



Environmental and biological controls on methyl halide emissions from southern California coastal salt marshes

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Abstract. Methyl bromide (CH₃Br) and methyl chloride (CH₃Cl) emission rates from southern California coastal salt marshes show large spatial and temporal variabilities that are strongly linked to biological and environmental factors. Here we discuss biogeochemical lines of evidence pointing to vegetation as the primary source of CH₃Br and CH₃Cl emissions from salt marshes. Sediments and macroalgae do not appear to be major producers of these compounds, based on observations that the highest fluxes are not inhibited by soil inundation; their emissions are not correlated with those of certain gases produced in soils; and emissions from mudflat- and macroalgae-dominated sites are relatively small. In contrast, the seasonal and spatial variabilities of methyl halide fluxes in these salt marshes are consistent with the production of these compounds by vascular plants, although the possibility of production by microflora or fungi associated with the salt marsh vegetation is not ruled out. Flux chamber measurements of emission rates are largely correlated to the overall plant biomass enclosed in the chamber, but appear also to be highly dependent on the predominant plant species. Emission rates follow a diurnal trend similar to the trends of ambient air temperature and photosynthetically active radiation, but not surface soil temperature. Diurnal variabilities in the carbon isotope compositions of CH₃Cl and CH₃Br and their relative ratios of emissions are consistent with simultaneously competing mechanisms of uptake and production.

1. Introduction

Methyl bromide (CH₃Br) and methyl chloride (CH₃Cl) are the chief carriers of bromine and natural chlorine to the stratosphere (Cicerone 1975; Cicerone et al. 1975; Schauffler et al. 1993; WMO 1995; Schauffler et al. 1998; WMO 1999) and thus are involved in the catalytic destruction of stratospheric ozone.

CH₃Br is also an agricultural fumigant whose production and use are scheduled to be phased out by international agreement (UNEP 1992). Despite the environmental and economic importance of CH₃Br and CH₃Cl, large gaps remain in our understanding of their atmospheric budgets. Estimates of sinks, which include oxidation by hydroxyl radicals, oceanic degradation, and soil consumption, greatly outweigh estimates of known sources, which include oceanic production, biomass burning, certain fungi and higher plants, and anthropogenic inputs (Graedel & Keene 1995; Khalil & Rasmussen 1999; Kurylo & Rodriguez 1999). Recent shipboard measurements of CH₃Br (Lobert et al. 1995; Moore & Webb 1996; Lobert et al. 1997; Groszko & Moore 1998) and CH₃Cl (Tait et al. 1994; Moore et al. 1996) have shown that the oceans are unlikely to make up the balance. Consequently, attention has turned toward the terrestrial biosphere to identify additional natural sources of these compounds.

Coastal salt marshes are regions of high primary productivity and carbon accumulation (Woodwell et al. 1973) and are tidally inundated with halogen-rich seawater. With their abundance of organic carbon, free halogens, and biological activity, coastal salt marshes are logical places to investigate as potential sources of CH₃Br and CH₃Cl. However, it was only recently reported that coastal salt marshes might be globally significant sources of these compounds (Rhew et al. 2000). Observed fluxes of CH₃Br and CH₃Cl were as high as 42 and 570 $\mu\text{mol m}^{-2} \text{ day}^{-1}$, respectively. The surprisingly high emission rates from coastal salt marshes lead to questions regarding the specific source of these compounds, the mechanism of their production, and the environmental and biological control of their fluxes.

Salt marshes are habitats for many halophytic plants, fungi (Padgett & Celio 1990; Mansfield & Barlocher 1993), benthic algae (Woodwell et al. 1973), and for aerobic and anaerobic soil microbes. All of these are candidates as possible sources of methyl halide production in salt marshes. CH₃Br and CH₃Cl fluxes are discussed here in the context of environmental and biological variabilities, and in conjunction with flux measurements of other gas species and carbon isotope measurements of the methyl halides. This analysis provides substantial support for the identification of salt marsh vegetation as the primary sources of CH₃Br and CH₃Cl, although the role of symbiotic microflora and fungi remains to be explored.

2. Site descriptions

Field studies were conducted at the Mission Bay Marsh (32°47' N, 117°13' W) and the San Dieguito Lagoon (32°58' N 117°15' W), both located in San Diego County in southern California. The Mission Bay Marsh is a tidal salt

marsh with little freshwater input, and the San Dieguito Lagoon is formed at the terminus of the San Dieguito River with the Pacific Ocean. The salt marsh vegetation communities at both sites have relatively low species diversity and demonstrate a vertical zonation similar to other southern California salt marshes. At the Mission Bay Marsh, cordgrass (*Spartina foliosa*) covers the lower marsh and tidal creek beds, pickleweed (*Salicornia virginica*, *Salicornia bigelovii*) dominates the expansive middle marsh, saltwort (*Batis maritima*) grows in the upper middle marsh, and a variety of grasses and succulents grow in the upper marsh. The San Dieguito Lagoon similarly has vertical zonation of vegetation. Small patches of *S. foliosa* exist in the lower marsh, the middle marsh is dominated by *S. virginica* and *Salicornia subterminalis*, the upper middle marsh contains alkali heath (*Frankenia grandifolia*), and the upper marsh contains a variety of species, including saltgrass (*Distichlis spicata*).

3. High emissions from coastal salt marshes were not predicted

The observation of large emissions of CH_3Br and CH_3Cl from coastal salt marshes was not expected, given previous research that suggested that salt marsh sediments are sinks for these compounds. Oremland et al. (1994) show that CH_3Br is degraded anaerobically in salt marsh sediments after reaction with sulfide. The product of this nucleophilic substitution is methane thiol (CH_3SH), which subsequently is converted to dimethyl sulfide (DMS) through chemical and bacterial reactions. A less significant reaction for CH_3Br is nucleophilic substitution by chloride, creating CH_3Cl . CH_3Cl is also degraded in the presence of HS^- (Braus-Stromeier et al. 1993), and CH_3Cl in salt marsh sediments is converted to CH_3SH in reactions mediated by anaerobic bacteria (Oremland et al. 1994).

