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Chlorofluorocarbons in the Hudson estuary during summer months

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Abstract. Chlorofluorocarbon (CFC) concentrations in the Hudson estuary were found to be greater than the atmospheric solubility equilibrium concentration, demonstrating that the entire reach is contaminated with CFCs from local wastewater discharge. Samples have been collected along the axis of the lower Hudson estuary over a 5-month period to assess temporal and spatial variability of their wastewater sources. The highest CFC concentrations were found in water collected near Manhattan. In this region, CFC-11 (CCl_3F) and CFC-12 (CCl_2F_2) were 3 to 5 and 10 to 20 times saturation, respectively. There appears to be a continuous CFC source in the New York City area, although the magnitude of this source declined during summer months. Other large CFC sources were found near Albany, and in Haverstraw Bay (60 km north of Manhattan).

Introduction

Background

Chlorofluorocarbons (CFCs) have become important transient tracers in oceanography [*Gammon et al.*, 1982; *Bullister and Weiss*, 1983; *Weiss et al.*, 1985; *Smethie*, 1993], hydrology [*Thompson and Hayes*, 1979; *Busenberg and Plummer*, 1992; *Ekwurzel et al.*, 1994], and limnology [*Weiss et al.*, 1991]. They are synthetic compounds with no known natural sources and have been distributed globally via atmospheric circulation. CFC-11 (CCl_3F) and CFC-12 (CCl_2F_2) are stable in oxygenated natural waters [*Bopp et al.*, 1981; *Lovley and Woodward*, 1992; *Ekwurzel et al.*, 1994]. However, under anaerobic conditions, consumption of these compounds by microbial communities has been observed [*Khalil and Rasmussen*, 1989; *Lovley and Woodward*, 1992; *Cook et al.*, 1995].

CFCs enter most natural waters through solubility equilibrium with the atmosphere. Hence their source functions are controlled primarily by water temperature and atmospheric concentrations [*Warner and Weiss*, 1985]. Atmospheric concentrations have been estimated for the last 50 years from a combination of industrial production records and direct atmospheric measurements [*Smethie et al.*, 1988; *Elkins et al.*, 1993; *Cunnold et al.*, 1994].

Concentrations of both CFC-11 and CFC-12 greater than those possible from equilibration of water with air have been observed in some continental waters that have been contaminated with wastewater [*Schultz et al.*, 1976; *Busenberg and Plummer*, 1992; *Clark et al.*, 1992a; *Böhkle et al.*, 1995]. Although elevated concentrations have not been reported from the open ocean, *Hammer et al.* [1978] identified coastal water from the Gulf of Maine that may have been locally contaminated.

Because of their association with wastewater, CFCs could potentially be used in many contamination studies. *Clark et al.* [1992a] used their distributions to quantify gas fluxes in the lower Hudson estuary. They have also been used to identify wastewater plumes in shallow groundwater [*Schultz et al.*, 1976;

Busenberg and Plummer, 1992; *Böhlke et al.*, 1995]. Despite these early studies that have used CFCs as tracers for wastewater, the characteristics of point source CFC inputs have been largely ignored. Before these compounds can be readily used as quantitative tracers of wastewater in hydrologic systems these functions must be examined.

Here, we present dissolved CFC data for water samples collected from the lower Hudson estuary during a 5-month period and for a single transect collected from the upper estuary. The temporal and spatial variability of the local inputs of these compounds are assessed. As was demonstrated earlier [*Clark et al.*, 1992a], these estuarine waters receive large quantities of dissolved CFCs presumably from wastewater treatment facility (WWTF) discharge.

The Hudson River Estuary

The tidal Hudson River can be divided into two regions, the upper and lower estuaries, on the basis of salinity. The upper estuary experiences semidiurnal stage changes but always remains fresh, and the lower estuary has increased salinity derived from coastal waters. The length of the salt intrusions varies seasonally. The upper estuary extends from the Federal Dam at Troy, New York, south for more than 140 km to the saltwater-freshwater interface. Tidal stage changes between 1 and 1.5 m occur along this reach of the estuary.

