UC Irvine

UC Irvine Previously Published Works

Title

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

Permalink

<https://escholarship.org/uc/item/3gc6x7rq>

Journal

Global Biogeochemical Cycles, 20(3)

ISSN

0886-6236

Authors

Manley, SL
Wang, NY
Waiser, ML
et al.

Publication Date

2006-09-01

DOI

10.1029/2005GB002578

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed

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

Steven L. Manley,¹ Nun-Yii Wang,² Maggie L. Walser,³ and Ralph J. Cicerone^{2,4,5}

Received 23 June 2005; revised 1 May 2006; accepted 23 May 2006; published 11 August 2006.

[1] Emissions of CH₃Cl, CH₃Br and CH₃I 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 CH₃Cl and 90% of CH₃Br emitted and only 41% of the emitted CH₃I. Unvegetated areas emitted 7.9% of CH₃Cl, 9.9% CH₃Br, and 59% of the emitted CH₃I. 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 CH₃Cl, CH₃Br, and CH₃I, respectively, or 1.2, 3.9, and 0.8% of total global fluxes of these gases.

Citation: Manley, S. L., N.-Y. Wang, M. L. Walser, and R. J. Cicerone (2006), Coastal salt marshes as global methyl halide sources from determinations of intrinsic production by marsh plants, *Global Biogeochem. Cycles*, 20, GB3015, doi:10.1029/2005GB002578.

1. Introduction

[2] Methyl chloride (CH₃Cl), methyl bromide (CH₃Br) and methyl iodide (CH₃I) 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 CH₃Br and CH₃Cl 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, CH₃I 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 (CH₃X) 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 CH₃Cl and CH₃Br [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,

¹Department of Biological Sciences, California State University, Long Beach, California, USA.

²Department of Earth System Science, University of California, Irvine, California, USA.

³Department of Chemistry, University of California, Irvine, California, USA.

⁴Also at Department of Chemistry, University of California, Irvine, California, USA.

⁵Now 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 $\times$ 0.53 mm Poraplot-Q column (Chrompack) and detected by electron-capture (Hewlett Packard 5890 Series II). Standards in N₂ (9.68 ppb CH₃Br and 479 ppb CH₃Cl; 25.4 ppb CH₃I) 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- μ m 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: 5×10^{-5} M Cl⁻; 5×10^{-6} M Br⁻; and 5×10^{-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. maritima*, 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/wwwcgi.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 CH₃Br and CH₃I 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 CH₃Br and CH₃I 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 CH₃I 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 CH₃Br 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 CH₃Cl and CH₃Br emission by *Frankenia* was correlated with flowering (Figure 3a). Flowering in *Batis* corresponded to a striking increase in biomass normalized CH₃I emission and a secondary spike in CH₃Br emission (Figure 3b). Area normalized emissions of CH₃Cl and CH₃Br 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 ($\mu\text{g m}^{-2} \text{d}^{-1}$; CH₃Cl, green squares; CH₃Br, red diamonds; CH₃I, purple triangles) from plant species with corresponding monthly mean temperature and insolation (solid circles). Emissions of CH₃Cl are shown on the y axis. Actual values for CH₃Br and CH₃I emissions can be determined by dividing graphed values by the factor indicated below: (a) *Spartina*, April 2003 to March 2005 (CH₃Br $\div$ 4, CH₃I $\div$ 2); (b) *Salicornia*, May 2004 to May 2005 (CH₃Br $\div$ 4, CH₃I $\div$ 8); (c) *Frankenia*, March 2002 to November 2003 (CH₃Br $\div$ 8, CH₃I $\div$ 80); and (d) *Batis*, May 2002 to April 2003 (CH₃Br $\div$ 4, CH₃I $\div$ 20). Shaded rectangles indicate flowering period.

Figure 3. Biomass (grams fresh weight) normalized methyl halide emissions ($\mu\text{g gfw}^{-1} \text{ d}^{-1}$; CH₃Cl, green squares; CH₃Br, red diamonds; CH₃I, purple triangles) and corresponding monthly mean temperature and insolation (solid circles). Emissions of CH₃Cl are shown on the y axis. Actual values for CH₃Br and CH₃I emissions can be determined by dividing graphed values by the factor indicated below: (a) *Frankenia*, March 2002 to November 2003 (CH₃Br $\div$ 8, CH₃I $\div$ 80) and (b) *Batis*, May 2002 to April 2003 (CH₃Br $\div$ 4, CH₃I $\div$ 20). Shaded rectangles indicate flowering period.

