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Coastal water source of short-lived halocarbons in New England

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[1] Short-lived halocarbon tracers were used to investigate marine influences on air quality in a coastal region of New England. Atmospheric measurements made at the University of New Hampshire's Observing Station at Thompson Farm (TF) in Durham, New Hampshire, indicate that relatively large amounts of halocarbons are emitted from local estuarine and coastal oceanic regions. Bromine-containing halocarbons of interest in this work include bromoform (CHBr_3) and dibromomethane (CH_2Br_2). The mean mixing ratios of CHBr_3 and CH_2Br_2 from 11 January to 5 March 2002 were 2.6 pptv and 1.6 pptv, and from 1 June to 31 August 2002 mean mixing ratios were 5.9 pptv and 1.4 pptv, respectively. The mean mixing ratio of CHBr_3 was not only highest during summer, but both CHBr_3 and CH_2Br_2 exhibited large variability in their atmospheric mixing ratios during this season. We attribute the greater variability to increased production combined with faster atmospheric removal rates. Other seasonal characteristics of CHBr_3 and CH_2Br_2 in the atmosphere, as well as the impact of local meteorology on their distributions at this coastal site, are discussed. Tetrachloroethene (C_2Cl_4) and trichloroethene (C_2HCl_3) were used to identify time periods influenced by urban emissions. Additionally, measurements of CHBr_3 , CH_2Br_2 , C_2Cl_4 , methyl iodide (CH_3I), and ethyl iodide ($\text{C}_2\text{H}_5\text{I}$) were made at TF and five sites throughout the nearby Great Bay estuarine area between 18 and 19 August 2003. These measurements were used to elucidate the effect of the tidal cycle on the distributions of these gases. The mean mixing ratios of CHBr_3 , CH_2Br_2 , CH_3I , and $\text{C}_2\text{H}_5\text{I}$ were $\sim 82\%$, 46% , 14% , and 17% higher, respectively, near the coast compared to inland sites, providing evidence for a marine source of short-lived halocarbons at TF. Correlation between the tidal cycle and atmospheric concentrations of marine tracers on the night of 18 August 2003 showed that the highest values for the brominated species occurred ~ 2 – 3 hours after high tide. Emission fluxes of CHBr_3 , CH_2Br_2 , CH_3I , and $\text{C}_2\text{H}_5\text{I}$ on this night were estimated to be 26 ± 57 , 4.7 ± 5.4 , 5.9 ± 4.6 , and $0.065 \pm 0.20 \text{ nmol m}^{-2} \text{ h}^{-1}$, respectively. Finally, the anthropogenic source strength of CHBr_3 was calculated to determine its impact on atmospheric levels observed in this region. Although our results indicate that anthropogenic contributions could potentially range from 15 to 60% of the total dissolved CHBr_3 in the Great Bay, based on the observed ratio of $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ and surface seawater measurements in the Gulf of Maine, it appears unlikely that anthropogenic activities are a significant source of CHBr_3 in the region.

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1. Introduction

[2] Halocarbons have anthropogenic and natural sources with atmospheric lifetimes varying from days to centuries.

The short-lived halocarbons bromoform (CHBr_3), dibromomethane (CH_2Br_2), methyl iodide (CH_3I) and ethyl iodide ($\text{C}_2\text{H}_5\text{I}$) have been shown to be sources of the halogen oxide radicals BrO and IO to the atmosphere. These radicals influence tropospheric oxidation processes in both polar [Barrie *et al.*, 1988; Bottenheim *et al.*, 2002] and temperate

regions [Allan *et al.*, 2000; Carpenter and Liss, 2000]. Under strong convective conditions, which are predominant in the tropics, even relatively short-lived gases such as CHBr_3 and CH_2Br_2 can be transported to the stratosphere or reach it as inorganic Br, thus contributing to ozone depletion [Solomon *et al.*, 1994; Davis *et al.*, 1996; Dvortsov *et al.*, 1999; Schauffler *et al.*, 1999; Montzka *et al.*, 2003]. In addition, short-lived marine halocarbons have been frequently used as tracers to investigate the marine influence on air masses [e.g., Atlas *et al.*, 1992; Blake *et al.*, 1996a; Blake *et al.*, 1999]. Measurements of these marine tracers are important for improving our understanding of the atmospheric processes that control the production and distribution of air pollutants along coastal marine regions.

[3] Marine macroalgae and microalgae are capable of producing a considerable number of different halocarbons [Gschwend *et al.*, 1985; Manley and Dastoor, 1988; Sturges *et al.*, 1992; Moore and Tokarczyk, 1993; Carpenter and Liss, 2000; Quack and Wallace, 2003]. It has been suggested that in macroalgae, the formation of halocarbons is initiated by an enzyme-catalyzed reaction of accumulated halide ions with hydrogen peroxide to form hypohalous acid. Halocarbons may be subsequently formed in the algal cells and transferred to seawater or alternatively, formed outside the cell by reaction of the released hypohalous acid with organic matter in seawater [Carpenter *et al.*, 1999, and references therein]. Field measurements and laboratory culture studies of microalgae suggest planktonic species produce and release halocarbons into the seawater, particularly in coastal areas [Klick and Abrahamsson, 1992; Moore *et al.*, 1996]. In these species, bromoperoxidase and iodoperoxidase enzymes are believed to be responsible for the production of bromocarbons and iodocarbons, respectively [Moore *et al.*, 1996]. Apart from biogenic sources, the anthropogenic chlorination of seawater also leads to the production of trihalomethanes (THMs) [Fogelqvist and Krysell, 1991; Jenner *et al.*, 1997; Allonier *et al.*, 1999; Quack and Wallace, 2003], with bromoform as the principal by-product [Allonier *et al.*, 1999]. In this process, hypochlorite and hypobromite react with organic material, producing THMs. The production of THMs by chlorination is greatly enhanced with increased bromide concentrations in the water [Jenner *et al.*, 1997].

[4] Atmospheric CHBr_3 is one of the most abundant biogenic organic bromine compounds and is a major source of reactive bromine to the atmosphere [Schauffler *et al.*, 1999; Carpenter and Liss, 2000]. A positive correlation between CHBr_3 and CH_2Br_2 has been observed in air masses with recent marine influences indicating that they have a common biological source [Carpenter *et al.*, 2003]. Photolysis and reaction with hydroxyl radical (OH) are the major atmospheric sinks of CHBr_3 , yielding a photochemical lifetime of $\sim 2\text{--}3$ weeks [Carpenter and Liss, 2000]. For CH_2Br_2 , reaction with OH is the major removal mechanism with a lifetime of $\sim 3\text{--}4$ months [Schauffler *et al.*, 1999]. The 1990 global average tropospheric concentrations of CHBr_3 and CH_2Br_2 were 0.2–0.3 pptv and 0.5–3 pptv, respectively [Brasseur *et al.*, 1999]. The source strength of CH_2Br_2 was estimated by Carpenter *et al.* [2003] to be between 15 and 25% of the global CHBr_3 flux, which is $\sim 2.2 \times 10^{11} \text{ g yr}^{-1}$ [Carpenter and Liss, 2000]. This implies that the higher global average atmo-

spheric concentration of CH_2Br_2 compared to CHBr_3 is likely because of its longer lifetime.

[5] Previously reported results indicate much higher production rates and subsequent emission of CHBr_3 in coastal regions compared to the open ocean (Table 1 and references cited therein). Estimates of algal biomass and halocarbon emissions suggest that macroalgae in coastal regions contribute about 70% of the global CHBr_3 production [Carpenter and Liss, 2000]. Mixing ratios of CHBr_3 measured at the coastal site Mace Head, Ireland, ranged from 1.0 to 22.7 pptv with a mean value of 6.8 pptv in September 1998 [Carpenter *et al.*, 2003] (Table 1). Coastal CHBr_3 concentrations presented by Quack and Wallace [2003] in the region $40^\circ\text{--}60^\circ\text{N}$ ranged between 1 and 8.3 pptv. In contrast to these coastal regions, a mean mixing ratio of 0.5 pptv was observed in the open ocean of the northern Atlantic in October 1996 [Fischer *et al.*, 2000] (Table 1). These results suggest that the coastal marine environment is a source region for CHBr_3 , with elevated mixing ratios that might strongly influence the atmospheric chemistry in these regions [Carpenter and Liss, 2000]. In some coastal regions, where numerous disinfection facilities and power plants dump effluent into coastal waters, chlorination of water may serve as an additional source of CHBr_3 . The current source estimate from water chlorination is $\sim 0.3 \text{ Gmol Br yr}^{-1}$, which accounts for a small part of the annual global flux of $\sim 10 \text{ Gmol Br yr}^{-1}$ [Quack and Wallace, 2003] but may be more significant locally [Fogelqvist and Krysell, 1991; Jenner *et al.*, 1997; Allonier *et al.*, 1999; Quack and Wallace, 2003].

[6] Atmospheric CH_3I and $\text{C}_2\text{H}_5\text{I}$ are marine derived iodocarbons that have been identified as significant sources of iodine to the atmosphere [Singh *et al.*, 1983a; Yokouchi *et al.*, 1997; Vogt *et al.*, 1999]. In addition to biological production, photochemical production in surface seawater has been indicated as an important source of CH_3I [Moore and Zafriou, 1994; Happell and Wallace, 1996]. The major sink for atmospheric CH_3I and $\text{C}_2\text{H}_5\text{I}$ is photolysis. Recently, microbial consumption has been identified as a loss process for CH_3I [Wingenter *et al.*, 2004]. The photolytic lifetime of CH_3I at low latitudes is reported to be 3–4 days, increasing to 2 weeks or more at higher latitudes [Blake *et al.*, 1999]. There is very little information on the lifetime of $\text{C}_2\text{H}_5\text{I}$ because even fewer atmospheric measurements are reported in the literature for this molecule. However, Carpenter *et al.* [1999] have suggested that $\text{C}_2\text{H}_5\text{I}$ and CH_3I have similar photochemical lifetimes. Previously reported mixing ratios of CH_3I and $\text{C}_2\text{H}_5\text{I}$ have ranged from 0.12–1.47 pptv and $<0.02\text{--}0.21$ pptv, respectively, from measurements at Mace Head [Carpenter *et al.*, 1999] and 0.24–2.0 pptv and $<0.03\text{--}0.31$ pptv, respectively, over the Asian seas [Yokouchi *et al.*, 1997]. Atmospheric mixing ratios of $\text{C}_2\text{H}_5\text{I}$ are significantly lower than those of CH_3I (Table 1), which may reflect the lower volatility, slower sea-to-air flux, and shorter lifetime of the heavier species rather than a lower oceanic production rate [Carpenter *et al.*, 1999].