The lower Hudson estuary (Figure 1) extends from the Narrows, about 12 km south of the southern tip of Manhattan (the Battery), northward to the upstream limit of saline water, which during summer months is typically found more than 100 km upstream (just north of the Hudson Highlands). The estuarine circulation of the lower Hudson has been examined in a number of previous studies [e.g., *Abood*, 1974; *Hunkins*, 1981]. It is a partially mixed estuary. Vertical density stratification is controlled primarily by variations in salinity with depth. Monthly mean freshwater discharge rates at the Battery reach a maximum during the spring (1000–1500 m^3 s^{-1}) and a minimum during the late summer (150–300 m^3 s^{-1}). During high discharge (>600 m^3 s^{-1}), freshwater replacement times (total equivalent volume of freshwater in the salt-intruded reach divided by mean freshwater discharge at the Battery) are less than 15 days while during low flow conditions (150–250 m^3 s^{-1}) replacement times are typically between 45 and 60 days, although
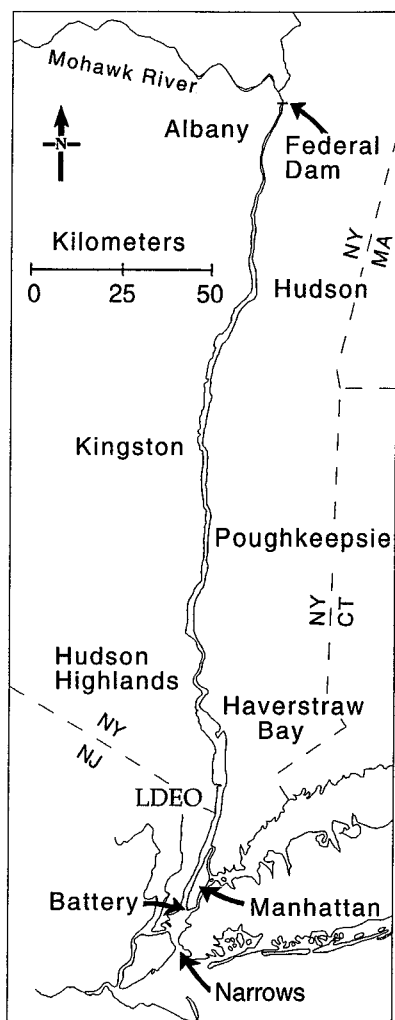
Figure 1. Map of the Hudson estuary. LDEO marks the location of Lamont-Doherty Earth Observatory.

they can be greater than 75 days during extreme dry periods [*Clark et al.*, 1992b].

Most of the wastewater (>90%) discharged into the salt-intruded reach of the Hudson enters near Manhattan from about two dozen large WWTFs. By 1990, more than 90% of the discharged waste water passed through secondary treatment, and direct discharge of untreated waste water had been stopped during dry weather conditions [*Dujardin et al.*, 1991]. The combined freshwater discharge rate from these treatment facilities, 59 m^3 s^{-1}, is a significant part of the freshwater budget for the lower Hudson estuary, especially during periods of low runoff, when it is generally 25% to 40% of the total freshwater flow.

The strong estuarine circulation near Manhattan tends to mix the point source discharges rapidly. Distributions of nutrients derived from wastewater vary smoothly as a function of salinity along the axis of the estuary [*Clark et al.*, 1992b]. Hence water collected in the channel near a WWTF does not show any local signature but rather tends to reflect the integrated loading of the regional WWTFs.

During summer 1992 the daily mean freshwater discharge rate at the Federal Dam at Troy decreased from more than 800 m^3 s^{-1} at the beginning of June to about 200 m^3 s^{-1} by the middle of June (Figure 2). Thereafter, base flow remained

relatively constant between 200 and 250 m^3 s^{-1}. Strong runoff events caused large deviations from this base flow several times each month. These high-runoff events increased the flow to as much as 600 m^3 s^{-1}. Discharge at the Federal Dam accounts for 50 to 80% of the freshwater flux across the saltwater-freshwater interface. The remainder of the freshwater discharge comes from lower basin tributaries. The transit time through the estuary is long, and during summer months the high frequency runoff events are damped considerably at the downstream end of the system.

Freshwater replacement times increased from about 14 days in early June to about 45 days in September through October (Table 1). Changes in replacement times reflect both changes in the mean freshwater discharge rate and the extent of saline water intrusion. The length of the salt intrusion increased in June, causing replacement times to increase while the average freshwater discharge rate remained constant. Thereafter, the length of the salt intrusion remained relatively stable, and variations in the replacement times reflect changes in freshwater discharge rates.

Surface water temperatures in the Hudson Highlands were 1°–4°C warmer than those in the water adjacent to Manhattan (Table 1). They reached a maximum in August of 25°C and were 6°–7°C cooler at the beginning of June and in the middle of October.

Methods

Samples were collected with a 1.5-L Niskin bottle about 1 m below the water surface and 1 m above the sediment (Table 2). A piece of rubber tubing was used to close the Niskin bottle. While such tubing has been identified as a source of CFC contamination to oceanographic samples, it did not significantly alter the Hudson estuary samples. The high CFC concentrations and very short residence time of samples in the Niskin bottle (less than 10 min) minimized the potential for contamination. Each day, samples were collected in sequence along the axis of the estuary from a small boat and thus are neither synoptic nor tidally averaged.

