 | 12 | 1.4 | $1.4 \times 10^3$ | 90 | $2.6 \times 10^3$ | 130 |
| $CH_3Br$ mg m$^{-2}$ yr$^{-1}$ | 2.8 | 0.32 | 3.2 | 0.36 | 230 | 19 | 340 | 25 |
| $CH_3I$ mg m$^{-2}$ yr$^{-1}$ | 7.6 | 0.88 | 2.0 | 0.59 | 16 | 40 | 25 | 26 |

[a]Net emission rates reported for plants (see text).

rates were similar to those in Table 2 ranging from $0.5-18$ µg $CH_3Cl$ gdwt$^{-1}$ yr$^{-1}$, $0-1.3$ µg $CH_3Br$ gdwt$^{-1}$ yr$^{-1}$, and $0.11-3.5$ µg $CH_3I$ gdwt$^{-1}$ yr$^1$, even though it was difficult to ensure a tight seal (the reason we changed to a permanent base). *Spartina* biomass normalized rates were determined 3 times (November, June and August) using biomass density determinations near the site where emission fluxes were measured. The rates were similar to those in Table 2 ranging from 0 to 38 µg $CH_3Cl$ gdwt$^{-1}$ yr$^{-1}$, $1.4-12.8$ µg $CH_3Br$ gdwt$^{-1}$ yr$^{-1}$, and $4-13$ µg $CH_3I$ gdwt$^{-1}$ yr$^1$.

[17] Tissue halide content for these plants is also shown in Table 2. Although the infrequent sampling probably masked any significant seasonal changes, values are shown to confirm that halides are present in high concentrations. The succulent species *Batis* and *Salicornia* contain more halides than the nonsucculent plants.

[18] Estimates of total annual emissions from two coastal salt marshes, one in the Upper Newport Bay (UNB) and the other in the Tijuana Estuary (TE, San Diego County, California), are based on descriptions of marsh area and percent plant cover of each marsh region (UNB [*Vogl*, 1966; U.S. Army Corp of Engineers *et al.* 2000]; TE [*Zedler*, 1977]). The description of each marsh varies dramatically and therefore different techniques were used to estimate total plant cover. Annual emissions (mg m$^{-2}$ yr$^{-1}$) were calculated for the four dominant marsh plant species studied from integration of the seasonal emission profile. The limited data set of *Rhew et al.* [2000] for another marsh

plant present, *Monathochloe littoralis* was also incorporated. It was assumed that emissions from these plants overwhelm emissions from any other species present. Furthermore, it is assumed that emissions are constant throughout a 24-hour day. *Rhew et al.* [2002] have shown putative diurnal $CH_3Cl$ and $CH_3Br$ emissions from *Batis*. The calculated yearly mean emission from the *Spartina* controls was used for an estimate of emission from unvegetated marsh mudflat of UNB.

[19] *Vogl* [1966] used a customary zonal classification scheme: littoral zone or salt marsh proper which is subject to tidal submersion, splash and spray, and the maritime zone comprising the bluff and dune vegetation. He also represented plant cover in the UNB salt marsh as a percent cover in three littoral zones, lower, upper and high, but he did not attempt to quantify the area of each zone. For this we relied upon the description in a report by U.S. Army Corp of Engineers (Upper Newport Bay Ecosystem Feasibility Study Final Report, 2003, available at http://www.ocwatersheds.com/watersheds/pdfs/Ecosystem_Restoration_Feasibility_Study.pdf) (Tables 3a and 3b) which states that there is $9.7 \times 10^5$ m$^2$ (240 acres) of intertidal mudflats. On the basis of Vogl's description we calculate $3.2 \times 10^5$ m$^2$ barren area or mudflat in the low salt marsh (Table 3b). This discrepancy is based on Vogl's description "the littoral zone was delimited by the plant species present, since plants were considered better indicators of zonation than physical factors...." The lower limit

**Table 2.** Halide Content and Annual Biomass Specific $CH_3X$ Production From Salt Marsh Plants[a]

| | Tissue | | | | |
|---|---|---|---|---|---|
| | | Salicornia | | | |
| | Spartina | This Study | Ralph and Manley [2006][b] | Batis | Frankenia |
| Number of samples | 5 | 4 | 39–216 | 18 | 30 |
| Percent dry weight | 25 (2) | 14 (0.5) | 13.2 (1.5) | 16 (1) | 37 (6) |
| $Cl^-$ content, % | 6.7 (1.5) | 20 (5) | 24 (4) | 21 (4) | 6.3 (1.4) |
| $Br^-$ content, ‰ | 1.1 (0.3) | 2.8 (0.8) | 3.7 (1) | 2.9 (0.7) | 1.0 (0.2) |
| $I^-$ content, ppm | 6.4 (3.2) | 10 (3) | 6.2 (3) | 8 (3) | 6.7 (3.6) |
| *Mean Annual Biomass Specific Production* | | | | | |
| µg $CH_3Cl$ gfwt$^{-1}$ yr$^{-1}$ | 18 | 2.2 | | 420 | $1.9 \times 10^3$ |
| µg $CH_3Cl$ gdwt$^{-1}$ yr$^{-1}$ | 70[d] | 16[e] | | $2.6 \times 10^3$ | $5.1 \times 10^3$ |
| µg $CH_3Br$ gfwt$^{-1}$ yr$^{-1}$ | 4.0 | 0.60 | | 67 | 260 |
| µg $CH_3Br$ gdwt$^{-1}$ yr$^{-1}$ | 16[d] | 4.3[e] | | 420 | 700 |
| µg $CH_3I$ gfwt$^{-1}$ yr$^{-1}$ | 11 | 0.38 | | 5.5 | 23 |
| µg $CH_3I$ gdwt$^{-1}$ yr$^{-1}$ | 44[d] | 2.7[e] | | 34 | 62 |

