Halogenated Trace Gas Fluxes From Salt Pond Ecosystems
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Abstract   Halogenated trace gases play an important role in atmospheric science change due to their potential to deplete stratospheric ozone. Consequently, international efforts are being made to mitigate anthropogenic contributions of these gases. The dominant atmospheric methyl halides, methyl chloride (CH_3Cl), -bromide (CH_3Br), and -iodide (CH_3I), all have more known sinks than sources. To help identify missing sources, this study examines salt ponds, which have not yet been analyzed for methyl halide fluxes. Based on past studies, the unique environmental factors within salt ponds, including high bacterial populations, high salinity, and high sunlight exposure, suggest they could potentially be large sources of methyl halides. Vegetation, a typical contributing factor in halomethane production, is scarce in this ecosystem and thus provided an opportunity to separate that environmental variable. Air samples were collected over four locations with varying cover types (water, soil, vegetation) at the salt ponds of the San Francisco Bay National Wildlife Refuge. Samples collected using a static flux chamber were analyzed by gas chromatography-mass spectrometry. Other environmental variables, including temperature and soil moisture content, were recorded to note correlations. Fluxes were found to be unimportant relative to their global budgets in all samples. Thus, salt ponds do not seem to be major contributors to global fluxes of methyl halides.

Introduction

Halogenated trace gases are a family of compounds containing one or more relatively unreactive halogen atoms (chlorine, bromine, fluorine, or iodine; abbreviated 'X'), and are present in the atmosphere in small amounts, typically parts per billion (ppb) or trillion (ppt) by volume. Of halogenated trace gases, halomethanes (or methyl halides, CH_3X) are the simplest in structure and have the lowest molecular weight. The dominant halomethanes in the atmosphere are methyl bromide (CH_3Br), methyl chloride (CH_3Cl), and methyl iodide (CH_3I). Despite their low concentrations, these compounds are very important in atmospheric chemistry because of their relatively stable halogen bonds. This quality allows a considerable fraction to travel through the troposphere and into the stratosphere, where they are photochemically degraded, enabling halogen atoms to catalyze the depletion of stratospheric ozone (Hammond and Maugh 1974). By examining the activity of halogenated trace gases in a particular natural environment, specifically salt ponds, this study will contribute to the understanding of halomethane cycling in the atmosphere.

Since stratospheric ozone loss was linked to the industrial use of chlorofluorocarbons (CFCs) in 1974 (Molina and Rowland 1974), rapid ozone loss has raised two major concerns: increased human exposure to harmful ultraviolet rays, given that the ozone layer acts as a protective barrier against high-energy radiation; and the effect of altered atmospheric composition on global climate change (Hammond and Maugh 1974). Focusing on CFCs, ensuing studies have revealed the important contribution of anthropogenic halogenated trace gases to ozone loss. These threats have generated large scale attempts to understand and mitigate emissions, as exemplified by the 1998 Montreal Protocol, an international agreement that outlines the phase-out of certain ozone-depleting chemicals. The Scientific Assessment of Ozone Depletion, the informational basis of the Montreal Protocol proceedings, has shown that both methyl bromide (CH_3Br) and methyl chloride (CH_3Cl) contribute significantly to ozone depletion (Montzka and Fraser 2002). Methyl iodide (CH_3I), the other dominant atmospheric methyl halide, is not monitored by the Montreal Protocol because its short lifetime causes it to be degraded before reaching the stratosphere, and because there are currently no substantial industrial sources (Ko and Poulet 2002). However, Solomon et al. (1994) note that CH_3I can be transported to the stratosphere via convective clouds and react to destroy ozone.

Intensive research has expanded the body of knowledge regarding the nature of ozone depletion; however, a more complete understanding is needed for making fair and effective policy decisions that minimize environmental threats. Many halogenated trace gases, for example CFCs, are purely anthropogenic in origin; therefore their sources are relatively well accounted for. Halomethanes, however, have both natural and anthropogenic sources, with the natural component being highly intricate and uncertain (Butler 2000). Given this incomplete understanding and the pressing nature of issues surrounding atmospheric methyl halides, research regarding their global biogeochemical cycles has accelerated.

