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Natural methyl bromide and methyl chloride emissions from coastal salt marshes

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Atmospheric methyl bromide (CH₃Br) and methyl chloride (CH₃Cl), compounds that are involved in stratospheric ozone depletion, originate from both natural and anthropogenic sources. Current estimates of CH₃Br and CH₃Cl emissions from oceanic sources, terrestrial plants and fungi, biomass burning and anthropogenic inputs do not balance their losses owing to oxidation by hydroxyl radicals, oceanic degradation, and consumption in soils, suggesting that additional natural terrestrial sources may

be important¹. Here we show that CH₃Br and CH₃Cl are released to the atmosphere from all vegetation zones of two coastal salt marshes. We see very large fluxes of CH₃Br and CH₃Cl per unit area: up to 42 and 570 μmol m⁻² d⁻¹, respectively. The fluxes show large diurnal, seasonal and spatial variabilities, but there is a strong correlation between the fluxes of CH₃Br and those of CH₃Cl, with an average molar flux ratio of roughly 1:20. If our measurements are typical of salt marshes globally, they suggest that such ecosystems, even though they constitute less than 0.1% of the global surface area², may produce roughly 10% of the total fluxes of atmospheric CH₃Br and CH₃Cl.

Field studies were conducted between June 1998 and June 1999 in two southern California coastal salt marshes: the Mission Bay marsh (32° 47' N, 117° 13' W) and the San Dieguito lagoon (32° 58' N, 117° 15' W). The climate at these locations is Mediterranean, with wet winters and dry summers. During the March to September growing season, the soils are typically hypersaline; this is because tidal sea water provides most of the soil moisture and because evaporation usually exceeds precipitation³. Study plots (Table 1) were chosen within predominant vegetation communities along a vertical zonation typical of California salt marshes, from the upper marsh (which is inundated only at the highest tides) down to the tidal channels which are devoid of vascular plants. Gas fluxes were measured using a dark static flux chamber⁴ which covers a surface area of 1 m² and encloses a volume of 850 litres; the large chamber size reduces possible 'edge effects' and allows for whole plants to be enclosed. Samples of air were extracted from the chamber, and

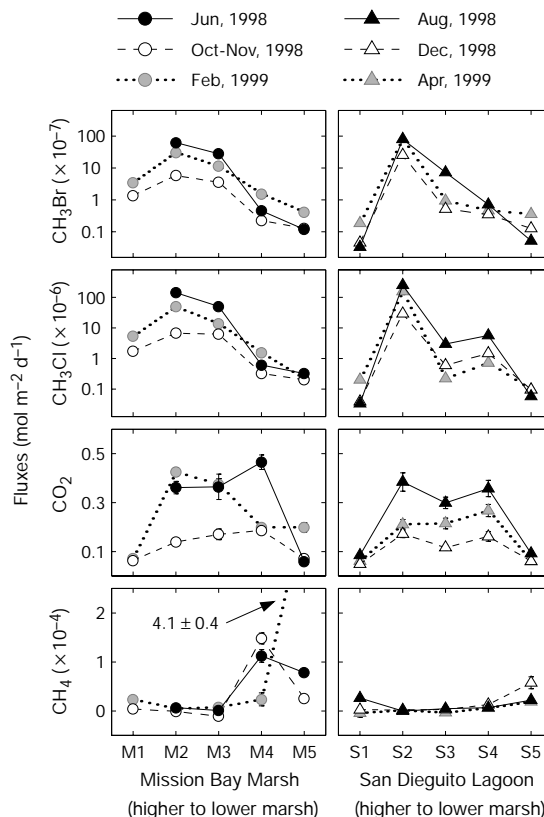


Figure 1 Daytime fluxes of CH₃Br, CH₃Cl, CO₂ and CH₄. Measurements were made between June 1998 and April 1999 at the Mission Bay marsh (circles, left panels) and the San Dieguito lagoon (triangles, right panels). Fluxes are highly variable, both seasonally and spatially, with the largest CH₃Br and CH₃Cl emissions from the upper-middle marsh during the growing season (March–September). The predominant types of vegetation and flux data for each site are listed in Table 1. Note the logarithmic scales for the CH₃Br and CH₃Cl fluxes. The error bars for CO₂ and CH₄ fluxes include analytical and curve-fitting errors.