[a]Parentheses: s.d.
[b]Values: n = 39 for % dwt, 216 for Cl- and Br- content, and 162 for I- content [*Ralph and Manley*, 2006].
[c]Excluding very high months of September and October [*Ralph and Manley*, 2006].
[d]Determined using a yearly mean biomass density of 171 gdwt m$^{-2}$ [*Zedler and Nordby*, 1986].
[e]Determined using a yearly mean biomass density of 750 gdwt m$^{-2}$ [*Boyer et al.*, 2001].

**Table 3a.** Habitat Area at Upper Newport Bay, California

| Marsh Habitat | Area, $m^2$ |
|---|---|
| Open water | $8.5 \times 10^5$ (209 acres) |
| Intertidal mudflat | $9.7 \times 10^5$ (240 acres) |
| Low salt marsh | $5.9 \times 10^5$ (146 acres) |
| Middle salt marsh | $6.2 \times 10^5$ (154 acres) |
| High salt marsh | $4.0 \times 10^4$ (10 acres) |
| Total salt marsh | $1.3 \times 10^6$ |

did not therefore include the mudflat exposed during low tides below the range of *Spartina;* the outer edge of *Spartina* delineated the lower marsh. The Corps of Engineers defined intertidal mudflats as bare areas between $-1.3$ m and $+0.46$ m mean sea level (MSL) and the low salt marsh between $+0.46$ m and $+0.91$ m above MSL. (J. B. Zedler empirically defined the lower marsh edge at $+0.3$ m MSL). Therefore, Vogl's barren area is most likely near or above $+0.3$ m MSL and excludes much of the estuarine mud that the Corps of Engineers included. Using the plant area coverage for UNB salt marsh and the calculated annual methyl halide emissions for each species, we estimated the total methyl halide flux coming from these plants (Table 4). The total contribution of each plant species is dependent on the emission rate from its tissue and the total area that it covers.

[20] An estimate of the total methyl halide emission from the entire Upper Newport Bay littoral zone, which, therefore, excludes salt pan ($2.8 \times 10^4$ $m^2$), uplands *(*in the sense of Vogl's maritime zone, $2.3 \times 10^5$ $m^2$) and fresh water marsh ($7.1 \times 10^5$ $m^2$), and which must exclude open water ($8.5 \times 10^5$ $m^2$) production for which we have no estimate, is shown in Table 5. To account for emissions from plants we did not measure, we assumed an emission rate equal to the total area weighted emission from the known plants ($\Sigma$ plant emission, g $yr^{-1}$, normalized to total area covered by these plants; e.g., 410 mg $CH_3Cl$ $m^{-2}$ $yr^{-1}$). Estimated annual contribution by plants was about 91% for $CH_3Cl$ and $CH_3Br$. Plants accounted for only 41% of $CH_3I$ emissions. The emission rate from mid and an upper marsh soil was determined from the mean emission from the controls from *Salicornia*, *Batis* and *Frankenia*. Soil in the mid/upper marsh accounted for 50% of $CH_3I$ emissions, much greater than that emitted from estuarine mud. The emission rate for estuarine mud was determined from the emissions from the *Spartina* control. Total mudflat area was equal to that of the "intertidal mudflat" plus the "barren low" littoral zone (Tables 3a and 3b). Mudflats accounted for less than 10% of the total $CH_3I$ released and less than 1% for the other gases.

[21] In estimating the total coverage of each plant species in TE salt marsh we relied on the detailed measurements of *Zedler* [1977] (see the auxiliary material[1]).

## 4. Discussion

[22] This work extends and refines the research of *Rhew et al.* [2000] in the estimation of methyl halide emission from coastal salt marshes. This present study differs signif-

icantly from the former in that only single plant species were chambered (no species mixtures), transparent chambers were used allowing for plant photosynthesis, and the sampling frequency was much greater and covered an entire year or more. Measuring emissions from individual species permitted direct interspecies comparisons, which, in conjunction with plant coverage data, allowed for a more accurate assessment of salt marsh methyl halide emissions. We also included production of methyl halides from barren areas in our estimations.

[23] The use of transparent chambers ensured that the plants were photosynthetically active. If methyl halide production is coupled to C fixation, the use of transparent chambers would maintain this relationship. Methyl halides are formed enzymatically (methyl transferases) using *S*-adenosyl-L- methionine (SAM) as the methyl donor to methylate halides [*Wuosama and Hager*, 1990; *Manley*, 2002]. Such methylations, however, are generally not directly coupled to primary metabolism (e.g., photosynthesis). The lack of coupling between methyl halide production and photosynthesis is supported by the observations that algal and rice methyl halide production is not enhanced in the light [*Manley and Dastoor*, 1987; *Redeker and Cicerone*, 2004]. Diurnal patterns in methyl halide emissions have been reported for various ecosystems including rice paddies [*Redeker and Cicerone*, 2004] and salt marshes [*Rhew et al.*, 2000, 2002]. However, some of these patterns may have been in response to changing ambient temperature rather than irradiance [*Redeker and Cicerone*, 2004].

