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Measurements of ambient atmospheric C₂H₅Cl and other ethyl and methyl halides at coastal California sites and over the Pacific Ocean

Jason C. Low,¹ Nun Yii Wang,² Jody Williams,³ Ralph J. Cicerone^{1,4}

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[1] Spatial and temporal distributions of atmospheric CH₃Cl, CH₃Br, C₂H₅Cl, and C₂H₅Br were determined by gas chromatography/mass spectrometry measurements at coastal California and inland sites from 1996 through 1999. The median concentrations observed at a clean coastal site were 585, 13.1, 3.3, and 0.3 ppt (parts per trillion) for CH₃Cl, CH₃Br, C₂H₅Cl, and C₂H₅Br, respectively. To our knowledge, these represent the first quantitative measurements of atmospheric C₂H₅Cl. High variation was seen in CH₃Br and C₂H₅Cl measurements from the other two California sites, a rural inland site and a coastal site with urban influence. When compared to the California stationary sites, the median Northern Hemispheric results from measurements taken along Pacific Ocean transects between California and New Zealand from 1996 through 1999 were similar for CH₃Cl (594 ppt) and C₂H₅Br (0.3 ppt) but lower for CH₃Br (10.4 ppt) and C₂H₅Cl (2.6 ppt). Median concentrations of Southern Hemispheric CH₃Br (9.4 ppt), C₂H₅Cl (1.6 ppt), and C₂H₅Br (less than 0.2 ppt) were lower than the Northern Hemispheric results. No significant correlation was found between the atmospheric concentrations of the methyl halides with the ethyl halides. **INDEX TERMS:** 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; **KEYWORDS:** ethyl chloride, chloroethane, California air measurements, Pacific Ocean air measurements, ethyl bromide, bromoethane

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1. Introduction

[2] Halocarbons, the general term given to most organic compounds containing halogens, have been well known since the 1940s for their industrial use as refrigerants, propellants and solvents. Atmospheric halocarbon measurements were prompted by the observations of Lovelock [1975] and Lovelock *et al.* [1973], which showed increased tropospheric concentrations of industrial chlorofluorocarbons (CFCs) and showed natural emissions of halogenated compounds, mostly from the oceans. Molina and Rowland [1974] proposed that halogenated compounds such as CFCs and CCl₄ were not subject to tropospheric removal and instead were transported into the stratosphere. Once in the stratosphere, they photochemically decompose and release halogen atoms, contributing to the subsequent catalytic destruction of ozone.

[3] Upon discovery of the Antarctic ozone hole, the Montreal Protocol was signed in an international attempt to protect the stratospheric ozone layer. Under the Montreal protocol, phase outs of CFCs and related chlorinated and brominated compounds were scheduled for 1996 for industrialized nations and by 2010 for developing nations. As a result of the mandate, tropospheric concentrations of all but CFC-12 are declining [Elkins *et al.*, 1993; Cunnold *et al.*, 1994; Prinn *et al.*, 2000]. In addition, atmospheric amounts and distributions of other halogenated organic compounds such as methyl chloride (CH₃Cl) and methyl bromide (CH₃Br) that can affect stratospheric ozone also have been observed [Khalil and Rasmussen, 1999; Butler and Rodriguez, 1996]. Methyl iodide (CH₃I), a relatively short-lived compound, and several other alkyl iodides have been detected in the air, mostly over oceans [Carpenter *et al.*, 1999; Yokouchi *et al.*, 1997]. By themselves, CH₃Cl and CH₃Br contribute 23% of inorganic chlorine [Khalil *et al.*, 1999] and 50 to 55% of inorganic bromine [Schauffler *et al.*, 1993, 1998, 1999] transported to the stratosphere. As the concentrations of anthropogenic halogenated species are reduced, the relative contributions of CH₃Cl and CH₃Br to stratospheric ozone depletion will increase.

[4] Shorter-lived halogenated species contribute to concentrations of atmospheric halogen radicals which are involved in the chemistry of tropospheric odd nitrogen (NO_x) and odd hydrogen (HO_x) [Platt and Janssen, 1995; Penkett

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et al., 1985]. Our research focuses on ambient measurements of relatively short-lived alkyl halides. We report the first quantification of C₂H₅Cl (ethyl chloride), present new data on atmospheric C₂H₅Br (ethyl bromide), and expand the current data set for the methyl halides, CH₃Cl and CH₃Br.

[5] Sources and concentrations of atmospheric C₂H₅Cl and C₂H₅Br are not well known. Both are produced in industry for use as ethylating agents, refrigerants, and flame retardants. Additionally, C₂H₅Cl is used as a topical anesthetic and as a starter compound for the production of tetraethyl lead. Previously, C₂H₅Cl was claimed to be detected in Los Angeles air [Pelizzari *et al.*, 1976], but was not quantified. Small emissions of C₂H₅Cl have been observed from cows [Williams *et al.*, 1999a], and C₂H₅Br has been shown to be released from a species of phytoplankton, *Sargassum fuciales* [Class and Ballschmiter, 1988]. Carpenter *et al.* [1999] reported atmospheric concentrations of C₂H₅Br at Mace Head, Ireland ranging from 0.09 to 0.49 ppt and suggested a correlation between CH₃Br and C₂H₅Br emissions. Recent evidence has shown minor natural production of the ethyl and propyl halides from organic matter degradation [Keppler *et al.*, 2000].

[6] Once thought to arise only from natural sources, CH₃Cl has been shown to be released from human-caused biomass burning [Andreae *et al.*, 1996]. Significant natural sources observed have included the ocean [Moore *et al.*, 1996] and wood fungi [Wailing and Harper, 1998]. Also, potentially large natural emissions of CH₃Cl and CH₃Br have been explored recently from natural wetlands [Varner *et al.*, 1999], salt marshes [Rhew *et al.*, 2000] and rice [Redeker *et al.*, 2000]. Higher plants have been shown to produce atmospheric CH₃Cl and CH₃Br through a methyl-transferase reaction [Saini *et al.*, 1995] and CH₃Br through soil Br- conversion in live plants from the Brassicaceae family [Gan *et al.*, 1998]. These natural sources of CH₃Br are significant contributors to a global budget once thought to be dominated by anthropogenic sources such as biomass burning [Andreae *et al.*, 1996], fumigation [Yagi *et al.*, 1993, 1995; Butler and Rodriguez, 1996; Yates *et al.*, 1997; Williams *et al.*, 1999b], and gasoline combustion [Thomas *et al.*, 1997; Chen *et al.*, 1999; Baker *et al.*, 1998].

[7] A lower limit to global emissions of relatively stable atmospheric species may be estimated by measuring atmospheric concentrations and calculating sink intensities. However, the reaction with OH, albeit the major pathway for alkyl halide removal, is not the only significant sink of these compounds. Oceanic uptake [Moore *et al.*, 1996] is a sink for CH₃Cl although the net flux is from the ocean to the atmosphere. CH₃Br sinks include ocean uptake [Lobert *et al.*, 1995], soil [Shorter *et al.*, 1995], and plants [Jeffers *et al.*, 1998]. Estimated sinks have been used to calculate CH₃Cl and CH₃Br tropospheric lifetimes at 1.4 years [Khalil and Rasmussen, 1999] and 0.7 years [Yvon-Lewis and Butler, 1997] respectively. Global sources and sinks of CH₃Cl and CH₃Br still are not well characterized and quantified [Butler, 2000].