[7] Both C_2Cl_4 and C_2HCl_3 are widely used as solvents and dry cleaning fluids [Wang *et al.*, 1995], with main sources located in the Northern Hemisphere. Previous measurements have shown a strong latitudinal gradient in the mixing ratios of these gases, with highest concentrations

Table 1. Halocarbon Mixing Ratios as Reported in the Literature^a

Location or Region	Latitude and Longitude, deg	Dates	CHBr ₃	CH ₂ Br ₂	CH ₃ I	C ₂ H ₅ I	C ₂ Cl ₄	C ₂ HCl ₃	Reference
Mace Head (shore)	53.3N, 9.9W	Sep 1998	6.8 (1.0–22.7)	1.44 (0.28–3.39)	3.8 (1.3–12.0)				Carpenter et al. [2003]
		July 1996			3.4 (1.9–8.7)				Bassford et al. [1999]
Cape Grim (open ocean air masses)	40.7S, 144.7E	May 1997	6.27 (1.9–16.3)		0.43 (0.12–1.47)	0.06 (<0.02–0.21)			Carpenter et al. [1999]
		Jan–Feb 1999	2.6 (0.7–8.0)	0.43 (0.10–1.39)	2.6 (1.0–7.3)				Carpenter et al. [2003]
		Oct–Nov 1996	2.4 ± 0.48						Fischer et al. [2000]
		Apr 1990	(0.79–1.71)	(0.70–1.28)					Sharp et al. [1992]
		1984 Sept., 1987	6.3 (2–11)						Cicerone et al. [1988]
Point Barrow, Alaska	71.3N, 156.6W	Jan 1992	2.6 (2.0–3.7)	0.8 (0.5–1.0)	(0.9–1.4)		8.3 (6.6–9.7)	8.4 (5.4–11.5)	Yokouchi et al. [1994]
		Apr 1992	1.6 (0.9–3.2)	0.8 (0.6–1.0)	0.4 (0.2–0.6)		6.8 (4.3–9.5)	2.4 (0.5–4.3)	
Alert (shelf)	83N, 64W	1982; 1983	0.85 ± 0.44	2.70 ± 0.59					Penkett et al. [1985]
		1982	1				(15–30)	(5–10)	Class and Ballschmiter [1986a, 1986b, 1988]
Atlantic (open ocean)	0–50N (Northern Hemisphere)								Koppmann et al. [1993]
Pacific (open ocean)	0–50N, E Atlantic 30–90N	Aug–Sep 1989					13 ± 6	3 ± 1	Wiedmann et al. [1994]
		Oct 1996	0.5 ± 0.1				1.0 ± 0.2		Fischer et al. [2000]
		Sep, Dec 1989, Mar, Jun 1990	0.35 ± 0.08	0.79 ± 0.03			(7–26)		Wang et al. [1995]
		Jan, Feb 1991	1.01 (0.28–2.9)	0.87 (0.47–1.36)			6.6 (0.68–40)		Schauffler et al. [1999]
		Sep, Oct 1992	0.63 (0.13–1.91)	0.59 (0.14–1.58)	0.87 (0.05–5.0)		1.9 (0.36–27.9)	0.48 (<0.1–13.5)	Yokouchi et al. [1997]
Pacific (open ocean)	36–41N (>2km) 35N–22S, W. Pacific 35N–40S, W. Pacific	Sep 1994	1.2 (0.38–10.67)				7 (0.83–128.7)	3.52 (0.03–141.2)	Quack and Suess [1999]
		Jan, Feb 1991			0.6 ^b (0.12–1.15)		7.2 ^b (2.1–231)		Blake et al. [1997]
		Sep, Oct 1992			0.32 ^b (0.18–1.81)		21 ^b (16–370)		
		4–43N, 113–150E					9.0 (0.9–250.3)		
		25–48N, 114–165E					29		
Pacific (open ocean)	25–48N, 114–165E	Sep, Oct 1991					5.4 (1.8–24.2)		Blake et al. [1996b]
		1982							Singh et al. [1983b]
		Feb, Mar 1990	2.30 (0.50–6.70)		1.07 (0.6–1.8)				Atlas et al. [1993]

Table 1. (continued)

Location or Region	Latitude and Longitude, deg	Dates	CHBr ₃	CH ₂ Br ₂	CH ₃ I	C ₂ H ₅ I	C ₂ Cl ₄	C ₂ HCl ₃	Reference
Pacific (open ocean)	39–55S, 135–160E	Nov 1995			0.3		1.4		Blake <i>et al.</i> [1999]
W. Pacific and Indian Ocean (open ocean)	15–35N, 115–140E	Dec 1996– Feb 1997			0.7 ± 0.1				Li <i>et al.</i> [2001]
E and SE Asian (open ocean)	15N–15S, 95–120E				1.2 ± 0.7				
Seas (open ocean)		Jan–Mar 1994	1.2 (0.32–7.1)	0.77 (0.38–1.42)	0.63 (0.24–2.0)	0.09 (<0.03–0.31)	9.5 (1.77–70.0)	14.7 (<0.1–261)	Yokouchi <i>et al.</i> [1997]
Antarctic (shelf)	60.5–66.5S, 54.5–69.16W	Oct–Dec 1987	6.3 (1.0–37.4)	3.7 (0.3–8.6)	2.4 ± 1.5				Reijnders <i>et al.</i> [1992a], Heumann [1992b]

^aValues are given in parts per trillion by volume.

^bMedian mixing ratios are given.

at high latitudes in the Northern Hemisphere and relatively low concentrations in equatorial regions and the Southern Hemisphere [Wang *et al.*, 1995; Blake *et al.*, 1999] (Table 1). These two compounds are frequently used as tracers of urban air masses [Blake *et al.*, 1996b]. The concentrations and ratios of these two compounds reflect the extent of anthropogenic influence and help to characterize the photochemical aging of contaminated air masses. High concentrations of C₂HCl₃ relative to C₂Cl₄ point to fresh anthropogenic emissions because of its short atmospheric lifetime of ~7 days [Quack and Suess, 1999] compared to C₂Cl₄ with an OH lifetime of about 3.5–4 months [Singh *et al.*, 1996; Olaguer, 2002]. Conversely, relatively high levels of C₂Cl₄ can indicate long-range transport of urban air masses. Therefore the ratio of C₂HCl₃/C₂Cl₄ can help constrain air mass processing times.

[8] The New England Air Quality Study (NEAQS) (available at <http://www.al.noaa.gov/NEAQS/>) took place in summer 2002 and was initiated jointly by AIRMAP, a UNH air quality and climate program, and by NOAA. A primary goal of NEAQS was to improve our understanding of the atmospheric processes that control the production and distribution of air pollutants in the New England region. Information on the distribution of short-lived marine halocarbons will help to elucidate processes related to the marine influence in this region. Here we present ambient concentrations of the marine derived halocarbons CHBr₃ and CH₂Br₂, and the anthropogenic halocarbons C₂Cl₄ and C₂HCl₃ measured from January–March and June–August 2002 at Thompson Farm (TF) in the seacoast region of New Hampshire. Also presented are measurements of CHBr₃, CH₂Br₂, C₂Cl₄, CH₃I and C₂H₅I from 18–19 August 2003 at TF and five other locations throughout the local Great Bay estuarine area. Emission fluxes of marine-derived halocarbons were estimated from these measurements. For CHBr₃, the results of the Great Bay study are compared with sea-to-air fluxes determined from air and surface seawater measurements made onboard the NOAA ship *Ronald H. Brown* as part of the NEAQS campaign. Finally, the potential anthropogenic source strength of CHBr₃ discharged into local water bodies from power plants and water treatment facilities was assessed.

2. Experimental Setup

2.1. Field Site Description

[9] The University of New Hampshire Observing Station at Thompson Farm (43.11°N, 70.95°W, elevation 24 m) is located in the southern, rural area of Durham, New Hampshire (Figure 1). TF is 24 km from the Gulf of Maine and 5 km northwest of Great Bay, New Hampshire, and is located on an active corn farm surrounded by a mixed forest. Air is drawn down a PFA Teflon lined manifold from the top of a 12 m tower. A subsample of this air is directed to our automated gas chromatographic (GC) system equipped with two flame ionization detectors (FIDs) and two electron capture detectors (ECDs) for the analysis of hydrocarbons, halocarbons, and alkyl nitrates (details on analysis are in the following section). The data record used in this paper covers the time periods from 11 January to 5 March 2002 and 1 June to 31 August 2002. There are gaps

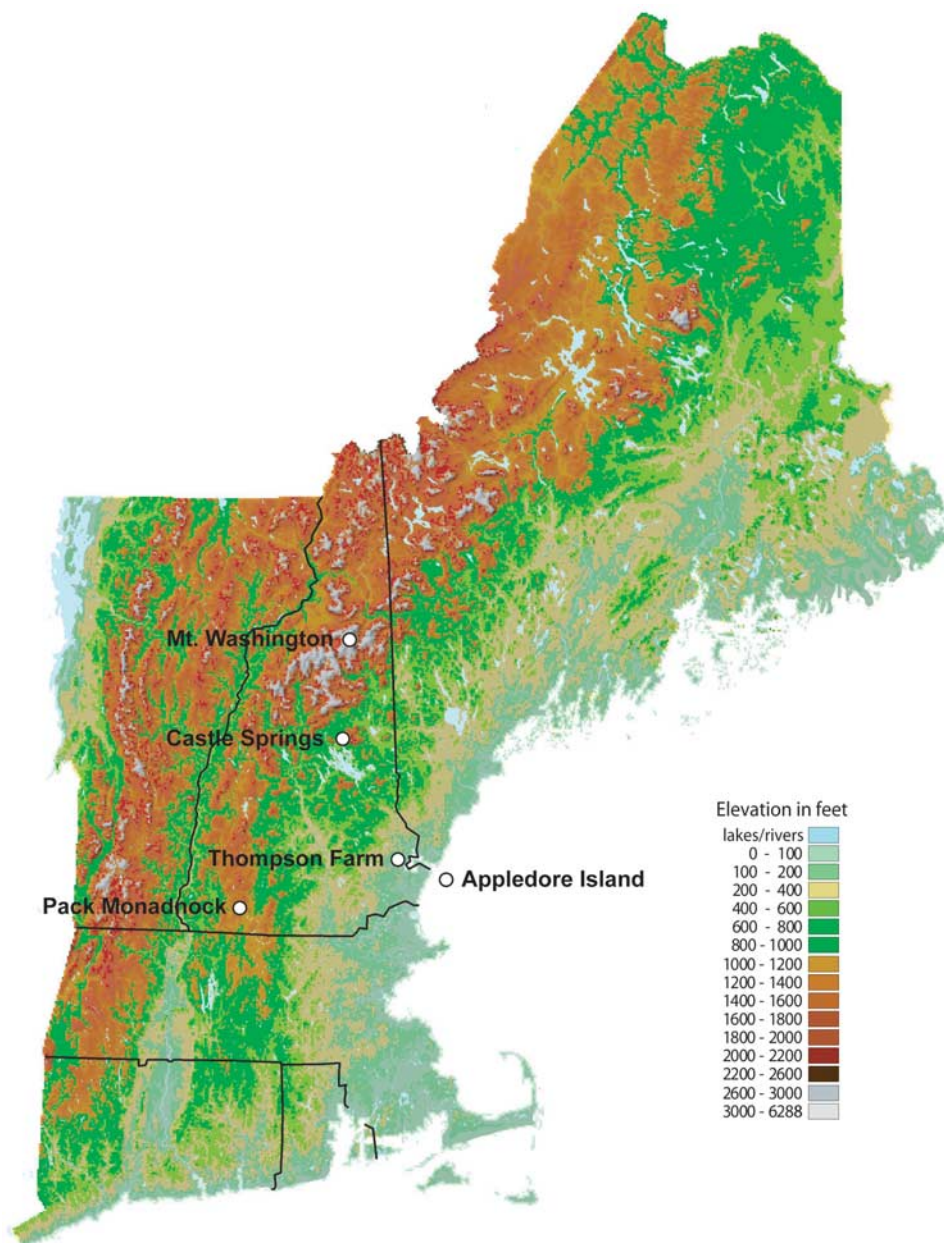


Figure 1. Locations of the AIRMAP monitoring stations, a University of New Hampshire air quality and climate program.

in data collection from 1–25 July and 29 July to 3 August because of instrument problems.