Current knowledge of methyl halide sources and sinks is summarized in Table 1 (Ko and Poulet 2002, Montzka and Fraser 2002), which shows the respective global budgets, or the balance of "sources" (where compounds are released) and "sinks" (where compounds are taken up). The budgets are not well understood for any of the three dominant halomethanes; many estimates have high uncertainties and all compounds have one or more unidentified sinks and/or overestimated sources.

Table 1 Estimated global budgets (in Gigagrams per year) and uncertainties of the three dominant atmospheric methyl halides.

Compound	Sources and estimated source strength (Gg/yr)	Sinks and estimated sink strength (Gg/yr)	Total estimated source (+) and sink (-) strength, magnitude of imbalance (Gg/yr)
Methyl Bromide (CH₃Br)	Ocean (63), fumigation (40.8), biomass burning (20), salt marshes (14), wetlands (4.6), gasoline (5), rapeseed (6.6), other (5.1)	Ocean (77), soils (47), photochemical and hydroxyl reactions (8), plants (not quantified)	- 159 + 204 = -45
Methyl Chloride (CH₃Cl)	Oceans (600), biomass burning (911), tropical plants (910), fungi (160), salt marshes (170), wetlands (40), anthropogenic source (160)	Hydroxyl reactions (3180), loss to stratosphere (200), reaction with Cl in MBL (376), microbial degradation in soil 180), loss to poles (75)	− 2951 + 4005 = -1049
Methyl Iodide (CH₃I)	Ocean (210), biomass burning (10), rice paddies (90), wetlands (7.3), peatlands (1.4)	Chemical loss in oceans and atmosphere (Not quantified)	Not quantified

However, what these figures do reveal is some overlap in their global chemical cycling. For example, biological systems such as plants and bacteria, aquatic environments including salt marshes, and the atmosphere all play an important role in the cycling of these compounds. The important role of biology in halomethane activity is evident in the estimated sources and sinks. Research has repeatedly shown both terrestrial and oceanic plants to be producers of halomethanes. Production has been observed by terrestrial higher plants (Gan et al. 1998), tropical plants (Yokouchi et al. 2002), agricultural rice paddies (Redeker et al. 2000), and macroalgae and phytoplankton (Manley et al. 1992 and Scarratt et al. 1997, respectively). Nonetheless, the multitude and diversity of different plant species and their individual biochemical operations sets hurdles for an understanding of this relationship. Bacteria have been shown both to produce and consume halogenated compounds, the activity being highly species dependent. Though the role of bacteria is variable, it is highly important (Shorter et al. 1995, Amachi et al. 2001, McAnulla et al. 2001), in part due to the omnipresent nature of such bacteria. The contribution of oceans and salt marshes to the global budgets of methyl halides illustrates the relationship between their production and saline environments. Much of these observed sources, however, are the result of biological functions within saline environments. The high levels of methyl chloride and methyl bromide production observed in salt marshes (Rhew et al. 2000), for example, were attributed to biochemical processes within the salt marsh vegetation. Alternatively, on the sink side, the dominance of atmospheric processes is apparent, putting into perspective the need for gaseous emissions regulations.

Salts consist of a halide (X^-) bonded to a cation, as in the dominant oceanic salt sodium chloride (NaCl). Accordingly, salinity levels have been directly linked to methyl halide production. In fact, soil salinity has been shown to be a key determinant in the magnitude of methyl halide emissions from terrestrial plants and from fungi (Gan et al. 1998 and Haper 1985, respectively). The relationship between salinity and halomethane production remains uncertain, most likely because ambiguity in biological mediation clouds this understanding. Surprisingly, very few studies have been conducted in high salinity/low vegetation environments. Perhaps this is because both the global percent cover of non-oceanic high salinity environments and the amount of vegetation within them may be presumed to be too low for important contributions to global budgets. However, this assumption merits further inspection for two reasons. First, the salinity factor should not be underestimated; the study by Rhew et al. (2000) concluded that "even though [salt marshes] constitute less than 0.1% of the global surface area, [they] may