High rates of biosynthesis of methyl halides by salt marsh vegetation were not predicted either, because earlier research suggested that salt marsh plants have low activities of methyl halide producing enzymes. Production of methyl halides has been observed to be enzymatically mediated through methyltransferases (White 1982; Harper 1985; Wuosmaa & Hager 1990). Saini et al. (1995) conducted a survey of methyltransferase activity in 118 herbaceous species by floating leaf discs of these plants in a potassium iodide solution and measuring the resultant methyl iodide (CH_3I) production. While finding that the ability to synthesize methyl halides was a widespread phenomenon in plants, they reported that the 21 tested species that were generally considered to be halophytic (salt-tolerant) had relatively low CH_3I emission rates. In addition, treating three salt-tolerant plants with 50% artificial seawater had no effect on their *in vivo* halide methylating activity. In contrast, far greater

methyltransferase activities were reported for the 15 species of Brassicaceae and one of Resedaceae, all in the taxonomic order Capparales.

There are several differences between these previous studies and the salt marsh field studies described by Rhew et al. (2000). The measurements of sediment uptake of methyl halides were made under elevated concentrations of these compounds and excluded vascular plants. The leaf disk study included only portions of the leaves floating in solution, while the field studies included whole plants with their root systems intact and growing under native conditions. Also, while two genera, *Salicornia* and *Spartina*, were represented both in the leaf disk assays and salt marsh field measurements, there were no species in common between the two studies. Perhaps more importantly, CH_3I might not serve as an accurate proxy for the capability of plants to produce CH_3Cl and CH_3Br .

4. Salt marsh surface sediments are small net sources of CH_3Br and CH_3Cl

At the San Dieguito Lagoon, six study sites were chosen for seasonal flux chamber measurements of CH_3Br , CH_3Cl , carbon dioxide (CO_2), and methane (CH_4). Fluxes from five of these intertidal sites were reported previously (Rhew et al. 2000), while those from the sixth site, a patch of middle marsh devoid of vascular plants, are reported here. This mudflat site shows relatively small net emissions of both CH_3Cl and CH_3Br , except for the December 1998 measurement which shows small uptake of CH_3Br (Figure 1). The average fluxes of CH_3Cl and CH_3Br from the mudflat site are smaller than any of the vegetated sites in the San Dieguito Lagoon as well as the Mission Bay Marsh.

The mudflat site also has very low dark chamber fluxes of CO_2 (-0.01 to $+0.02 \text{ mol m}^{-2} \text{ day}^{-1}$, where positive values denote net fluxes to the atmosphere) compared to sites containing vegetation ($+0.05$ to $+0.5 \text{ mol m}^{-2} \text{ day}^{-1}$). CH_4 is consumed at the mudflat site, showing that activity of aerobic methanotrophs in the surface soil was greater than the activity of anaerobic methanogens. The small CH_4 fluxes are similar in magnitude to those observed at other sites in the middle marsh. Chloroform (CHCl_3) and nitrous oxide (N_2O) were also measured (instrumentation described in Prinn et al. 2000; O'Doherty et al. 2001), and net fluxes of these compounds are determined to be small at this mudflat site. As reported previously by Rhew et al. (2000), methyl halide fluxes from vegetated sites do not appear to be inhibited by complete soil inundation which would inhibit emissions from the submerged soil surface but not from the above-ground plants. Thus, the majority of the CH_3Br , CH_3Cl , and CO_2 from the middle marsh appears to

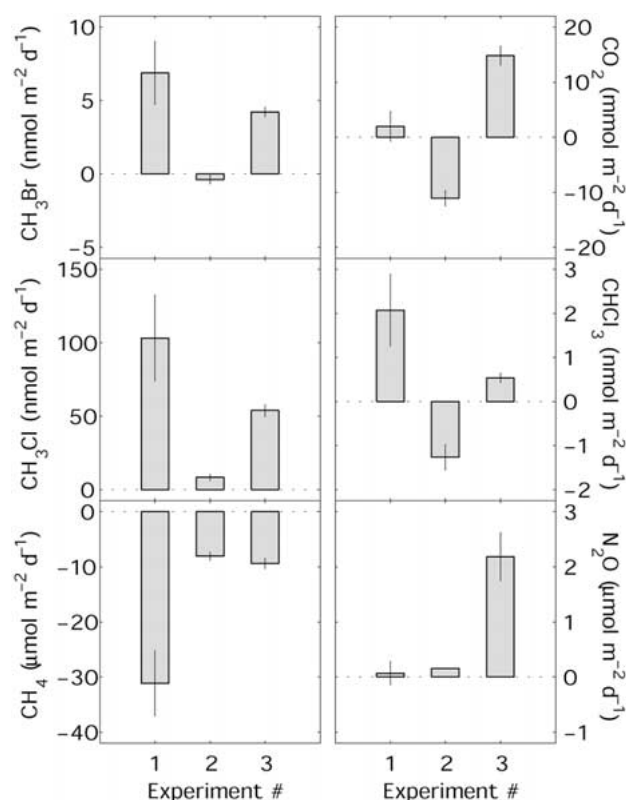


Figure 1. Net fluxes of CH₃Br, CH₃Cl, CH₄, CO₂, CHCl₃ and N₂O from the San Dieguito Lagoon mudflat site (S6). Measurements show that the mudflat site is a minor net source of CH₃Br and CH₃Cl and a net sink of CH₄. CO₂ and CHCl₃ emissions from this site are small compared to vegetated zones of the salt marsh. CH₃Br and CH₃Cl emissions show no correlation with N₂O emissions. Experiment numbers refer to measurements on the following dates: (1) August 8, 1998, (2) December 5, 1998, and (3) April 21, 1999. Plotted error bars for the fluxes include curve fit and chamber temperature, volume, and pressure errors.

emanate from the above ground vegetation rather than from the microbes in the sediments.