CFC samples were drawn from the Niskin bottle immediately into 100-mL glass syringes and stored submerged in a bucket containing Hudson estuarine water until analyses were completed. Upon returning to the lab, CFC-11 and CFC-12 concentrations were determined following procedures outlined
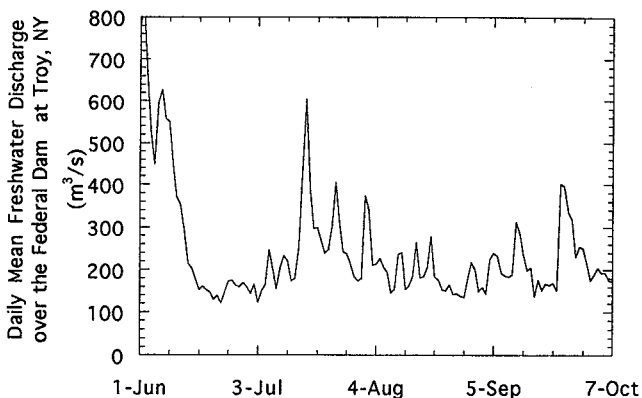

Figure 2. Daily mean freshwater discharge measured at the Federal Dam, Troy, New York (260 km upstream of the Narrows), during the summer of 1992.

Table 1. Physical Characteristics of the Hudson Estuary at the Time of Each Transect, Peak CFC Concentrations, CFC/SRP Ratios, and Calculated Fluxes of CFCs

Date, 1991	Freshwater Discharge,[a] m^3/s	Replacement Time, days	Temperature, °C		Peak Concentrations, pmol L^{-1}		Peak Ratio, pmol/μmol		Mass Flux,[b] μmol s^{-1}	
			Manhattan	Highlands	CFC-11	CFC-12	CFC-11/SRP	CFC-12/SRP	CFC-11	CFC-12
Oct. 2–4[c]	140	96	20	22	9.0	15	1.9	3.3	10 ± 1	20 ± 3
June 4	554	14	17	...	15	49	5.8	20	46	173
June 29–30	541	24	19	23	8.0	32	3.5	13	21	94
Aug. 5–6	363	35	24	25	9.9	20	2.8	5.8	18	38
Sept. 4–5	271	42	23	24	9.4	18	2.4	5.4	14	39
Oct. 7–10	272	43	18	19	8.2	12	2.1	2.6	13	17

[a]Average freshwater discharge rates were calculated from mean daily flows of the main stem of the Hudson River at the Federal Dam and the mean daily flows of the tributaries that enter the upper Hudson estuary following the procedures described by Clark et al. [1992b]. The discharge rates reported are 30-day averages for all transects except for the one collected on June 4, 1992, where a 15 day average was used.
[b]The flux calculated for the lower Hudson estuary. It is the sum of the loss across the air-water interface and exchange through the Narrows with the coastal ocean.
[c]Data from Clark et al. [1992a].

by Smethie et al. [1988]. Briefly, CFC-11 and CFC-12 were stripped from 6-mL aliquots of water with nitrogen gas that had been cleaned with a molecular sieve 13× column and trapped on Porasil C at −60°C. The trap was subsequently heated to 100°C, and the CFCs liberated were flushed into a Shimadzu Mini 2 gas chromatograph equipped with an electron capture detector. CFC-11 and CFC-12 were separated on a Porasil B precolumn followed by a SP2100 main column. CFC-12 and N_2O, which pass through these columns together, were further separated with a short column filled with molecular sieve 5a. The molecular sieve was taken out of line after CFC-12 was detected and before CFC-11 had passed through the SP2100 column. Concentrations of replicate samples were reproducible to within 3%. CFC loss within the glass syringes did not appear to be a problem. Duplicate samples analyzed about 6 hours and 24 hours after collection had CFC concentrations that were indistinguishable. However, because of the potential problem of syringe samples becoming anaerobic (followed by CFC consumption) and in situ production of N_2O, all CFC analyses were completed within 12 hours of sample collection.

Water samples were also collected for measurement of nutrients and chloride ion concentrations. These samples were immediately filtered (Whatman GF/F filters) and stored in the dark on board the small boat. Once back in the lab, the samples were transferred to a refrigerator. Soluble reactive phosphorus (SRP; SRP is defined as molybdate-reactive phosphate) concentrations were determined using standard methods outlined by Strickland and Parsons [1972]. Salinity was calculated from chloride concentrations [Pickard and Emery, 1982] which were measured with an Ag electrode autotitrator.

Air samples were collected periodically from a forest area more than 100 m from any buildings at Lamont-Doherty Earth Observatory. These samples were collected in dry 100-mL glass syringes and were analyzed immediately (within 5 min) after collection.

Results and Discussion

CFC Distributions Along the Axis of the Lower Hudson Estuary

Distributions of chlorofluorocarbons along the axis of the lower Hudson estuary (Table 2) can be described by four

general characteristics. First, concentrations at all stations were greater than concentrations in solubility equilibrium with the atmosphere. Second, maximum concentrations were found in estuarine water adjacent to Manhattan (at salinities between 15 and 25‰) (parts per thousand). Third, concentrations of CFCs from surface and bottom samples with similar salinities were essentially the same. Fourth, local maxima were often observed at low salinities (2–5‰ ppt).