produce roughly 10% of the total fluxes of CH_3Br and CH_3Cl." Second, abiotic production mechanisms have been proposed. Keppler et al. (2000) showed that oxidation of organic matter by Iron (III) in soils and sediments can release volatile halogenated organic compounds without bacterial mediation. Another finding, more applicable to the salt pond environment and perhaps more widely accepted, is the role of sunlight alone in halogenated trace gas production, including CH_3Br and CH_3I (Swanson et al. 2002). Furthermore, salt lakes, while environmentally different from salt ponds due mostly to higher vegetative abundance, have been shown to produce inorganic halogenated compounds (Weissflog et al. 2004). Several possible mechanisms were proposed, including biotic production in the saline soils and abiotic production in the soils or the salt crystals. In theory, any of these production mechanisms can take place in salt pond ecosystems.

The complex and poorly understood interaction of environmental factors that dictate halomethane cycling is especially pronounced in the case of salinity and biological mediation. These uncertainties, as well as the lack of related studies, create a gap in the understanding of global halomethane fluxes that ought to be addressed. Filling these knowledge gaps is not only crucial in addressing ozone depletion; it is also interesting and useful in understanding general ecosystem dynamics concerning these chemicals. This study will seek to address these knowledge gaps by quantifying halogenated trace gas emissions from both the water surface and the surrounding sediment of the salt ponds and to answer the question: Do salt pond environments exhibit globally important fluxes of methyl halides? I have arbitrarily defined importance as a globally averaged flux greater than or equal to one percent of a given compound's global budget, which provides some consistency with flux values reported in scientific literature.

Materials and Methods

Field Sites Salt ponds bordering the south San Francisco Bay, in the Don Edwards San Francisco Bay National Wildlife Refuge in Ravenswood (Fig. 1a), served as the study area for this project. Though salt pond systems in the south San Francisco Bay are currently in various stages of restoration from commercial salt pond use (Martin, 2004), our site was not actively undergoing either process at the time of sample collection, providing an accessible and undisturbed site for experimentation relative to surrounding areas.

While salt pond environments may be variable on a global scale, the individual salt pond system from which samples were collected was very homogenous in terms of environmental variables. Due to this relative homogeneity, large geographic spread is not necessary for sampling locations. Sampling was therefore done at two different locations of varying cover type within each of two different salt ponds, one in plot R3 and one in plot R4. In plot R4, sampling was done over the water surface near the edge of the pond (referred to as water or FC 2) and over the adjacent soil surface (FC 1 soil). In plot R3, the two sample sites were both on the soil surface, again adjacent to water. One of the sites was bare soil (FC4 soil). The other site was vegetated (vegetation or FC 3), with approximately 95% of the covered with *Spergularia marina*, a common California salt marsh plant. Note that the vegetated site was on the periphery of the salt pond, in a somewhat transitional area between the marshes and the ponds. All samples were collected on January 11, 2007. The weather was sunny and cool with slight winds, and there were very few salt crystals because the salt ponds experience their lowest evaporation rates in the winter.

Similar to other salt ponds, these are characterized by flat and uniform topography, scarcity in surrounding vegetation, anaerobic soils, high exposure to sunlight, simple community structure, and high and varying salinity levels. Salt ponds are typically colored blue/green due to different stages of evaporation (Fig. 1b). Some are also colored pink due to the abundance of algae and/or bacteria in highly evaporated salt ponds. The salt ponds from which samples were collected contained bacteria and brine shrimp, but did not contain any macroalgae. It is possible that there were microalgae present, but this was neither detectable nor likely because of the lack of other forms of vegetation.

Figure 1 a) Study site within the South San Francisco Bay: Plots R3 and R4 in Ravenswood, and b) general color variations of Salt ponds in Alviso (Martin, 2004).

Data Collection/Sampling Process For each site, a quantitative and qualitative description of the area was recorded. This included applicable site-specific environmental factors such as water salinity, weather conditions, geographic positioning, soil water content, air temperature, and atmospheric pressure. Soil temperature and vegetative composition were also recorded post-sampling. Due to the typically strong role of vegetation, one of the most determinant variables in organic halogenated trace gas activity is seasonality. However, the scarcity of vegetation in salt ponds strengthens this assumption and precludes seasonal sampling.

