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Journal

Geophysical Research Letters, 19(11)

ISSN

0094-8276

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Publication Date

1992-06-02

DOI

10.1029/92gl00558

Peer reviewed

GEOPHYSICAL RESEARCH LETTERS, VOL. 19, NO. 11, PAGES 1133-1136, JUNE 2, 1992

GAS EXCHANGE IN A CONTAMINATED ESTUARY INFERRED FROM CHLOROFLUOROCARBONS

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Abstract. A new method of quantifying mean rates of gas exchange for natural water systems using the distribution of pollutant chlorofluorocarbons (CFCs) is presented. Concentrations of dissolved CCl_3F (F-11), CCl_2F_2 (F-12), and CCl_2FCClF_2 (F-113) in the Hudson estuary are supersaturated with respect to the remote troposphere by as much as an order of magnitude. The most plausible source appears to be discharges from waste water treatment facilities. Loss of these compounds from the estuary water to the atmosphere occurs both upstream and downstream of the zone of input. Using a multi-box model, gas exchange coefficients were calculated to be between 2 and 4 cm hr^{-1} based on the observed concentrations. This rate of gas exchange is similar to values determined in lakes and coastal bays and substantially lower than the mean value for the open ocean.

Introduction

Exchange of dissolved gases across the air-water interface is an important physical process which influences many properties of natural waters. Water quality assessment often requires quantitative estimates of this parameter both for the determination of reaeration rates [O'Conner and Dobbins, 1958] and loss of volatile pollutants [Bopp, 1983; Dyrssen et al., 1990]. Unfortunately, in many environments it is difficult to employ geochemical techniques which have been valuable in estimating gas exchange rates for the ocean [e.g. ^{222}Rn deficit, natural and bomb ^{14}C methods; Peng et al., 1979; Broecker et al., 1985]. Estuaries, which often receive large quantities of municipal and industrial wastes, are such environments.

A relatively new method in which a volatile tracer, sulfur hexafluoride (SF_6), is purposefully added to lakes and streams has assisted in determining gas exchange rates in systems not suited for oceanographic methods [Wanninkhof et al., 1985 and 1990; Upstill-Goddard et al., 1990].

Here, we attempt to determine the spatially and temporally averaged gas exchange rate in the lower Hudson estuary using a method which is conceptually similar to the SF_6 approach. Rather than monitoring a gas that has been purposefully added to the system, we have estimated gas exchange rates from the distribution of chlorofluorocarbons (CFCs). The CFCs measured were CCl_3F (F-11), CCl_2F_2 (F-12), and CCl_2FCClF_2 (F-113). As with SF_6, these gases are synthetic compounds with no known natural source and are chemically very stable in solution. CFCs have a variety of industrial uses and thus are likely to be found in waste water. Common uses are refrigeration (F-12), foam blowing (F-11 and F-12), solvents (F-11 and F-113), and washing of semiconductors (F-113).

Paper number 92GL00558
0094-8534/92/92GL-00558$03.00

The Hudson Estuary

The lower Hudson estuary (Figure 1), as defined here, extends from the seaward opening at the Narrows, northward to the upstream limit of saline water. Tidal stage changes occur for about 270 km upstream of the Narrows and the area-weighted mean water depth of the salt-intruded reach is about 9 m. During summer months, saline water typically extends more than 110 km upstream of the Narrows.