The northern hemisphere mean CFC-11 and CFC-12 concentrations in 1992 were about 278 pptv (parts per trillion by volume) and 515 pptv, respectively [Elkins et al., 1993]. Concentrations of CFCs in a series of grab samples of air collected at Lamont-Doherty Earth Observatory, approximately 45 km north of the Narrows on the western bank of the Hudson estuary (Figure 1), were generally higher than the northern hemisphere means, showing influences of local urban sources. CFC-11 and CFC-12 concentrations ranged between 278 and 330 pptv and between 553 and 1052 pptv, respectively (Table 3). Large deviations from tropospheric mean concentrations have been reported in a number of continental settings and are not unique to the lower Hudson Valley [Fraser and Pearman, 1978; Prather, 1985]. The mean deviation of CFC-12 (+43%) from the northern hemisphere mean was much greater than that for CFC-11 (+8%), indicating that local urban sources of the former were proportionally greater.

Atmospheric solubility equilibrium concentrations of CFC-11 and CFC-12 calculated for the Hudson estuary transects were substantially lower than the observed dissolved CFC data using air concentrations equal to either the mean of our random air samples or to northern hemisphere values (Figure 3). The peak CFC-11 and CFC-12 concentrations in the water adjacent to Manhattan (salinities between 15 and 25‰) were 3–5 times and 10–20 times greater than the atmospheric solubility equilibrium values, respectively. Although the specific sources of CFC to the Hudson estuary have not been identified, Clark et al. [1992a] showed that they were coincident with the wastewater nutrient peaks. Our surveys also showed this general feature.

Upstream of the peak, CFC concentrations decreased rapidly. At the freshwater-saltwater interface, CFC-11 and CFC-12 concentrations were typically less than 30% and 100% supersaturated, respectively. The peak concentration of CFC-12 decreased throughout the summer months from about

Table 2. Lower Hudson Estuary Chlorofluorocarbon Data From 1992

Location	Distance Upstream,[a] km	Depth[b]	June 4 Salinity, ‰	June 4 CFC-11 pmol L⁻¹	June 4 CFC-12 pmol L⁻¹	June 29–30 Salinity, ‰	June 29–30 CFC-11 pmol L⁻¹	June 29–30 CFC-12 pmol L⁻¹	August 4–5 Salinity, ‰	August 4–5 CFC-11 pmol L⁻¹	August 4–5 CFC-12 pmol L⁻¹	September 5–6 Salinity, ‰	September 5–6 CFC-11 pmol L⁻¹	September 5–6 CFC-12 pmol L⁻¹	October 7–10[c] Salinity, ‰	October 7–10[c] CFC-11 pmol L⁻¹	October 7–10[c] CFC-12 pmol L⁻¹
Cornwall	102	S				0.1	4.51	4.3	0.1	3.70	3.54						
		B				0.3	4.58	4.9	0.1	3.54	3.57						
Foundry Cove	95	S				0.9	4.84	5.5	0.1	3.60	3.44						
		B				1.3			0.2	3.61	3.47						
Bear Mountain Bridge	88	S				2.6	5.33	7.7	0.3	3.70	3.45	1.2	4.32	3.09	1.6	4.39	
		B				3.1			0.4			2.0	4.94	3.63	5.4	5.61	
Stony Point	75	S				4.3	5.55	9.0	1.6	5.22	4.47	2.4	5.45	4.05	2.8	5.39	
		B				5.7	5.72	11.7	2.2	6.61	4.92	3.8	5.56	3.90	12.2		
Croton Point	69	S				5.2			2.2	7.08	4.89	4.0	4.64	3.74	3.0	6.65	
		B				7.4	5.78	13.7	3.2	6.48	4.85	6.8	5.15	4.78	14.6	6.62	
Tappan Zee Bridge	53	S				6.5			3.7	5.25	4.34	5.4	4.68	3.64	3.6	5.13	
		B				9.7	6.11	18.6	4.7	4.81	4.72	10.7	6.07	8.36	15.1	6.25	
Piermont	50	S	5.8	7.1	11.9	6.4	5.69	12.1	4.4	4.81	4.50	5.8	4.83	3.70	7.0	6.15	4.67
		B	6.5			11.6	6.53	21.1				10.7	6.05	8.77	11.8	6.19	6.53
Alpine	43	S	7.4	7.1	12.1	8.9	6.16	17.0	5.6	4.75	5.50	7.4	4.85	4.53	8.7	5.74	5.10
		B	8.2			15.6	7.24	29.3	9.4	6.12	11.5	15.4	7.47	12.2	13.0	6.50	6.82
George Washington Bridge	29	S	11.1	9.1	22.5	14.4	6.91	32.0	8.5			8.6	5.08	5.48	13.1	7.24	8.19
		B	15.1			19.9	7.94	33.6	14.2	10.1	18.7	17.4	7.92	13.8	17.0		
79th Street	22	S	12.9	10.0	33.9	18.4	7.96	27.9	9.5	6.75	11.7	9.6	5.16	5.92	19.6	8.18	9.69
		B	19.8			22.8	7.76	29.4	18.1	9.90	21.2	20.2	8.14	16.8	21.2	8.16	9.77
Battery	12	S	16.7	13.4	46.8	20.1	7.87	26.1	12.0	8.01	13.8	13.4			21.3	8.25	9.15
		B	23.8	14.4	41.7	26.7	7.26	19.7	23.4	7.70	16.4	25.4	9.14	22.1	25.1	7.06	8.63
Harbor	6	S	23.1	15.7	49.7	19.9			16.0	9.83	18.0	20.2	9.43	33.3	25.1	7.34	9.54
		B	24.9			27.9	6.56	15.2	24.3	7.09	15.1	27.9			26.7	6.51	6.59
Verrazzano Narrows Bridge	0	S	24.0	15.1	45.0	25.0	8.52	23.7	21.4	8.86	20.1	25.5	9.49	18.9	25.3	7.91	12.0
		B	27.8	8.3	19.0	27.0	6.65	15.5	26.0	5.32	9.20	29.6	5.41	6.45	28.1	4.56	4.78
New York Harbor[d]	6			3.54	2.36		3.22	2.17		2.57	1.78		2.69	1.85		3.37	2.26