[10] Additionally, TF was also used as one of the sites in our study of the marine influence on air quality during 18–19 August 2003. The other sites in this study included Sandy Point Discovery Center, Stratham (43.05°N, 70.90°W), Wagon Hill, Durham (43.13°N, 70.87°W), Fort Constitution, Newcastle (43.07°N, 70.71°W), Downtown Boat Launch, Exeter (42.98°N, 70.95°W), and Pease Weather Station, Portsmouth (43.08°N, 70.82°W). The first three sites are located on the shores of Great Bay, while the others are 3.2–8.0 km inland from the coast. Great Bay, a 21.4 km² estuary, is located 16 km inland from the coast of New Hampshire and the Maine border and is a mesotidal estuary with the average tidal range varying from 2 to 2.5 m.

Throughout most of the year, the tidal component of the estuary dominates over the freshwater influence (see <http://www.nerrs.noaa.gov/GreatBay/>). Individual canister samples were collected at each site every hour from 6 P.M. on 18 August to 7 P.M. on 19 August 2003. The samples were returned to our laboratory at the University of New Hampshire for analysis within 1 week of collection.

[11] As part of the NEAQS-2002 campaign, we deployed an automated GC system for hydrocarbon, halocarbon and alkyl nitrate measurements aboard the NOAA ship *Ronald H. Brown*. Trace gases were sampled simultaneously from ambient air and equilibrator head space above fresh surface seawater to determine the concentration of dissolved gases. The shipboard data for CHBr₃, CH₃I, C₂Cl₄ and isoprene were obtained from 30 July to 7 August 2002 and covered

the geographic region extending from the New Hampshire seacoast south to Boston Harbor.

2.2. Analytical Methods

2.2.1. Thompson Farm GC System

[12] The Thompson Farm GC system is designed for dual-stage trapping using liquid nitrogen such that there are two individual dewars containing cold regions: The first stage is for water management and is cooled to -20°C , while the second stage is used for sample concentration and is cooled to -185°C . The first stage cooling unit contains an empty 6-inch \times 1/8-inch Silonite coated (Entech Instruments, Inc., Simi Valley, California) stainless-steel sample loop while the second stage contains a 6-inch \times 1/8-inch Silonite coated stainless steel sample loop filled with glass beads (60/80 mesh) for sample concentration. From work conducted at TF, we have determined that -20°C is adequate for water management during the sample trapping procedure, even during extremely high-humidity episodes. After the loops reach their initial set point temperatures, a downstream mass flow controller and pump are used to draw a 1000 cm^3 aliquot from the sampling manifold at a rate of $200\text{ cm}^3\text{ min}^{-1}$. After sample trapping is complete, 100 cm^3 of UHP helium is passed through both sample loops at a rate of $100\text{ cm}^3\text{ min}^{-1}$. After the helium sweep, the glass bead-filled sample loop is isolated, rapidly heated ($\sim 10\text{ sec}$) to 100°C , and then injected. Helium carrier gas flushes the contents of the loop and the stream is split into four, with each substream feeding a separate GC separation column housed in a single gas chromatograph. One $50\text{ m} \times 0.53\text{ mm}$ I.D., $10\text{ }\mu\text{m}$ film thickness CP-A $1_2\text{O}_3/\text{Na}_2\text{SO}_4$ PLOT column (Varian, Inc., Walnut Creek, CA), one $60\text{ m} \times 0.32\text{ mm}$ I.D., $0.5\text{ }\mu\text{m}$ film thickness Cyclodex-B column (J&W Scientific, Folsom, California), one $60\text{ m} \times 0.25\text{ mm}$ I.D., $1\text{ }\mu\text{m}$ film thickness OV-1701 column (Ohio Valley, Marietta, Ohio), and one $60\text{ m} \times 0.25\text{ mm}$ I.D., $1.4\text{ }\mu\text{m}$ film thickness OV-624 column are used for trace gas separation (Ohio Valley, Marietta, Ohio). The OV-624 and OV-1701 columns are plumbed into the ECDs and are used for measuring the halocarbons and alkyl nitrates. The PLOT and Cyclodex-B columns are connected to the FIDs and are used for the C $_2$ –C $_{10}$ nonmethane hydrocarbon (NMHC) measurements. For the standard analysis protocol, a 1000 cm^3 (STP) aliquot from one of two working standards was assayed every fifth analysis, thereby quickly drawing attention to any drift or malfunction of the analytical system. The measurement precision for each of the halocarbons, hydrocarbons and alkyl nitrates ranged from 0.3–15%.

2.2.2. Great Bay Canister Samples

[13] Measurements of C $_2$ –C $_{10}$ NMHCs, C $_1$ –C $_2$ halocarbons and C $_1$ –C $_5$ alkyl nitrates were made from canister samples collected around Great Bay. Samples were collected hourly from 6 P.M. on 18 August to 7 P.M. on 19 August 2003 at each location in 2-L electropolished stainless steel canisters (University of California, Irvine (UCI)). After filling, the samples were then returned to the laboratory at UNH for analysis by gas chromatography using FID and ECD in conjunction with mass spectrometry.

[14] The trace gas analytical system used for sample analysis has been described by *Sive et al.* [2003]. Current modifications of the system are described below. Briefly, the

system utilizes two GCs and one GC-mass spectrometer (GC-MS). The samples are analyzed by cryotrapping 1000 cm^3 (STP) of air on a glass bead filled loop immersed in liquid nitrogen. After the sample is trapped, the loop is isolated, warmed to 80°C and injected. Helium carrier gas flushes the contents of the loop and the stream is split into five, with each substream feeding a separate GC column. One $50\text{ m} \times 0.53\text{ mm}$ I.D., $10\text{ }\mu\text{m}$ film thickness CP-A $1_2\text{O}_3/\text{Na}_2\text{SO}_4$ PLOT column, one $60\text{ m} \times 0.25\text{ mm}$ I.D., $1\text{ }\mu\text{m}$ film thickness OV-1701 column, one $60\text{ m} \times 0.32\text{ mm}$ I.D., $1.0\text{ }\mu\text{m}$ film thickness DB-1 column (J&W Scientific, Folsom, CA), and two $60\text{ m} \times 0.25\text{ mm}$ I.D., $1.4\text{ }\mu\text{m}$ film thickness OV-624 columns are used for trace gas separation. One of the OV-624 columns and the OV-1701 are plumbed into ECDs and used for measuring the halocarbons and alkyl nitrates. The PLOT and DB-1 columns are connected to FIDs and used for the C $_2$ –C $_{10}$ NMHC measurements. The second OV-624 column provides separation for the MS, resulting in duplicate measurements for certain halocarbons and NMHCs. This enables us to accurately quantify certain gases that we are unable to using the FIDs or ECDs. For the GC-MS, electron impact mode is used for sample ionization along with single ion monitoring. Finally, the gas separation is unique for each of the columns, and thus any gases coeluting on one column are usually resolved on another. The standard analysis protocol is identical to that used at Thompson Farm (section 2.2.1). The measurement precision for each of the halocarbons, hydrocarbons, alkyl nitrates ranged from 0.1 to 12%.

2.2.3. Air and Surface Seawater Sampling Aboard the NOAA Ship *Ronald H. Brown*

[15] Ambient air was drawn from an inlet situated at the crow's nest of the bow mast, which was located approximately 15 m above the average waterline. The air was drawn through 1/4-inch stainless steel tubing by a diaphragm pump operating at a rate of 15 L min^{-1} with a back pressure of 1.5 atmospheres. The air traveled a distance of $\sim 80\text{ m}$ from the sample inlet to the laboratory located near the stern of the *Ronald H. Brown*. A portion of the airflow ($200\text{ cm}^3\text{ min}^{-1}$) was drawn by the concentrator system for five minutes and a 1000 cm^3 sample was cryogenically trapped before injection. The ship's crew took measures to ensure that the bow was pointed into the wind, and thereby avoided most contamination from the ship's exhaust. Water from the ship's uncontaminated seawater system flowed to the equilibrator at 4 L min^{-1} . Air was drawn from the equilibrator at $200\text{ cm}^3\text{ min}^{-1}$ by the concentrator system for concentration of the stripped gases from the surface seawater. Make-up gas for the equilibrator was provided by a zero air cylinder with a flow rate of $300\text{ cm}^3\text{ min}^{-1}$, with the excess air vented to the lab. The equilibrator used during the NEAQS cruise was a smaller version of the original Weiss design.

[16] After the sample was concentrated, it was injected and the carrier stream was split and sent to two independent Shimadzu GC-17A gas chromatographs. One GC contained a $60\text{ m} \times 0.25\text{ mm}$ I.D., $1.4\text{ }\mu\text{m}$ film thickness OV-624 capillary column, which was coupled to an ECD and used to separate and quantify various halocarbons and alkyl nitrates. The second GC contained a $50\text{ m} \times 0.53\text{ mm}$ I.D., $10\text{ }\mu\text{m}$ film thickness CP-A $1_2\text{O}_3/\text{Na}_2\text{SO}_4$ PLOT column coupled to an FID for the separation and quantification of the C $_2$ –C $_6$

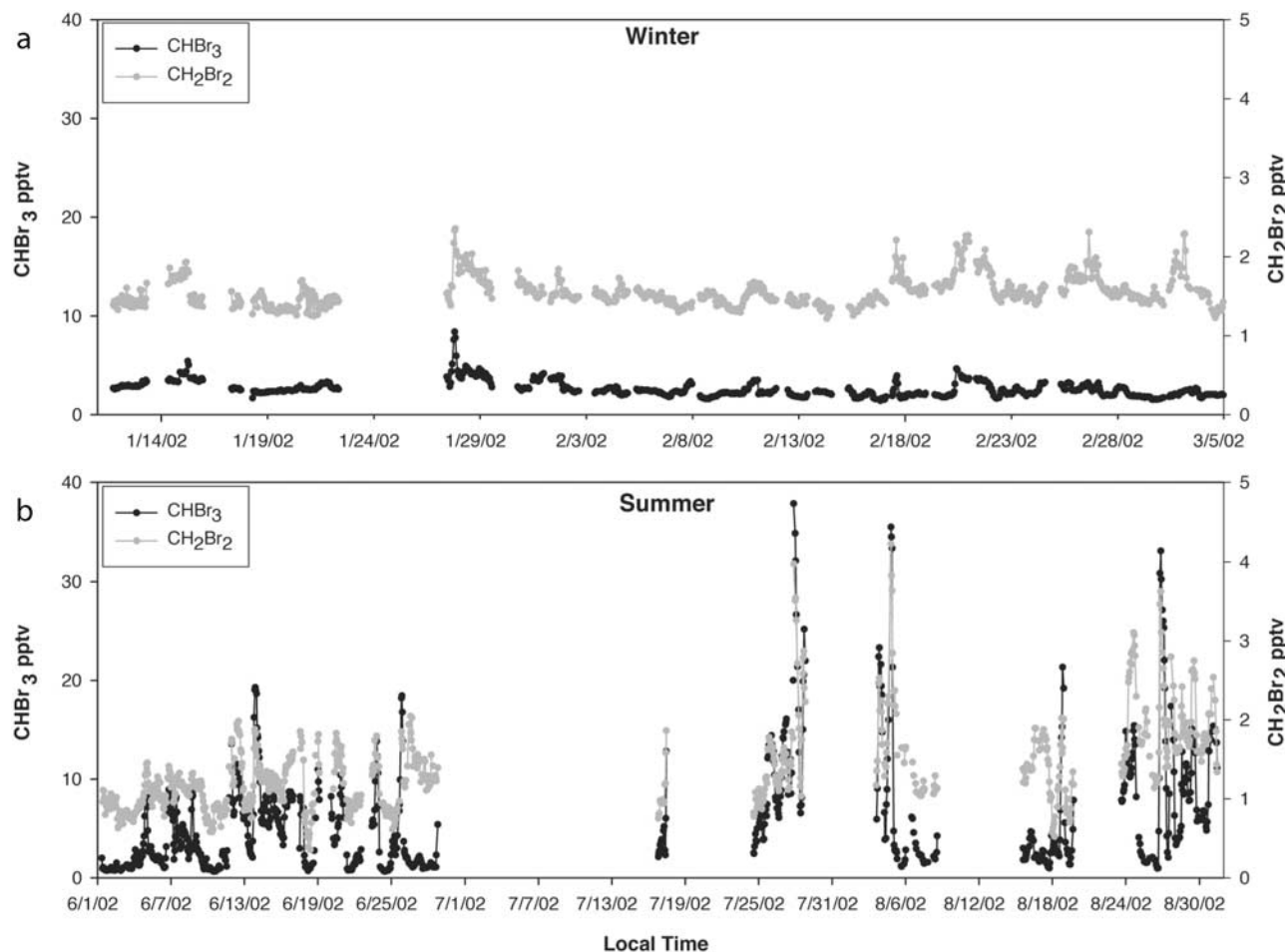


Figure 2. CHBr_3 and CH_2Br_2 distributions at Thompson Farm for (a) 11 January to 5 March and (b) June–August 2002.