**Table 3b.** Area of Plant Coverage at Upper Newport Bay, California[a]

| Species | Plant Cover, % | Area Covered, $m^2$ | Total Area $m^2$ | Total Area Percent |
|---|---|---|---|---|
| *Spartina* | | | $2.3 \times 10^5$ | 18 |
| low | 38 | $2.2 \times 10^5$ | | |
| mid | 1 | $6.2 \times 10^3$ | | |
| high | np | 0 | | |
| *Salicornia* | | | $1.8 \times 10^5$ | 14 |
| low | 4 | $2.4 \times 10^4$ | | |
| mid | 23 | $1.4 \times 10^5$ | | |
| high | 40 | $1.6 \times 10^4$ | | |
| *Batis* | | | $1.2 \times 10^5$ | 10 |
| low | 4 | $2.4 \times 10^4$ | | |
| mid | 15 | $9.3 \times 10^4$ | | |
| high | 1 | $4.0 \times 10^2$ | | |
| *Frankenia* | | | $2.0 \times 10^4$ | 1.6 |
| low | np | 0 | | |
| mid | 3 | $1.9 \times 10^4$ | | |
| high | 2 | $8.0 \times 10^2$ | | |
| *Monanthochloe* | | | $6.0 \times 10^3$ | 0.48 |
| low | np | 0 | | |
| mid | np | 0 | | |
| high | 15 | $6.0 \times 10^3$ | | |
| Other plants | | | $9.8 \times 10^4$ | 7.8 |
| low | 0 | 0 | | |
| mid | 14 | $8.7 \times 10^4$ | | |
| high | 27 | $1.1 \times 10^4$ | | |
| Barren | | | $6.0 \times 10^5$ | 48 |
| low | 54 | $3.2 \times 10^5$ | | |
| mid | 44 | $2.7 \times 10^5$ | | |
| high | 14 | $5.6 \times 10^3$ | | |

[a]Abbreviation: np, not present.

**Table 4.** Estimated Annual Emission From Salt Marsh Plants at Upper Newport Bay, California[a]

| | Spartina | Salicornia | Batis | Frankenia | Monanthochloe[b] | Total |
|---|---|---|---|---|---|---|
| | | | Coverage of Salt Marsh | | | |
| $\times 10^5$ m$^2$ | 2.3 | 1.8 | 1.2 | 0.20 | 0.06 | 5.6 |
| Percent of plant cover | 35 | 27 | 18 | 3.0 | 0.91 | 85[c] |
| | | | Emissions | | | |
| CH$_3$Cl | | | | | | |
| mg m$^{-2}$ yr$^{-1}$ | 12 | 12 | $1.4 \times 10^3$ | $2.6 \times 10^3$ | 65 | 410[d] |
| g yr$^{-1}$ | $2.8 \times 10^3$ | $2.2 \times 10^3$ | $1.7 \times 10^5$ | $5.2 \times 10^4$ | 390 | $2.3 \times 10^5$ |
| Percent total | 1.2 | 0.97 | 75 | 23 | 0.17 | |
| CH$_3$Br | | | | | | |
| mg m$^{-2}$ yr$^{-1}$ | 2.8 | 3.2 | 230 | 340 | 35 | 64[d] |
| g yr$^{-1}$ | 640 | 580 | $2.8 \times 10^4$ | $6.8 \times 10^3$ | 210 | $3.6 \times 10^4$ |
| Percent total | 1.8 | 1.6 | 77 | 19 | 0.58 | |
| CH$_3$I | | | | | | |
| mg m$^{-2}$ yr$^{-1}$ | 7.6 | 2.0 | 16 | 25 | nd | 8.0[d] |
| g yr$^{-1}$ | $1.7 \times 10^3$ | 360 | $1.9 \times 10^3$ | 500 | nd | $4.5 \times 10^3$ |
| Percent total | 38 | 8.1 | 43 | 11 | | |

[a]Excludes intertidal mudflat, other barren area, and other plant species not investigated; see Tables 3a and 3b.
[b]Emission data from *Rhew et al.* [2000].
[c]Remaining 15% coverage by other plants not measured for emissions.
[d]Mean weighted flux based on $5.6 \times 10^5$ m$^2$.

[24] Higher sampling frequency and determination of emissions on the basis of chambered area and plant biomass allowed for a more accurate description of the seasonal patterns of methyl halide emissions. Emissions showed a pronounced seasonality caused not only by seasonal changes in biomass density, but also due to a physiological activation of the emission process. Such an approach identified flowering as an important event (see below).