Salicornia flowering corresponded with a peak in CH₃I 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* CH₃Br and CH₃I emissions during non-flowering periods were poorly correlated to average chamber temperature ($r = 0.5$ and 0.3 , respectively), however, CH₃Cl 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) CH₃I emissions by *Spartina* during 2003 ($n = 8$; $r = -0.71$), (2) CH₃Br emissions by *Salicornia* ($n = 8$; $r = -0.71$) and (3) CH₃Cl emissions by *Frankenia* during 2003 ($n = 8$, $r = +0.69$). However, CH₃I emissions by *Spartina* during the flowering period of 2004 and CH₃Cl 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 $\div$ time since last high tide; $r < 0.05$).

[15] Annual emissions of CH₃Cl and CH₃Br 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 CH₃I throughout the year with peak emissions in the late summer. The emission of CH₃I 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 CH₃I 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 (gfw and gdw, 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 gdw m^{-2} , determined at Mugu Lagoon (Ventura County, California [Boyer et al., 2001]), and the yearly mean *Spartina* biomass density of 171 gdw 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 CH₃X Emissions From Salt Marsh Plants and Controls^a

Species	<i>Spartina</i>		<i>Salicornia</i>		<i>Batis</i>		<i>Frankenia</i>	
	Plant	Control	Plant	Control	Plant	Control	Plant	Control
CH ₃ Cl mg m ⁻² yr ⁻¹	12	1.6	12	1.4	1.4 × 10 ³	90	2.6 × 10 ³	130
CH ₃ Br mg m ⁻² yr ⁻¹	2.8	0.32	3.2	0.36	230	19	340	25
CH ₃ I mg m ⁻² yr ⁻¹	7.6	0.88	2.0	0.59	16	40	25	26

^aNet emission rates reported for plants (see text).

rates were similar to those in Table 2 ranging from 0.5–18 µg CH₃Cl gdw⁻¹ yr⁻¹, 0–1.3 µg CH₃Br gdw⁻¹ yr⁻¹, and 0.11–3.5 µg CH₃I gdw⁻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 CH₃Cl gdw⁻¹ yr⁻¹, 1.4–12.8 µg CH₃Br gdw⁻¹ yr⁻¹, and 4–13 µg CH₃I gdw⁻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 CH₃Cl and CH₃Br 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 × 10⁵ m² (240 acres) of intertidal mudflats. On the basis of *Vogl*'s description we calculate 3.2 × 10⁵ m² 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 CH₃X Production From Salt Marsh Plants^a

	Tissue					
	<i>Spartina</i>	<i>Salicornia</i>			<i>Batis</i>	<i>Frankenia</i>
		This Study	<i>Ralph and Manley</i> [2006] ^b			
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)	
<i>Mean Annual Biomass Specific Production</i>						
µg CH ₃ Cl gfw ^{−1} yr ^{−1}	18	2.2		420	1.9 × 10 ³	
µg CH ₃ Cl gdw ^{−1} yr ^{−1}	70 ^d	16 ^c		2.6 × 10 ³	5.1 × 10 ³	
µg CH ₃ Br gfw ^{−1} yr ^{−1}	4.0	0.60		67	260	
µg CH ₃ Br gdw ^{−1} yr ^{−1}	16 ^d	4.3 ^c		420	700	
µg CH ₃ I gfw ^{−1} yr ^{−1}	11	0.38		5.5	23	
µg CH ₃ I gdw ^{−1} yr ^{−1}	44 ^d	2.7 ^c		34	62	

^aParentheses: s.d.

^bValues: n = 39 for % dwt, 216 for Cl⁻ and Br⁻ content, and 162 for I⁻ content [*Ralph and Manley*, 2006].

^cExcluding very high months of September and October [*Ralph and Manley*, 2006].

^dDetermined using a yearly mean biomass density of 171 gdw⁻¹ m⁻² [*Zedler and Nordby*, 1986].