[8] The influence of the short-lived halogenated species on tropospheric chemistry remains to be determined because their impacts are likely to be localized rather than global. Photochemical degradation of these alkyl halides can release halogen radicals which then react with hydro-

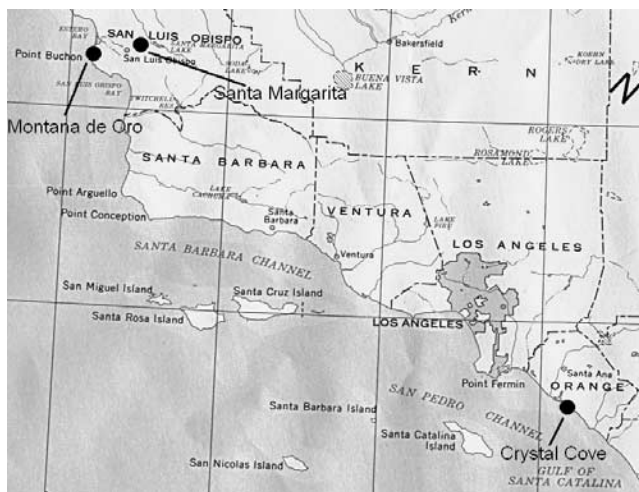


Figure 1. Locations (solid circles) of three California stationary sites chosen for measurements of CH₃Cl, CH₃Br, C₂H₅Cl, and C₂H₅Br in ambient air.

carbons, ozone [Platt and Janssen, 1995], and OH [Sekusak *et al.*, 1995]. The alkyl halide regional effects on tropospheric oxidation may be similar to the chemistry suggested with other shorter lived trace gases such as CH₃I and CHBr₃ [Davis *et al.*, 1996]. Also, shorter lived halocarbons and other trace gases can experience fast vertical transport depending on season and location of emissions [Olsen *et al.*, 2000], suggesting that alkyl halides could reach the stratosphere episodically in a time span shorter than their average tropospheric lifetime. Once in the stratosphere, they can photolyze and release chlorine and bromine radicals which would affect ozone chemistry. A recent suggestion [O'Dowd *et al.*, 2002] could implicate organic iodine compounds in the formation of marine clouds.

[9] Our goals are to quantify atmospheric amounts of C₂H₅Cl and C₂H₅Br in relatively clean air and to determine if these amounts correlate with concentrations of CH₃Cl and CH₃Br. We report data for each species from air samples taken from three stationary sites in California data and from multiple Pacific Ocean transects from 1996 through 1999. Regional alkyl halide concentrations will be reported for each of the California sites and cruise and will be compared to reported Northern Hemispheric clean air concentrations.

2. Sampling Locations and Methods

2.1. California Coastal Sites

[10] The three land-based sites (Figure 1) in California were Montaña de Oro (35°15'N and 120°53'W), Santa Margarita (35°22'N and 120°34'W), and Crystal Cove (33°36'N, and 117°54'W). Montaña de Oro is a remote coastal park with a dominant onshore breeze. Methane and CO (indicator for combustion) studies overlapping the dates of this study [Tyler *et al.*, 1999] show that small foothills parallel to the coastline protect the site from pollution from San Luis Obispo. A location 3 miles southeast of Santa Margarita was chosen to compare Montaña de Oro to a site 20 miles inland along the same latitude. Last, Crystal Cove State Park was chosen to compare Montaña de Oro to a coastal site at a different latitude. Ambient air measurements

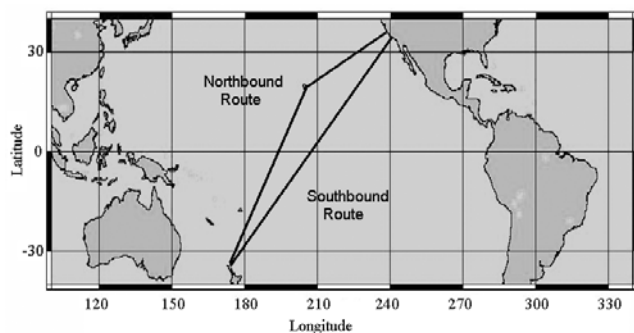


Figure 2. Pacific Ocean transects for sampling alkyl halides. Seven southbound trips and one northbound trip were done between June 1996 and November 1999. The transects covered from 35°N to 35°S within 21 days.

were done from Montaña de Oro and Santa Margarita since June 1996 and from Crystal Cove from March 1998 through December 1999. One to three times monthly, samples were collected in the middle-to-late afternoon when the prevailing winds were the strongest and consistently blowing from the west and northwest [Tyler *et al.*, 1999; California Energy Commission, 1985]. We present our methyl halide data from June 1996 through December 1999, C₂H₅Cl data from January 1998 through December 1999, and C₂H₅Br data from September 1996 through December 1999. Each measurement at the onshore California sites consisted of simultaneous ambient air collection by preevacuated, electropolished, 2-L stainless steel canisters (M. G. Weldtek, Inc.). The canisters (typically four) simultaneously were filled up to 40 psi through a custom manifold that accommodated from two to eight canisters. A full discussion of the sampling methodology can be found elsewhere [Low, 2001].

[11] Surface wind direction and speed were measured at the times of air sampling. The winds at Montaña de Oro were always from the northwest, consistent with surface winds observed by Tyler *et al.* [1999]. Surface winds from both Santa Margarita and Crystal Cove were from the west and northwest but were more variable than winds observed from Montaña de Oro. In the summers of 1998 and 1999, the winds at Santa Margarita and Crystal Cove came from the east in 10% of the measurements. Wind speeds at the three sites were typically between 3 and 10 km hr⁻¹, but winds at Montaña de Oro sometimes reached up to 23 km hr⁻¹.

2.2. Pacific Ocean Transect

[12] Eight Pacific Ocean transects (Figure 2) were done aboard freighter ships (Blue Star Services) on a direct southbound route from Los Angeles, California to Auckland, New Zealand except for one northbound transect that went from Auckland, New Zealand then to San Francisco, California after a stopover in Hawaii. The route overlaps with earlier investigations [Moore *et al.*, 1996; Groszko and Moore, 1998] in the equatorial Pacific Ocean but was usually about 7° north of their measurements in Southern Hemisphere and 7° south of their Northern Hemispheric measurements. Studies were done in the northern hemispheric summer (June 1997, July 1998 and June 2000),

autumn (November 1997, 1998, and 1999), spring (April 1999) and in a transition period between summer and fall (September 1998). The September 1998 study, following a slightly different route (Figure 2), was the only northbound trip, immediately preceding the November 1998 southbound study.

[13] Sampling lines composed of 5/8" Dekobon tubing (Furon) were located on both starboard and port sides up on the ship bridge extending ~100 feet above the water and were thoroughly flushed before sampling with a compressor (Rix). The sampling line was oriented to collect air on the windward side of the ship. After flushing the line, samples were pressurized either with a DC pump (KNF Neuberger) or an AC bellows pump (Metal Bellows) into 6L, 2L (Weldtek, Inc.) or 3L (Mereter) stainless steel, electropolished canisters. From 10 to 30 samples were collected each trip at a spatial resolution of either 2.5° or 5° latitude. Occasional replicate samples were taken to check variability. Results from samples taken near simultaneously at the front, back and through the bridge sampling line were within 5% of each other.

3. Analysis Methodology

[14] Samples were analyzed by gas chromatography/mass spectrometry (GC/MS) at the University of California, Irvine, normally within five days of collection for the stationary sites and within 1 month for the Pacific Ocean samples. For analysis, canisters were attached to a stainless steel vacuum line of a determined volume (341.8 mL at 22°). Known amounts of sample were preconcentrated into a 1/8" stainless steel injection loop packed with glass beads (2 mm) cooled to liquid nitrogen temperatures (77°K). Samples were then thermally desorbed (90°C) for one minute and then injected onto a Poraplot-Q column (25 m × 0.53 mm, Chrompack) with an oven cycle of 45°C for 2 min with a subsequent steady increase of 10°C per minute to 170°C. The column was baked out between samples for at least 10 min at 200°C. Selective ion monitoring detection of two natural stable isotopes for each alkyl halide (m/z = 50 and 52 for CH₃Cl, m/z = 94 and 96 for CH₃Br, m/z = 64 and 66 for C₂H₅Cl, and m/z = 108 and 110 for C₂H₅Br) eluting from the column was accomplished by an Automass Model 150 (UNICAM) MS in the electron impact (EI) mode at 70 eV. A combination of retention times, mass to charge ratios (m/z), and correct isotope signal ratios (3.06:1 for ³⁵Cl and ³⁷Cl, 1.02:1 for ⁷⁹Br and ⁸¹Br) identified the peaks.