NMHCs. Analytical accuracy of the assayed compounds ranged from 2–20%.

3. Halocarbons at Thompson Farm: 2002

3.1. Seasonal Distributions

[17] High concentrations of short-lived halocarbons were frequently observed in air masses at TF. Figure 2 shows distributions of CHBr_3 and CH_2Br_2 , measured at TF from 11 January to 5 March 2002 (Figure 2a) and 1 June to 31 August 2002 (Figure 2b). Previously published data for these species and results from this work are listed in Tables 1 and 2, respectively. From 11 January to 5 March 2002, the mixing ratios of CHBr_3 and CH_2Br_2 ranged 1.4–8.4 pptv (mean = 2.6 pptv; RSD = 30%) and 1.2–2.4 pptv (mean = 1.6 pptv; RSD = 12%), respectively. Ambient concentrations of CHBr_3 and CH_2Br_2 from 1 June to 31 August 2002, ranged from 0.6–37.9 pptv (mean = 5.9 pptv; RSD = 99%) and 0.4–4.2 pptv (mean = 1.4 pptv; RSD = 40%), respectively. These values are comparable with previously reported results from coastal regions between 40°–60°N [e.g., Carpenter *et al.*, 2003; Quack and Wallace, 2003] (Table 1). During both the winter and summer months of 2002, CHBr_3 and CH_2Br_2 were well correlated, most likely reflecting their similar marine sources as observed in

previous studies [Carpenter and Liss, 2000; Carpenter *et al.*, 2003]. The variability observed in their mixing ratios during summer was likely a result of several factors, including increased marine production rates, increased sunlight and surface water temperatures [Carpenter *et al.*, 2003], greater variability in their emissions from Great Bay, and a faster removal rate from the atmosphere. In both seasons, much greater relative standard deviations were documented for CHBr_3 compared to CH_2Br_2 , which is consistent with its higher reactivity in the atmosphere. In addition, the background (minimum) concentrations of both gases were lower in summer than in winter because of enhanced summertime photodecomposition rates and removal by OH.

[18] The anthropogenic halocarbons C_2Cl_4 and C_2HCl_3 were measured for comparison to marine halocarbons. The halocarbon mixing ratios during June 2002 and 25 July to 31 August 2002 are shown in Figures 3a and 3b, respectively. Ambient mixing ratios of C_2Cl_4 and C_2HCl_3 during June to August at Thompson Farm were 4.3–91.9 pptv (mean = 17 pptv, RSD = 79%) and 0.1–41.7 pptv (mean = 3.3 pptv, RSD = 112%), respectively. These values are slightly higher than ones reported previously for nonurban coastal regions (Table 1), suggesting a moderate urban/industrial influence in the eastern New Hampshire region.

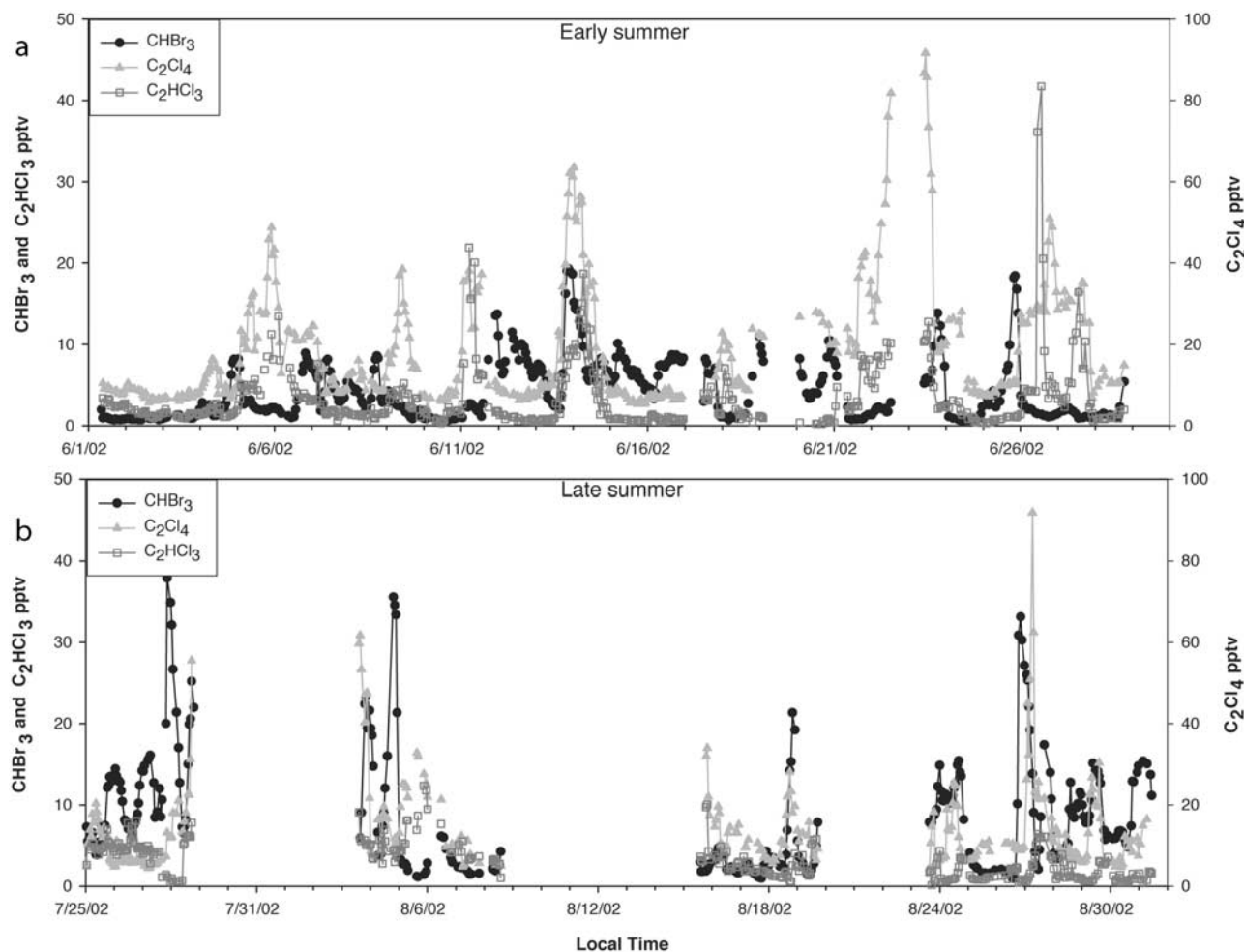


Figure 3. Mixing ratios of halocarbons at Thompson Farm: (a) June and (b) 25 July to 31 August 2002.

Measurements of C_2HCl_3 show larger variability in its mixing ratios compared to C_2Cl_4 , which is consistent with its higher reactivity with OH radicals. Additionally, higher OH concentrations during the summer lead to lower average background mixing ratios of C_2Cl_4 observed at TF (see Table 2). Figure 3 also shows that C_2HCl_3 and C_2Cl_4 tracked each other well throughout the period indicating

that they share a similar anthropogenic source. In contrast, $CHBr_3$ and CH_2Br_2 were generally not correlated with either of C_2HCl_3 or C_2Cl_4 , indicating that enhancements observed regularly at TF, particularly for $CHBr_3$, are probably not related to inputs from anthropogenic sources. Although no general correlation existed, we note that coincident enhancements of $CHBr_3$ and the urban tracers

Table 2. Halocarbons Measured at Thompson Farm in Durham, New Hampshire^a

Compounds	Mean	Median	Minimum	Maximum	Relative Standard Deviation, %	N
<i>January–March 2002</i>						
$CHBr_3$	2.6	2.4	1.4	8.4	30	797
CH_2Br_2	1.6	1.5	1.2	2.4	12	796
C_2Cl_4	24	17.8	7.2	147.3	73	788
C_2HCl_3	2.9	2.1	0.5	70	121	804
<i>June–August 2002</i>						
$CHBr_3$	5.9	3.9	0.6	37.9	99	810
CH_2Br_2	1.4	1.2	0.4	4.2	40	788
C_2Cl_4	17	11.2	4.3	91.9	79	786
C_2HCl_3	3.3	2.1	0.1	41.7	112	789

^aValues are given in parts per trillion by volume.

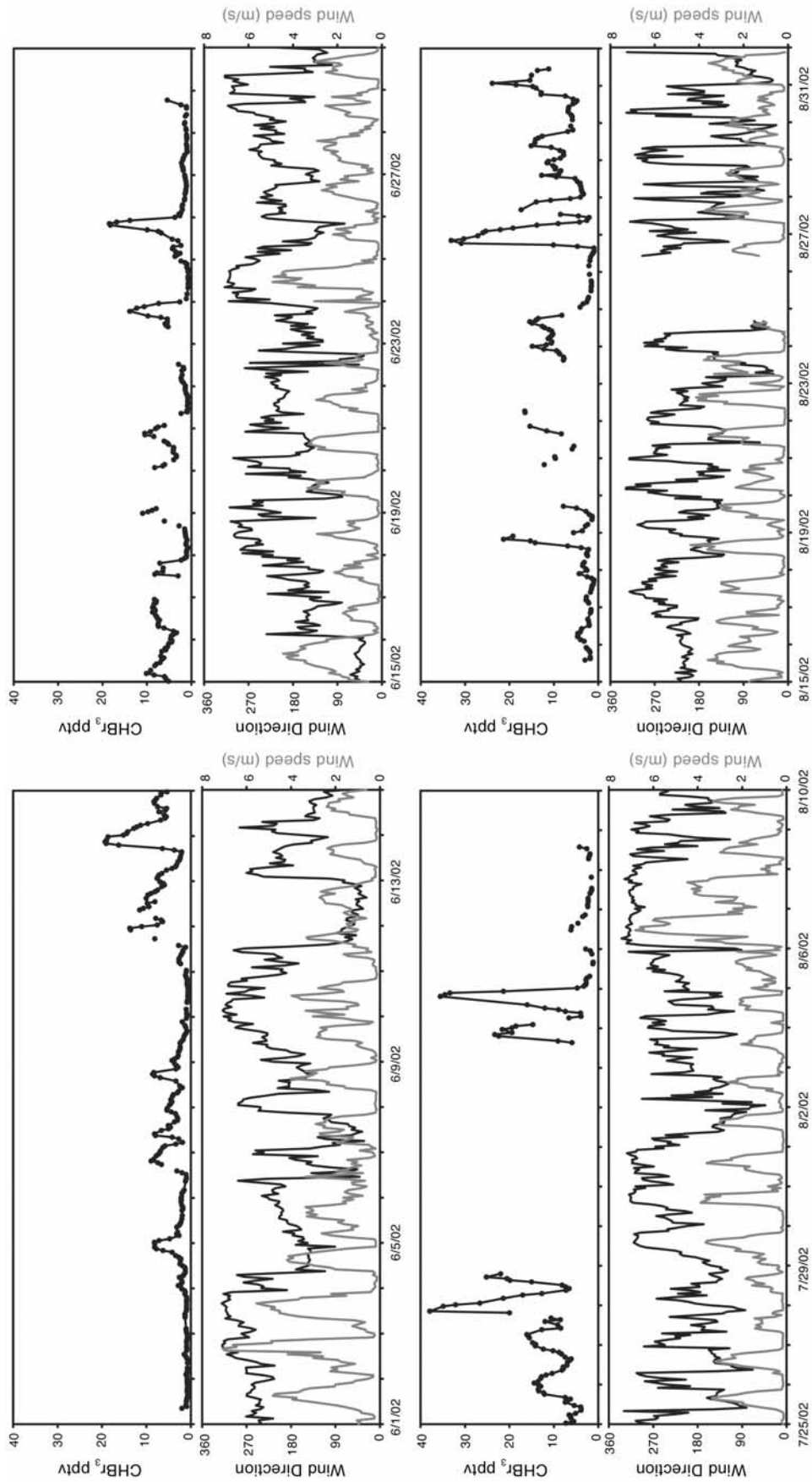


Figure 4. CHBr₃, wind direction, and wind speed at Thompson Farm from June to August 2002.