stored in stainless steel canisters that were lined with fused silica. The concentrations of CH₃Br, CH₃Cl, methane (CH₄) and carbon dioxide (CO₂) in these air samples were measured by gas chromatography. (See Methods for details.)

To quantify fluxes for each gas species, mole fractions within the chamber were plotted versus time of sampling, weighted linear least-squares fits were applied to these data, and the resulting slopes were multiplied by the number of moles of air in the chamber. Chamber measurements represent the net fluxes of the enclosed soil and plants, with positive slopes representing net production. Control experiments demonstrate no significant reactivity of the measured gases on the flux chamber surfaces over the length of the experiment, and the storage of air samples in the canisters has been tested for stability; there was no significant degradation, or production, of the compounds of interest⁵.

The results of our study of seasonal variations across the vegetation zones of these two marshes (Table 1, Fig. 1) show that CH₃Br and CH₃Cl are released from all salt-marsh sites, with greater emissions in the growing season than in the non-growing season. The magnitudes of these daytime fluxes, which vary widely from site to site, show patterns corresponding to the intertidal vegetation

zones of the salt marsh. The greatest emissions of the methyl halides are from the middle to upper-middle marsh, where *Salicornia* species, *Batis maritima*, and *Frankenia grandifolia* are the predominant vascular plants. Large methyl halide fluxes are typically associated with relatively high densities of above-ground green biomass, and do not seem to be inhibited by complete soil inundation. Fluxes at several sites decrease tenfold during the non-growing season, exhibiting a seasonality that corresponds with plant growth. These observations are consistent with the biogenic production of methyl halides by salt-marsh vegetation or microflora intimately associated with the plants. Also, sites with relatively large CH₄ fluxes (M4, M5, and S5; see Table 1) have low emissions of CH₃Br and CH₃Cl, suggesting that the highly reduced soils and/or vegetative cover of the lower marsh are less favourable for methyl halide emissions, even though the methyl halides are partially reduced compounds. In salt marshes, high CH₄ emissions are not only associated with lower-marsh *Spartina* grasses but are also typically associated with lower salinity^{6,7} which may affect methyl halide production rates.

The results from the upper-middle salt marsh (M2a, S2) during the growing season (April, June and August measurements)