[a]Distance upstream of the Narrows along the axis of the river.
[b]S, surface (1 m below the surface); B, bottom (1 m above the sediments).
[c]CFC-12 data from samples collected upstream of Piermont during the October 7–10, 1992, transect were discarded because of a temporary contamination of the analytical system.
[d]Solubility equilibrium value calculated using the mean CFC concentrations observed in the local air (Table 3), the observed water temperature (Table 1), and a salinity of 20 ppt [Warner and Weiss, 1985].

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Table 3. Atmospheric Chlorofluorocarbon Concentrations at Lamont-Doherty Earth Observatory

	CFC-11, pptv	CFC-12, pptv	CFC-11/CFC-12, pptv/pptv
LDEO			
June 5, 1992	278	651	0.43
June 28, 1992	286	589	0.49
June 30, 1992	305	1052	0.29
Aug. 6, 1992	301	553	0.54
Aug. 13, 1992	296	613	0.48
Sept. 4, 1992	315	842	0.37
Sept. 5, 1992	284	568	0.50
Sept. 15, 1992	330	1003	0.33
Mean	299 ± 17	734 ± 203	0.43 ± 0.09
Northern hemisphere[a]	278	515	0.54

[a] Data from *Elkins et al.* [1993]

50 pmol L^{-1} in early June to about 10 pmol L^{-1} in mid-October. A similar decrease was not observed in the peak concentration of CFC-11, which remained approximately the same (8–10 pmol L^{-1}) from late June through the middle of October. The maximum concentration of CFC-11 in early June was appreciably higher (15 pmol L^{-1}).

Upstream of the peak region, CFC concentrations in surface and bottom samples, when plotted versus salinity, form a single smoothly varying function (Figure 3). In this region, which is away from the New York City area point sources, CFC concentrations are controlled largely by estuarine mixing and gas exchange across the air-water interface. Degradation of CFCs within the water column is unlikely because dissolved oxygen concentrations were always greater than 140 μmol L^{-1}. The agreement between surface and deep samples with similar salinities is somewhat surprising because they were typically separated by more than 8 km. However, because the spatial variation of temperature was small compared with that of salinity, the salinity surfaces approximate density surfaces. Mixing along these surfaces is rapid compared with gas transfer across the air-water interface. In the peak region, good agreement between surface and bottom samples was not always observed. This could be the result of the finite amount of time needed to mix episodic point source releases of CFCs into the estuarine water.

At low salinities, local maxima were often observed in the CFC profiles, especially for CFC-11. The local maxima were most pronounced during the August and September transects (Figures 3c and 3d), although they are present in all four of the transects collected after June 4, 1992. The maxima were found in Haverstraw Bay (70 km north of the Narrows) at salinities of 2–5‰.

CFC-11/CFC-12 Ratios in the Lower Hudson Estuary

Distributions of CFC-11/CFC-12 ratios plotted versus salinity show minimum values in the region of maximum CFC-11 and CFC-12 concentrations (Figure 4). The ratios increase both up and downstream from this area. The minimum values of this ratio were about 0.3 in June and increased through the summer to a value of about 0.8 in October. The increase of the ratio was due primarily to the decrease in the CFC-12 concentrations. These ratios were substantially lower than those expected for water that is in solubility equilibrium with the local air (2.1) and much closer to the local air ratio (0.4). The highest ratios were found near the saltwater-freshwater inter-

face, where the absolute CFC concentrations were the lowest. The agreement between the local atmosphere and water column CFC ratios suggests that the respective sources are similar.

Temporal Variability of Wastewater Source

The temporal variability of the integrated CFC wastewater source can be inferred by the changes in the CFC concentrations of estuarine water near Manhattan. In addition to the loading rate, concentrations of dissolved species derived from WWTFs, such as nutrients, are largely controlled by the freshwater discharge rate. The relationship between peak concentration and freshwater discharge rate is best illustrated by SRP, which has a relatively constant WWTF input rate and behaves almost conservatively in the lower Hudson estuary [*Clark et al.*, 1992b]. Maximum concentrations of SRP are found in the water adjacent to Manhattan at salinities between 15 and 25‰ and vary systematically with freshwater discharge.