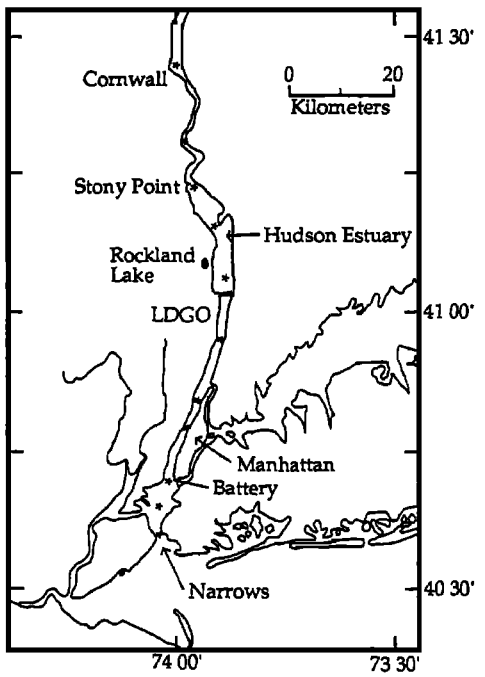

Fig. 1. Hudson River and estuary: sample locations are indicated by *. LDGO indicates Lamont-Doherty Geological Observatory.

The lower Hudson is a partially-mixed estuary in which the surface and bottom salinities generally differ by less than 5 ‰ during periods of low freshwater discharge. Upper basin runoff usually reaches a maximum during early spring and a minimum during late summer. Extreme values of monthly mean river discharge at the Battery (12 km upstream of the Narrows) are typically 1200 $m^3\ s^{-1}$ and 150 $m^3\ s^{-1}$. During high discharge (>600 $m^3\ s^{-1}$), freshwater replacement times are less than 15 days while during low flow conditions (150 - 250 $m^3\ s^{-1}$) they are between 45 and 60 days [Clark et al., 1992].

Approximately 10^7 m^3 of waste water per day is discharged into the lower Hudson estuary [Dajardiam et al., 1991] of which more than 90% presently pass through secondary treatment during dry weather conditions. Although treatment facilities are scattered along the entire tidal reach,

most of the waste water is discharged near the downstream end from about two dozen facilities serving the greater New York City metropolitan area. The combined freshwater inflow from all treatment facilities into the NY harbor complex is a significant part of the freshwater budget, especially during summer months when it is generally between 25-40% of the riverine discharge rate.

Methods

Samples were collected about one meter below the water surface and one meter above the sediment (Figure 1) with a 2.5 liter Niskin bottle in which the rubber tubing was replaced with a nylon-covered metal spring. The southern half of the lower estuary was sampled on October 2, 1991 and the northern half on October 4, 1991. Each day, samples were collected in sequence along the axis from a small boat and thus are neither synoptic nor tidally averaged.

CFC samples were drawn from the Niskin bottle immediately into 100 cm^3 glass syringes and stored submerged in water until analyses were completed. Upon returning to the lab, F-11, F-12, and F-113 concentrations were determined following modified procedures outlined in Smethie et al. [1988]. CFCs were stripped from 35 ml of water with pure nitrogen gas 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 GC–8a gas chromatograph equipped with an electron capture detector. The three CFCs were separated on a Porasil B precolumn followed by a SP2100 (20% supported on supercoport) main column. F-12 and N_2O, which pass through together, were further separated with a short column filled with molecular sieve 5a. The molecular sieve was taken out of line after F-12 was detected and before F-11 and F-113 had passed through the Porasil B column. F-11 and F-12 concentrations are relative to SIO 1986 scale. The F-113 calibration is preliminary at this time. Concentrations of replicate samples were reproducible to within 5%. All CFC analyses were completed within 14 hours of sample collection.

Water samples for measurement of nutrient and chloride ion concentrations were filtered immediately after collection (Whatmann 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. Analysis of nutrients were completed within 48 hours of collection, following procedures outlined by Strickland and Parsons [1972]. Replicate nutrient analyses were reproducible to within 3%. Salinity was calculated from chloride concentrations [Pickard and Emery, 1982] which were measured with an Ag electrode auto-titrator.

Results

Both NH_4 and SRP (solubly reactive phosphate) had large concentration maxima at salinities between 15 to 25 ‰ (Figure 2). Maxima of CFC concentrations were also observed in the same salinity range (Figure 3). Based on CFC solubility data of Warner and Weiss [1985], F-11 and F-12 at maximum concentrations were supersaturated with respect to the current remote troposphere (F-11 = 270 pptv, F-12 = 460 pptv; M. Prather personal communication) by 300% and 1000%, respectively. Upstream from the maxima, the CFC concentrations decreased rapidly, reaching values close to atmospheric equilibrium.