Table 1 Measured CH₃Br and CH₃Cl fluxes by study site

Site	Predominant vegetation	Date (dd/mm/yy)	Hour*	T† (°C)	CH ₃ Br‡ (μmol m ⁻² d ⁻¹)	CH ₃ Cl‡ (μmol m ⁻² d ⁻¹)
Seasonal salt marsh flux study results, arranged from upper tidal zone to lower tidal zone						
Mission Bay marsh						
M1	<i>Monanthochloe littoralis</i> (shoregrass)	10/10/98	10	24	0.14 ± 0.03	1.7 ± 0.2
		23/02/99	16	26	0.35 ± 0.07	5.3 ± 0.6
M2a	<i>Batis maritima</i> / <i>Salicornia bigelovii</i> (saltwort/annual pickleweed)	13/06/98	10	25	6.2 ± 2.1	140 ± 30
		10/10/98	08	19	0.58 ± 0.11	6.7 ± 1.0
		23/02/99	13	31	3.09 ± 0.12	49 ± 2
M3	<i>Salicornia virginica</i> (common pickleweed)	13/06/98	11	27	2.8 ± 0.7	51 ± 6
		10/10/98	09	21	0.36 ± 0.14	6.3 ± 1.6
M4	<i>Spartina foliosa</i> (cordgrass)	23/02/99	15	29	1.13 ± 0.07	13.9 ± 0.7
		13/06/98	13	26	0.045 ± 0.003	0.62 ± 0.04
		10/10/98	06	16	0.0227 ± 0.0006	0.325 ± 0.012
M5	Tidal creek/ <i>Enteromorpha</i> spp. (algal mat)	23/02/99	11	29	0.154 ± 0.004	1.56 ± 0.04
		13/06/98	14	29	0.0119 ± 0.0011	0.324 ± 0.017
		20/11/98	14	24	0.0130 ± 0.0006	0.203 ± 0.010
		23/02/99¶	11	29	0.041 ± 0.003	0.213 ± 0.011
San Dieguito lagoon						
S1	<i>Distichlis spicata</i> (saltgrass)	08/08/98	10	27	0.0034 ± 0.0009	0.034 ± 0.006
		05/12/98	15	17	0.0046 ± 0.0003	0.039 ± 0.002
		21/04/99¶	11	27	0.019 ± 0.003	0.20 ± 0.08
S2	<i>Frankenia grandifolia</i> (alkali heath)	08/08/98	06§	19	7.9 ± 0.7	250 ± 20
		05/12/98	11§	18	2.5 ± 0.3	30 ± 3
		21/04/99	09	24	8.1 ± 2.7	160 ± 30
S3	<i>Salicornia subterminalis</i> (glasswort)	08/08/98	07§	19	0.73 ± 0.06	3.0 ± 0.2
		05/12/98	12§	17	0.052 ± 0.004	0.60 ± 0.05
		21/04/99	08	20	0.094 ± 0.008	0.22 ± 0.03
S4	<i>Salicornia virginica</i> (common pickleweed)	08/08/98	08§	21	0.071 ± 0.007	5.7 ± 0.5
		05/12/98	13§	18	0.035 ± 0.004	1.5 ± 0.2
		21/04/99	10	28	0.047 ± 0.004	0.72 ± 0.07
S5	<i>Spartina foliosa</i> (cordgrass)	08/08/98	11§	29	0.0052 ± 0.0006	0.058 ± 0.005
		05/12/98	16§	14	0.0128 ± 0.0007	0.096 ± 0.006
		21/04/99¶	12§	23	0.036 ± 0.003	0.097 ± 0.018
Diurnal salt marsh study results						
Mission Bay marsh						
M2a	See above	30/06/99	06	20	3.63 ± 0.14	78 ± 3
		30/06/99	13	27	10.0 ± 0.4	99 ± 4
		30/06/99	16	24	6.5 ± 0.2	65 ± 2
M2b	<i>S. bigelovii</i>	30/06/99	07	20	7.1 ± 0.3	155 ± 6
		30/06/99	12	26	13.5 ± 0.5	186 ± 7
		30/06/99	17	24	7.2 ± 0.3	103 ± 4
M2c	<i>B. maritima</i>	30/06/99	07§	21	11.8 ± 0.6	460 ± 60
		30/06/99	12§	26	42 ± 6	570 ± 30
		30/06/99	17§	23	29 ± 3	490 ± 20

* Pacific Standard Time (GMT minus 8 h).

† Average chamber air temperature.

‡ Flux errors (1σ) include analytical and curve-fitting errors.

§ Soils inundated.

|| High *S. foliosa* mortality; *S. virginica* established at site.

¶ New site within 5 m of original site.