### 4.1. Seasonal Emission Pattern

[25] Our degree of sampling allowed for the detection of a strong seasonal signal and monthly differences. Monthly emissions of CH$_3$Cl, CH$_3$Br from *Spartina* and *Frankenia* were more highly correlated with monthly insolation than monthly temperature because of its dramatic effect on seasonal biomass via growth. These two species show a pronounced biomass change with the seasons, with presumably day length having the greatest effect on growth. During

the winter, aboveground biomass of *Spartina* senesced and disappeared, with new shoots emerging. During the winter, green tissue of *Frankenia* also disappeared leaving only woody twigs. Whereas CH$_3$I emission was strongly correlated to monthly temperature for *Spartina*, that was not the case for *Frankenia*. Clearly CH$_3$I emissions from these two species are controlled by different physiological processes than are the emissions of the other methyl halides. *Batis* showed little change in biomass with seasons, and the area-based emissions were less highly correlated with either temperature or insolation as compared to the other plants. Biomass-based CH$_3$I emissions by *Batis* do show a strong temperature influence suggesting greater metabolic activity in the production of this gas during the warmer months. *Salicornia* is a plant with a woody base supporting succulent tissue and the ratio of woody stem to succulent tissue increases dramatically in the winter [*Boyer et al.*, 2001]. In the winter there was a decrease in CH$_3$I emissions; CH$_3$Br

**Table 5.** Estimated Annual Emission From Upper Newport Bay, California

| Habitat | Measured Plants | Unmeasured Plants[a] | Total Mud[b] | Barren Soil[c] | Total |
|---|---|---|---|---|---|
| | | Area | | | |
| $\times 10^5$ m$^2$ | 5.6 | 0.98 | 13.0 | 2.8 | 22.0 |
| | | Emissions | | | |
| CH$_3$Cl | | | | | |
| mg m$^{-2}$ yr$^{-1}$ | 410 | 410 | 1.6 | 73 | |
| g yr$^{-1}$ | $2.3 \times 10^5$ | $4.0 \times 10^4$ | $2.1 \times 10^3$ | $3.1 \times 10^4$ | $2.9 \times 10^5$ |
| (Percent) | (78) | (14) | (0.7) | (7.2) | |
| CH$_3$Br | | | | | |
| mg m$^{-2}$ yr$^{-1}$ | 64 | 64 | 0.32 | 15 | |
| g yr$^{-1}$ | $3.6 \times 10^4$ | $6.3 \times 10^3$ | $4.2 \times 10^2$ | $4.2 \times 10^3$ | $4.7 \times 10^4$ |
| (Percent) | (77) | (13) | (0.9) | (9.0) | |
| CH$_3$I | | | | | |
| mg m$^{-2}$ yr$^{-1}$ | 8.0 | 8.0 | 0.88 | 22 | |
| g yr$^{-1}$ | $4.5 \times 10^3$ | 630 | $1.1 \times 10^3$ | $6.2 \times 10^3$ | $1.2 \times 10^4$ |
| (Percent) | (36) | (5.1) | (8.8) | (50) | |

[a]Assumed same area weighted emission rate as measured plants.
[b]Total area equal to that of intertidal mudflat plus barren lower littoral (Table 3); total emission rate calculated as integrated yearly emission from *Spartina* controls (Table 1).
[c]Total area equal to mid and high littoral; total emission calculated as mean of integrated yearly emission from *Salicornia*, *Batis* and *Frankenia* controls (Table 1).

emissions showed a slight decline and $CH_3Cl$ emission were relatively unchanged. There was much more biomass and succulent tissue present in the spring of 2005 than present in the spring and summer of 2004 which corresponded to overall greater methyl halide emissions in the spring of 2005. Although there were poor correlations between methyl halide emissions from *Salicornia* and monthly temperature, $CH_3Cl$ and $CH_3Br$ emissions did correlate slightly with insolation showing succulent tissue dependency. A stronger correlation may have been masked by the large increase in emissions and biomass that occurred in 2005 after heavy summer rains.

[26] We could not correlate emissions with tidal or rainfall patterns on a daily, weekly or monthly scale. Presumably tides and rainfall did not influence emissions directly, apart from their effect on overall plant health and growth. In most cases, mean chamber incubation temperatures were weakly correlated to daily emissions, even when those emissions were separated into flowering and nonflowering categories. Positive correlations between emissions (e.g., $CH_3Cl$ emissions from *Spartina*, nonflowering) and temperature may have been due to the effect of temperature on diffusion and the rate of enzyme catalyzed methyl halide synthesis. Negative correlation between emissions (e.g., $CH_3I$ emissions by *Spartina* during 2003 flowering and $CH_3Br$ emissions by flowering *Salicornia*) and temperature may have been a result of inhibition of methyl halide biosynthesis at high temperature. The highest chamber temperatures were not generally associated with average monthly temperatures (e.g., chamber temperature for *Spartina* of 34.6°C occurred 12/03) and thus did not amplify the seasonal signal. The negative correlations between temperatures and emissions during flowering period may have resulted in an underestimation of emission peaks associated with flowering. The use of temperature controlled chambers would have been beneficial.