Air samples were then collected in 1L canisters using an inert and opaque flux chamber, which enclosed 0.18 m^3 of air over a ground level area of interest. For each of the four locations, air withdrawals were made from the flux chamber into pre-evacuated, inert air canisters at time t=2, 17, and 32 minutes after initiation. In addition, two ambient (or "background") air samples were collected for comparison, totaling ((3*4) +2=) 14 air samples. The comparison against ambient air is mostly done for quality control, i.e. verifying that any abnormal fluxes are the result of the sampling site and not leakage through the sampling apparatus.

Within one week of data collection, the chemical composition of the air samples were analyzed using gas chromatography and mass spectrometry (GC/MS) (Agilent Technologies, 6890N/5973, Santa Clara, CA). The resulting values were plugged into a calibration curve that relates GC/MS output data with standard gases of known concentration to determine actual

chemical concentrations within the samples (resulting concentrations were thus corrected for systemic errors). Due to availability of standard gases, a total of eight halogenated trace gases were analyzed (Table 2). However, the three methyl halides (or monohalomethanes) were of particular interest because of intensive research surrounding them, especially by the Rhew Laboratory.

Table 2 Gases analyzed.

Full Compound Name	Chemical Formula	Abbreviation	
Methyl Chloride	CH_3Cl	MeCl	Methyl Halides
Methyl Bromide	CH_3Br	MeBr	(CH_3X)
Methyl Iodide	CH_3I	MeI	
Carbon Tetrachloride	CCl_4	CT	Other Halogenated
Dichlorodifluoromethane	CF_2Cl_2	F12	Trace Gases
Trichlorofluoromethane	$CFCl_3$	F11	
Chloroform	$CHCl_3$	CF	
Methyl Chloroform	CH_3CCl_3	MeCF	

The resulting data is a collection of concentrations (moles per volume) of individual gases at individual time points (t=2, 17, and 32 minutes) for each sampling area. When plotted against time, the slope of the best-fit (linear or polynomial) function divided by the enclosed surface area reveals the average flux of that gas in moles per area per time. Fluxes can be either positive, showing net release (or production) of the gas, or they can be negative, showing net uptake (or consumption). The flux is assumed to be representative for other times and similar locations, in order to make the extrapolation to a global flux in the next step. This assumption introduces error; however the complexity of natural ecosystems, their global spatial and temporal variability, the lack of well-defined relationships between halogenated trace gas fluxes and environmental variables, and the limited scope of this study makes it unavoidable.

To isolate unidirectional fluxes for methyl bromide and methyl chloride, an isotopic spiking technique was incorporated into the sample collection and analysis (see, for example, Rhew et al., 2003). This technique, which utilizes the mass difference of isotopes or their fragments that are detectable by a mass spectrometry but do not translate to significant behavioral differences within the environment, involves the injection of carbon-13 labeled methyl bromide and methyl

chloride of known concentration into the headspace of the flux chamber at time t=0. Given that 13-C isotope makes up about 1% of the C found in nature, changes in the concentration of 13-C over time relative to the input amount expose the gross fluxes within a system. When 13-C is injected into an enclosed system, it can either 1) remain stagnant in the air, showing no concentration change over time, or 2) decrease in concentration, showing uptake by one or more components of the enclosed system. Concentrations will rarely increase, since the injected amount is much greater than the background 1%. After adjusting for any leakage out of the enclosure by monitoring a tracer gas (F113) and adjusting for 13-C fractionation, a value of uptake for the specific 13-C labeled compound can be measured. When compared to the net flux measured by the three air samples, the uptake value can be subtracted from the net value, isolating consumption and production.