[15] Tests for storage were conducted to ensure the integrity of the air in canisters from the time of collection to the time of analysis. Evacuated canisters were filled with ultra high purity helium and showed no detectable growth of the methyl and ethyl halides after 11 days. Additional tests for storage stability compared the concentration of an ambient air sample analyzed the day after collection and again several days to two weeks later. Tests were repeated several times and the results showed that the halogenated gases of this study at typical ambient levels were usually within 7% for CH₃Cl, 5% for CH₃Br, 10% for C₂H₅Cl and 15% for C₂H₅Br which is similar to the canister precision (Table 1). The large deviation percentages for C₂H₅Cl and C₂H₅Br are mainly due to the sub-ppt level concentrations, just above the detection limits, observed at ambient level.

Table 1. Detection Limits, the Storage Reproducibility, and the Canister Variability are Shown^a

	CH ₃ Cl	CH ₃ Br	C ₂ H ₅ Cl	C ₂ H ₅ Br
Detection Limit, ^b ppt	1.5	1.2	0.7	0.2
Storage Stability, %	7	5	10 ^c	15
Unpressurized Canister Variability, ^d %	5	5	15	20
Pressurized Canister Variability, ^e %	4	3	7	10

^aStorage stability was calculated on the basis of analyzing a known quantity of ambient air sample at the time of sampling and analyzing the same sample up to a week later. Canister variability was determined by same day analysis of air collected from connected canisters in parallel to the same inlet.

^bObtained by processing 3000 std cc of sample.

^cAfter storage issues were resolved.

^dApplicable to measurements before 1998.

^eApplicable to measurements after 1998.

[16] The detection limits (Table 1), defined as the lowest concentration of analyte with a 2:1 ratio of signal to noise, of CH₃Cl, CH₃Br, and C₂H₅Cl were well below atmospheric concentrations. However, atmospheric concentrations approach the detection limit for C₂H₅Br. The reproducibility of the instrument for analyzing a sample in replicate was better than ±1% for the methyl halides and ±3% for the ethyl halides.

[17] Calibration curves were constructed by analyzing varied absolute amounts of gravimetrically prepared primary standards (39.7 ppb CH₃Cl and 1.0 ppb CH₃Br in N₂ by the National Institute of Standards and Technology (NIST) and 8.8 ppb CH₃Br, 4.4 ppb C₂H₅Cl, and 4.14 ppb C₂H₅Br in air from Scott Specialty Gases. NIST and the Scott Specialty gas standards were checked against each other using CH₃Br to ensure their integrity. The NIST standard had a quoted accuracy of 1% for CH₃Cl and 3% for CH₃Br, whereas the Scott Specialty Gas quoted accuracy of 20% for its standard; thus the NIST standard was used as our primary standard. Calibrations were done the same day the samples were run. Because the mixing ratios of the standards were higher than the sampled air, proportionally smaller amounts (~0.2 to 40 standard ml) of standard were injected to cover the mass range of the samples so that extrapolation of the calibration curve was not essential. That is, the absolute amount of analyte injected from the standard gas spanned the range of absolute amounts in the sample. Linearity (R² > 0.99) was seen for the observed concentration ranges of all species.

4. Results and Discussion

4.1. Ethyl Chloride

[18] Most C₂H₅Cl concentrations (Figures 3a–3c) range between 3 to 7 ppt at the three California Coastal sites. Enhanced C₂H₅Cl concentrations of greater than 10 ppt were seen at Montaña de Oro and Santa Margarita in October of 1998 and also at Crystal Cove in the spring and early summer of 1998 and 1999. The C₂H₅Cl distribution (Figure 4a) shows that the majority of the observations at the sites fall in the 2.5 to 4.9 ppt range with very few observations greater than 12.5 ppt. The C₂H₅Cl mean mixing ratio observed at Crystal Cove was more than 25% higher than those observed at Montaña de Oro and Santa Margarita and was more variable (Table 2). This enhancement, while not strong statistically, may be due to the urban influence of Los Angeles.

[19] A lack of seasonal variation of C₂H₅Cl can be seen in the monthly averages of the raw data (Figure 5). Apart from local sources and sinks, seasonal cycles should be complementary to an OH derived sink. The fluctuations of C₂H₅Cl and other alkyl halide concentrations should be opposite the fluctuations of OH concentrations, which reach a maximum in the summer and a minimum in the winter [Carslaw *et al.*, 1999]. The monthly average C₂H₅Cl concentrations (Figure 5) for the three sites fluctuated around 3.5 ppt with a seasonal pattern that was smaller than the variability of the data.

[20] Similar to other short-lived anthropogenic compounds such as CH₃Br, CHCl₃, C₂HCl₃ and C₂Cl₄ [Koppman *et al.*, 1993; Atlas *et al.*, 1993], mean C₂H₅Cl concentrations observed over the Pacific Ocean were higher in the Northern Hemisphere (3.0 ppt) than the Southern Hemisphere (2.2 ppt). When calculating the hemispheric average concentrations of the oceanic data, the data points were weighted by the cosine of the latitude to account for the total atmospheric mass at each latitude. Concentrations greater than 10 ppt were observed in both Northern and Southern Hemispheres in July 1998 and April 1999 with no correlation to the other alkyl halides studied (Figure 6). There were enhanced concentrations in northern points of the November 1998 cruise but were most likely influenced from the Port of Los Angeles. All C₂H₅Cl results from samples collected on the June 1997 and November 1997 transects were removed from the data set because its storage was unreliable in the 6 L canisters. The average Northern Hemisphere to Southern Hemisphere ratio was 1.4 ± 0.3, while the difference of gradients between Northern and Southern midlatitudes was 3.8. Median C₂H₅Cl concentrations decreased steadily as a function of latitude (Figure 7a). Although there was little difference of the June/July and November medians in the Northern Hemisphere to each other and the total median, the June/July medians were about 1.4 ppt higher than the November median below the ITCZ, the Intertropical Convergence Zone (5 to 10°N). The November median was well constrained to the total data median. This could reflect the OH seasonality in the Southern Hemisphere in which more OH would be present in November. The histogram analysis of the C₂H₅Cl data (Figure 8a) showed an overwhelming difference in concentration distributions between the hemispheres. In the Southern Hemisphere, 73% of the C₂H₅Cl were below 2.5 ppt and frequencies sharply drop in the higher concentration ranges. The majority of the Northern Hemispheric C₂H₅Cl was between 2.5 and 5 ppt which was consistent with C₂H₅Cl reported at the three stationary California sites.

4.2. Ethyl Bromide

[21] Nearly 35% of the C₂H₅Br stationary site measurements were below the detection limit of the GC/MS, but when detected, the data (Figures 3d–3f) concentrated near 0.3 ppt which are similar to the values reported by Carpenter *et al.* [1999]. At Crystal Cove, two measurements in early June 1999 were 1.8 and 3.0 ppt in the atmosphere, much higher than any other observed concentration. Those two measurements provide a contrast to the other 16 measurements taken from May through October, which were below the detection limit.