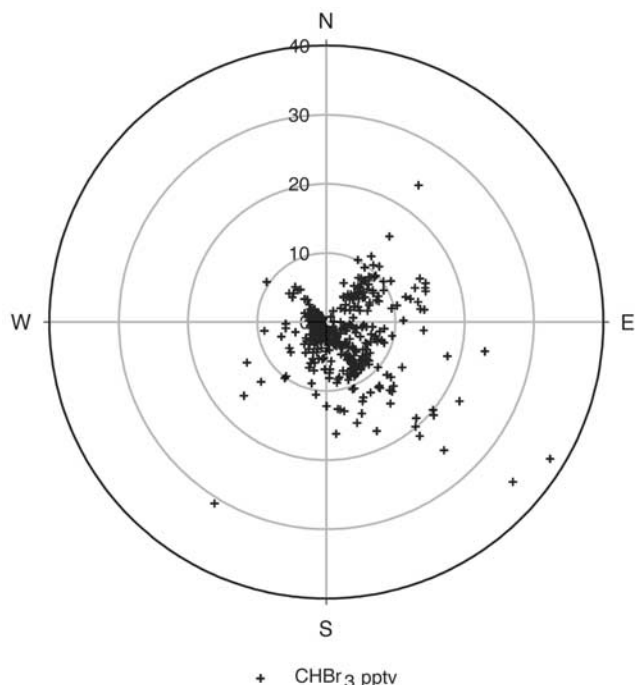


Figure 5. Wind rose of CHBr_3 from June to August 2002 for wind speeds $>0.5 \text{ m s}^{-1}$.

were observed on certain occasions such as 13 June, from 4 P.M. to midnight (local time). At this time winds were from SE (Figure 4), suggesting that urban tracers and marine tracers were potentially transported to TF from the Boston coastal metropolitan area.

3.2. Source Region Relationships

[19] Figure 4 shows the relationship between wind direction and CHBr_3 mixing ratios at TF from 1 June to 31 August 2002. During 1–4 and 9–10 June and 15–18 August, when westerly winds prevailed, there was no diurnal variation in CHBr_3 and its atmospheric mixing ratios were consistently low. The average CHBr_3 mixing ratios during these three periods were $1.1 (\pm 0.5)$ pptv, $1.2 (\pm 0.6)$ pptv, and $2.5 (\pm 0.9)$ pptv respectively, which are much lower than the mean mixing ratio of 5.9 pptv during the entire sampling period. If we only include data from time periods when wind speeds were larger than 0.5 m s^{-1} , it is evident that transport of CHBr_3 was primarily from the SE ($90^\circ\text{--}180^\circ$) and NE ($0^\circ\text{--}90^\circ$) (Figure 5), and that the highest mixing ratios were associated with wind speeds $>2 \text{ m s}^{-1}$. These results suggest that elevated mixing ratios of CHBr_3 occurred during periods when winds were from the SE and NE sectors, two source regions having estuarine and coastal marine influences.

[20] Figure 6 shows the mean mixing ratios of CHBr_3 and CH_2Br_2 (Figure 6a) and C_2Cl_4 , C_2HCl_3 , and O_3 (Figure 6b) measured in air masses arriving from the four primary wind sectors (all data included). For CHBr_3 , air masses arriving from the NE and SE sectors had mean CHBr_3 mixing ratios of 8.2 and 8.4 pptv, respectively, while air masses from the SW and NW were 4.7 pptv and 3.8 pptv, respectively. For CH_2Br_2 , mean mixing ratios for the NE and SE sectors had higher mixing ratios (1.6 and 1.5 pptv, respectively) than

those from SW and NW sectors (1.3 and 1.1 pptv, respectively). In all cases, air masses from the NE and SE had higher levels of CHBr_3 and CH_2Br_2 (by about 50–140% and 15–35%, respectively) than those from the SW and NW sectors, indicative of a coastal marine influence. The marginal difference in the mean CH_2Br_2 concentrations between the different wind sectors probably reflects the longer atmospheric lifetime of CH_2Br_2 . The $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ ratio was ~ 0.14 for the $0^\circ\text{--}180^\circ$ wind sector, which is in agreement with the ratio of 0.15 for fresh coastal marine emissions reported by *Carpenter et al.* [2003].

[21] Mixing ratios of the urban tracers C_2Cl_4 and C_2HCl_3 were higher in the SW sector ($\sim 26\text{--}150\%$ and $10\text{--}80\%$, respectively) than those arriving in air masses from other wind sectors. These results reflect the urbanization in the SW region (i.e., the northeastern urban corridor of the U.S.) compared with the other sectors and correlate well with the higher average O_3 mixing ratios from this sector [*Mao and Talbot, 2004*]. The lowest average concentrations of C_2Cl_4 and C_2HCl_3 correspond to the NE and NW sectors, reflecting transport of cleaner air masses to the study area [*Moody et al., 1998*]. Although air masses originating from the SE demonstrate the chemical characteristics of a coastal marine influence, they also exhibited a higher average concentration of O_3 compared to air masses from the NW and NE sectors, as well as the second highest mixing ratios of C_2Cl_4 and C_2HCl_3 . Possible explanations for this chemical signature include inputs from the Boston urban area and transport of polluted air from the Mid-Atlantic States out over the

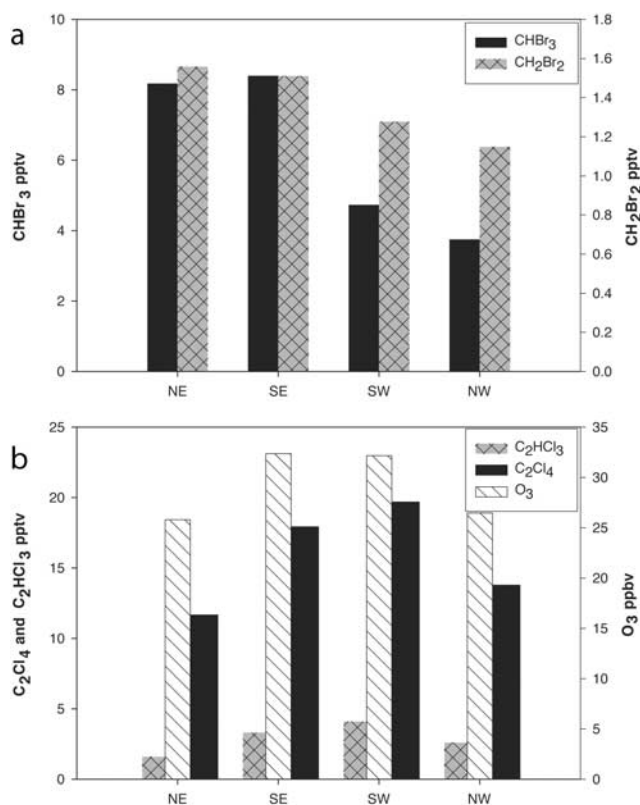


Figure 6. Mean mixing ratios of (a) CHBr_3 and CH_2Br_2 and (b) C_2Cl_4 , C_2HCl_3 , and O_3 from June to August 2002.

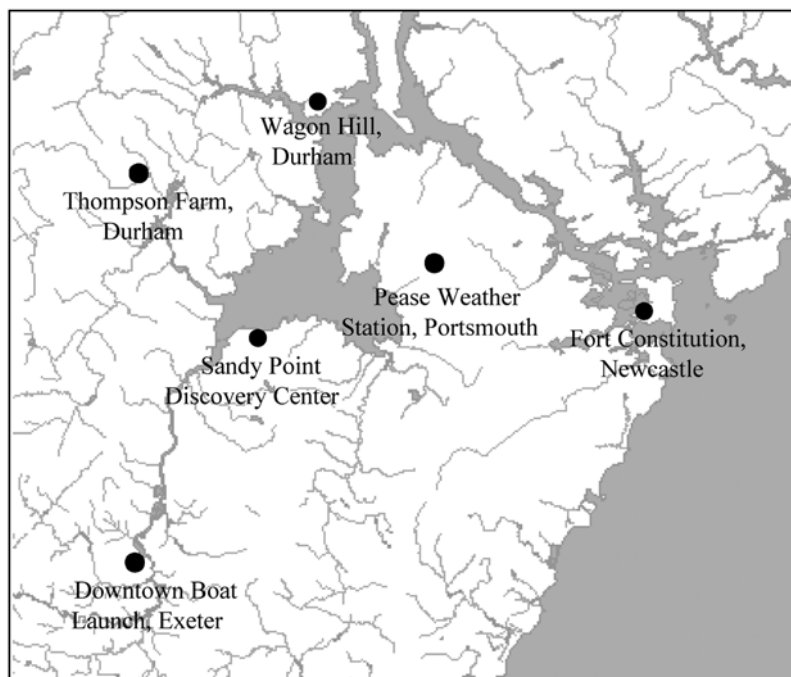


Figure 7. Sampling sites at Great Bay, New Hampshire on 18–19 August 2003.

Atlantic and then wrapping backward to make landfall in eastern New England under influence from the subtropical high [Mao and Talbot, 2004].