Using flux calculations, and their associated errors, from each site, an average flux magnitude and direction is computed for the salt pond subsystem in nanomoles per square meter per day. Provided that the various sample locations are in reasonable agreement in flux magnitude/direction, this will be a reasonable demonstration of salt pond activity. This average is then extrapolated over the global surface area of salt ponds and over a time of one year to give an amount of gas per year that is either produced or consumed by salt pond environments. Extrapolation to global surface cover of salt ponds introduces much error because there is a lack of aerial estimates. Here, a surface area of 1×10^{12} m^2 is used, which is equal to the global surface cover of salt marshes (Rhew et al. 2000). This surface area value will overestimate flux magnitudes, but will be more representative than any other reported surface area values for terrestrial water bodies, which are overwhelmingly for freshwater bodies. For the vegetated site, 10% of this surface area value was used based, on a crude estimate of their percent cover within salt ponds during the time of sampling. The percent cover of this vegetation within salt marshes would be much higher, but an evaluation of salt marshes was not the purpose of this study. For each compound, the flux magnitude obtained is compared to the estimated global budget of that compound, and an arbitrarily defined 1% minimum will be used to evaluate flux importance. Extrapolating measured values is the common approach used in literature for reporting ecosystem-specific trace gas fluxes.

Results

Environmental variables ranged only slightly among sample locations in both plots R3 and R4 (Table 3). For the purposes of this project, the important distinctions between the two sample areas are salinity and bacterial population. Both ponds are highly evaporated, allowing the bacterial populations to color the waters pink. The pond water of R4 was less pink than R3 pond water, indicating a lower bacterial population. Salinities were measured from the water adjacent to the sampling sites in each plot. Plot R3 had higher salinity than plot R4, though not by very much. These values show the extent of salt pond hypersalinity relative to seawater (~ 35 ppt).

Table 3. Environmental factors of study areas at time of sampling

Plot	R4 - FC 1	R4 - FC 2	R3 - FC 3	R3 - FC 4
Ground Cover Type	Soil	Water	Vegetation	Soil
Average Air Temperature (°C)	12.9	13.0	10.4	10.8
Average Soil Temperature (°C)	8.35	10.45	7.85	9.05
Soil Moisture (%)	46.5	-	40.6	38.1
Water Temperature (°C)	-	12.0	-	-
Bacterial Population	Lower		Higher	
Salinity (parts per thousand)	262		223	