During the summer of 1992 maximum SRP concentrations increased from 2.5 μmol L^{-1} in early June to 3.9 μmol L^{-1} in October as the freshwater discharge rate decreased from 550 m^3 s^{-1} to 270 m^3 s^{-1} (Figure 5). Assuming that the loading rate of SRP was relatively constant and that the CFCs are conservative tracers, we would expect that the maximum CFC-11 and CFC-12 concentrations in October would have been about 50% more than in early June. Of course, in water that can exchange with the atmosphere, CFCs are not conservative tracers.

Calculations were made using a single-layer, multibox model (see *Clark et al.* [1992a, b] for a description of the model) to assess the relative importance of gas exchange and freshwater discharge on peak CFC concentrations. In these calculations, axial transport and mixing were determined by the mean freshwater discharge rate and salinity distributions observed at the time of the transects listed in Table 1. The gas transfer velocity was assumed to be constant over the entire estuary and equal to 3 cm h^{-1} [*Clark et al*, 1994]. CFC loading was scaled to the WWTF discharge rate and held constant. The calculations showed, for freshwater discharge rates between 140 and 550 m^3 s^{-1}, that the peak CFC concentrations increased with decreasing freshwater discharge and that the CFC/SRP ratio at maximum CFC concentrations remained relatively constant (±20%).

During summer 1992, both peak CFC concentrations and peak CFC/SRP ratios decreased (Figure 5; Table 1). The CFC-11/SRP and CFC-12/SRP decreased from 5.8 to 2.1 and from 20 to 2.6, respectively. Assuming that the loading rate of SRP was approximately constant, we estimate that the loading rate of CFC-11 decreased by a factor of 3 while the loading rate of CFC-12 decreased by an order of magnitude. Therefore the relative loading rates of CFCs changed over the course of the summer.

The peak CFC-11/SRP and CFC-12/SRP ratios in October 1991 were 1.9 and 3.3, respectively [*Clark et al.*, 1992a]. These ratios were very close to the ratios observed 1 year later. Hence provided that the loading rate of SRP remained the same, the loading rate of CFCs were similar in October 1991 and 1992. It appears that there may be a seasonal cycle associated with the WWTF loading rate of CFCs into the lower Hudson estuary, although more data would be needed to confirm this suggestion.