^eDetermined using a yearly mean biomass density of 750 gdw⁻¹ m⁻² [*Boyer et al.*, 2001].

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

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

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 (2.8×10^4 m²), uplands (in the sense of Vogl's maritime zone, 2.3×10^5 m²) and fresh water marsh (7.1×10^5 m²), and which must exclude open water (8.5×10^5 m²) 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 (Σ plant emission, g yr⁻¹, normalized to total area covered by these plants; e.g., 410 mg CH₃Cl m⁻² yr⁻¹). Estimated annual contribution by plants was about 91% for CH₃Cl and CH₃Br. Plants accounted for only 41% of CH₃I 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 CH₃I 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 CH₃I 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 material¹).

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	Percent
<i>Spartina</i>			2.3×10^5	18
low	38	2.2×10^5		
mid	1	6.2×10^3		
high	np	0		
<i>Salicornia</i>			1.8×10^5	14
low	4	2.4×10^4		
mid	23	1.4×10^5		
high	40	1.6×10^4		
<i>Batis</i>			1.2×10^5	10
low	4	2.4×10^4		
mid	15	9.3×10^4		
high	1	4.0×10^2		
<i>Frankenia</i>			2.0×10^4	1.6
low	np	0		
mid	3	1.9×10^4		
high	2	8.0×10^2		
<i>Monanthochloe</i>			6.0×10^3	0.48
low	np	0		
mid	np	0		
high	15	6.0×10^3		
Other plants			9.8×10^4	7.8
low	0	0		
mid	14	8.7×10^4		
high	27	1.1×10^4		
Barren			6.0×10^5	48
low	54	3.2×10^5		
mid	44	2.7×10^5		
high	14	5.6×10^3		

¹Auxiliary materials are available at <ftp://ftp.agu.org/apend/gb/2005gb002578>.

^aAbbreviation: np, not present.

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

	<i>Spartina</i>	<i>Salicornia</i>	<i>Batis</i>	<i>Frankenia</i>	<i>Monanthochloe</i> ^b	Total
<i>Coverage of Salt Marsh</i>						
$\times 10^5 \text{ m}^2$	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
<i>Emissions</i>						
<i>CH₃Cl</i>						
mg m ⁻² yr ⁻¹	12	12	1.4×10^3	2.6×10^3	65	410 ^d
g yr ⁻¹	2.8×10^3	2.2×10^3	1.7×10^5	5.2×10^4	390	2.3×10^5
Percent total	1.2	0.97	75	23	0.17	
<i>CH₃Br</i>						
mg m ⁻² yr ⁻¹	2.8	3.2	230	340	35	64 ^d
g yr ⁻¹	640	580	2.8×10^4	6.8×10^3	210	3.6×10^4
Percent total	1.8	1.6	77	19	0.58	
<i>CH₃I</i>						
mg m ⁻² yr ⁻¹	7.6	2.0	16	25	nd	8.0 ^d
g yr ⁻¹	1.7×10^3	360	1.9×10^3	500	nd	4.5×10^3
Percent total	38	8.1	43	11		

^aExcludes intertidal mudflat, other barren area, and other plant species not investigated; see Tables 3a and 3b.^bEmission data from *Rhew et al.* [2000].^cRemaining 15% coverage by other plants not measured for emissions.^dMean weighted flux based on $5.6 \times 10^5 \text{ m}^2$.

[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 *CH₃Cl*, *CH₃Br* 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 *CH₃I* emission was strongly correlated to monthly temperature for *Spartina*, that was not the case for *Frankenia*. Clearly *CH₃I* 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 *CH₃I* 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 *CH₃I* emissions; *CH₃Br*

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

Habitat	Measured Plants	Unmeasured Plants ^a	Total Mud ^b	Barren Soil ^c	Total
<i>Area</i>					
$\times 10^5 \text{ m}^2$	5.6	0.98	13.0	2.8	22.0
<i>Emissions</i>					
<i>CH₃Cl</i>					
mg m ⁻² yr ⁻¹	410	410	1.6	73	
g yr ⁻¹	2.3×10^5	4.0×10^4	2.1×10^3	3.1×10^4	2.9×10^5
(Percent)	(78)	(14)	(0.7)	(7.2)	
<i>CH₃Br</i>					
mg m ⁻² yr ⁻¹	64	64	0.32	15	
g yr ⁻¹	3.6×10^4	6.3×10^3	4.2×10^2	4.2×10^3	4.7×10^4
(Percent)	(77)	(13)	(0.9)	(9.0)	
<i>CH₃I</i>					
mg m ⁻² yr ⁻¹	8.0	8.0	0.88	22	
g yr ⁻¹	4.5×10^3	630	1.1×10^3	6.2×10^3	1.2×10^4
(Percent)	(36)	(5.1)	(8.8)	(50)	