Of the eight compounds examined, the non-monohalomethanes ($CHCl_3$, CCl_4, CF_2Cl_2, $CFCl_3$, CH_3CCl_3) showed negligible net fluxes with respect to their global budgets, and will therefore not be discussed in depth. For most of these compounds, this result is expected because they have negligible natural sources in their global budgets.　　However the three monohalomethanes, which were the primary interest of this study, did show interesting results with regard to the magnitude of global flux (Fig. 2) and/or the relationship between flux and environmental conditions. Gross fluxes for each cover type are also shown for methyl bromide (Fig. 3a) and methyl chloride (Fig. 3b) to elucidate the directional components of the overall fluxes. Error bars represent a 5% experimental error.
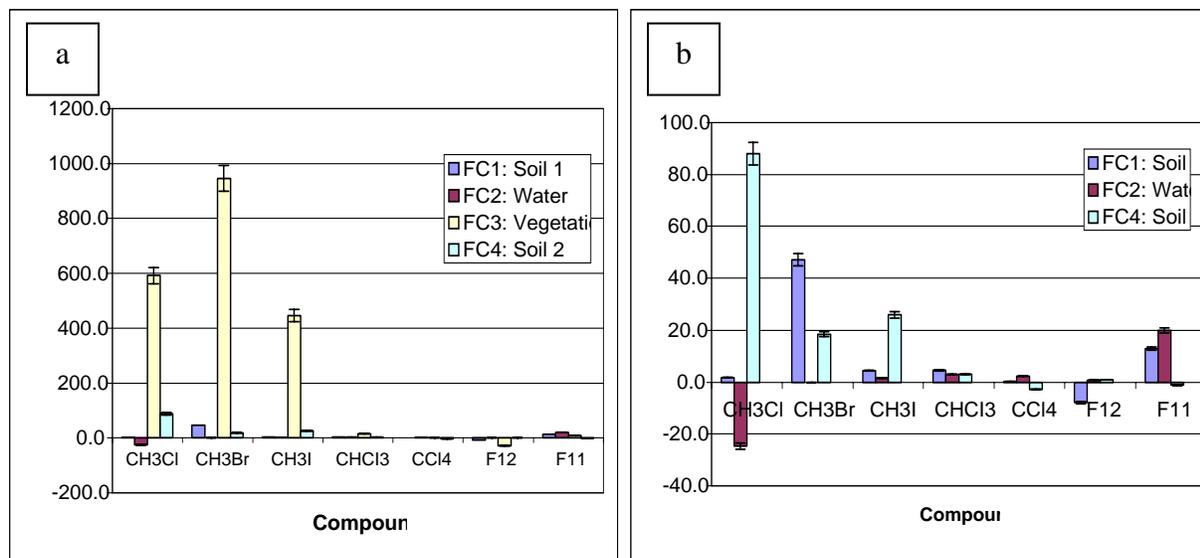
Figure 2. Net flux measurements for a) all cover types, and b) all cover types excluding vegetation (FC 3) for clarity.
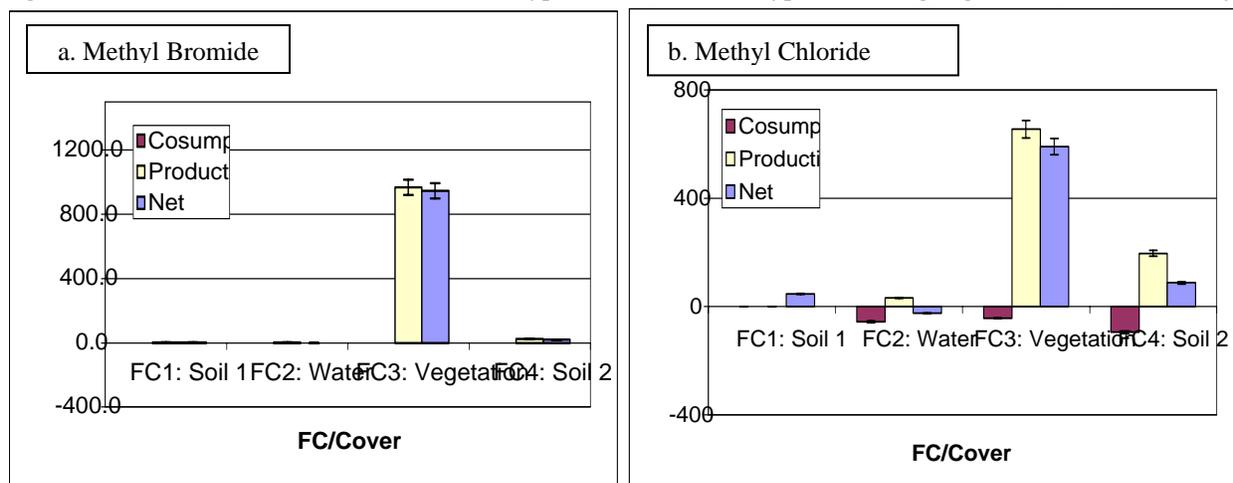

Figure 3. Gross flux measurements for a) methyl bromide and b) methyl chloride.

Discussion

The water site (FC 2) and the FC 1 soil site were located in the same area, as were the vegetation site (FC 3) and the FC 4 soil site (in a different area). The weak flux correlations between neighboring sample sites suggests that variability in activity is perhaps more related to cover type than micro-locations within the salt ponds. The sample area that contained vegetation (species *Spergularia marina*; a common California salt marsh plant) clearly showed the most halomethane activity, both in production and consumption (Fig. 2a). While production was much higher than any other site, the amounts of CH_3Cl (1.09 Gg/yr), CH_3Br (3.28 Gg/yr), and CH_3I (2.31 Gg/yr) produced were insignificant relative to their global sources (2951 Gg/yr, 159 Gg/yr, and 304 Gg/yr, respectively) (Ko and Poulet 2002, Montzka and Fraser 2002). Similarly, all

three non-vegetated sites showed negligible activity for all compounds. Most of these sites showed release of methyl halides, with the consumption of CH_3Cl in the water site being an apparent exception (Fig. 2b). What is surprising, however, is the ratio of $CH_3Cl:CH_3Br$ produced by this plant in the salt ponds- about 0.3:1. Rhew et al. (2000) observed production ratios of $CH_3Cl:CH_3Br$ in salt marsh plants to be on the order of 20:1, which better reflects the typical ratio of Cl:Br in saltwater of about 650:1. The explanation of this species' strong preference for Br^- is worth addressing, but is beyond the scope of this paper.