[22] The C₂H₅Br frequency distribution (Figure 4b) was dominated by the <0.25 ppt range and diminishes in the

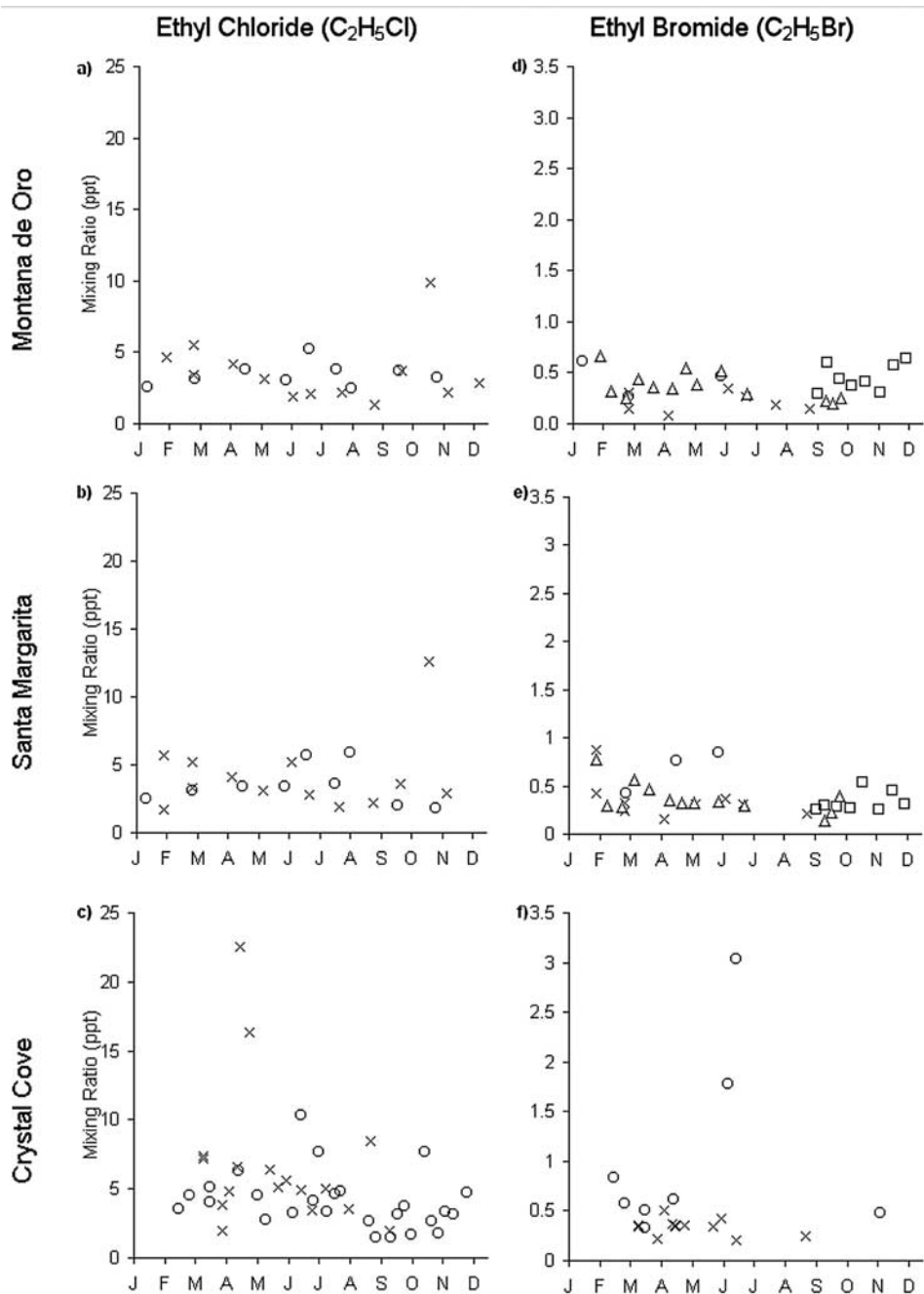


Figure 3. Time series of each alkyl halide at the California stationary sites Montana de Oro (unpolluted coastal), Santa Margarita (unpolluted continental), and Crystal Cove (polluted coastal). The data points represent the averages of four replicate samples for each sampling date, and the symbols denote different years that the samples were collected.

>1 ppt range for the three sites. The <0.25 ppt category includes samples for which C₂H₅Br was below our detection limit. The high variability seen in these regional measurements exceeded any seasonal cycle.

[23] In the Pacific Ocean transects, the C₂H₅Br measurements were highly variable across all latitudes (Figure 6b) and ranged from 5.5 ppt to below our detection limit (0.2 ppt). About 30% of the C₂H₅Br data points were below our detection limit, most of which were in the Southern

Hemisphere. Northern Hemispheric measurements agree with previous measurements at Mace Head, Ireland [Carpenter *et al.*, 1999], in the lower troposphere as part of the THESEO (Third European Stratospheric Experiment on Ozone) campaign [Pfeilsticker *et al.*, 2000], at the three stationary sites cited in this paper, and at urban locations in California (J. C. Low *et al.*, Urban measurements of atmospheric alkyl halides in Los Angeles, California, submitted to *Journal of Geophysical Research*, 2003). Observ-