^aAssumed same area weighted emission rate as measured plants.^bTotal 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).^cTotal 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 ($\sim 1000 \text{ gdw m}^{-2}$, 20–40% succulent tissue) compared to the winter ($\sim 500 \text{ gdw m}^{-2}$, 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 gdw m^{-2} , which is similar to the yearly mean of 750 gdw 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 gdw 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 $211\text{--}898 \text{ gdw m}^{-2}$ [Zedler and Nordby, 1986; Covin and Zedler, 1988]. The mean annual biomass density calculated for *Batis* and *Frankenia* were 520 and 470 gdw 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 $\text{CH}_3\text{Cl}:\text{CH}_3\text{Br}$ ratios as do *Frankenia* and *Batis*. The latter two species also share similar $\text{CH}_3\text{Cl}:\text{CH}_3\text{I}$ and $\text{CH}_3\text{Br}:\text{CH}_3\text{I}$ 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 CH₃X Production From Plants and Controls

Species	CH ₃ Cl Versus CH ₃ Br		CH ₃ Cl Versus CH ₃ I		CH ₃ Br Versus CH ₃ I	
	r	Ratio	r	Ratio	r	Ratio
<i>Spartina</i>	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
<i>Salicornia</i>	0.54	7.4	0.25	17	0.73	1.8
Control	0.50	7.8	0.22	6.9	0.59	0.90
<i>Frankenia</i>	0.98	15	-0.10	299	-0.17	21
Control	0.62	9.9	-0.21	14	-0.07	1.4
<i>Batis</i>	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 CH₃Cl and CH₃Br ($r = 0.98$) because the emission of these gases were enhanced during flowering, whereas with the other species only CH₃I emissions were primarily enhanced during flowering. The correlation between CH₃Cl and CH₃Br for a Tasmanian coastal wetland site (Cape Grim, 40°S, 145°E) dominated by the succulent halophyte *Pachyornia arbuscula* (basonym *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 CH₃Cl and CH₃Br 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 CH₃I 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 CH₃I production in this species. The peak in CH₃I in March of 2005 corresponded with the development of new green succulent tissue associated with renewed growth.

[34] The mean molar ratio of CH₃Cl: CH₃Br: CH₃I produced by the plants (determined from Table 5) was 144: 11: 1 which was smaller than for tissue halides, 5.4×10^4 : 420: 1 (determined from Table 2) and seawater, 5.4×10^6 : 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 CH₃Cl: CH₃Br 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 CH₃I 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 CH₃Cl: CH₃Br: CH₃I ratios were more similar, and the *Salicornia* control was closer to the other sites. The CH₃Cl: CH₃Br: CH₃I 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 CH₃Br [Schaefer et al., 2002], indicating the greater influence of emission differences.

[36] Emissions of CH₃Cl and CH₃Br from mudflats and mid marsh soil were smaller than that from plants (Table 5). A weak seasonal signal for CH₃Cl emissions was detectable only for mid marsh soil and for CH₃Br emissions from mud. The uptake of CH₃Cl and CH₃Br 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 CH₃Cl and CH₃Br 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 CH₃I 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 CH₃I [Tait and Moore, 1995; Scarratt and Moore, 1996, 1998; Manley and de la Cuesta, 1997]. Methyl iodide is the major alkyl iodide found in estuarine sediments, with a concentration range of 1–3.5 pg gdw⁻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 CH₃I 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 ₃ Cl	CH ₃ Br	CH ₃ I
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

^aCalculated from total production, Table 5.

^bAssuming significant rhizosphere production, see text.