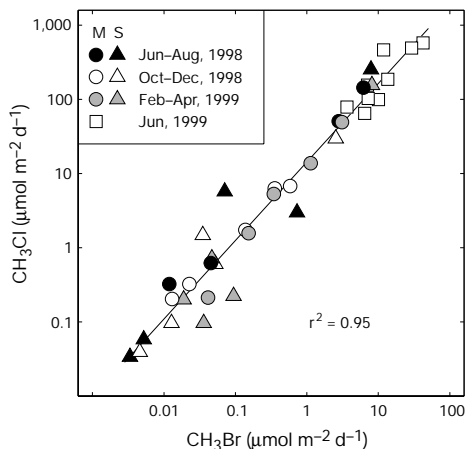


Figure 2 Correlation between CH_3Cl and CH_3Br fluxes. Fluxes are highly correlated over four orders of magnitude, despite the differences between Mission Bay marsh (M) and San Dieguito lagoon (S) sites, vegetation zones, and seasons of study. As both axes are on a logarithmic scale, the slope of near unity indicates that the fluxes are linearly correlated. The equation of the least-squares fitted line is: $\ln(\text{CH}_3\text{Cl flux}) = 1.06 \ln(\text{CH}_3\text{Br flux}) + 2.66$.

dominate the observed methyl halide fluxes. In order to characterize better the fluxes in this region, an additional study of growing-season diurnal and spatial variability was conducted at three upper-middle marsh sites at the Mission Bay marsh (Table 1). Experiments were 15 minutes in duration. These fluxes exhibit strong diurnal trends that follow the incident sunlight and air temperature changes, but not the soil surface (0–3 cm depth) temperature changes, suggesting that the methyl halides are emitted from the above-ground rather than subsurface biomass. The maximum observed fluxes per unit area of CH_3Br and CH_3Cl from salt marshes (site M2c) exceed those from freshwater wetlands⁸ by factors of about 750 and 500, respectively. Diurnal flux (ϕ) variations were modelled by the least-squares fitting of the daytime measurements to the function

$$\phi = a + b \left(1 + \cos \frac{t\pi}{8} \right)$$

where t is the difference in hours from the mean of the times of the midday temperature and sunlight maxima, and a and b are fitted constants; a represents the night-time baseline flux.

Averaged daily fluxes, determined by integrating the modelled fluxes over a 24-hour cycle at the three sites (M2a, M2b and M2c, respectively), are 5.0, 7.2 and 20 $\mu\text{mol m}^{-2} \text{d}^{-1}$ for CH_3Br and 75, 130 and 480 $\mu\text{mol m}^{-2} \text{d}^{-1}$ for CH_3Cl . During the course of the day, fluxes ranged from 0.5 to 2 times the daily average for CH_3Br and from 0.9 to 1.3 times the daily average for CH_3Cl . Spatial variability may be roughly assessed by comparing these averages from the upper-middle marsh. Assuming a lognormal distribution, the mean value of 9 $\mu\text{mol m}^{-2} \text{d}^{-1}$ for CH_3Br varies by a factor of 2.1, while the mean value of 170 $\mu\text{mol m}^{-2} \text{d}^{-1}$ for CH_3Cl varies by a factor of 2.6. Of the three upper-middle marsh sites sampled, the lowest flux emanated from the original site (M2a). Thus, the overall salt-marsh flux may be even higher than our seasonal sampling would suggest. Within a single vegetation zone, the spatial representation of fluxes can pose a larger uncertainty than the diurnal variability.

Certain reactions involving methyltransferase enzymes are known to produce CH_3Br and CH_3Cl through the *S*-adenosyl-L-methionine (SAM)-dependent methylation of bromide (Br^-) and chloride (Cl^-)^{9–11}; methyltransferase activity has also been identified in several salt-marsh plant species^{9,12}. Our observations of high

methyl halide emissions from salt marshes were not predicted, however, because the leaves of certain halophytic (salt-tolerant) plants were found to have relatively low methyltransferase activities compared to the leaves of Brassicaceae species¹². Possible explanations for the surprisingly large salt-marsh emissions involve the different species of halophytic plants under study, the influence of the whole plant on emissions, the interaction between the plant and associated microflora, and the high concentrations of readily available bromide and chloride ions.