The source in Haverstraw Bay was episodic. Large releases occurred only in August and September. This source differed
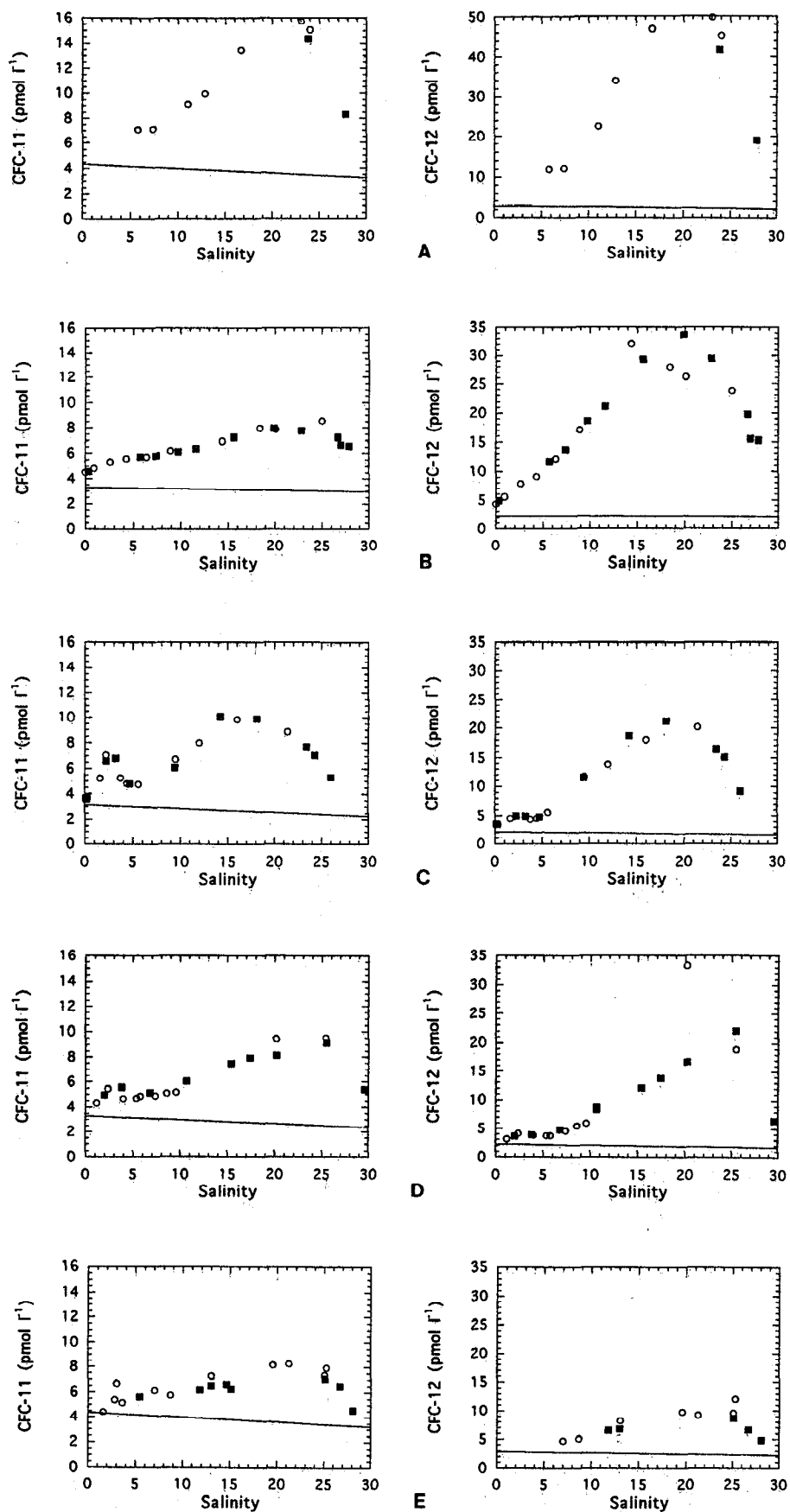
Figure 3. Distributions of dissolved CFCs plotted versus salinity in the lower Hudson estuary: (a) June 4, 1992; (b) June 29–30, 1992; (c) August 5–6, 1992; (d) September 4–5, 1992; and (e) October 7–10, 1992. The line shows the solubility equilibrium concentration calculated with the local air mean CFC concentrations (see Table 3); open circles indicate surface samples, and solid squares indicate bottom samples.
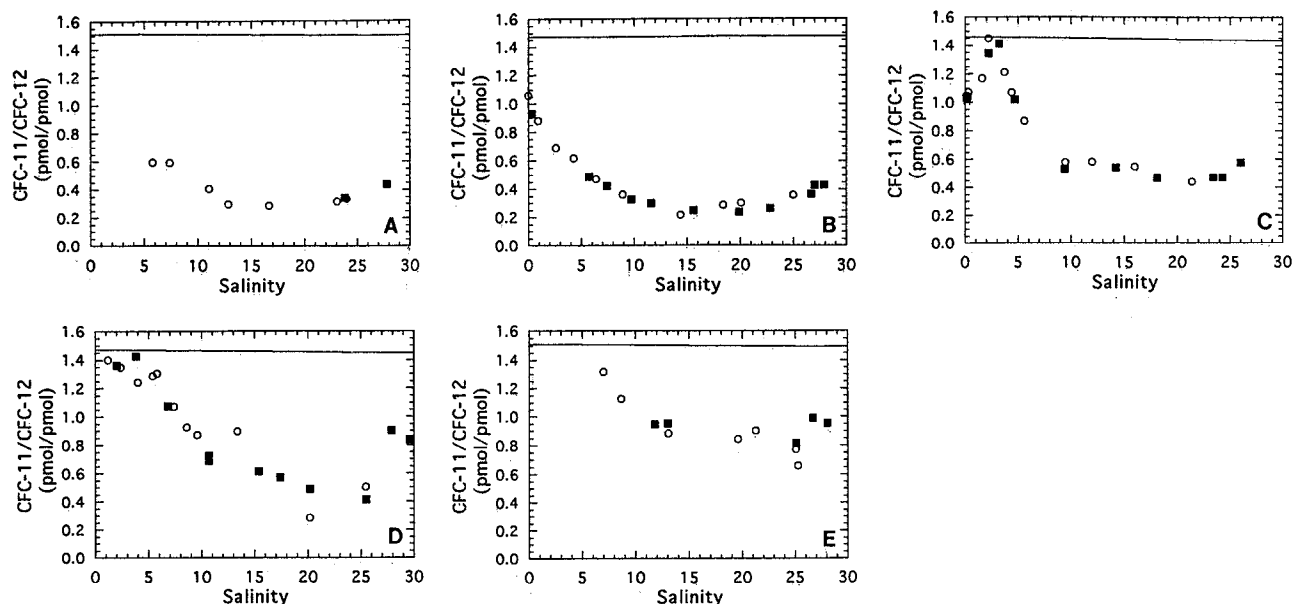
Figure 4. CFC-11/CFC-12 ratios from the lower Hudson estuary plotted as a function of salinity: (a) June 4, 1992; (b) June 29–30, 1992; (c) August 5–6, 1992; (d) September 4–5, 1992; and (e) October 7–10, 1992. The line shows the CFC-11/CFC-12 ratios of water in solubility equilibrium with the local air mean CFC concentrations (see Table 3), open circles indicate surface samples, and solid squares indicate bottom samples.

from the source near Manhattan in two ways. First, the Haverstraw Bay source was much stronger for CFC-11 than for CFC-12. Second, although the source strength near Manhattan weakened during the summer, it appears to have been relatively continuous, unlike the Haverstraw Bay source.