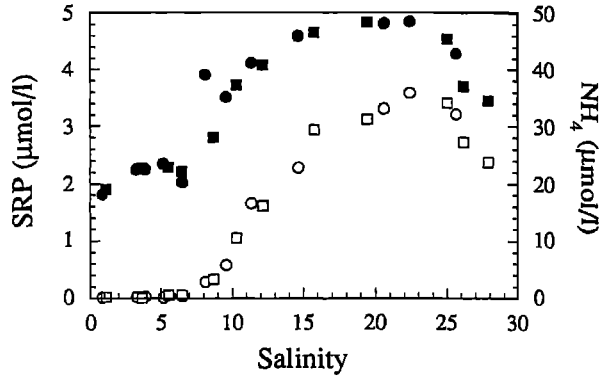

Fig. 2. Distribution of SRP and NH_4 measured on October 2-4, 1991. Filled symbols = SRP and open = NH_4; ○ = surface samples and □ = bottom samples.

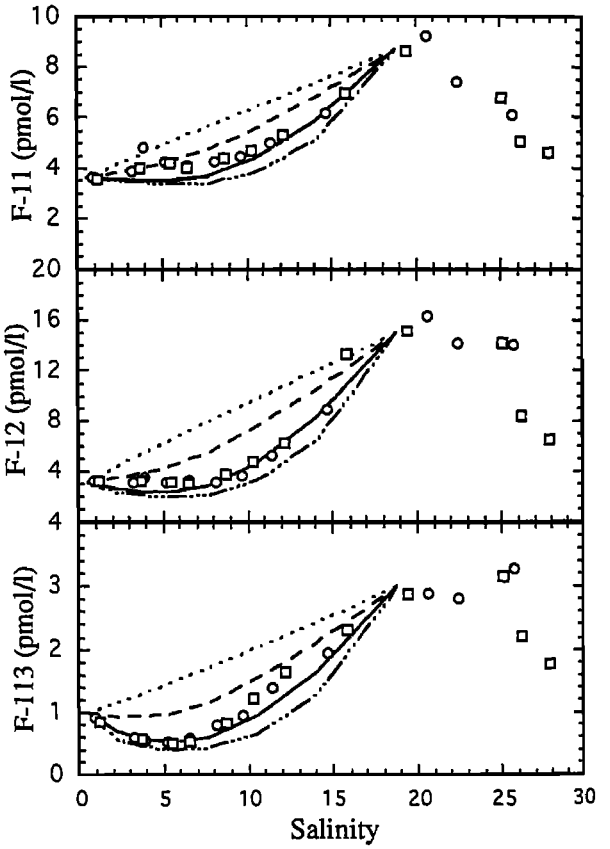

Fig. 3. Distribution of CFCs measured on October 2-4, 1991. The dotted, dashed, plain, and dashed/dotted lines were calculated with gas exchange coefficients = 0 cm hr^{-1}, 0.5 cm hr^{-1}, 3 cm hr^{-1}, and 8 cm hr^{-1}, respectively. ○ = surface samples and □ = bottom samples.

Concentration ratios of F-11/F-12 and F-11/F-113 in the region of highest waste water discharge were relatively constant, 0.5 and 3, respectively (Figure 4). The F-11/F-12 ratio observed was approximately one quarter of the ratio of water in equilibrium with the remote troposphere and similar to the current global industrial production ratio. Upstream of Manhattan both ratios increased, reaching maxima of 1.4 and 9, respectively. For salinities less than 5 ‰ these CFC ratios decreased, suggesting possible influence from waste water discharges upstream of our northern most samples.