## 4.2. Intrinsic Plant Variation in Methyl Halide Emissions

[27] Calculating the yearly biomass specific methyl halide emission rates, especially those based on dry weights (Table 2) demonstrates an inherent difference in emissions amongst species. *Frankenia* and *Batis* biomass specific emission rates for $CH_3Cl$ and $CH_3Br$ were at least an order of magnitude greater than the rates for the other two species. The biomass specific emission rates for $CH_3I$ by *Frankenia* were also greater than the rates from *Spartina* and *Salicornia*, but the $CH_3I$ emissions from *Batis* exceeded only those of *Salicornia*. The values were empirically determined for *Batis* and *Frankenia*; they were calculated based on seasonal determinations of biomass for *Salicornia* and *Spartina* from other studies. The biomass of above ground tissue of *S. virginica* in a southern California salt marsh reaches a maximum in the summer ($\sim$1000 gdwt m$^{-2}$, 20–40% succulent tissue) compared to the winter ($\sim$500 gdwt m$^{-2}$, 3% succulent tissue), with slightly more succulent tissue peaking in June and woody tissue peaking in August [*Boyer et al.*, 2001]. Biomass normalized emissions calculated for *Salicornia* (Table 2) were very similar to those few direct measurements. The mean biomass density from these limited

determinations was 649 gdwt m$^{-2}$, which is similar to the yearly mean of 750 gdwt m$^{-2}$ [*Boyer et al.*, 2001], validating our approach. *S. foliosa* aerial biomass (using height and numbers of stems as a proxy) in a southern California salt marsh peaks in July and again in September when fruiting, and is at a minimum throughout the winter [*Zedler and Nordby*, 1986; *Covin and Zedler*, 1988]. The limited measurements of *Spartina* biomass densities (570 gdwt m$^{-2}$) was 3 times the yearly mean determined from the work of *Zedler and Nordby* [1986] but well within reported growing season maximums of 211–898 g dwt m$^{-2}$ [*Zedler and Nordby*, 1986; *Covin and Zedler*, 1988]. The mean annual biomass density calculated for *Batis* and *Frankenia* were 520 and 470 gdwt m$^{-2}$, respectively.

[28] Normalizing emissions to the amount of chambered aerial tissue biomass revealed seasonal emissions inherent to each plant species independent of biomass density (Figure 3). This increase in methyl halide emission demonstrates physiological control of the process. Such control could involve the increase in the synthesis of the methyl transferase(s) involved in methyl halide production and/or increased activity of the enzyme. The seasonal emission peak of certain methyl halides corresponded with flowering in *Batis* ($CH_3I$ in August) and *Frankenia* ($CH_3Cl$ and $CH_3Br$ in late spring early summer). The $CH_3I$ emission peak for *Spartina* in August 2004 and for *Salicornia* in October 2004 also corresponded with flowering, but because data are not normalized to biomass but to chambered area, the peaks may be influenced by biomass increases. Clearly flowering is related in the production of certain methyl halides, depending on the plant species. Flowering in rice corresponded to a large increase in $CH_3Br$ emissions and a minor peak in $CH_3I$ emissions [*Redeker et al.*, 2000].

[29] Plants contain many different types of SAM utilizing methyltransferases defined by the different organic substrates that they methylate [*Manley*, 2002]. A variety of purified methyltransferases (caffeic acid OMT, caffeoyl-CoA OMT, flavanol OMT, salicylic acid carboxyl MT) have been shown to catalyze the methylation of bromide in the presence of SAM (S. L. Manley, unpublished data, 2002). The latter enzyme had the highest specific activity in producing $CH_3Br$. Salicylic acid carboxyl MT isolated from petals of the plant *Clarkia breweri*, functions to create the volatile compounds associated with this flower to attract insects [*Ross et al.*, 1999]. Such a methyl transferase may be present during flowering of these salt marsh species and secondarily methylate the respective halides. Although *Spartina* is a wind pollinator and may not produce volatile insect attractants, increased $CH_3I$ emissions was correlated with flowering for both years studied.

[30] Intrinsic differences in methyl halide production by plants are also revealed by examination of the molar ratios of emissions (Table 6). Each plant has its own distinct ratio pattern. However, *Spartina* and *Salicornia* have similar $CH_3Cl: CH_3Br$ ratios as do *Frankenia* and *Batis*. The latter two species also share similar $CH_3Cl:CH_3I$ and $CH_3Br:CH_3I$ ratios reflecting similar emission fluxes for all compounds.

[31] The linear correlation between $CH_3Cl$ and $CH_3Br$ monthly emissions was moderate to high (r > 0.7) for all

**Table 6.** Linear Correlation Coefficients (r) and Molar Ratios for Monthly $CH_3X$ Production From Plants and Controls

| Species | CH₃Cl Versus CH₃Br | | CH₃Cl Versus CH₃I | | CH₃Br Versus CH₃I | |
|---|---|---|---|---|---|---|
| | r | Ratio | r | Ratio | r | Ratio |
| *Spartina* | 0.84 | 8.3 | 0.53 | 4.6 | 0.67 | 0.55 |
| Control | 0.87 | 9.7 | 0.81 | 5.2 | 0.88 | 0.53 |
| *Salicornia* | 0.54 | 7.4 | 0.25 | 17 | 0.73 | 1.8 |
| Control | 0.50 | 7.8 | 0.22 | 6.9 | 0.59 | 0.90 |
| *Frankenia* | 0.98 | 15 | −0.10 | 299 | −0.17 | 21 |
| Control | 0.62 | 9.9 | −0.21 | 14 | −0.07 | 1.4 |
| *Batis* | 0.78 | 12 | 0.25 | 252 | 0.21 | 21 |
| Control | 0.14 | 9.1 | 0.92 | 6.3 | −0.06 | 0.71 |