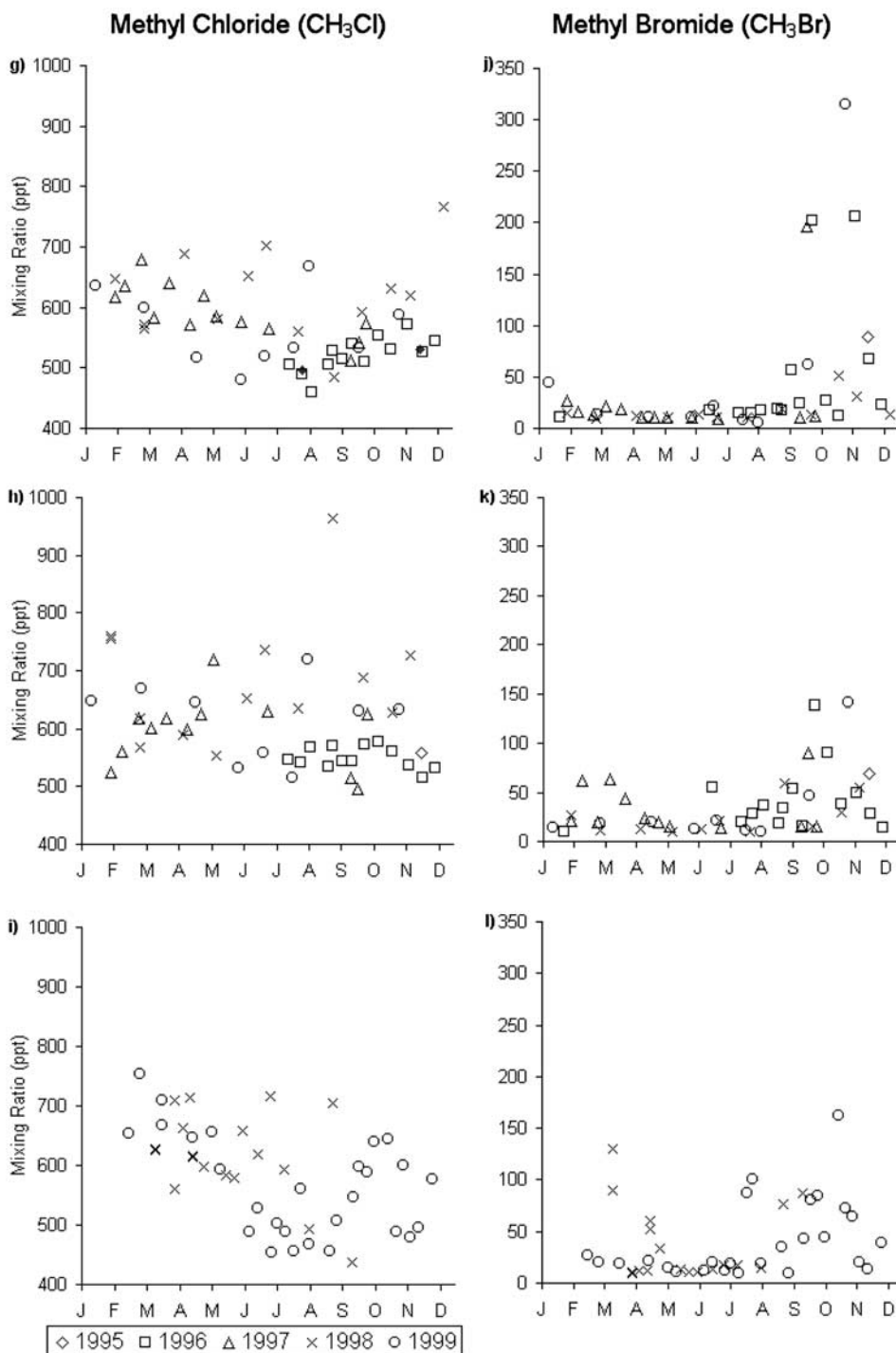


Figure 3. (continued)

able median Northern Hemispheric midlatitude C₂H₅Br values (Figure 7b) were ~0.3 ppt but steadily drop below our detection limit south of the ITCZ. Measurable values were too limited and variable to form reasonable conclusions from the seasonal medians. Almost 65% of oceanic C₂H₅Br observations in the Northern Hemisphere were below 0.25 ppt and the frequency declined steadily to 1 ppt (Figure 8b). This agrees well with distributions observed in California (Figure 4b) but is different from

the oceanic Southern Hemispheric distribution which had over 85% C₂H₅Br below 0.25 ppt.

4.3. Methyl Chloride

[24] CH₃Cl concentrations (Figures 3g–3i) at all three stationary sites fluctuate in the range of 450 to 700 ppt with a few exceptions. The average mixing ratio was 583 ppt, which is similar to middle Northern Hemispheric observations reported at 597 ppt by *Khalil and Rasmussen* [1999]

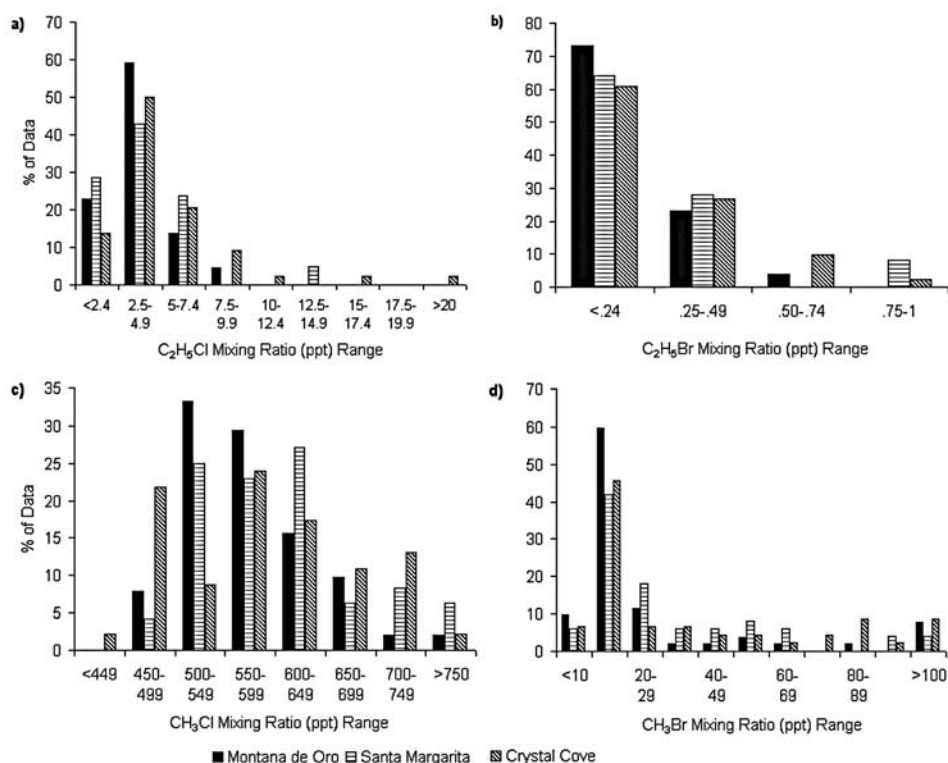


Figure 4. Histogram analysis for percentage observed of the total measurements versus mixing ratio ranges for Montana de Oro, Santa Margarita, and Crystal Cove between 1996 and 2000. The histogram analysis shows CH₃Cl, CH₃Br, C₂H₅Cl, and C₂H₅Br mixing ratios divided into 50, 10, 2.5, and 0.25 ppt bins, respectively, for each site.

and similar to other reported background concentrations for clean air [Yokouchi *et al.*, 2000a, Khalil *et al.*, 1999; Moore *et al.*, 1996]. An isolated high anomaly to the CH₃Cl observations was 965 ppt in August 1998, at Santa Margarita. We note that a value of 945 ppt was reported by Atlas *et al.* [1993] from a marine atmospheric sample. No corresponding spike in CH₃Cl was observed at Montaña de Oro but the winds were from the southwest during this time. This suggests that this particular CH₃Cl plume could have been due to a local source either just inland of the bluffs (coastal shrub) or the surrounding foothills (mostly grasslands). There were no visible biomass burning or chemical signatures (e.g., largely enhanced CH₃Br or CO) which yielded other information regarding this CH₃Cl plume.

[25] The CH₃Cl concentrations observed at each stationary site varied over a wide range. Data was plotted versus the frequency measured (Figure 4c). The distribution for

CH₃Cl concentration varied between the three sites although the mean concentrations were within 10% of each other (Table 2). The distribution observed at Montaña de Oro was dominated by two bins in the 500–600 ppt range whereas the majority of the Santa Margarita and Crystal Cove distributions gave a wider range of values from 500 to 650 ppt and 450 through 750 ppt, respectively.

[26] Concentrations of CH₃Cl range from 450 to 850 ppt (Figure 6c) over the Pacific Ocean with averages of 598 ± 81 ppt in the Northern Hemisphere and 589 ± 109 ppt in the Southern Hemisphere. The CH₃Cl difference between the hemispheres was not significant. Previous studies [Moore *et al.*, 1996; Koppman *et al.*, 1993] also showed that the hemispheric difference is not significant but did show CH₃Cl averages slightly higher in the Southern Hemisphere. Also, our values were similar to those reported by Yokouchi *et al.* [2000a] and Moore *et al.* [1996]. In the majority of the cruises, CH₃Cl concentrations decreased going away from

Table 2. Alkyl Halide Median Values Calculated From Measured Values for Montana de Oro, Santa Margarita, and Crystal Cove and Their Annual Variation (1 σ) Compared to the Median Concentrations Observed in the Northern and Southern Hemispheres Over the Pacific Ocean Transects

Location	Mixing Ratio Medians, ppt \pm 1 σ			
	CH ₃ Cl	CH ₃ Br	C ₂ H ₅ Cl	C ₂ H ₅ Br
Montana de Oro (1995–1999)	585 \pm 62	13.1 \pm 59.3	3.3 \pm 1.8	0.3 \pm 0.2
Santa Margarita (1995–1999)	626 \pm 92	19.2 \pm 28.0	3.2 \pm 2.4	0.3 \pm 0.2
Crystal Cove (1998–1999)	595 \pm 86	19.9 \pm 37.8	4.6 \pm 3.8	0.4 \pm 0.7
Pacific Ocean: Northern Hemisphere (1996–1999)	594 \pm 81	10.4 \pm 2.0	2.6 \pm 1.9	0.3 \pm 0.1
Pacific Ocean: Southern Hemisphere (1996–1999)	593 \pm 109	9.4 \pm 1.4	1.6 \pm 2.0	N.D.