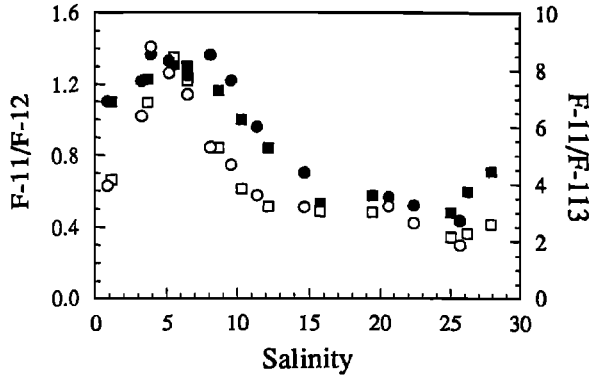

Fig. 4. CFC ratios (pmol/pmol) plotted as a function of salinity. Filled symbols = F-11/F-12 and open symbols = F-11/F-113; ○ = surface samples and □ = bottom samples.

Discussion

The distributions of SRP and NH_4 as a function of salinity observed during the October, 1991 transect were typical of low river discharge conditions in the Hudson estuary. The locations of nutrient maxima coincided with the region of highest waste water loading. As previously reported by Simpson et al. [1975] and others, the SRP distribution is largely controlled by (1) waste water loading (geometry and amounts) and (2) conservative transport by physical mixing. Other possible processes (e.g. uptake by the biological community or desorption from suspended material) represent minor perturbations of SRP distributions in the Hudson estuary water [Clark et al., 1992]. Significant removal of NH_4 relative to SRP at low salinities has also previously been observed in the Hudson. Deck [1981] demonstrated that nitrification is the dominant sink of NH_4 in this region.

The distributions of CFCs as a function of salinity in the Hudson estuary are remarkably similar to those of nutrients suggesting that the locations of their inputs are similar. Unlike SRP, however, CFC concentrations upstream of the maxima fall well below conservative mixing lines. This departure probably is in response to loss from solution by gas exchange; hence, these distributions can be used to estimate the mean gas exchange rate.

We employed a multi-box model of water transport and gas exchange in the Hudson estuary [Deck, 1981; Clark et al., 1992] to calculate the mean gas exchange rate. In the model description, the lower Hudson estuary was divided into a single-layer of boxes of roughly equal volume, either 4 or 8 miles long. Steady-state distributions of dissolved constituents were calculated iteratively with the model. Estuarine transport was simulated using observed riverine plus waste water discharge rates and inter-box exchange fluxes which were calculated from observed salinity distributions. External point sources were included by inputs to the appropriate boxes. Gas exchange was calculated from the degree of saturation with respect to the atmosphere as follows:

$$\frac{dC}{dT} = k\,(C - C_o)$$

where C is the observed CFC concentration in surface water, C_o is the equilibrium CFC concentration with air, and k is the gas exchange coefficient.

The mean salinity distribution was calculated by fitting a third order polynomial to the depth-averaged salinities of all the water samples as a function of location along the axis of the estuary. The salinity for the midpoint of each model segment was then derived directly from the polynomial curve.

Riverine inflow was averaged over the previous 30 days using the sum of: (1) USGS daily mean discharges from the main stem of the Hudson upstream of tidal waters, (2) gauged discharges from tributaries to tidal waters and (3) estimated runoff from ungauged sub-basin areas scaled on the basis of yield per unit area, following the method outlined in Clark et al. [1992]. For the period of interest, average total riverine discharge at the Battery was 140 ± 50 m^3 s^{-1}.

Average atmospheric concentrations of CFCs (n=3) measured at Lamont-Doherty Geological Observatory (45 km north of the Narrows) were 270, 530, and 80 pptv for F-11, F-12, and F-113, respectively, slightly higher than global mean tropospheric air concentrations. Equilibrium concentrations of F-11 and F-12 have been calculated from the solubility data of Warner and Weiss [1985], using the observed mean surface water temperature during our sampling transect (20° C). The F–113 equilibrium concentration was estimated from the observed distribution, assuming that the minimum observed value was supersaturated with respect to the atmosphere by 30%. In the same region, F-11 and F-12 were supersaturated by as little as 10% and 60%, respectively.