The observed fluxes of CH_3Br and CH_3Cl are linearly correlated (Fig. 2), despite the major differences in salt-marsh zones, predominant vegetation, and month of the year. This correlation spans four orders of magnitude of fluxes, and points to a common mechanism of formation and release for these compounds. The average molar ratio of chloride ion to bromide ion in sea water is approximately 650, while the ratio of emissions of methyl chloride to methyl bromide from the salt marsh is 17 ± 14 . Therefore the mechanism appears to favour strongly the production of CH_3Br to that of CH_3Cl . This observation is generally consistent with the behaviour of the methyltransferases isolated from certain plants and wood-rot fungi^{9–11,13}, in which the enzymatic production of CH_3Br is kinetically favoured over that of CH_3Cl . The ratios of emissions of these compounds from phytoplankton¹⁴ and macroalgae¹⁵ incubated in sea water also show that the production of CH_3Br is favoured relative to CH_3Cl , when compared to the ratio of halide ion concentrations in sea water. A more quantitative comparison of the observed emission ratios from field studies to those predicted by enzyme kinetics is complicated by the possibility that chloride and bromide concentrations in seawater differ from the concentrations at the active site of the enzyme, due to selective uptake or exclusion of ions by the cell.

Global extrapolations indicate that salt marshes may contribute significantly towards balancing the known global budgets of CH_3Br and CH_3Cl . The global contribution of salt marshes to these source fluxes can be estimated if we make the following assumptions: that our seasonal flux-chamber sites are representative of their respective salt marshes; that the diurnal trend (adjusted for length of day) and spatial variability of fluxes observed in our upper-middle marsh study are representative of each salt-marsh vegetation zone and season of study; that our study sites are representative of salt marshes globally; and that the global salt marsh area is $0.38 \times 10^{12} \text{ m}^2$ (ref. 2). Accordingly, we estimate that salt marshes globally may be responsible for annual releases to the troposphere of 0.14 Gmol (14 Gg) of CH_3Br and 3.3 Gmol (170 Gg) of CH_3Cl (Gmol, 10^9 mol ; Gg, 10^9 g). The full range of estimates, based on the spatial variability of fluxes, is 0.08 – 0.31 Gmol (7 – 29 Gg) per year of CH_3Br and 1.3 – 8.6 Gmol (65 – 440 Gg) per year of CH_3Cl . Before this present work, the largest estimated natural terrestrial sources for these compounds were 7 Gg $\text{CH}_3\text{Br yr}^{-1}$ from *Brassica* plants¹⁶ and 160 Gg $\text{CH}_3\text{Cl yr}^{-1}$ from wood-rot fungi¹⁷. Consequently, salt marshes may constitute the largest natural terrestrial source of CH_3Br , and possibly of CH_3Cl , identified thus far.

Because our sampling is both temporally and spatially limited, global extrapolations are subject to large uncertainties. The estimate of salt-marsh area alone has an uncertainty of 50% or more². Furthermore, southern California salt marshes differ in structure and composition from other salt marshes. For example, salt marshes on the east coast of the United States are dominated by *Spartina alterniflora*², and at lower latitudes, salt marshes are replaced by mangrove forests which have greater productivity and higher-density above-ground biomass¹⁸. Fluxes are much higher during the growing season, which may be significant when interpreting the seasonal cycles of background atmospheric concentrations¹⁹. If high concentrations of halide ions are critical to the production of CH_3Br and CH_3Cl by plants, then halophytic plants of tropical mangrove and semi-arid environments may also release significant amounts of these compounds.

Methods

Sampling

The aluminium flux chamber consists of a collar, which is seated in the soil first, and a lid, which is placed on top to initiate the measurement period. Three whole air samples are drawn from the flux chamber into previously evacuated 6-litre fused-silica-lined stainless steel canisters at 15- or 20-minute intervals. Small electric fans circulate the chamber air before the last two samplings, and a chamber vent tube is opened during sampling to allow for pressure equilibration. Ambient temperature, chamber temperature, and atmospheric pressure are monitored, and ambient air samples are taken at the beginning and end of each flux chamber experiment.