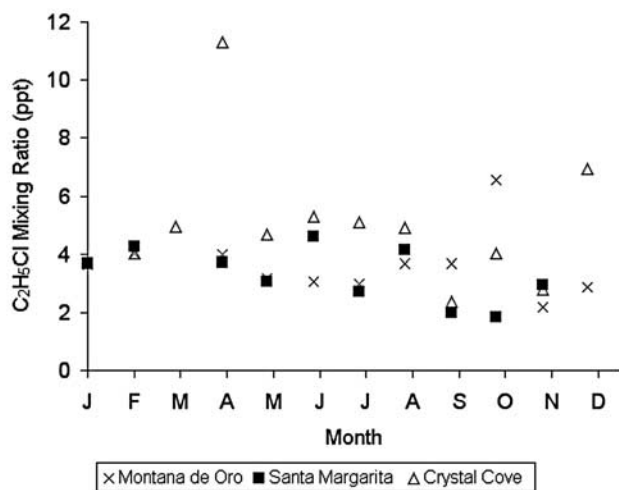


Figure 5. Monthly average of C₂H₅Cl mixing ratios of the three California stationary sites. A seasonal cycle is not evident.

the northeast coastal Pacific until reaching a local minimum at 20°N when they increased approaching the ITCZ. Going southward from the ITCZ, CH₃Cl concentrations decreased until near 20°S where the concentrations increase at a local maximum. This relative pattern was similar between trips (although absolute concentrations vary) and was also observed in the CH₃Cl median distribution (Figure 7c). This provides further evidence of tropical CH₃Cl sources as previously suggested [Yokouchi *et al.*, 2000a; Khalil and Rasmussen, 1999]. Enhanced CH₃Cl was observed off the coastal waters west of North America in November but not in June (Figure 7c). Histogram CH₃Cl distributions separated into 50 ppt bins (Figure 8c) show a Gaussian distribution approximately for both hemispheres with a lower peak in the Southern Hemisphere.

4.4. Methyl Bromide

[27] Observed CH₃Br concentrations (Figures 3j–3l) for the coastal sites have similar patterns over the year. Most concentrations ranged from 13 to 18 ppt, but high perturbations were observed at all sites. At Montaña de Oro, concentrations peaked consistently each year from September through November. The maximum observed concentration was 315 ppt in October 1999. No other alkyl halide

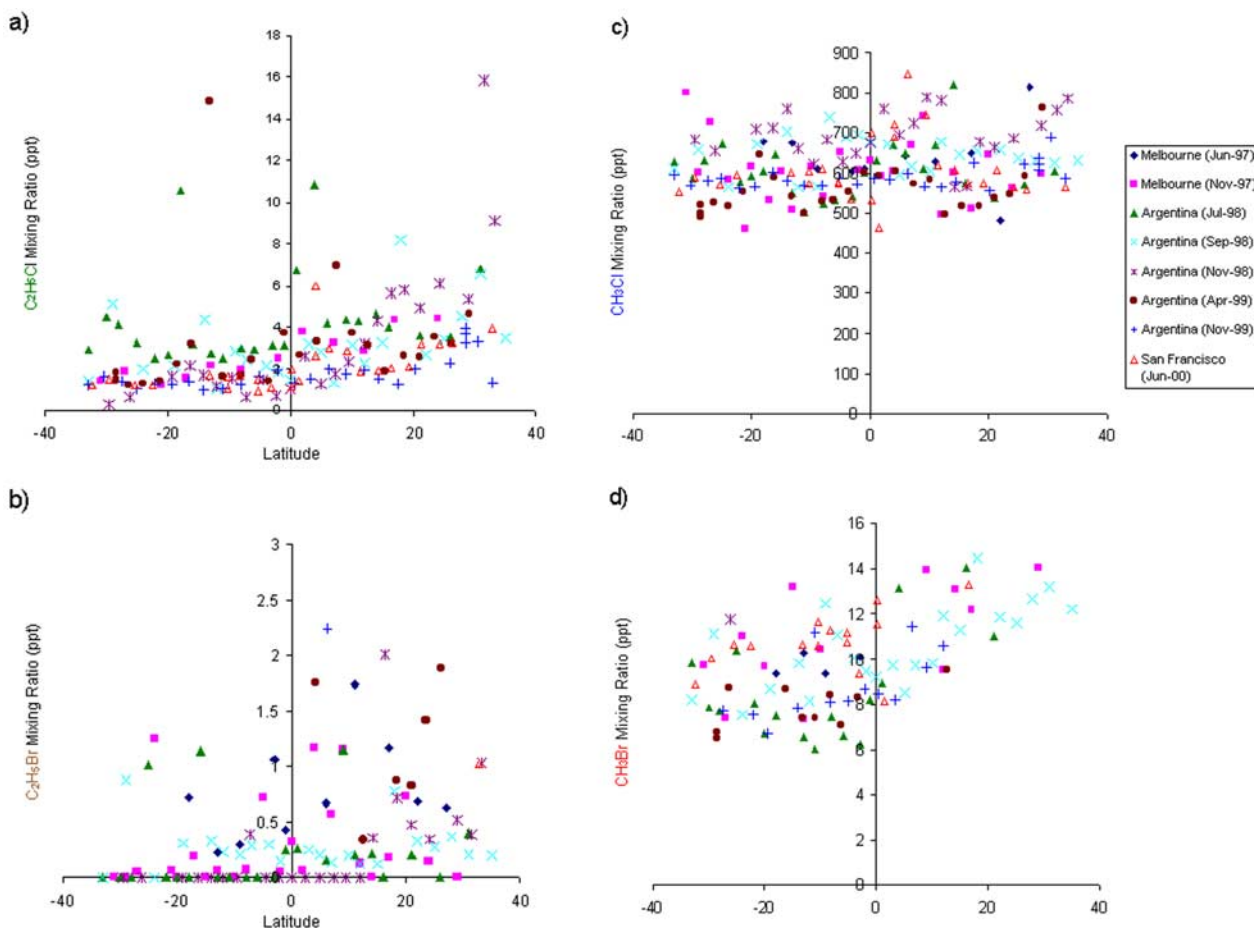


Figure 6. Latitudinal distributions of all data points over the Pacific Ocean for (a) C₂H₅Cl, (b) C₂H₅Br (c) CH₃Cl, and (d) background CH₃Br. Background CH₃Br included all CH₃Br data points that were within 2 standard deviations of the uncontaminated September 1998 cruise.