It is nonetheless possible that gas transport from the sediments may be plant-mediated, especially through plants like *Spartina* grasses that contain aerenchyma, a spongy tissue that facilitates gas exchange through intracellular air spaces called lacunae. This mechanism effectively transports CH₄ from the anaerobic zones of wetlands to the atmosphere (Chanton & Whiting 1995). The hypothesis that methanogens could be major methyl halide producers was supported by the finding that rice cultivars emit high fluxes of methyl iodide (Muramatsu & Yoshida 1995). This has prompted

significant efforts to quantify CH_3Br and CH_3Cl fluxes from major methane sources, including cattle (Williams et al. 1999), freshwater wetlands (Varner et al. 1999; Dimmer et al. 2001), and rice paddies (Redeker et al. 2000). These studies show that methane sources indeed emitted CH_3Br and CH_3Cl , but the net fluxes of these compounds are small relative to their respective global budgets. Furthermore, the seasonal trend of CH_4 emissions from rice paddies has a different temporal pattern and a much greater dependence on soil organic matter than methyl halide emissions, suggesting that the methyl halides and methane are produced by different biological processes (Redeker et al. 2000).

In the salt marsh, the anaerobic conditions of the *Spartina* sites in the lower marsh are manifested by high CH_4 emissions. However, the methyl halide fluxes in the salt marsh were neither correlated with CH_4 fluxes nor with the presence of grasses that have effective gas transport mechanisms. In fact, there appeared to be an inverse correlation between methyl halide and CH_4 emissions along different vegetation zones, which is inconsistent with the suggestion that methyl halides, being partially reduced compounds, could be metabolic by-products of methane generation in the sediments.

5. Algal mats are small net sources of CH_3Br and CH_3Cl

Algal mats consisting of green filamentous (*Enteromorpha* spp.) and blue-green algae appear to contribute a minor part of the methyl halide emissions, as shown by the small positive fluxes observed from tidal creek sites where algal mats are present (Rhew et al. 2000). Among the three study dates, the algal mat is thickest on February 23, 1999, but the fluxes of CH_3Br are only slightly greater than the other 2 measurements, and the CH_3Cl emissions are roughly the same. In southern California salt marshes, dense algal mats can have primary productivity levels that match or exceed those of the canopy vegetation (Zedler et al. 1992). However, there is no visible evidence of widespread algal mats at the Mission Bay Marsh and the San Dieguito Lagoon during the flux chamber studies, and the only sites with visible algal mats also emit relatively low amounts of methyl halides.

6. CH_3Cl and CH_3Br fluxes are partly related with overall plant biomass

In the salt marsh study described by Rhew et al. (2000), CH_3Br and CH_3Cl emissions show a strong seasonality, with fluxes up to an order of magnitude greater during the growing season than during the non-growing season.

Table 1. Above-ground plant biomass dry weight for Mission Bay (M1–M5) on November 20–22, 1998, and San Dieguito Lagoon (S1–S6) on December 5, 1998. Woody stems and senescent leaves or shoots are classified as ‘brown’ parts; separable algae and green leaves or stems are classified as ‘green’ parts. Number of samples (*n*) is 2, unless otherwise specified

Site	Predominant vegetation	‘green’ parts (g/m ²)	‘brown’ parts (g/m ²)
Mission Bay Marsh			
M1	<i>Monanthochloe littoralis</i>	190 ± 30	480 ± 3
M2	<i>Batis maritima</i> / <i>Salicornia bigelovii</i>	210 ± 100	350 ± 20
M3	<i>Salicornia virginica</i>	370 ± 70	1210 ± 350
M4	<i>Spartina foliosa</i>	250 ± 80	710 ± 160
M5	tidal creek/ <i>Enteromorpha</i> spp. and blue green algal mat	55 (<i>n</i> = 1)	none
San Dieguito Lagoon			
S1	<i>Distichlis spicata</i>	14 ± 13	610 ± 320
S2	<i>Frankenia grandifolia</i>	330 ± 260	1400 ± 790
S3	<i>Salicornia virginica</i>	420 ± 50	1660 ± 570
S4	<i>Salicornia subterminalis</i>	440 ± 130	1990 ± 20
S5	<i>Spartina foliosa</i>	270 ± 40	430 ± 70
S6	mudflat	none	none

The seasonal variation in above-ground plant biomass is coherent with the seasonal nature of the fluxes. The plants are visibly more productive and have greater above-ground biomass in the growing season (March to September) than in the non-growing season (October to February), consistent with observed seasonal trends in other southern California salt marshes (Zedler et al. 1992).

The spatial variability of the fluxes between different vegetation zones of the salt marsh also appears to be related, at least partially, to the amount of above-ground live vegetation. The relative amounts of above-ground biomass between the five salt marsh study sites at the Mission Bay Marsh and between the six sites at the San Dieguito Lagoon were compared in the fall of 1998 (Table 1). Plant samples were taken from the Mission Bay Marsh on November 20–22, 1998 and from the San Dieguito Lagoon on December 5, 1998. Above-ground plant material was harvested from two separate 10 cm × 10 cm plots adjacent to each of the study plots and stored in a freezer until processing. Plots were chosen randomly at sites with dense vegetation or

centered on a plant stem at sites with less dense vegetation. Plants were rinsed and separated into 'brown' (woody stems and senescent leaves or shoots) and 'green' parts, oven dried at 60 °C overnight, and then weighed. For this categorization, the 'green' parts include all separable algae, green leaves and green stems. Although the biomass estimates were made during the non-growing season, the plants were still photosynthetically active. Substantial errors are possible due to the limited number of samples at each site (2), the small size of the sub-plots, and the complications in separating green and brown parts of the sampled vegetation. Nevertheless, these measurements illustrate the large spatial variability of above-ground plant biomass among different vegetation zones of the salt marsh.

In general, the salt marsh sites with large CH_3Br and CH_3Cl fluxes have relatively high CO_2 emissions and relatively high densities of above-ground biomass (Figure 2 and Table 1). All sites are net emitters of CO_2 in these studies because the flux chamber is opaque to sunlight and thus inhibits photosynthesis while respiration continues. Conversely, most sites with low methyl halide fluxes typically have low densities of above-ground green biomass and low CO_2 emissions. While these observations are consistent with the biogenic production of methyl halides by salt marsh vegetation, this rough relationship clearly does not explain all of the variability in the fluxes. Emissions appear also to be strongly dependent on vegetation type. The Mission Bay *Batis maritima* site (M2) and the San Dieguito Lagoon *Frankenia grandifolia* site (S2) have the largest CH_3Br and CH_3Cl emission rates but have smaller biomass densities than other salt marsh sites, such as those containing *Spartina foliosa* (M4), *Salicornia virginica* (S3), and *Salicornia subterminalis* (S4). Further studies will need to compare the change in biomass for each particular vegetation type with the variability in the fluxes.