Gas measurements

CH₃Br and CH₃Cl were measured by capillary column gas chromatography with cryogenic preconcentration on a Porapak Q capillary microtrap, separation on a PoraPLOT Q column, and oxygen-doped electron capture detection^{5,20}. Calibration curves are constructed with a suite of synthetic primary standards prepared in-house³ which span the range of the concentrations. CH₄ was measured by packed-column gas chromatography, with separation on a silica gel precolumn and a molecular sieve 5-Å column, and flame ionization detection²¹. CO₂ was measured by packed-column gas chromatography, with separation on a Porapak Q column, nickel catalyst reduction, and flame ionization detection. Flask sub-samples are measured twice on each of these instruments, with relative analytical precisions typically ranging from 0.2 to 2%.

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A strong source of methyl chloride to the atmosphere from tropical coastal land

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Methyl chloride (CH₃Cl), the most abundant halocarbon in the atmosphere, has received much attention as a natural source of chlorine atoms in the stratosphere^{1,2}. The annual global flux of CH₃Cl has been estimated to be around 3.5 Tg on the grounds that this must balance the loss through reaction with OH radicals (which gives a lifetime for atmospheric CH₃Cl of 1.5 yr)^{3–5}. The most likely main source of methyl chloride has been thought to be oceanic emission^{2,6–8}, with biomass burning the second largest source⁹. But recent seawater measurements¹⁰ indicate that oceanic fluxes cannot account for more than 12% of the estimated global flux of CH₃Cl, raising the question of where the remainder comes from. Here we report evidence of significant CH₃Cl emission from warm coastal land, particularly from tropical islands. This conclusion is based on a global monitoring study and spot measurements, which show enhancement of atmospheric CH₃Cl in the tropics, a close correlation between CH₃Cl concentrations and those of biogenic compounds emitted by terrestrial plants, and OH-linked seasonality of CH₃Cl concentrations in middle and high latitudes. A strong, equatorially located source of this nature would explain why the distribution of CH₃Cl is uniform between the Northern and Southern hemispheres, despite their differences in ocean and land area.

The seasonality of sources and sinks of atmospheric CH₃Cl at different latitudes was studied by periodical monitoring at Hateruma Island, Japan, a small island (12.5 km²) situated 250 km east of Taiwan in the subtropics (latitude 24.1° N, longitude 123.8° E); at Alert, Canada, in the Arctic (latitude 82.5° N, longitude 62.3° W); and over the northwest Pacific Ocean. Over the northwest Pacific Ocean, 7 samples were collected between 42° N and 54° N with an interval of 2° on board the cargo ship *Skaugran*, which sails regularly between Japan and Canada. Figure 1 shows the sampling locations as well as those for the other observations in this study. All samples were collected using evacuated stainless steel canisters, 6-litre fused-silica lined canisters (Silico-can, Restek), or 3-litre electro-chemical buffering canisters (ECB, Ultrafinish Technology), in both of which CH₃Cl was stable for more than six months (ref. 11). Samples were analysed using pre-concentration/capillary gas chromatography/mass spectrometry after being transported to the laboratory. Details of our analytical method have been published elsewhere^{11,12}. Data on CH₃Cl obtained from the three data sets for July 1996 to December 1998 are plotted in Fig. 2 to show seasonal variation; each year is represented by a different symbol (one data point from the 12 May 1998 sample from the northwest Pacific (761 p.p.t.) that was far beyond the average was omitted for the following discussion). The data sets from Alert and the northwest Pacific showed clear seasonal variation (Fig. 2a and b). Abundance and seasonal pattern, exhibiting a slight decrease of CH₃Cl in autumn, are very similar for the data sets from Alert and the northwest Pacific, and both data sets