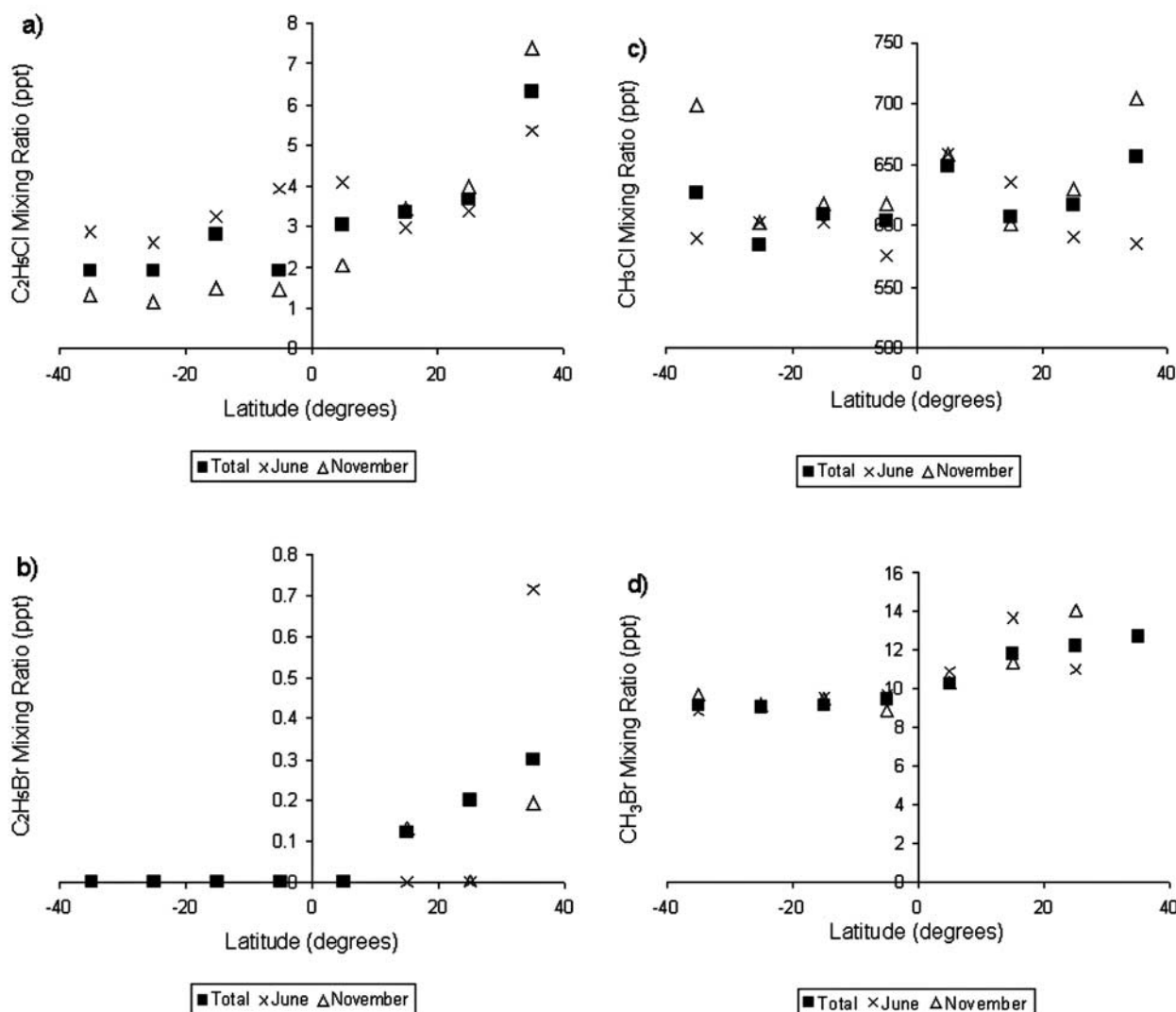


Figure 7. Latitudinal distribution of total, June/July and November medians of (a) C₂H₅Cl, (b) C₂H₅Br (c) CH₃Cl, and (d) CH₃Br calculated from dividing the cruise data into 10° latitudinal bins.

species were observed to have a significant increase during these periods of enhanced concentrations. High CH₃Br concentrations during this time period were also seen at Santa Margarita but were not as high as observed at Montaña de Oro. This indicated a possible coastal source from coastal upwelling or phytoplankton [Scarratt and Moore, 1998] because the surface wind directions consistently showed onshore breeze from the west and northwest at both sites during late fall. In Santa Margarita with its prominent agricultural community, CH₃Br fumigations possibly influenced the results, especially during the fall. Around 75% of the CH₃Br fumigation occurs during the months of August through November according to California studies in 1995 [Environmental Working Group, 1998]. Fumigation enhancement would be less likely, although still possible with certain meteorology, at Montaña de Oro. At Santa Margarita, significant CH₃Br enhancements (~50 ppt) were observed from February through April in 1997. Measurements at Crystal Cove showed CH₃Br concentrations up to 150 ppt in March and May of 1998 and

during autumn of 1998 and 1999, similar timing to the enhanced CH₃Br concentrations observed at the Montaña de Oro and Santa Margarita sites.

[28] High concentrations of CH₃Br were seen at Crystal Cove when the wind was blowing from the south and southeast but were also observed even with a dominant onshore breeze. Air from Crystal Cove analyzed by a reduction gas analyzer (RGD2, Trace Analytical) revealed high carbon monoxide concentrations (>300 ppb) in some samples. This suggests that Crystal Cove has an occasional urban influence that could contribute anthropogenic CH₃Br, C₂H₅Cl, and C₂H₅Br, which would elevate their atmospheric concentrations. Meteorology studies [Lu et al., 1997] indicate the Pacific High affects the Southern California basin. The high pressure can create offshore rather than onshore flow which transport air from LA county and other urban areas to the coast. Thus, in these conditions, air observed from Crystal Cove could have recirculated from the nearby coastal urban regions causing the enhanced urban signature in the measurements.

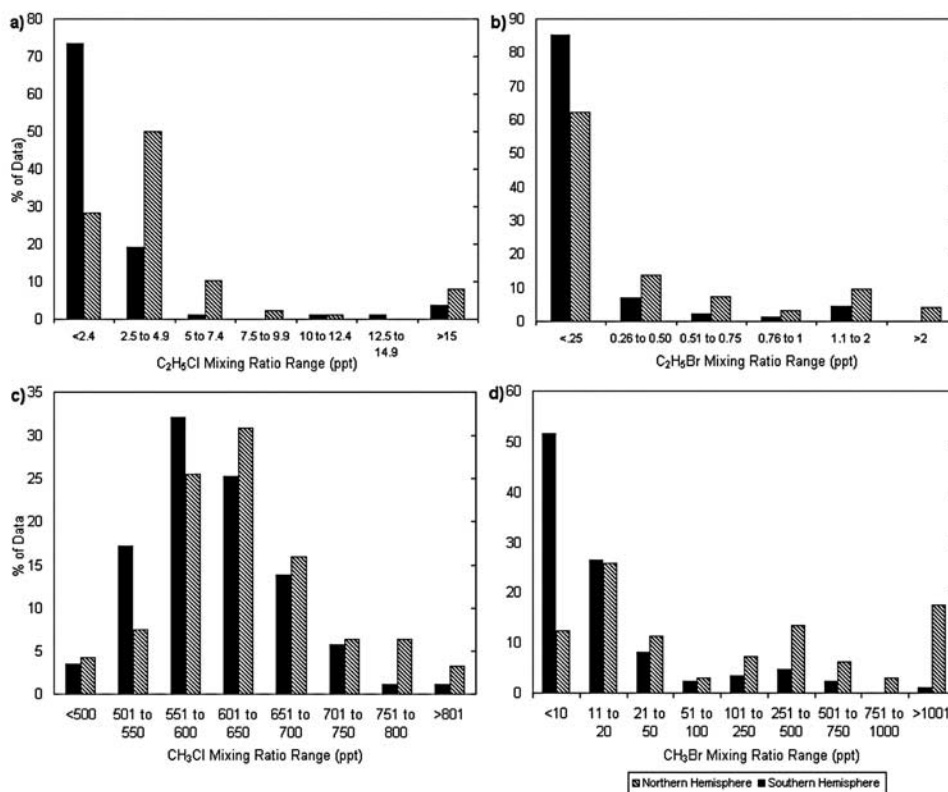


Figure 8. Histogram analysis for percentage observed of the total measurements versus mixing ratio ranges for the data points obtained in the Southern Hemisphere and the Northern Hemisphere on the Pacific Ocean transects between 1996 and 2000.