plant species except *Salicornia*, suggesting synchronized production (Table 6). *Frankenia* showed the highest correlation between $CH_3Cl$ and $CH_3Br$ (r = 0.98) because the emission of these gases were enhanced during flowering, whereas with the other species only $CH_3I$ emissions were primarily enhanced during flowering. The correlation between $CH_3Cl$ and $CH_3Br$ for a Tasmanian coastal wetland site (Cape Grim, 40°S, 145°E) dominated by the succulent halophyte *Pachycornia arbuscula* (basionym *Salicornia arbuscula*) was also high (r = 0.86 [*Cox et al.*, 2004]), however, we found the correlation based on our integrated mean with related species *S. virginica* low (r = 0.35).

[32] Except for the species *Salicornia* [*Ralph and Manley*, 2006], this is the first time all three halides have been measured in these halophytes (Table 3a). *Batis* and *Salicornia* contain more halides than *Frankenia* or *Spartina*, because of their strategy to survive in saline soils by maintaining a large amount of tissue water (succulence) with which to sequester salts in cell vacuoles [*Jennings*, 1968]. It is anticipated that other halophytes would also be prolific methyl halide producers because of their high tissue halide levels.

[33] The frequency of analysis for tissue halides may have missed any significant seasonal differences in tissue halide content for the various halophytes. *Salicornia* chloride and bromide levels were slightly lower in the late winter of 2003 as compared to summer of 2002, presumably as a response to increased succulence [*Ralph and Manley*, 2006]. This conceivably could affect $CH_3Cl$ and $CH_3Br$ emissions. However, in the winter, much of the green tissue of *Salicornia* disappeared, leaving mostly woody stems above ground, and the decline is most likely a response to overall lack of metabolic activity. In marked contrast, during the flowering period of September and October of 2002, iodide tissue levels increased by several orders of magnitude [*Ralph and Manley*, 2006]. The peak emission of $CH_3I$ also corresponded with flowering during a different year (Figure 2b). This excess iodide possibly in concert with flower methyl transferase activity may be responsible for the October peak in $CH_3I$ production in this species. The peak in $CH_3I$ in March of 2005 corresponded with the development of new green succulent tissue associated with renewed growth.

[34] The mean molar ratio of $CH_3Cl$: $CH_3Br$: $CH_3I$ produced by the plants (determined from Table 5) was 144: 11: 1 which was smaller than for tissue halides, $5.4 \times 10^4$: 420: 1 (determined from Table 2) and seawater, $5.4 \times 10^6$: 8.2 ×

$10^3$: 1. There is selective uptake of halides with I > Br > Cl and there is selective methylation following the same trend. Methyl transferase isolated from *Batis* shows a higher affinity with I > Br > Cl [*Wuosmaa and Hager*, 1990]. Our molar ratio of $CH_3Cl$: $CH_3Br$ plant emission of 12 ± 3 (sd) compared to 17 ± 14 reported by *Rhew et al.* [2000] for all plants.

### 4.3. Methyl Halide Emission From Mud and Soil

[35] The soil/mud mixed control for *Salicornia* was more similar in methyl halide flux to the estuarine mud control for *Spartina*, except the *Spartina* control showed greater $CH_3I$ production. The *Batis* and *Frankenia* soil controls were also more similar in emissions suggesting similar production mechanisms. For our estimations of annual emissions from UNB (Table 5), however, we chose to categorize emissions from estuarine mud as equivalent to the *Spartina* control and those from marsh soil as equivalent to mean of the *Salicornia*, *Frankenia* and *Batis* controls. We did this because their $CH_3Cl$: $CH_3Br$: $CH_3I$ ratios were more similar, and the *Salicornia* control was closer to the other sites. The $CH_3Cl$: $CH_3Br$: $CH_3I$ molar ratio from mudflats (5.2:0.53:1) and mid marsh soil (10:1:1), respectively is much different from the plant ratio. These ratios are different than those of plants and may represent differences in production mechanisms or the effects of differential consumption processes. Biological degradation, however, has been shown to favor $CH_3Br$ [*Schaefer et al.*, 2002], indicating the greater influence of emission differences.

[36] Emissions of $CH_3Cl$ and $CH_3Br$ from mudflats and mid marsh soil were smaller than that from plants (Table 5). A weak seasonal signal for $CH_3Cl$ emissions was detectable only for mid marsh soil and for $CH_3Br$ emissions from mud. The uptake of $CH_3Cl$ and $CH_3Br$ was more pronounced in the mid marsh soil occurring primarily, but not exclusively, in the winter. Rarely were these gases taken up by mud. Microbial production in mud throughout the year may have accounted for the very low level emission of these gases. Their emission from mid marsh soil during the summer may have also been microbially produced, with production ceasing in the winter. Emissions from mud in a tidal channel with the green seaweed *Enteromorpha* present [*Rhew et al.*, 2000] were approximately 2.6 times greater than our average emissions of $CH_3Cl$ and $CH_3Br$ from mud. Green seaweeds are known producers of methyl halides [*Manley et al.*, 1992; *Nightingale et al.*, 1995].