7. Diurnal variabilities of fluxes correspond with variations in air temperature, sunlight, and CO_2 emissions

Diurnal studies of the net fluxes of CH_3Br and CH_3Cl were conducted during the growing season on June 30, 1999 (Rhew et al. 2000) and July 18–19, 2000 (Bill et al. 2002). Sites were chosen in the upper-middle intertidal zone of the Mission Bay Marsh (near Site M2) because this region was overwhelmingly the largest source of methyl halides among the original vegetation zones and therefore dominated the spatially and temporally averaged fluxes. The high tides in the 1999 and 2000 measurements occurred at approximately noon and 22:00 local time.

In the 1999 study, three sites that contained *Batis maritima* and/or *Salicornia bigelovii* were selected and fluxes were each measured at three

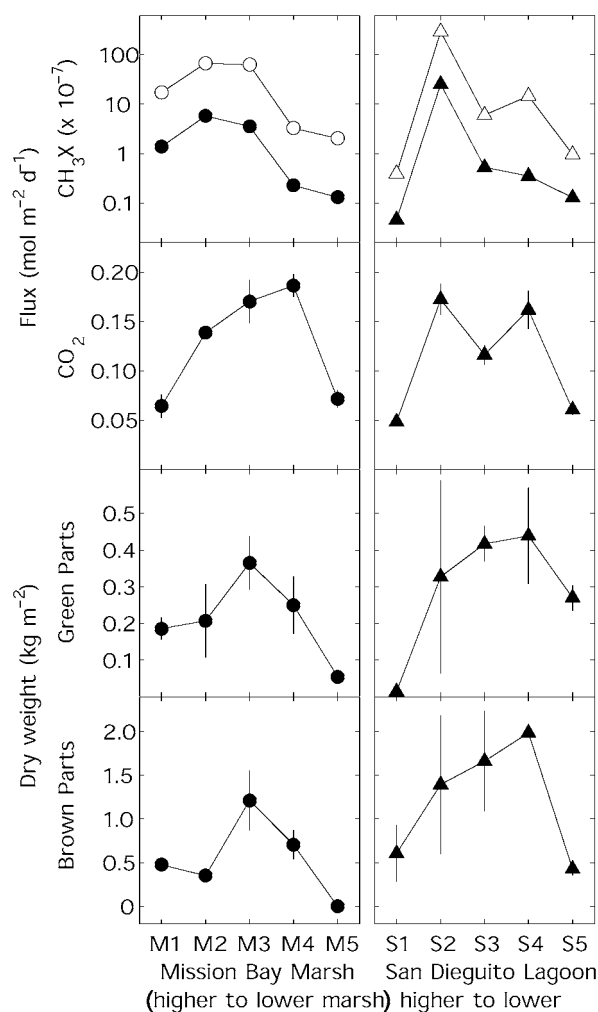


Figure 2. Salt marsh fluxes and above-ground biomass estimates between October and December, 1998. Daytime fluxes of CH_3Br (top panels, closed symbols), CH_3Cl (top panels, open symbols), and CO_2 were measured using dark flux chambers at the Mission Bay Marsh (circles, left panels) and the San Dieguito Lagoon (triangles, right panels). The predominant vegetation types and above-ground biomass estimates at sites M1–M5 and S1–S5 are listed in Table 1. Note the logarithmic scale used for the methyl halide fluxes.

different times of the day using 15-minute enclosures. At the sampling times, the surface soils of the site containing only *Batis maritima* were inundated, while the surfaces of the other two sites were partially covered with seawater only during high tide. The strong diurnal variability in the observed fluxes of CH_3Br and CH_3Cl is similar to diurnal cycles of air temperature and photo-

synthetically active radiation (Figure 3). Diurnal variations of the flux (ϕ) are modeled by the least-squares fitting of the daytime measurements to the function

$$\phi = a + b \left(1 + \cos \frac{t\pi}{d/2} \right) \quad (1)$$

where t is the difference (in hours) from the mean of the times of the midday temperature and sunlight maxima; a and b are fitted constants (units of $\text{mol m}^{-2} \text{ d}^{-1}$) with a representing the nighttime baseline flux and b representing the amplitude; and d is the approximate length of daytime (as opposed to nighttime) in hours. For these calculations, d is taken as 16 hours, and the 8-hour nighttime baseline flux, a , is assumed to be positive and constant. Using Eq. 1, the averaged diel flux may be calculated as $a + bd/24$.

During this study, the fluxes of other biologically active trace gases also were measured and are reported here. The diurnal cycles of CO_2 emissions in these dark flux chambers show a similar midday maximum in emissions (Figure 3). However, the fluxes of CH_4 , N_2O , and CHCl_3 , gases produced by soil microbes, do not follow the same diurnal cycle. The lack of correlation between soil temperatures (0-3 cm depth) and the fluxes of CH_3Br and CH_3Cl is consistent with the production of methyl halides by the above ground biomass as opposed to by microbes or fungi in the surface sediments.

The July 18–19, 2000 study was designed to better characterize the diurnal variability of CH_3Br and CH_3Cl fluxes, especially during nighttime. Two different *Batis maritima* sites were chosen: Site A had standing water for the entire time of the study and was temperature-controlled with an air cooling unit, while the surface of Site B was inundated only during the high tides and temperatures were moderated by insulating the chamber. The vegetation canopy at both sites was always above seawater level. Over a 24-hour period, seven fluxes of CH_3Br and CH_3Cl were measured at each of the two sites (Table 2), with each flux measurement requiring samples at 1 and 20 minutes after closure. The first three flux measurements at Site B were compromised by a poor seal between the chamber lid and base, which was corrected prior to the subsequent measurements.