[29] Over half of the CH₃Br concentrations observed for Montaña de Oro ranged between 10 to 19 ppt, characteristic of northern hemispheric background concentrations. Although the highest frequencies of concentrations observed were within the 10 to 19 ppt range for Santa Margarita and Crystal Cove, this range of values was less than 50%. For each of these sites, observations in the higher concentration ranges were more common than for Montaña de Oro.

[30] This was comparable to other reported concentrations ranging from 11 to 14 ppt for the Northern Hemisphere [Yokouchi *et al.*, 2000b; Carpenter *et al.*, 1999; Butler and Rodriguez, 1996]. Thus California coastal air may have a regional CH₃Br enhancement.

[31] Over the Pacific Ocean, the latitudinal background CH₃Br medians were 10.4 ± 2 (Northern Hemisphere) and 9.4 ± 1.4 ppt (Southern Hemisphere). They were consistent between the eight cruises (Figure 6d) and with previous studies [Yokouchi *et al.*, 2000b; Groszko and Moore, 1998; Lobert *et al.*, 1995]. For the purposes of determining background CH₃Br concentrations, many data points were not included into our calculation. Most of these excluded data points had greater than 50 ppt CH₃Br and were located in the Northern Hemisphere out of the Port of Los Angeles, California. We believe that these high data points were from fumigation contamination from the commercial cargo. Another set of high CH₃Br concentrations (>100 ppt) appeared in the Southern Hemisphere, near the Fiji islands where the ship typically docked, but

where no container fumigation occurred. These CH₃Br enhancements are most likely influenced from heavy structural fumigations in Fiji. The clearest latitudinal profile is the September 1998 study in which no CH₃Br fumigation was done to the cargo en route from New Zealand to North America. Analysis of CH₃Br on a similar October 2002 cruise had hemispheric averages within 5% of the September 1998 cruise and also had a profile that was not indicative of fumigation contamination. Thus we determined background CH₃Br points by only including data within 30% deviation of the September 1998 data. This corresponded to 2 standard deviations to the September 1998 data and exceeds instrumental, seasonal, and natural variation.

[32] There was little seasonal variation between the June/July and November background CH₃Br data but a gradient clearly was observed between the Northern Hemisphere and Southern Hemisphere (Figure 7d). The June/July and November background interhemispheric ratios were both 1.2. Wingenter *et al.* [1998] showed that the CH₃Br interhemispheric ratio demonstrates seasonality and predicts both July and November ratios to be ~ 1.15 , which is between the March/April maximum (1.3–1.4) and September minimum (1.1). However, the background interhemispheric ratio for our April 1999 data was 1.2. A histogram analysis of the CH₃Br data (Figure 8d) showed a trimodal distribution of the total data from both hemispheres in which most of the uncontaminated data reside in the first mode (0 to 50 ppt). The other modes were indicative of

contamination from fumigated cargo in the Northern Hemisphere best indicated by the November 1998 cruise where there was a persistent enhancement of CH₃Br that declined sharply with distance (time) away from the port.

4.5. Other Observations

[33] Correlations between concentrations of methyl halides to ethyl halides are useful for establishing similar sources and/or sinks. *Kepler et al.* [2000] reported the correlated emissions of methyl, ethyl, and propyl halides coming from emissions from oxidative biodegradation processes and *Carpenter et al.* [1999] observed an occasional correlation between CH₃Br and C₂H₅Br at a coastal site in Mace Head, Ireland. However, analyzing correlations between atmospheric concentrations of CH₃Cl with CH₃Br, CH₃Cl with C₂H₅Cl, CH₃Br with C₂H₅Br and C₂H₅Cl with C₂H₅Br showed correlation coefficients that were unconvincing to extrapolate similar sources in the stationary California site data and the Pacific Ocean transect data. Also, correlations were poor between the alkyl halides and environmental conditions such as temperature and relative humidity.

5. Conclusion

[34] The first quantification of atmospheric C₂H₅Cl has been presented along with further observations of CH₃Cl, CH₃Br and C₂H₅Br. The observed median ambient CH₃Cl, CH₃Br, C₂H₅Cl and C₂H₅Br mixing ratios averaged over the three California sites were 602 ± 21, 17.4 ± 3.7, 3.7 ± 0.8, and <0.3 ± 0.1 ppt. Higher variability was seen with the CH₃Br, C₂H₅Cl, and C₂H₅Br data from Crystal Cove than the other sites. This possibly provides further evidence of urban source emissions of CH₃Br and new evidence of significant sources of the ethyl halides in polluted air as indicated by high CO concentrations.

[35] Measurements have characterized CH₃Cl, CH₃Br, C₂H₅Cl, C₂H₅Br across the Pacific Ocean from June 1997 to June 2000 with area-weighted medians of 594, 10.4, 2.6, and 0.3 ppt for the Northern Hemisphere and 593, 9.4, 1.6, and <0.2 ppt for the Southern Hemisphere. The CH₃Cl and C₂H₅Br Northern Hemispheric medians over the Pacific Ocean were similar to their respective median mixing ratios in California. However, the CH₃Br and C₂H₅Cl medians over the ocean were lower than their respective coastal California mixing ratios (Table 2). Enhanced CH₃Cl concentrations were observed near the ITCZ that did not appear to be a function of seasonality. Well-defined, repeatable gradients were observed for CH₃Cl, CH₃Br, C₂H₅Cl and C₂H₅Br and CO to which the concentration ratios between Northern and Southern Hemispheres were 1.0, 1.1, 1.6, not determinable, and 1.4 respectively. This is consistent with the fact that Northern Hemisphere produces more anthropogenic emissions. The interhemispheric ratios were consistent with other short-lived halocarbons [*Koppmann et al.*, 1993; *Wingenter et al.*, 1998]. Since natural emissions of these compounds are few, the gradient most likely is from uneven distribution of sources. However, localized enhancements of C₂H₅Cl in the Southern Hemisphere could indicate an unidentified source.

[36] The Pacific Ocean median concentrations for the methyl halides corresponded well with accepted back-

ground values of oceanic air. Thus the data suggest that our reported ethyl halide oceanic concentrations also are representative of background concentrations. Rates for reactions with OH radicals [*Kasner et al.*, 1990; *Hsu and DeMore*, 1995] at an average OH radical tropospheric concentration, 9.7×10^5 radicals cm⁻³ [*Prinn et al.*, 1995], would imply (lower limit) a C₂H₅Cl atmospheric lifetime of 24 days. A rate constant for the reaction of C₂H₅Br with OH was determined to be 2.25×10^{-13} cm³ molecule⁻¹ s⁻¹ by using a structure-activity relationship estimate [*Kwok and Atkinson*, 1995; *Atkinson*, 1987]. This suggests that the C₂H₅Br lifetime against OH would be 41 days. Very short-lived halogenated compounds are not equally distributed vertically. *Pfeilsticker et al.* [2000] reported vertical profiles for many trace organic bromine compounds, including C₂H₅Br, which decrease an order of magnitude in concentration from 9 km to 16 km. It is reasonable to hypothesize that C₂H₅Cl and C₂H₅Br behave similarly which would yield a latitudinal (30°N to 30°S) and altitudinal (0 to 16 km) global burden of 10.8 ± 2.4 Gg C₂H₅Cl and an upper limit of 1.4 ± 0.4 Gg C₂H₅Br.

[37] The short lifetimes and small global burden of C₂H₅Cl and C₂H₅Br suggest that these compounds will not play a dominant role in the global tropospheric halide budget. However, they can contribute as much chlorine and bromine as HCFCs and other halogenated organic compounds measured [*Schauffler et al.*, 1993, 1999]. Because most significant sources of ethyl halides are industrial, local and regional impacts as well as stratospheric effects are plausible if these urban emissions are high.

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