CFC Fluxes

The mass flux of CFCs out of the lower Hudson estuary can be calculated with the transect data. Total fluxes are the sum of the loss across the air-water interface and the loss through the Narrows to the Atlantic Ocean. The loss across the air-water interface was calculated with a gas exchange coefficient of 3 cm h^{-1} [*Clark et al.*, 1994] and surface areas listed by *Clark et al.* [1992b]. The loss through the Narrows was calculated from the freshwater discharge rate, an exchange term that was calculated assuming a steady state salt distribution and a seawater end-member. The seawater end-member was assumed to have a salinity of 30‰ and CFC concentrations equal to the solubility equilibrium value. Total fluxes of CFC-11 and CFC-12

Figure 5. Peak CFC-12 and soluble reactive phosphorus (SRP) concentrations plotted as a function of freshwater discharge rate (see Table 1). Crosses indicate SRP, and solid circles indicate CFC-12.

were 46–13 μmol s^{-1} and 173–17 μmol s^{-1}, respectively (Table 1). The loss due to gas exchange was 25–50% of the total flux.

CFC Concentrations in the Upper Hudson Estuary

In mid-September and early October 1992, surface samples were collected for CFCs upstream of the saltwater-freshwater interface along the axis of the Hudson River to Albany, New York (Figure 6). As in the lower estuary, CFC concentrations were always greater than atmospheric solubility equilibrium values. The lowest values observed were south of Kingston, New York (about 150 km upstream of the Narrows). A very large CFC source was found near Albany. CFC-11 concentrations near Albany were about as large as the maximum value found near Manhattan. This was not the case for CFC-12. Maximum values of CFC-12 near Albany were 3 to 10 times lower than those near Manhattan.

Summary

CFC concentrations throughout the Hudson estuary were substantially greater than atmospheric solubility equilibrium values. Large sources have been identified near Manhattan, in Haverstraw Bay, and near Albany. The temporal variability of the sources near Manhattan and in Haverstraw Bay were examined over a 5-month period during summer 1992. The Haverstraw Bay source was highly variable. The integrated sources of CFC-11 and CFC-12 near Manhattan were more continuous, although the source strengths decreased over the period of several months by a factor of 3 and by an order of magnitude, respectively. Despite the decrease, the source near Manhattan remained the dominant feature in the CFC distributions in the lower Hudson estuary throughout the summer and early fall.

Once CFCs reached the water, estuarine circulation rapidly mixed and transported them away from the dominant source areas. Distributions show that CFCs vary smoothly as a func-
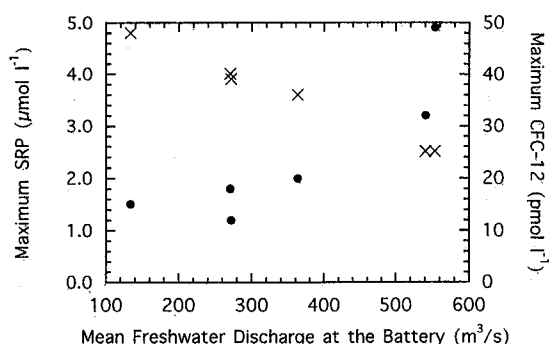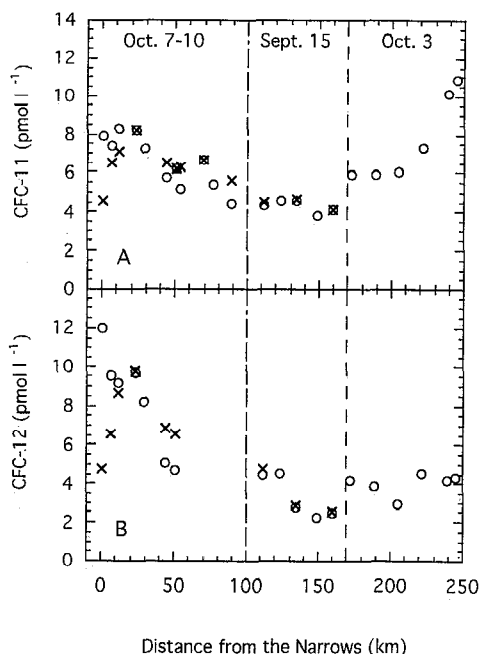
Figure 6. Distribution of CFCs along the axis of the Hudson estuary collected between September 15 and October 10, 1992. On September 15 the saltwater-freshwater interface was about 100 km upstream of the Narrows. Circles indicate surface samples, and crosses indicate bottom samples.

tion of salinity, with surface and bottom samples that have similar salinities also having similar CFC concentrations. The one area of the lower Hudson estuary where this feature was not as consistent was in the dominant source region near Manhattan. Here CFCs were not always well mixed as a function of salinity. We calculated that the flux of CFC-11 and CFC-12 out of the lower estuary ranged between 46 and 13 μmol s^{-1} and 173 and 17 μmol s^{-1}, respectively.

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