The daytime cycle of CH_3Br and CH_3Cl emissions in the 2000 study (Figure 4) is very similar to those in the 1999 study (Figure 3), with maximum fluxes at midday. Minimum emission rates occur during the night but still exceed $4 \mu\text{mol m}^{-2} \text{ d}^{-1}$ CH_3Br and $120 \mu\text{mol m}^{-2} \text{ d}^{-1}$ CH_3Cl at these two *Batis maritima* sites. The diurnal cycle in methyl halide emissions follows the diurnal cycle in photosynthetically active radiation (PAR) (Figures 4 and 5), consistent with the observations of Dimmer et al. (2001) at an Irish coastal peatland site. Our measurements also show a similar diurnal cycle in ambient

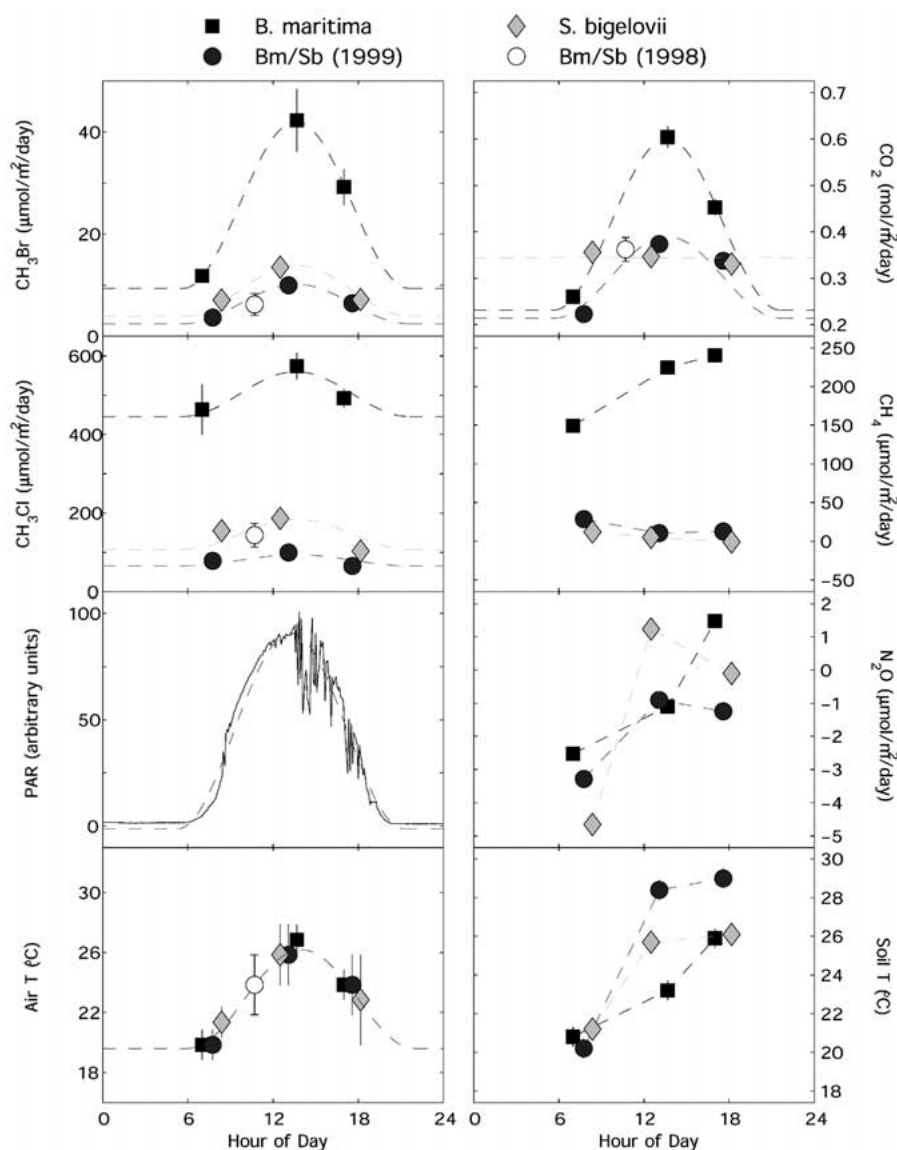


Figure 3. Diurnal variations in the salt marsh fluxes, photosynthetically active radiation (PAR), and soil and average chamber air temperatures on June 30, 1999, at selected sites in the Mission Bay Marsh. Fluxes of CH_3Br , CH_3Cl , and CO_2 in these dark flux chamber studies show similar diurnal trends to PAR and air temperature (dashed lines represent modeled diurnal flux variations, as described in the text), but not to CH_4 fluxes, N_2O fluxes, or surface (0–3 cm) soil temperatures. PAR was measured at the Scripps Institution of Oceanography (SIO) pier ($32^{\circ}52' \text{ N}$, $117^{\circ}15' \text{ W}$). *S. bigelovii* = *Salicornia bigelovii*; *B. maritima* = *Batis maritima*; Bm/Sb = *Batis maritima*/*Salicornia bigelovii* mix. Hour of day refers to local time, Pacific Daylight Savings Time (GMT –7 hours).

Table 2. Diurnal fluxes of CH₃Br and CH₃Cl and chamber air temperatures at two *Batis maritima* sites in the Mission Bay Marsh on July 18–19, 2000

Site	Date	Time hour*	CH ₃ Br $\mu\text{mol m}^{-2}$	CH ₃ Cl $\mu\text{mol m}^{-2}$	Air Temp (°C)
A	July 18	10:10	22.8 ± 0.9	318 ± 13	26.6 ± 1.1
B [†]	July 18	10:53	10.5 ± 0.4	123 ± 5	27.0 ± 0.4
A	July 18	12:57	33.3 ± 1.3	493 ± 19	31.4 ± 0.7
B [†]	July 18	13:55	8.7 ± 0.3	107 ± 4	29.2 ± 0.8
A	July 18	17:00	23.9 ± 0.9	437 ± 17	27.9 ± 1.0
B [†]	July 18	18:03	19.1 ± 0.7	231 ± 9	27.9 ± 2.0
A	July 18	20:04	10.0 ± 0.4	287 ± 11	20.8 ± 0.9
B	July 18	21:02	7.1 ± 0.3	184 ± 7	19.8 ± 0.2
A	July 18	23:59	4.7 ± 0.2	218 ± 9	18.5 ± 1.2
B	July 19	01:21	4.5 ± 0.2	123 ± 5	18.2 ± 0.2
A	July 19	05:00	6.9 ± 0.3	306 ± 12	18.9 ± 0.4
B	July 19	05:53	4.3 ± 0.2	146 ± 5	18.9 ± 0.2
A	July 19	10:00	23.0 ± 0.9	342 ± 14	25.6 ± 0.6
B	July 19	11:04	39.0 ± 1.5	400 ± 15	29.5 ± 0.6
Diurnal average [§]			14.9	284	

*Local time when the flux chamber closure was initiated.