3.3. Marine Influence and Great Bay Emission Estimates

[22] An intensive study was conducted to determine the factors that influence the emission pattern and rate of short-lived halocarbons in the New Hampshire seacoast area. The sampling locations around the Great Bay estuary, New Hampshire (Figure 7), were divided into an inland site group (less coastal influence) and a near-coast group (more estuarine and marine influence). Concentration gradients existed for marine tracers from the coastal to inland regions (Table 3). At the coastal sites, the average mixing ratios of CHBr_3 and CH_2Br_2 were 8.8 and 1.9 pptv, respectively. The average mixing ratios of these two gases were much lower

at the inland sites (4.9 and 1.3 pptv for CHBr_3 and CH_2Br_2 , respectively). Slightly higher mixing ratios of CH_3I were also observed at the coastal sites (average 1.43 pptv) in contrast to the sites inland (average 1.25 pptv). The mean mixing ratios at the near-coast sites were approximately 82%, 46%, 14%, and 17% higher than at the inland sites for CHBr_3 , CH_2Br_2 , CH_3I , and $\text{C}_2\text{H}_5\text{I}$, respectively. These results provide evidence for the influence of marine emissions from Great Bay on the atmospheric composition at sites near the coast. Mixing ratios of CH_3I and $\text{C}_2\text{H}_5\text{I}$ were well correlated in a manner similar to CHBr_3 with CH_2Br_2 (Figure 8), a trend generally observed at TF. This result confirms that there are local colocated marine sources for CH_3I and $\text{C}_2\text{H}_5\text{I}$. The slopes of the regression lines for $\text{C}_2\text{H}_5\text{I}/\text{CH}_3\text{I}$ and $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ were 0.034 and 0.12, respectively (Figure 8). Although the observed mixing ratios were higher at the near-coast sites, the respective

Table 3. Statistics for Halocarbons on 18–19 August 2003 at Great Bay, New Hampshire^a

Compounds	Mean	Median	Minimum	Maximum	Standard Deviation	N
<i>Inland Sites</i>						
CHBr_3	4.9	4.7	0.7	16.0	3.9	78
CH_2Br_2	1.3	1.4	0.6	2.5	0.5	78
CH_3I	1.25	1.2	0.34	2.97	0.68	78
$\text{C}_2\text{H}_5\text{I}$	0.06	0.06	0.02	0.13	0.03	78
C_2Cl_4	25.9	17.1	5.18	98.6	21.6	78
<i>Near Coast Sites</i>						
CHBr_3	8.8	8.1	0.9	26.4	6.0	78
CH_2Br_2	1.9	1.8	0.8	3.9	0.8	78
CH_3I	1.43	1.41	0.44	3.1	0.66	78
$\text{C}_2\text{H}_5\text{I}$	0.07	0.07	0.02	0.12	0.02	78
C_2Cl_4	23.8	17.2	3.9	118.7	18.5	78

^aValues are given in parts per trillion by volume.

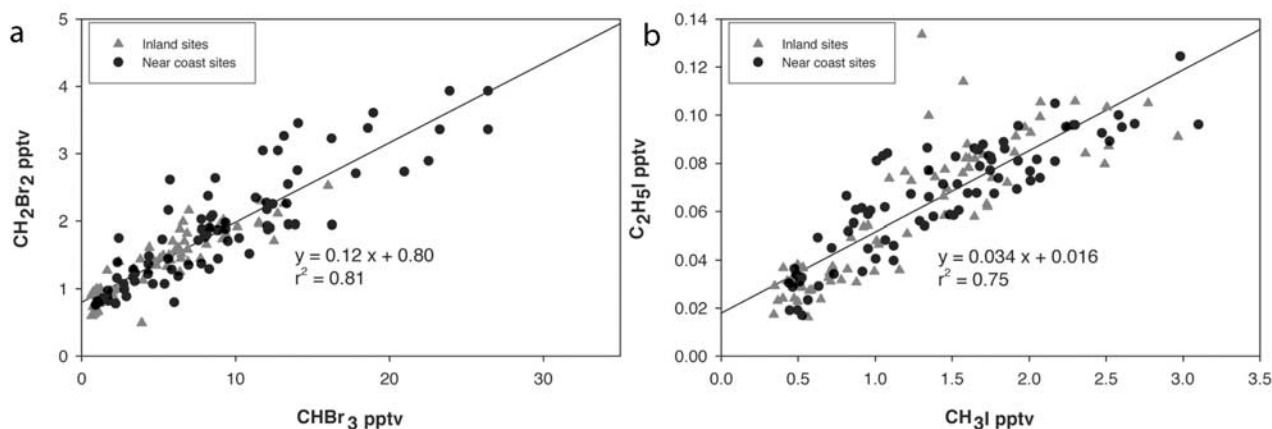


Figure 8. Correlations of (a) $\text{CHBr}_3/\text{CH}_2\text{Br}_2$ and (b) $\text{CH}_3\text{I}/\text{C}_2\text{H}_5\text{I}$ at Great Bay, New Hampshire on 18–19 August 2003.

compound ratios were similar at both locations, demonstrating the pervasiveness of the marine influence throughout the region.

3.4. Relationship Between Atmospheric Abundance and Tidal Cycle

[23] A tidal influence on the atmospheric mixing ratios of marine halocarbons in intertidal regions has been reported recently. *Carpenter et al.* [1999, 2001] suggested a link between the tidal cycle and marine influence of alkyl iodides and bromides at Mace Head, Ireland. Elevated mixing ratios of these gases were observed at low-tide periods, most likely because of higher emission rates when seaweed beds are exposed to the atmosphere. In contrast to Mace Head, short-lived halocarbon concentrations around Great Bay were observed to be highest following high tide, especially when it occurred during nighttime. Interpretation of the tidal influence on atmospheric mixing ratios can be complicated by factors such as the diurnal cycle of atmospheric boundary layer height and wind speed and direction. Nonetheless, the study conducted around Great Bay on 18–19 August 2003 appears to provide evidence that CHBr_3 and CH_2Br_2 , and to a lesser extent CH_3I and $\text{C}_2\text{H}_5\text{I}$ mixing ratios at the six sampling locations (section 2.1) are influenced by the tidal cycle. However, instead of reaching their highest mixing ratios at low tide, average values over inland and near coast sites peaked 2–3 hours after the nighttime high tide occurred (Figures 9a–9d). This phenomenon was most evident for CHBr_3 and CH_2Br_2 , which had the largest mixing ratio enhancements. These results suggest that large amounts of organic halocarbons were emitted from the seawater and/or directly by the macroalgae in surface seawater of Great Bay. The relationship of CHBr_3 measured at TF and tidal height for 4–5 June 2002 is shown in Figure 10. During this 2-day period, the prevailing winds at TF were onshore from the ocean, minimizing influences from inland air mass sources. Maximum mixing ratios of CHBr_3 were observed 2–3 hours after nighttime high tide, which is consistent with our observations around Great Bay and longer-term measurements at TF.

[24] There was little or no correlation of these gases and the daytime tidal cycle. This could possibly be due to dilution related to increased boundary layer height or

reduced contact with coastal source regions associated with increased wind speed from other directions. All reported compounds show a trend of decreasing mixing ratio after 6 a.m. When the boundary layer height was lowest, the mixing ratios of C_2Cl_4 were highest (between 2 and 6 A.M. local time, Figure 9e). This indicates that the C_2Cl_4 diurnal variation was not coupled to the tidal cycle. In addition to changes in boundary layer height, the 4–5 fold change in C_2Cl_4 is likely to be primarily associated with transport by S-SE winds (hourly wind speed $>1.5 \text{ m s}^{-1}$) that occurred from midnight to 6 A.M. on 19 August 2003.

[25] Figures 9c and 9d show decreased CH_3I and $\text{C}_2\text{H}_5\text{I}$ mixing ratios in the morning of the same magnitude as those for CHBr_3 and CH_2Br_2 . This result indicates the importance of dilution and transport resulting from an increase in boundary layer height and wind direction as indicated by the variation of C_2Cl_4 . To put this into perspective, we first calculate the loss rate from 6 A.M. to 8 A.M. on 19 August 2003 using the measured mixing ratios and obtain values of 0.55 pptv h^{-1} and 0.02 pptv h^{-1} for CH_3I and $\text{C}_2\text{H}_5\text{I}$, respectively. Next, we calculate the expected loss of each gas from its reaction with OH by using the integrated form of the rate law for a second-order reaction involving either CH_3I or $\text{C}_2\text{H}_5\text{I}$ and OH. If we overestimate the average OH concentration for the early morning and assume a concentration of $1 \times 10^6 \text{ molecules cm}^{-3}$, we get OH destruction rates of $5.6 \times 10^{-4} \text{ pptv h}^{-1}$ and $1.0 \times 10^{-5} \text{ pptv h}^{-1}$ for CH_3I ($k_{\text{OH}} = 0.07 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$) and $\text{C}_2\text{H}_5\text{I}$ ($k_{\text{OH}} = 0.03 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$) [*Cotter et al.*, 2001]. Additionally, if the photolytic lifetimes for CH_3I and $\text{C}_2\text{H}_5\text{I}$ are calculated for this latitude and season using noontime values for the actinic flux, we get comparable lifetimes of approximately 2 days. This implies that mixing and dilution are the driving forces during the daytime for these observations, but photolysis can also be considered as a secondary loss process. The sink due to reaction with OH is insignificant for these gases during the time frame under consideration. Moreover, both CH_3I and $\text{C}_2\text{H}_5\text{I}$ showed similar mixing ratios for the inland sites and the near-coast sites during the nighttime. This may reflect a lower emission rate of the iodocarbons compared to the bromocarbons (see below), resulting in the smaller enhancements observed. Overall, small nighttime differences in

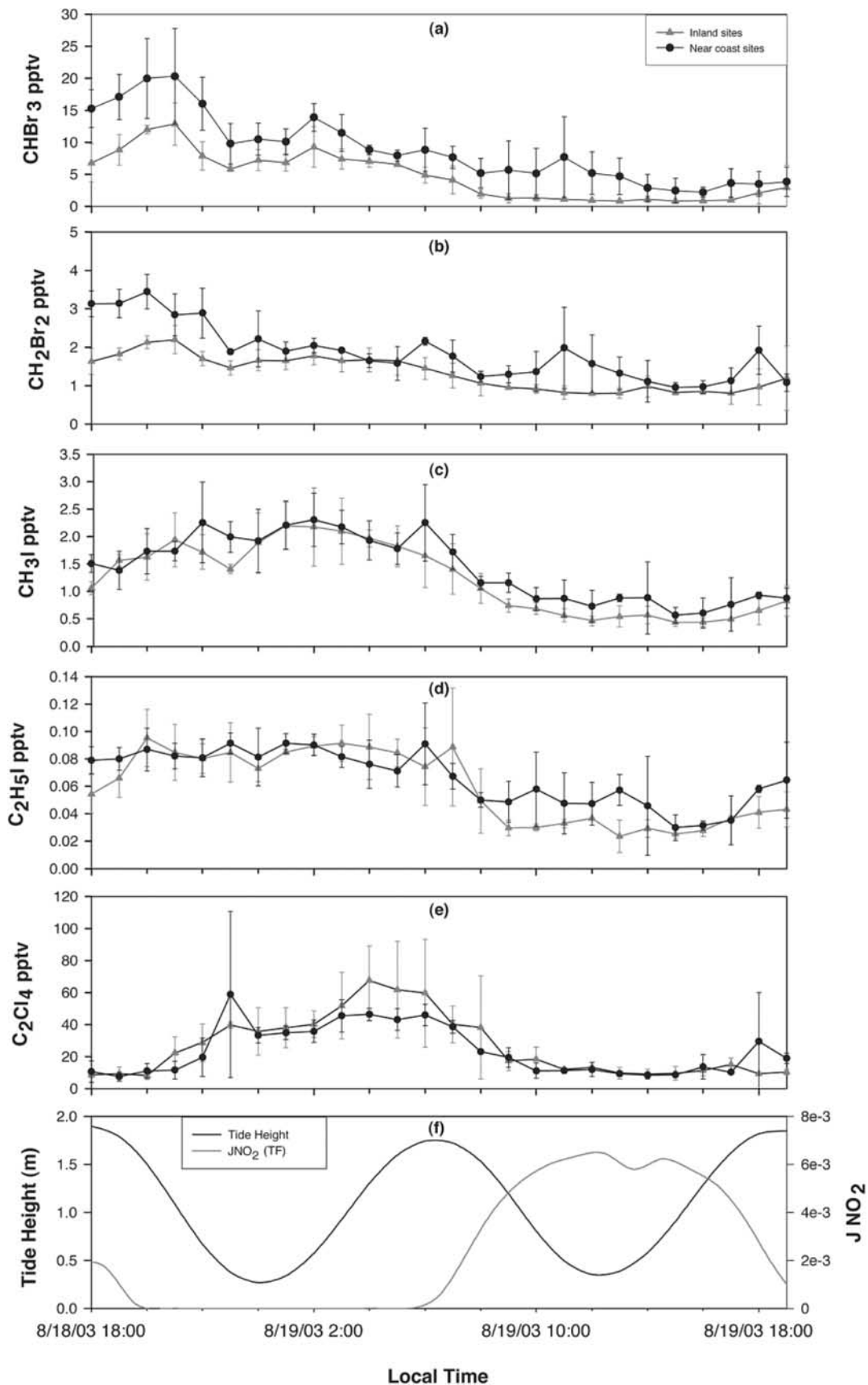


Figure 9. Mixing ratios of (a) CHBr₃, (b) CH₂Br₂, (c) CH₃I, (d) C₂H₅I, (e) C₂Cl₄, and (f) tidal height and JNO₂ at Great Bay, New Hampshire, 18–19 August 2003. Tide data in this work were obtained from <http://www.tideworld.com>.