^cGlobal salt marsh area (including mangroves) = 3.8×10^{11} m² [Woodwell et al., 1973]; global estimated sinks (Gg yr⁻¹): 4005 CH₃Cl [Montzka et al., 2003], 205 CH₃Br and 258 CH₃I (based on lower sink estimates [Cox et al., 2005]).

5.6 times that of the estuarine mud (Table 5). We attribute this large CH₃I 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 CH₃I emission rates from these soils were surprisingly similar (Table 1). Root mycorrhizal fungi, known producers of CH₃I [Redeker et al., 2004] may have also contributed to this large CH₃I 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 CH₃Cl and CH₃Br 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 CO₂. 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 CH₃Cl and CH₃Br 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 CH₃I produced with 41% coming from the plants and 8.8% from mudflats. As previously discussed, CH₃I 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 CH₃I 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 8.4×10^3 g CH₃I yr⁻¹, equal to the flux (22 mg m⁻² yr⁻¹) $\times$ the total area soil area covered by plants (3.8×10^5 m²), would need to be added to the total UNB CH₃I emissions for a total of 2×10^4 g CH₃I 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 CH₃Cl yr⁻¹ and 8.0 Gg CH₃Br yr⁻¹ is smaller than the 170 Gg CH₃Cl and 14 CH₃Br 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 CH₃Cl yr⁻¹ is very close to theirs while our estimate of 24 Gg CH₃Br 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 CH₃Cl m⁻² yr⁻¹, 1.7 mg CH₃Br m⁻² yr⁻¹, 2.2 mg CH₃I 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), $3.8 \times 10^{11} \text{ m}^2$ [Woodwell *et al.*, 1973] was stated to be highly unreliable, $\pm 50\%$. Recent work by Duarte *et al.* [2005] estimates that salt marshes cover $4 \times 10^{11} \text{ m}^2$ and global mangroves cover $2 \times 10^{11} \text{ m}^2$, 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 $1.3 \times 10^{13} \text{ m}^2$, 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_3Cl signal has been detected from tropical coastal land [Yokouchi *et al.*, 2000]. They could be very significant sites of methyl halide emissions.

[47] **Acknowledgments.** This work was supported by NSF grant ATM-0121153 and NSF-ROA to R. J. C. and NSF grant OCE-0350746 to S. L. M., and M. L. W. was supported by the NSF Graduate Research Fellowship Program. We thank Brian Shelton, Orange County Ecological Reserve Manager, California Department of Fish and Game for access and support and Michael Goulden (UCI) for the insolation data.