Again, the measured fluxes were net amounts for all compounds except CH_3Br and CH_3Cl, so it cannot be said with certainty that there is unimportant gross activity for these halogenated trace gases. For CH_3Br and CH_3Cl, however, the isotope spiking technique allowed activity to be broken down into unidirectional fluxes (Fig. 3a and 3b, respectively). CH_3Br is produced in all sample sites, though in negligible amounts except in the vegetated site. Unfortunately, an analytical error has prevented gross CH_3Cl flux analysis for soil site FC 1. The other sample sites show, however, that CH_3Cl is both produced and consumed, and in the same relative amounts across each site.

Though these salt ponds are characterized in part by scarcity of vegetation, production was still feasible because of the other unique environmental factors present at the salt ponds that contribute to production elsewhere. Ruling out production mediated by vegetation, other possible mechanisms (summarized previously) included production mediated by bacteria, photochemistry, or other abiotic production in the sediments or the salt crystals in the ponds. In light of these possible production mechanisms and the corresponding environmental variables (high salinity, high bacterial population, and high exposure of both the water and the soil surface to sunlight), the low production level at sites other than the vegetated one was somewhat surprising. Production also seemed plausible because of the lack of similar studies in salt pond systems to suggest otherwise. The low gross and net activity in the water, where the bacteria are most concentrated, suggests that these bacteria in particular are not especially active with regard to these compounds. In the salt pond ecosystem, either that activity is reduced by the lack of vegetation and/or that there is another missing element that would otherwise enhance local production.

Conclusion

Analyzing trace gas activity in salt ponds that were located near salt marshes presented an opportunity to compare the non-vegetative components of production to the vegetative components within the same environment. While non-vegetative production mechanisms were not evident in this study, it does not suggest that they are not important contributors to halomethane production in other ecosystems. For example, it is possible that there is more photochemically induced activity, whether in the salt crystals or the water itself, when sunlight is more intense, such as in the summer. In addition, if photochemical activity operates on a very short tie scale (i.e., instantaneously), then changes would not have been detected because a dark flux chamber (one that block incident sunlight) was used. Photochemical activity could be assessed in future studies by using a clear flux chamber.

An unmistakable result from this study is the central role of vegetation, at least in these salt ponds, which is somewhat supported by literature (as noted previously; Gan et al. 1998, Redeker et al. 2000, Yokouchi et al. 2002, etc.). The cumulative results of other studies show the contribution of vegetation to halogenated trace gas activity, but more importantly, studies of the most comparable ecosystems- salt marshes- show the same finding (Rhew et al. 2000). The demarcation between salt ponds and salt marshes can be vague because they blend into one another as parts of temperate coastal areas. An important distinction, however, is the vegetative abundance. This seems to be the factor that separates unimportant production, such as at the salt ponds, from large levels of production observed in salt marshes. For this reason, the large fluxes observed in the vegetated site should not be attributed to salt ponds, but rather salt marshes.

It is important to remember that other salt ponds may contain other types of bacteria, as well as algae, which could potentially be highly active in halogenated trace gas exchange with the atmosphere. Thus, salt ponds should not be completely discounted as potential halogenated trace gas sources. However, if these salt ponds are representative of others, it is unlikely. While this study shows that salinity alone does not determine halomethane production, it remains an important factor. Inspection of other salt ponds or hyper-saline environments would solidify these results. Because the goal of research such as this is to constrain the global budgets of these gases, it would probably be more worthwhile to explore other ecosystems to find the missing source(s) that would balance the sinks of these compounds. This study adds to the prediction

from several other studies that the missing source is likely terrestrial vegetation, perhaps in the tropics.

Acknowledgements

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