[†]These chamber experiments had excess leakage due to a poor seal between the base and the lid and are excluded from the plots and diurnal average calculations.

[§]The diurnal average is based on the integrated curve fit to the combined measurements from Sites A and B.

air (and enclosed chamber air) temperatures (Figures 4 and 5). Given that nighttime emission rates are relatively constant while PAR is zero and that sunlight is excluded from these dark chamber studies, the similarity between the diurnal cycles of methyl halide emissions and air temperature suggests that temperature variations may strongly affect emission rates. However, this contrasts the results of Dimmer et al. who report strong diurnal cycles in methyl halide emissions while air temperatures varied only 3–4 °C over the monitoring period.

In both diurnal studies at the Mission Bay Marsh, the flux measurements were not conducted at a high enough frequency to clarify the role of the tides in the net emissions of the methyl halides. It is possible that methyl halide consumption in salt marsh sediments (Oremland et al. 1994) may be inhibited due to partial or complete tidal inundation of the sediment surface. This effect has been demonstrated to be important for dimethylsulfide (CH₃SCH₃) and methane thiol (CH₃SH), methylated compounds produced in the leaves of

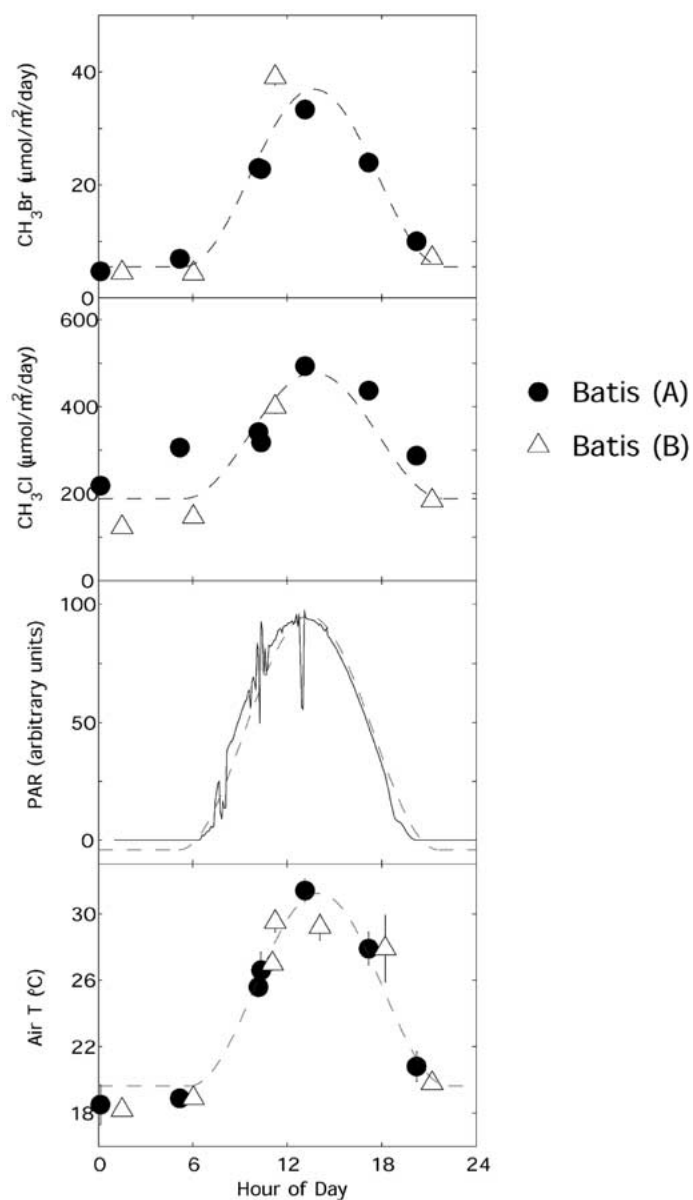


Figure 4. Diurnal flux study, July 18–19, 2000 at two *Batis maritima* sites (A and B) in the Mission Bay Marsh. Emissions are highest during midday hours, roughly coincident with maxima in PAR and air temperatures. Nighttime fluxes are positive but much lower than daytime emissions. Dashed lines represent modeled diurnal variations in flux, PAR, and air temperatures, using a length of daytime value of 16.5 hours. Hour of day refers to local time, Pacific Daylight Savings Time (GMT –7 hours).