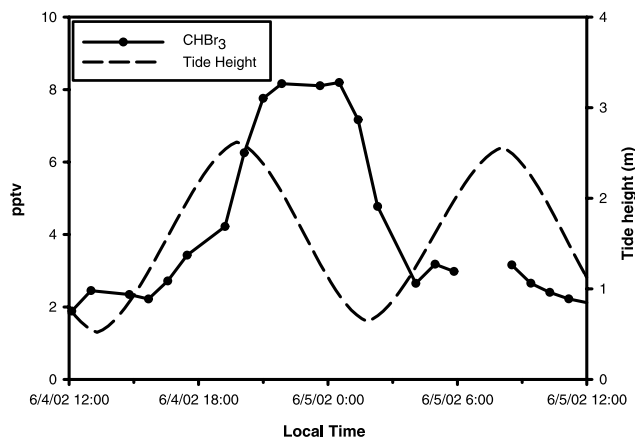


Figure 10. Tidal height and CHBr₃ mixing ratios at Thompson Farm from 4–5 June 2002.

mixing ratios for the iodocarbons were observed between the near coast and inland regions, while pronounced differences occurred during the daytime. Figure 9f shows the tidal cycle at the Great Bay and upwelling J_{NO_2} measured at Thompson Farm on 18–19 August 2003. The highest J values were observed from noon to 2 P.M., corresponding to the lowest mixing ratios of these gases, as discussed above.

3.5. Emission Fluxes From Marine Sources

[26] Short-lived bromocarbons and iodocarbons can play an important role in chemical processes that influence the composition of the troposphere. Estimates of emission rates of these gases from their primary sources are very useful for quantifying the impact on atmospheric chemistry. Emission fluxes of marine derived halocarbons are generally estimated using atmospheric lifetimes and concentrations or are calculated from surface seawater and atmospheric concentration measurements. Large uncertainties may be involved in determining parameters such as atmospheric lifetime and atmosphere-ocean transfer velocities. In this work, we calculated emission fluxes of marine-derived halocarbons from Great Bay using a simple box model approach. Parameters used in the model included wind speed, boundary layer height, and observed mixing ratios. In estimating the fluxes, the difference in mixing ratios between 6 P.M. and 10 P.M. were used to eliminate the effect of photochemical degradation. Under southerly winds on 18 August 2003 with an average speed of 1.8 m s^{-1} between 6 P.M. and 10 P.M., the observed mixing ratios primarily reflected local marine emissions from Great Bay. The fluxes were calculated from the time-dependent difference in mixing ratios at each of the six sites, divided by the area of Great Bay. The emission rates were determined from the product of the number of moles of air that pass through the box per unit time and the measured mole fraction enhancements.

[27] For these calculations, we assumed an average boundary layer height of 600 m and that mixing ratio enhancements were only due to emissions from local sources. The boundary layer height we used is a reasonable estimate based on the work of Talbot *et al.* [2005]. To

reduce uncertainty in these flux estimates, long-term observations of atmospheric concentrations and tidal influences are necessary. Combining boundary layer dynamics with the investigation of biogenic production variability in conjunction with surface seawater measurements is needed to fully understand the impact of coastal production of marine derived halocarbons.

[28] The emission flux estimates for CHBr₃, CH₂Br₂, CH₃I, and C₂H₅I were 26 ± 57 , 4.7 ± 5.4 , 5.9 ± 4.6 , and $0.065 \pm 0.20 \text{ nmol m}^{-2} \text{ h}^{-1}$, respectively. The large standard deviations in the flux estimates are a result of the variability in mixing ratios observed around Great Bay, which was likely caused by inhomogeneities in the emission distribution and subsequent atmospheric mixing. These emission fluxes yield an average emission ratio for CH₂Br₂/CHBr₃ of ~ 0.18 , which is consistent with our 2002 measurements. This value is very similar to the emission ratio of ~ 0.15 estimated for Mace Head, which is strongly influenced by local macroalgae [Carpenter *et al.*, 2003].

[29] The emission flux of $26 \text{ nmol m}^{-2} \text{ h}^{-1}$ (or $4.3 \times 10^8 \text{ molecules cm}^{-2} \text{ s}^{-1}$) for CHBr₃ is roughly double the average coastal emission flux of $2 \times 10^8 \text{ molecules cm}^{-2} \text{ s}^{-1}$ calculated by Carpenter *et al.* [2003] using air and seawater concentrations. Although there is a twofold difference between these flux estimates, our estimate is (1) obtained from Great Bay and the adjacent Gulf of Maine, which is an inhomogeneous body of water with a complex bathymetry and circulation patterns which can influence trace gas emissions, (2) based solely on atmospheric measurements, and (3) based on a 25-hour measurement period with large spatial coverage from six different locations around Great Bay. There are many additional factors, such as boundary layer height, mixing processes and biogenic production patterns that can contribute to variable fluxes. Moreover, our data represent one snapshot in time; the daily emissions fluxes are likely to be highly variable [Ekdahl *et al.*, 1998]. This work, nonetheless, represents the first flux estimates of CHBr₃, CH₂Br₂, CH₃I, and C₂H₅I for Great Bay and the seacoast region of New Hampshire.

3.6. Dissolved Halogenated Gases in the Gulf of Maine

[30] Dissolved surface seawater concentrations of CHBr₃, C₂Cl₄, CH₃I and isoprene were measured onboard the NOAA ship *Ronald H. Brown* from 30 July to 7 August 2002 as part of the NEAQS campaign (Figures 11a–11d). The highest concentrations of dissolved CHBr₃, CH₃I and isoprene, were observed along the coastal region off of New Hampshire near the mouth of the Piscataqua River, which flows through the Great Bay estuary, and is adjacent to the Hampton-Seabrook estuary (Figures 11a, 11c and 11d). In contrast to the distributions observed for these gases, low dissolved concentrations of C₂Cl₄, a good anthropogenic tracer, were observed in this region. Concentrations of C₂Cl₄ were approximately a factor of 2 higher in Boston Harbor, suggesting inputs from urban runoff (Figure 11b).

[31] The measurements aboard the *Ronald H. Brown* clearly indicate that CHBr₃, isoprene and CH₃I are from similar or colocated surface seawater sources. Biogenic production of isoprene has been observed in surface sea-

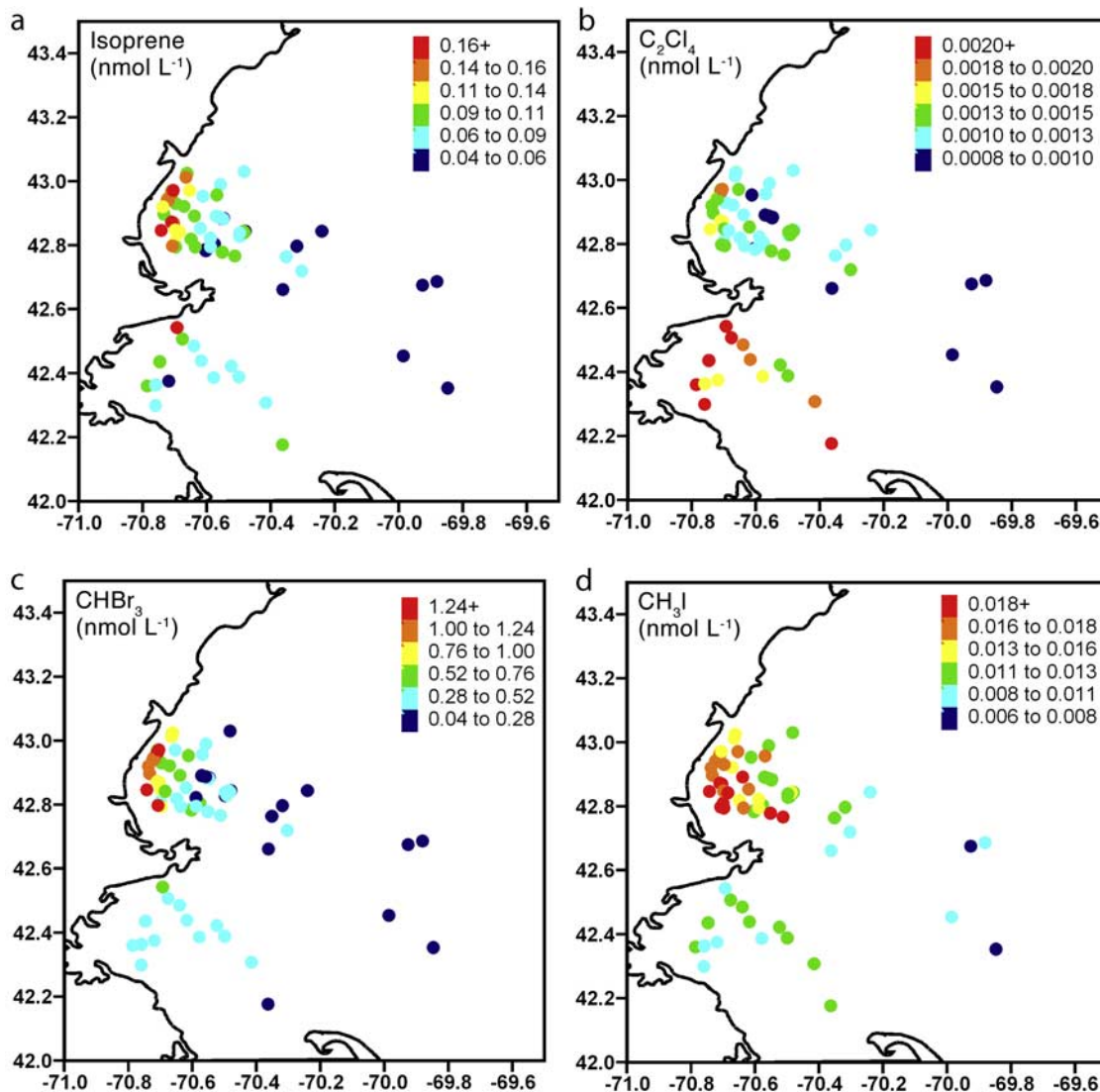


Figure 11. Surface seawater concentrations of (a) isoprene, (b) C₂Cl₄, (c) CHBr₃, and (d) CH₃I made from 30 July to 7 August 2002 during the NEAQS campaign.

water in the Mediterranean Sea and Pacific Ocean [Bonsang *et al.*, 1992], the Straits of Florida [Milne *et al.*, 1995], the North Sea and Southern Ocean [Broadgate *et al.*, 1997; Wingenter *et al.*, 2004]. Broadgate *et al.* [2004] established that isoprene is emitted from the same species of seaweed as reported by Carpenter *et al.* [2000], which in fact also emit CHBr₃ and CH₃I. Two of these macroalgae, *Chondrus crispus* and *Ascophyllum nodosum*, are common in the Great Bay estuary, the Hampton-Seabrook estuary and along the seacoast of New Hampshire [Mathieson and Fralick, 1972; Mathieson and Hehre, 1986].