[37] Mudflats contributed a significant amount of $CH_3I$ to the total salt marsh emissions (8.8%, Table 5). Its production occurred throughout the years studied (April 2004 was the only instance of no production) and consistently peaked in the summer. Benthic diatoms are a common component of estuarine mud [*Admiraal*, 1984] and micro algae, including diatoms, are known to produce $CH_3I$ [*Tait and Moore*, 1995; *Scarratt and Moore*, 1996, 1998; *Manley and de la Cuesta*, 1997]. Methyl iodide is the major alkyliodide found in estuarine sediments, with a concentration range of $1-3.5$ pg gdwt$^{-1}$ sediment [*Tessier et al.*, 2002]. It may also be formed abiotically during oxidation of organic matter in sediment [*Keppler et al.*, 2000].

[38] Highly significant $CH_3I$ emissions also occurred from barren soil. The magnitude of emission (g yr$^{-1}$) was

**Table 7.** Estimated Annual Emission From Global Salt Marshes

| Emissions | Unit | $CH_3Cl$ | $CH_3Br$ | $CH_3I$ |
|---|---|---|---|---|
| UNB vegetated and bare areas[a] | mg m$^{-2}$ yr$^{-1}$ | 130 | 21 | 5.5 (9.0)[b] |
| Global salt marsh emissions[c] | Gg yr$^{-1}$ | 49 | 8.0 | 2.1 (3.4)[b] |
| | Percent[c] | 1.2 | 3.9 | 0.81 (1.3)[b] |
| UNB vegetated area only | mg m$^{-2}$ yr$^{-1}$ | 410 | 64 | 8.0 |
| Global salt marsh emissions[c] | Gg yr$^{-1}$ | 160 | 24 | 3.0 |
| | Percent[c] | 4.0 | 12 | 1.2 |

[a]Calculated from total production, Table 5.

[b]Assuming significant rhizosphere production, see text.

[c]Global salt marsh area (including mangroves) = $3.8 \times 10^{11}$ m$^2$ [*Woodwell et al.*, 1973]; global estimated sinks (Gg yr$^{-1}$): 4005 $CH_3Cl$ [*Montzka et al.*, 2003], 205 $CH_3Br$ and 258 $CH_3I$ (based on lower sink estimates [*Cox et al.*, 2005]).

5.6 times that of the estuarine mud (Table 5). We attribute this large $CH_3I$ emission to plant roots and associated microbes presumably present under the barren surface. Controls for *Batis* and *Frankenia* were routinely close to the standing plants and the $CH_3I$ emission rates from these soils were surprisingly similar (Table 1). Root mycorrhizal fungi, known producers of $CH_3I$ [*Redeker et al.*, 2004] may have also contributed to this large $CH_3I$ emission.

### 4.4. Methyl Halide Emissions From Coastal Salt Marshes

[39] The results of this study demonstrate that the plants inhabiting the salt marsh community have dramatically different intrinsic abilities to produce methyl halides (Table 2). Also, a plant species that covers a relatively small area (e.g., *Batis, Frankenia*) can make a significant contribution to the total methyl halide emitted from the marsh (Table 4; also see the auxiliary material). Conversely, a plant species that covers a large area, such as *Spartina*, can be an overall minor contributor of methyl halides. The accuracy of the estimated methyl halide emissions can be dramatically improved by increasing the number of species being measured. Our estimation of methyl halide emissions from coastal salt marshes could still be low because we did not measure eight species present in UNB and TE, including *Scirpus californicus* (Bulrush) with 14% cover in the UNB upper marsh and *Tiglochin maritime* (Sea lavender) with 11% cover in UNB middle marsh.

[40] We did not account for possible diurnal patterns in methyl halide emission from plants. It is unclear if any or all halophytes exhibit this response, and if so, the amplitude of the response wave. *Batis* and *Salicornia* have shown increased $CH_3Cl$ and $CH_3Br$ emission with a peak corresponding with maximum daylight [*Rhew et al.*, 2000, 2002]. The magnitude of the response varied depending on the methyl halide emitted and the plant species examined. It is possible, however, that these diurnal emissions were artifactual owing to changes in plant metabolism. The chambers used by *Rhew et al.* [2000, 2002] blocked the plants from sunlight during the incubation period of 15 to 40 min. During that period the plant would undergo a dramatic metabolic shift, from photosynthesis to respiration as indicated by an increase in chamber $CO_2$. The effect of these metabolic changes on methyl transferase activity is unknown. Ambient air temperature also increased and may

have had a direct effect on respiration and methyl halide production. Similar incubations in transparent chambers with regulated temperature would confirm the existence of a diurnal response. If the diurnal response is real, and occurs with other plant species, then our estimation of methyl halide emissions is high because our measurements were made during daylight hours.

[41] The two southern California salt marshes that were modeled for plant-emitted methyl halides, UNB (Table 4) and TE (see the auxiliary material) have nearly identical species composition but different plant cover percentages. *Spartina* percent cover at both locations was similar but it was *Salicornia* that dominated the TE salt marsh. *Monanthochloe* was more prevalent at TE salt marsh. However, the total fluxes of methyl halides (mg m$^{-2}$ yr$^{-1}$; mean weighted flux, Table 4; see the auxiliary material) from the vegetated area in each marsh are similar because the most prolific producers, *Batis* and *Frankenia*, have similar emission rates (Table 1) and combined percent coverage (21% UNB and 19% TE).