Unfortunately, the external loading rate of CFCs is not presently known for the Hudson estuary. However, less than 10% of the total waste water input volume occurs upstream of Manhattan. By limiting model calculations to this region, variations of dissolved CFC concentrations in the estuary due to external sources can be ignored as a first approximation.

Results of the model calculations indicate that gas exchange coefficients between 2 and 4 cm hr^{-1} are most consistent with the observed CFC data (Figure 3). Although distributions calculated using these gas exchange coefficients miss some details, the model distributions match the observed data quite well. Most of the differences occur in the northern part of the estuary. In particular, the calculated concentrations for water with salinities < 7 ‰ are consistently lower than observed for both F-11 and F-12. A number of factors may account for this. Firstly, the gas exchange rate in this region, which lies north of Stony Point (Figure 1) could be lower because the Hudson flows through the Hudson Highlands, which shelters it from the wind and may lower the mean gas exchange rate. Secondly, additional inputs upstream of this area are suggested by the local maximum observed in the F-11 distribution at low salinities. Thirdly, our model calculations assumed a steady state distribution, which may not be an appropriate assumption.

Having derived a mean gas exchange coefficient from observations upstream of Manhattan, the total CFC loading rate from waste waters may be estimated by calculating CFC distributions for the entire estuary. In these calculations, the gas exchange coefficient was specified (2 to 4 cm hr^{-1}) and CFC input rates were varied to approximately match observed dissolved CFC distributions in the zone of maximum concentrations. These CFC loading rates were estimated by assuming a single waste water concentration for each compound and scaling the loading rates according to each facilities waste water discharge rate. Calculated CFC loading rates were 10±1 μmol s^{-1}, 20±3 μmol s^{-1}, and 3.5±0.5 μmol

s^{-1}, respectively, for F-11, F-12, and F-113, equivalent to mean concentrations in the waste water for these same gases of 160±20 pmol l^{-1}, 320±40 pmol l^{-1}, and 55±5 pmol l^{-1}. For comparison, Busenberg and Plummer [1991] measured F-12 concentrations in excess of 500 pmol l^{-1} in some ground waters from central Oklahoma which were contaminated with waste water.

Sensitivity tests showed that the calculated gas exchange rate is most sensitive to the CFC loading rate north of Manhattan. If CFC concentrations in waste water treatment facilities north of Manhattan are greater than the mean waste water values calculated above, then the gas exchange rate we obtained is too low. Hence, the estuarine gas exchange rates reported here should probably be considered as minimum values for the Hudson.

Gas exchange rates calculated here for the Hudson estuary are considerably lower than estimates of the mean oceanic gas exchange rate, but similar to previous estimates for coastal bays and lakes. The Hudson estuary gas exchange rate is 13-25% of the oceanic mean assuming an equal weighing between the ^{222}Rn deficit method (12 cm hr^{-1}) and the ^{14}C methods (19 and 20 cm hr^{-1}, respectively, for the natural and bomb methods) [Peng et al., 1979; Broecker et al., 1985]. The mean exchange rate estimated for San Francisco Bay from ^{222}Rn mass balances, 4 cm hr^{-1} [Hartman and Hammond, 1984], is similar to what we estimate here from CFCs for the Hudson estuary. The range of exchange rates, 0.8 to 8 cm hr^{-1}, observed at Rockland lake (Figure 1) using the SF_6 method [Wanninkhof et al. [1985] also is consistent with the mean gas exchange rate calculated for the Hudson estuary.

Acknowledgements. This research was initiated to complement a field study of nutrient geochemistry supported by the Hudson River Foundation (grant #010/88A/027). We are indebted to E. Busenberg and N. Plummer who initially showed us that high CFC concentrations can be found in natural waters contaminated with waste water. This is contribution number 4927 from Lamont-Doherty Geological Observatory of Columbia University.

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(Received January 13, 1992
accepted March 2, 1992)