[32] Sea-to-air fluxes of CHBr₃ were calculated for the Gulf of Maine using surface seawater and ambient air concentrations measured onboard the *Ronald H. Brown* (Figure 12). Emission fluxes of CHBr₃ from surface seawater to the atmosphere were derived from the measured surface water concentrations, atmospheric mixing ratios and the instantaneous wind speed [Fogelqvist and Krysell, 1991; Carpenter *et al.*, 2003; Quack and Wallace, 2003; Quack *et al.*, 2004]. The flux (F) of CHBr₃ across the air-sea interface

was calculated as the product of a gas transfer coefficient k_w and the air-sea concentration difference:

$$F = k_w(C_w - C_a/H),$$

where C_w and C_a are the concentrations in the surface seawater and air, respectively, H is the dimensionless Henry's law constant calculated using the following equation:

$$H_{(\text{CHBr}_3)_T} = \exp(13.16 - 4973/T),$$

where T is the water temperature (K). The transfer coefficient k_w depends on the wind speed, the identity of the gas, water temperature and salinity. A parameterization of the transfer coefficient suitable for CHBr₃ is

$$k_w \text{ CHBr}_3 = 0.31u^2(660/Sc_{\text{CHBr}_3})^{1/2},$$

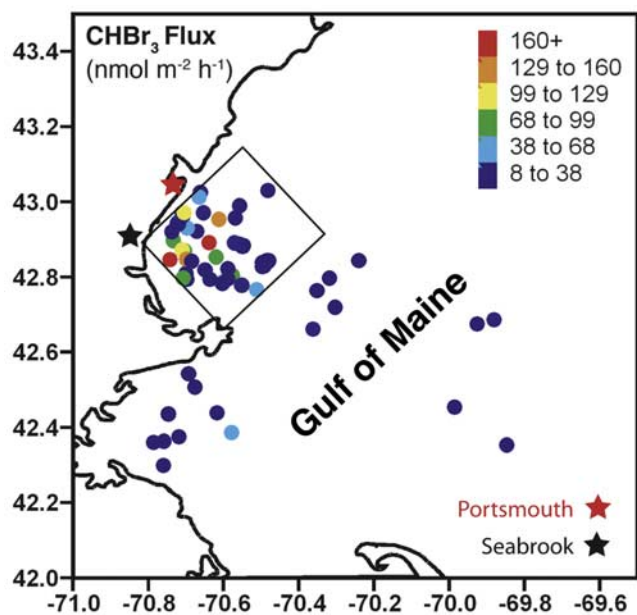


Figure 12. Emission fluxes of CHBr_3 from the Gulf of Maine during 31 July to 7 August 2002. The boxed in area represents measurements from 1–7 August 2002.

where u is the wind speed in m s^{-1} and Sc is the Schmidt number, which describes the kinematic viscosity of the solvent and diffusion coefficient of the compound of interest. The Sc for CHBr_3 at a salinity of 35 and various temperatures can be expressed as follows:

$$Sc_{\text{CHBr}_3} = 4662.8 - 319.45 T + 9.9012 T^2 - 0.1159 T^3,$$

where T ($^{\circ}\text{C}$) is the water temperature [Quack and Wallace, 2003]. Thus simultaneous measurements of the sea surface water concentration, the atmospheric mixing ratio, water temperature, and wind speed provide the necessary information to estimate sea-to-air fluxes of CHBr_3 .

[33] The fluxes of CHBr_3 from 1–7 August 2002, when the ship was cruising within the Gulf of Maine (boxed-in area of Figure 12), ranged from approximately 1.4 to 183 $\text{nmol m}^{-2} \text{h}^{-1}$. The median flux of 19.4 $\text{nmol m}^{-2} \text{h}^{-1}$ based on air-seawater measurements is in good agreement with our purely atmospheric-based flux of 26 $\text{nmol m}^{-2} \text{h}^{-1}$. The Great Bay is inundated with Gulf of Maine water during high tide. Therefore the source of the observed enhancements in atmospheric CHBr_3 surrounding Great Bay is potentially due to biogenic production in the Gulf of Maine, its transport into the Great Bay estuary and its subsequent release to the atmosphere, as suggested in section 3.4.

3.7. Estimate of Anthropogenic Source Strength of CHBr_3

[34] The various measurement sites around Great Bay and TF are close to populated areas which discharge chlorinated water into Great Bay. Coastal power plants also use and discharge millions of cubic meters of water for cooling

every day. Local to Great Bay are power plants in Sea Brook and Portsmouth, New Hampshire, that utilize water from nearby sources. In the process the water is chlorinated to prevent biofouling and is then discharged back into Great Bay and the Gulf of Maine. Thus a portion of the CHBr_3 emitted to the atmosphere from the Great Bay estuary might have an anthropogenic component. To assess the potential impact on our measured sea-to-air fluxes, we estimated the contribution to CHBr_3 levels in Great Bay from local wastewater treatment facilities and power plants.

[35] The World Resource Institute (see <http://earthtrends.wri.org>) reports that annual water withdrawals for domestic and industrial use are 238 and 825 m^3 per person, respectively, in the United States. New Hampshire has three counties (Carroll, Strafford, and Rockingham) that discharge wastewater into the Great Bay. The water volume of Great Bay varies from $2.3 \times 10^8 \text{ m}^3$ at high tide to $1.5 \times 10^8 \text{ m}^3$ at low tide [Brown and Arrelano, 1979]. The total population of these three counties is about 450,000 (see <http://www.ci.concord.nh.us>), and the CHBr_3 concentration in effluents from chlorination of wastewater, drinking water, and recreational water ranges from 4–40 nmol L^{-1} [Quack and Wallace, 2003]. From this, we estimate that the discharge of CHBr_3 to the Great Bay is about $2.2\text{--}22 \times 10^8 \text{ nmol h}^{-1}$, which could potentially contribute $\sim 0.032\text{--}0.32 \text{ nmol L}^{-1}$ of dissolved CHBr_3 . Using the flux value determined in the previous section and the measured atmospheric mixing ratios, we estimate an average concentration of CHBr_3 of about 3.1 nmol L^{-1} for Great Bay. Therefore the contribution from chlorination of wastewater, drinking water, and recreational water in this region could range from $\sim 1\text{--}10\%$.

[36] Quack and Wallace [2003] report that concentrations of 60 to 200 nmol L^{-1} of CHBr_3 have been measured in coastal power plant effluents. The total capacity of the power plants that discharge chlorinated cooling water into the Great Bay is about 1000 megawatts of electricity (MWe) (see <http://www.eia.doe.gov/cneaf/electricity/page/capacity/capacity.html>). The water usage of cooling water for these power plants is 30 $\text{m}^3 \text{ s}^{-1}$ per 1000 MWe [Quack and Wallace, 2003]. Therefore we estimate the contribution of CHBr_3 from coastal power plants to be $\sim 0.46\text{--}1.53 \text{ nmol L}^{-1}$, which is about 15–50% of the CHBr_3 concentration in the Great Bay. From these estimates, anthropogenic sources of CHBr_3 that discharge into Great Bay could potentially account for $\sim 15\text{--}60\%$ of its total atmospheric source strength. It should be noted that there is a large range of effluent concentrations reported in the literature, so our estimates have significant uncertainties associated with them. To more accurately evaluate the contribution of these sources, field studies are needed to measure the flow rates and concentrations of CHBr_3 in effluents of wastewater treatment facilities and power plants that discharge into Great Bay.

4. Conclusions

[37] From measurements conducted at the University of New Hampshire's Thompson Farm Observing Station, we have found that air masses encountered at this site are frequently influenced by emissions from coastal marine and estuarine waters. The mean mixing ratio of CHBr_3

observed in summer was higher than in the winter, and the mixing ratios for CHBr_3 and CH_2Br_2 were more variable during the summer most likely because of increased production rates and faster removal from the atmosphere. Mixing ratios of CHBr_3 and CH_2Br_2 were well correlated during both the winter and the summer of 2002 indicating that they have similar sources. Much greater variability of CHBr_3 compared with CH_2Br_2 was most likely a result of its higher reactivity with OH in the atmosphere. The urban tracers C_2HCl_3 and C_2Cl_4 tracked each other well from June–August 2002 indicating that they share similar anthropogenic sources. In contrast to these gases, CHBr_3 and CH_2Br_2 generally did not correlate with any of the anthropogenic halocarbons (though they correlated well with each other), suggesting biogenic sources. Air masses from the NE and SE had higher levels of CHBr_3 and CH_2Br_2 indicating an estuarine and coastal marine influence. For C_2Cl_4 and C_2HCl_3 , air masses from the SW showed higher levels than those from other sectors, confirming a strong urban influence from these directions. Additionally, there were periods when air masses from the SE showed a strong marine signature as well as enhancements of urban tracers, illustrating the complexity of the dynamic processes encountered in this region.

[38] For samples collected around Great Bay, mixing ratios of short-lived marine halocarbons at the near-coast sites were generally higher than those at the inland sites. This indicates a significant influence of emissions from Great Bay on the local distribution of these gases. During 18–19 August 2003, the mean CHBr_3 , CH_2Br_2 , CH_3I , and $\text{C}_2\text{H}_5\text{I}$ mixing ratios were 82%, 46%, 14%, and 17% higher, respectively, at near-coast sites as compared to the inland sites. Correlations of the tidal cycle and atmospheric concentrations of the marine tracers were observed during the night of 18 August 2003, with peak mixing ratios being observed about 2–3 hours after high tide. Using atmospheric concentrations observed at nighttime, we estimated the emission flux of CHBr_3 , CH_2Br_2 , CH_3I , and $\text{C}_2\text{H}_5\text{I}$ from the local coast region of New Hampshire to be 26 ± 57 , 4.7 ± 5.4 , 5.9 ± 4.6 , and $0.065 \pm 0.20 \text{ nmol m}^{-2} \text{ h}^{-1}$, respectively. Sea-to-air fluxes calculated from surface seawater and ambient air measurements on the *Ronald H. Brown* in the Gulf of Maine suggest a coastal marine source of CHBr_3 and are in very good agreement with the CHBr_3 fluxes estimated from atmospheric measurements around Great Bay. The anthropogenic source strength of CHBr_3 was also estimated, and is potentially 15–60% of the total CHBr_3 in Great Bay. However, we believe this estimate is an upper limit, at best, because of the types of macroalgae found in this region in addition to the $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ ratios measured at TF and the sampling sites around the Great Bay. The emission ratio of $\text{CH}_2\text{Br}_2/\text{CHBr}_3$ from measurements at the Great Bay is approximately 0.12, which is in good agreement with the emission ratio of ~ 0.15 that was estimated by *Carpenter et al.* [2003] at Mace Head, which is strongly influenced by local macroalgae.

[39] Coastal and estuarine environments are potentially significant sources of short-lived halogenated compounds to the atmosphere and play an important role in numerous processes which influence the chemistry of the atmosphere. Long-term continuous observations are needed at both inland and near-coast regions, including macroalgae bed

areas for atmospheric and surface seawater measurements. Dynamic processes such as boundary layer height variation need further investigation in order to improve our understanding of the factors controlling the diurnal cycles of the marine derived halocarbons. Finally, a more detailed anthropogenic source inventory, such as effluent concentration and water usage, is also needed in order to deconvolute anthropogenic from natural sources in coastal areas.

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