References

- Admiraal, W. (1984), The ecology of estuarine sediment inhabiting diatoms, in *Progress in Phycological Research*, vol. 3., edited by F. E. Round and D. J. Chapman, pp. 269–322, Biopress, Bristol, U. K.
- Boyer, K. E., P. Fong, R. R. Vance, and R. F. Ambrose (2001), *Salicornia virginica* in a southern California salt marsh: Seasonal patterns and a nutrient-enrichment experiment, *Wetlands*, 21, 315–326.
- Carpenter, L. J., W. T. Sturges, S. A. Penkett, P. S. Liss, B. Alicke, K. Hebestreit, and U. Platt (1999), Short-lived alkyl iodides and bromides at Mace Head, Ireland: Links to biogenic sources and halogen oxide production, *J. Geophys. Res.*, 104, 1679–1689.
- Covin, J. D., and J. B. Zedler (1988), Nitrogen effects on *Spartina foliosa* and *Salicornia virginica* in the salt marsh at Tijuana estuary, California, *Wetlands*, 8, 51–65.
- Cox, M. L., P. J. Fraser, G. A. Sturrock, S. T. Siems, and L. W. Porter (2004), Terrestrial sources and sinks of halomethanes near Cape Grim, Tasmania, *Atmos. Environ.*, 38, 3839–3852.
- Cox, M. L., G. A. Sturrock, P. J. Fraser, S. T. Siems, and P. B. Krummel (2005), Identification of regional sources of methyl halides from AGAGE observations at Cape Grim, Tasmania, *J. Atmos. Chem.*, 50, 59–77.
- Davis, D., J. Crawford, S. Liu, S. McKeen, A. Bandy, D. Thornton, F. Rowland, and D. Blake (1996), Potential impact of iodine on tropospheric levels of ozone and other critical oxidants, *J. Geophys. Res.*, 101, 2135–2147.
- Duarte, C. M., J. J. Middelburg, and N. Caraco (2005), Major role of marine vegetation on the oceanic carbon cycle, *Biogeosciences*, 2, 1–8.
- Finlayson, C. M., N. C. Davidson, A. G. Spiers, and N. J. Stevenson (1999), Global wetland inventory—Current status and future priorities, *Mar. Freshwater Res.*, 50, 171–727.
- Gran, G. (1952), Determination of the equivalence point in potentiometric titrations: Part II, *Analyst*, 77, 661–673.
- Hamilton, J. T., W. C. McRoberts, F. Keppler, R. M. Kalin, and D. B. Harper (2003), Chloride methylation by plant pectin: An efficient environmentally significant process, *Science*, 301, 206–209.
- Hogarth, P. J. (1999), *The Biology of Mangroves*, Oxford Univ. Press, New York.
- Jennings, D. H. (1968), Halophytes, succulence and sodium in plants: A unified theory, *New Phytol.*, 67, 899–911.
- Keppler, F., R. Eiden, V. Niedan, J. Pracht, and H. F. Schöler (2000), Halocarbons produced by natural oxidation processes during degradation of organic matter, *Nature*, 403, 298–301.
- Manley, S. L. (2002), Phytochemistry of halomethanes: A product of selection or a metabolic accident?, *Biogeochemistry*, 60, 163–180.
- Manley, S. L., and M. N. Dastoor (1987), Methyl halide (CH_3X) production from the giant kelp, *Macrocystis*, and estimates of global CH_3X production by kelp, *Limnol. Oceanogr.*, 32, 709–715.
- Manley, S. L., and J. L. de la Cuesta (1997), Methyl iodide production from marine phytoplankton cultures, *Limnol. Oceanogr.*, 42, 142–147.
- Manley, S. L., K. Goodwin, and W. J. North (1992), Laboratory production of bromoform, methylene bromide, and methyl iodide by macroalgae and distribution in nearshore southern California waters, *Limnol. Oceanogr.*, 37, 1652–1659.
- Montzka, S. A., et al. (2003), Controlled substances and other source gases, in *Scientific Assessment of Ozone Depletion: 2002*, chap. 1, pp. 1.1–1.83, *Global Ozone Res. Monit. Proj. Rep. 47*, World Meteorol. Org., Geneva.
- Nightingale, P. D., G. Malin, and P. S. Liss (1995), Production of chloroform and other low molecular weight halocarbons by some species of macroalgae, *Limnol. Oceanogr.*, 40, 680–689.
- O'Dowd, C. D., J. L. Jimenez, R. Bahreini, R. C. Flagan, J. H. Seinfeld, K. Hamerl, L. Pirjola, M. Kulmala, S. G. Jennings, and T. Hoffmann (2002), Marine aerosol formation from biogenic iodine emissions, *Nature*, 417, 632–636.
- Ralph, Y. J., and S. L. Manley (2006), Spatial and temporal variation in tissue halide levels of *Salicornia virginica*, *Wetlands*, 26, 97–106.
- Redeker, K. R., and R. J. Cicerone (2004), Environmental controls over methyl halide emissions from rice paddies, *Global Biogeochem. Cycles*, 18, GB1027, doi:10.1029/2003GB002092.
- Redeker, K. R., N.-Y. Wang, J. C. Low, A. McMillan, S. C. Tyler, and R. J. Cicerone (2000), Emissions of methyl halides and methane from rice paddies, *Science*, 290, 966–969.
- Redeker, K. R., K. K. Treseder, and M. F. Allen (2004), Ectomycorrhizal fungi: A new source of atmospheric methyl halides?, *Global Chang. Biol.*, 10, 1009–1016.
- Rhew, R. C., B. R. Miller, and R. F. Weiss (2000), Natural methyl bromide and methyl iodide emissions from coastal salt marshes, *Nature*, 403, 292–295.
- Rhew, R. C., B. R. Miller, M. Bill, A. H. Goldstein, and R. F. Weiss (2002), Environmental and biological controls on methyl halide emissions from southern California coastal salt marshes, *Biogeochemistry*, 60, 141–161.
- Ross, J. R., K. H. Nam, J. C. D'Auria, and E. Pichersky (1999), S-adenosyl-L-methionine:salicylic acid carboxyl methyltransferase, an enzyme involved in floral scent production and plant defense, represents a new class of plant methyltransferases, *Arch. Biochem.*, 367, 9–16.
- Scarratt, M. G., and R. M. Moore (1996), Production of methyl chloride and methyl bromide in laboratory cultures of marine phytoplankton, *Mar. Chem.*, 54, 263–272.
- Scarratt, M. G., and R. M. Moore (1998), Production of methyl chloride and methyl bromide in laboratory cultures of marine phytoplankton II, *Mar. Chem.*, 59, 311–320.
- Schaefer, J. K., K. D. Goodwin, I. R. McDonald, J. C. Murrell, and R. S. Oremland (2002), *Leisingera methylohalidivorans* gen. nov., sp. nov., a