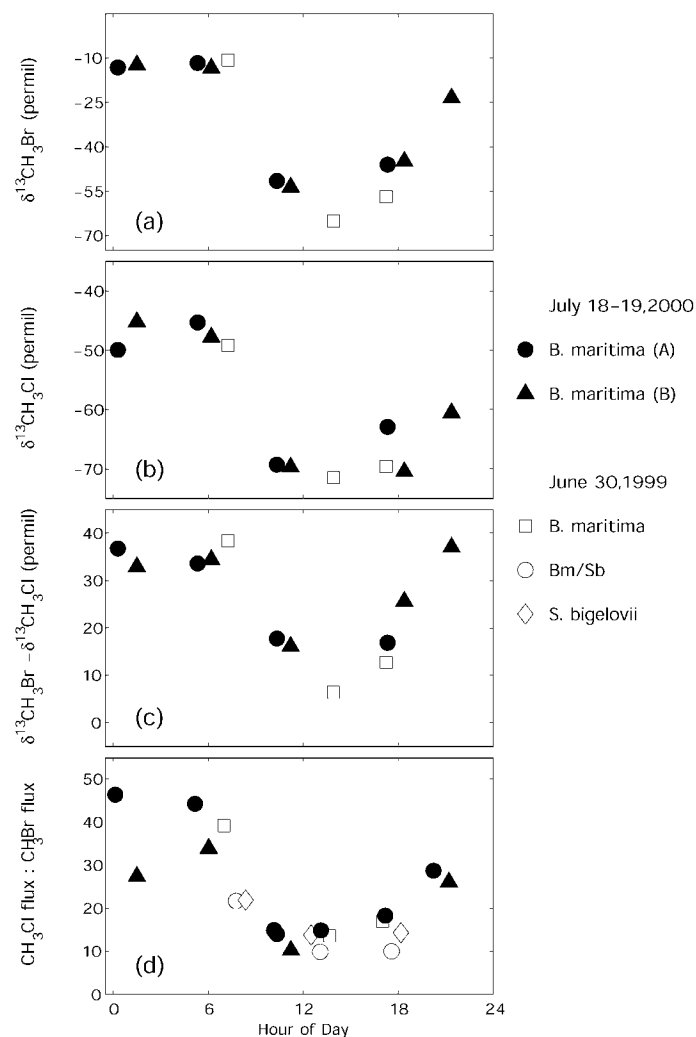


Figure 5. Diurnal observations of $\delta^{13}\text{C}$ in CH_3Br and CH_3Cl emissions (from Bill et al. 2001) and $\text{CH}_3\text{Cl}:\text{CH}_3\text{Br}$ emission ratios from selected sites in the upper-middle Mission Bay Marsh. $\delta^{13}\text{C}$ values of CH_3Br (a) and of CH_3Cl (b) in flux chamber air samples after 15–20 minutes of closure show a large diurnal variability with a more depleted isotopic signature during the middle of the day, coincident with maximum rates of emission. (c) The differences between the $\delta^{13}\text{C}$ values of CH_3Br and CH_3Cl illustrate that the diurnal change in $\delta^{13}\text{C}$ is greater for CH_3Br than for CH_3Cl . (d) The molar ratios of CH_3Cl to CH_3Br emissions show a diurnal trend as well, with a much higher $\text{CH}_3\text{Cl}:\text{CH}_3\text{Br}$ ratio at night than during the day. Hour of day is local time, Pacific Daylight Savings Time (GMT –7 hours).

Spartina grasses, whose net emissions increase when the sediment surfaces are covered with seawater (Dacey et al. 1987; Morrison & Hines 1990). Indeed, during our 1999 study, the site that was inundated throughout the day had the largest emissions, although this may also be explained by the species composition of the enclosed plants. Results from the 2000 study do not show a clear effect of tidal inundation on the emissions of these compounds.

8. Diurnal trends in emissions ratios and carbon isotopic values

The carbon isotope compositions of CH_3Br and CH_3Cl emitted from the upper-middle Mission Bay Marsh sites show large diurnal changes (Bill et al. 2002). Compared to the overall $\delta^{13}\text{C}$ of southern California salt marsh C-3 succulent plants of -27‰ (Kwak & Zedler 1997), the $\delta^{13}\text{C}$ of CH_3Br and CH_3Cl emitted at midday, the time of maximum emissions, is extremely depleted, roughly -70‰ for both compounds (Figures 5(a) and 5(b)). During the nighttime both gases are isotopically enriched in $\delta^{13}\text{C}$, from -10‰ for CH_3Br and -40‰ for CH_3Cl . The similarity in daytime isotopic values for CH_3Br and CH_3Cl and the differences from nighttime isotopic values (Figure 5(c)) suggest that different processes dominate the daytime and nighttime isotopic signals.

The observed emission rates of CH_3Cl and CH_3Br are correlated, with an average molar ratio of roughly 20:1 (Rhew et al. 2000). However, the molar ratios of fluxes have a diurnal trend as well, with a relatively high ratio at night (~ 40) and a lower ratio during the daytime (~ 10) (Figure 5(d)). This provides further evidence that different processes regulate the daytime versus nighttime CH_3Br and CH_3Cl emissions.

It is possible that the diurnal variabilities in the $\text{CH}_3\text{Cl}:\text{CH}_3\text{Br}$ molar ratios and/or carbon isotope signatures are due to competing mechanisms of production and consumption. During the daytime, production may be much faster than consumption, thus obscuring the consumption signature. At night, when production rates are lower, the consumption signature may become more important. If CH_3Br consumption exceeds CH_3Cl consumption, and if the isotopically lighter $^{12}\text{CH}_3\text{X}$ ($\text{X} = \text{Cl}^-$ or Br^-) molecules are consumed faster than the heavier $^{13}\text{CH}_3\text{X}$, then this could explain the higher $\text{CH}_3\text{Cl}:\text{CH}_3\text{Br}$ flux ratios at night as well as the enrichment of the remaining gas in $^{13}\text{CH}_3\text{Cl}$ and $^{13}\text{CH}_3\text{Br}$. Alternatively or in addition, there may be two different sources of the methyl halides, each with distinct isotopic signatures and emission ratios, but with one dominating emissions during the day and the other at night (Bill et al. 2002). Further experiments are necessary to elucidate the processes responsible for the diurnal shift in the net fluxes of CH_3Cl and CH_3Br , their ratio of emissions, and their carbon isotopic contents.

9. Production of CH₃Br and CH₃Cl appears to be mediated enzymatically

The production of CH₃Br and CH₃Cl has been identified in certain methyltransferase reactions through the *S*-adenosyl-L-methionine (SAM)-dependent methylation of bromide (Br⁻) and chloride (Cl⁻) (White 1982; Wuosmaa & Hager 1990; Attieh et al. 1995; Saxena et al. 1998). The enzyme-catalyzed reaction is:



Methyltransferase activity has been identified in several salt marsh plant species (Wuosmaa & Hager 1990; Saini et al. 1995). Methyltransferase reactions also methylate HS⁻ to CH₃SH (Attieh et al. 1995; Saini et al. 1995) and may account for the observed emissions of CH₃SH from other salt marshes (Morrison & Hines 1990; Devai & DeLaune 1995). Unfortunately, we are not able to quantify CH₃I and CH₃SH fluxes using our current gas chromatographic configurations. CH₃I is detected on one of our instruments as a shoulder on the CFC-113 peak, and many of the salt marsh sites show large increases of CH₃I. In addition, two of the air samples from June 1998 have been analyzed by gas chromatography-mass spectrometry at Bristol University (S. O'Doherty, personal communication) confirming the presence of elevated concentrations of CH₃I in samples with elevated CH₃Br and CH₃Cl.