[42] A more detailed methyl halide inventory was constructed for UNB salt marsh (Table 5). The major contributor of $CH_3Cl$ and $CH_3Br$ were plants, producing over 90% of both gases. Mid and upper marsh soil contributed nearly all of the remaining 10%. In contrast, the mid and upper marsh soil accounted for 50% of the $CH_3I$ produced with 41% coming from the plants and 8.8% from mudflats. As previously discussed, $CH_3I$ production from soil may have come from the roots and the organisms associated in the rhizosphere (e.g., mycorrhizae). If this is the case, we have not accounted for the large $CH_3I$ emission (22 mg m$^{-2}$ yr$^{-1}$, Table 5) by the soil under the plants in the mid and high salt marsh because control emissions (bare soil) were subtracted from chamber emissions (plant + soil). Therefore an additional $8.4 \times 10^3$ g $CH_3I$ yr$^{-1}$, equal to the flux (22 mg m$^{-2}$ y$^{-1}$) $\times$ the total area soil area covered by plants ($3.8 \times 10^5$ m$^2$), would need to be added to the total UNB $CH_3I$ emissions for a total of $2 \times 10^4$ g $CH_3I$ yr$^{-1}$.

[43] On the basis of our analysis of methyl halide emissions in Table 5, the annual global emission of methyl halides from salt marshes was estimated (Table 7). When taking into account the total barren area of the salt marsh, including the large area of mudflats in the lower salt marsh, exposed at low tides, our estimate of 49 Gg $CH_3Cl$ yr$^{-1}$ and 8.0 Gg $CH_3Br$ yr$^{-1}$ is smaller than the 170 Gg $CH_3Cl$ and 14 $CH_3Br$ Gg yr$^{-1}$ reported by *Rhew et al.* [2000]. If we extrapolate using only vegetated area as representative of the entire marsh, as did *Rhew et al.* [2000], then our estimate of 160 Gg $CH_3Cl$ yr$^{-1}$ is very close to theirs while our estimate of 24 Gg $CH_3Br$ yr$^{-1}$ is 1.7 times larger.

[44] Methyl halide fluxes have been measured from the coastal salt marsh in Cape Grim which is dominated by *Pachycornia arbuscula* (means fluxes were 2.6 mg $CH_3Cl$ m$^{-2}$ yr$^{-1}$, 1.7 mg $CH_3Br$ m$^{-2}$ yr$^{-1}$, 2.2 mg $CH_3I$ m$^{-2}$ yr$^{-1}$) and the emissions showed pronounced seasonality [*Cox et al.*, 2004]. The ranges of values fit well with our findings for the closely related species *Salicornia* (Table 1) but were much lower than our estimated annual emission for UNB (Table 7), because of our inclusion of other more prolific methyl halide emitting species.

[45] Estimates of global salt marsh methyl halide production are highly uncertain because of the error associated with estimates of global salt marsh area and methyl halide source strengths. The estimate of global marsh area (salt marsh + mangrove), $3.8 \times 10^{11}$ m$^2$ [*Woodwell et al.*, 1973] was stated to be highly unreliable, ±50%. Recent work by *Duarte et al.* [2005] estimates that salt marshes cover $4 \times 10^{11}$ m$^2$ and global mangroves cover $2 \times 10^{11}$ m$^2$, an increase of >50%. Our estimation of global emissions does not consider the variability in species composition that exists between temperate salt marshes and mangroves, and even among temperate salt marshes worldwide. Indeed, cover estimates of a northern California salt marsh showed *Salicornia* comprising 80% of the marsh and *Spartina* only 14% [*Zhang et al.*, 1997]. Certain genera are well distributed globally (e.g., *Spartina*), but many are not. The work reported here reveals the importance of determining emissions from all species present, not just those that dominate in coverage. Differences in growing season lengths were also not considered but may also dramatically impact estimates of methyl halide emissions from global salt marshes.

[46] The estimate of total global wetlands (freshwater, saline, inland, and coastal) is $1.3 \times 10^{13}$ m$^2$, and therefore they are ecologically highly significant [*Finlayson et al.*, 1999]. Assessments of these wetland areas as methyl halide sources has begun, including fens [*Varner et al.*, 1999], rice paddies [*Redeker et al.*, 2000] and coastal wetlands [*Rhew et al.*, 2000; *Cox et al.*, 2004] (also this study). On the basis of size, yearly solar irradiance and coastal location, mangroves, coral reefs and seagrass-based systems need to be investigated for methyl halide emissions. Mangroves replace salt marshes at approximately the 20°C winter ocean isotherm and as such cover approximately 60–70% of the coastline between 25°N and 25°S latitudes [*Hogarth*, 1999]. Their community structure is also much different than temperate salt marshes, with much greater plant biomass density and productivity. To date, no mangrove plant species has been studied for methyl halide emissions, although a strong CH$_3$Cl signal has been detected from tropical coastal land [*Yokouchi et al.*, 2000]. They could be very significant sites of methyl halide emissions.

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