- marine methylotroph that grows on methyl bromide, *Int. J. Syst. Evol. Microbiol.*, **52**, 851–859.
- Solomon, S., R. R. Garcia, and A. R. Ravishankara (1994), On the role of iodine in ozone depletion, *J. Geophys. Res.*, **99**, 20,491–20,499.
- Tait, V. K., and R. M. Moore (1995), Methyl chloride production in phytoplankton cultures, *Limnol. Oceanogr.*, **40**, 189–195.
- Tessier, E., D. Amouroux, G. Abril, E. Lemaire, and O. F. X. Donald (2002), Formation and volatilization of alkyl-iodides and -selenides in macrotidal estuaries, *Biogeochemistry*, **59**, 183–206.
- Varner, R. K., P. M. Crill, and R. W. Talbot (1999), Wetlands: A potentially significant source of atmospheric methyl bromide and methyl chloride, *Geophys. Res. Lett.*, **26**, 2433–2436.
- Vogl, R. J. (1966), Salt-marsh vegetation of upper Newport Bay, California, *Ecology*, **47**, 80–87.
- Woodwell, G. M., P. H. Rich, and C. A. S. Hall (1973), Carbon in estuaries, in *Carbon and the Atmosphere: Proceedings of the 24th Brookhaven Symposium in Biology*, edited by G. M. Woodwell and E. V. Pecan, pp. 221–240, Tech Inf. Cent., Off. of Inf. Serv., U.S. Army Environ. Cent., Washington, D. C.
- Wuosmaa, A. M., and L. P. Hager (1990), Methyl chloride transferase: A carbocation route for biosynthesis of halometabolites, *Science*, **249**, 160–162.
- Yokouchi, Y., Y. Nojiri, L. A. Barrie, D. Toom-Sauntry, T. Machida, Y. Inuzuka, H. Akimoto, H.-J. Li, Y. Fujinuma, and A. Aoki (2000), A strong source of methyl chloride to the atmosphere from tropical coastal land, *Nature*, **403**, 295–298.
- Yokouchi, Y., Y. Inuzuka, and T. Yukawa (2002), Strong emissions of methyl chloride from tropical plants, *Nature*, **416**, 163–165.
- Zedler, J. B. (1977), Salt marsh community structure in Tijuana Estuary, California, *Estuarine Coastal Mar. Sci.*, **5**, 39–53.
- Zedler, J. B., and C. S. Nordby (1986), The ecology of Tijuana Estuary, California: An estuarine profile, *Biol. Rep.* **85** (7.5), 104 pp., U.S. Fish and Wildlife Serv., Washington, D. C.
- Zhang, M., S. L. Ustin, E. Rejmankova, and E. W. Sanderson (1997), Monitoring Pacific coast salt marshes using remote sensing, *Ecol. Appl.*, **7**, 1039–1053.
-
- R. J. Cicerone, National Academy of Sciences, 500 Fifth St., NW, Washington, D. C. 20001, USA.
- S. L. Manley, Department of Biological Sciences, California State University, Long Beach, Long Beach, CA 90840, USA. (almanley@csulb.edu)
- M. L. Walser, Department of Chemistry, University of California, Irvine, 1102 Natural Sciences 2, Irvine, CA 92697, USA.
- N.-Y. Wang, Department of Earth System Science, University of California, Irvine, Croul Hall 3327, Irvine, CA 92697, USA.