The production of CH₃Br has been observed for several higher terrestrial plants of the *Brassicaceae* family (Gan et al. 1998), which have high methyltransferase activities (Saini et al. 1995). If salt marsh methyl halide production occurs in the above-ground green biomass, then our measurements suggest that the average plant CH₃Br production rate in the salt marsh exceeds the production rates of *Brassica* plants grown in native soils which have much lower Br⁻ levels (Gan et al. 1998). Thus, the high production rates of CH₃Br and CH₃Cl from salt marshes are likely influenced by the high concentrations of available Br⁻ and Cl⁻ as well as by the presence of methyltransferase activity.

SAM:halide methyltransferases from several different species of plant and fungi have been isolated, and the kinetic parameters of K_M (the Michaelis-Menten constant) and V_{max} (the maximum rate of production) have been determined for different substrates, including Cl⁻ and Br⁻. The species include *Endocladia muricata*, a marine red alga (Wuosmaa & Hager 1990); *Phellinus pomaceus*, a wood-rot fungus (Saxena et al. 1998); and *Brassica oleracea*, a cabbage (Attieh et al. 1995). In addition, the kinetic parameters of methyltransferase extracted from *Batis maritima*, the salt marsh plant which our studies show are associated with very high rates of methyl halide

production, have been partially characterized (Ni & Hager 1998; Ni & Hager 1999).

Assuming that the methyl source (SAM) and methyltransferase are the same for both CH_3Cl and CH_3Br , and assuming non-competitive Michaelis-Menten kinetics, we can calculate an expected molar ratio of production of CH_3Cl to CH_3Br as follows:

$$\frac{V_{0,Cl}}{V_{0,Br}} = \left(\frac{V_{\max,Cl}[Cl]_0}{K_{M,Cl} + [Cl]_0} \right) / \left(\frac{V_{\max,Br}[Br]_0}{K_{M,Br} + [Br]_0} \right) \quad (2)$$

where $V_{0,X}$ is the rate of production of CH_3X , and $[X]_0$ is the initial concentration of the substrate (X^-). Assuming further that these enzymes are exposed to seawater concentrations of $545 \text{ mM Cl}^- \text{ kg-soln}^{-1}$ and $0.9 \text{ mM of Br}^- \text{ kg-soln}^{-1}$ (Millero & Sohn 1992) and are not limited by SAM concentrations, we estimate ratios of CH_3Cl to CH_3Br production to be 20.5 for *Endocladia muricata*, 6.9 for *Phellinus pomaceus*, and 5.4 for *Brassica oleracea*. These ratios are similar to those that we have observed from coastal salt marshes. The ratios are also similar to those observed from three species of phytoplankton (~ 10) (Scarratt & Moore 1996) and giant kelp ($\sim 10\text{--}40$) (Manley & Dastoor 1988) incubated in seawater. This favoring of CH_3Br relative to CH_3Cl production in coastal salt marshes, given the concentrations of available Cl^- and Br^- in seawater, is generally consistent with the methyltransferase activities of these various species that show faster reactions with Br^- than Cl^- as a substrate. A more quantitative comparison between field or laboratory studies of emissions and those predicted by enzyme kinetics is complicated by the possibility that there are different halide ion concentrations at the active site of the enzyme compared to those in seawater.

S-Adenosyl-L-methionine methyltransferases are key enzymes for metabolic pathways of biological importance, and the genetic sequences for these enzymes have been identified in many different plants (Joshi & Chiang 1998). The recent sequencing of chromosome 2 of the *Arabidopsis* plant (Lin et al. 1999), which is a member of the Brassicaceae family, may assist efforts to screen plants for the SAM:halide methyltransferase gene. The putative methyltransferase gene has been identified in this chromosome, and it is likely that this gene will be identified in the other plants of the Brassicaceae family. A similar genetic sequence for a SAM:methyltransferase has also been identified in *Batis maritima* of the Bataceae family (Ni & Hager 1998), the salt marsh plant which had the highest emissions of the CH_3Br and CH_3Cl in the Mission Bay Marsh. The other salt marsh plant that was demonstrated to have a very high production of CH_3Br and CH_3Cl is *Frankenia grandifolia* of the Frankeniaceae family. These three families, the Brassicaceae, Bataceae, and Frankeniaceae, all belong to the same Subclass Dilleniidae. If the genetic

sequence for SAM:halide methyltransferase is shared and expressed along taxonomic lines, we may expect to find large emissions of CH_3Cl and CH_3Br from the many species of plants from other Families in this Subclass.

It is not currently understood why certain plants produce methyl halides. It has been speculated that the production and emission of methyl halides may be a mechanism by plants to eliminate Br^- and Cl^- ions from their cells. However, this is a very limited desalinization method, as the highest diurnally averaged growing season salt marsh fluxes (Table 2) are equivalent to the debromination of less than $20 \text{ ml m}^{-2} \text{ d}^{-1}$ of seawater and the dechlorination of only about $0.5 \text{ ml m}^{-2} \text{ d}^{-1}$ of seawater. Furthermore, SAM is an energetically expensive intermediate, suggesting that this is a metabolically inefficient method to eliminate halide ions (Harper 2000).

10. Summary

Salt marshes cover a very limited portion of the global surface area (Woodwell et al. 1973), limiting the influence that they can play in the global budgets of most biogenic trace gases, such as methane (Bartlett 1985) and certain sulfur compounds (Steudler & Peterson 1984; Rennenberg 1991). However, the high rates of coastal salt marsh emissions of CH_3Br and CH_3Cl per unit area suggest that they are globally significant sources of these compounds. (Rhew et al. 2000). Detailed mechanistic studies of production and consumption processes and the factors which control them are essential in efforts to quantify the global salt marsh source. Relevant environmental factors include temperature, sunlight, and tidal inundation. Present measurements of biological and environmental parameters and of the fluxes of other trace gases strongly suggest that the emissions of CH_3Br and CH_3Cl derive from the above-ground vegetation; although the roles of the subsurface roots, microbes, and fungi remain to be explored. Further research questions will involve the genetics and biochemistry of plants, fungi, and bacteria in the salt marsh; taxonomy, biogeography, and physiology of salt marsh vegetation; and flux measurements over a range of temporal and spatial scales.

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