

Reevaluation of the open ocean source of carbonyl sulfide to the atmosphere

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Abstract. Carbonyl sulfide (COS) concentrations were measured in surface seawater samples and the overlying marine boundary layer of the Pacific Ocean by using gas chromatography (GC) and electron capture sulfur detection (ECD-S). A wide latitudinal range was covered (55°N–70°S) on two cruises 9 months apart. COS saturation ratios (SRs) in seawater were found to be less than 1 (undersaturated) across wide regions of the open ocean, especially in the subtropical gyres and wintertime subpolar waters. SRs were highest in coastal/shelf regions and in spring/summertime temperate waters. Extensive undersaturation is attributed to a low COS photoproduction potential of the water, limited sunlight, and/or a rapid hydrolysis rate constant. Decreasing COS concentrations during diurnal cycles in tropical waters were fitted to first-order exponentials, with resulting decay times agreeing with calculated hydrolysis lifetimes to within 15%. Air-sea fluxes of COS from the open ocean were calculated by using two different expressions for the transfer velocity and averaged into six latitude bands and three seasons. On the basis of these data we report a global open ocean sea-air flux of -0.032 (-0.010 to -0.054) Tg COS/yr, which is much lower than and of different sign from the current global estimate (0.14–0.58 Tg COS/yr). Atmospheric COS mixing ratios averaged 470 pptv on the first cruise and 442 pptv on the second cruise, with much of the difference possibly a result of a seasonal decrease in the northern hemisphere COS mixing ratio of up to 10%.

Introduction

Carbonyl sulfide (COS) is unique among naturally occurring sulfur gases in the atmosphere because of its relatively slow reaction with the OH radical [Wahner and Ravishankara, 1987], giving it a tropospheric lifetime of 1 year or more and an average mixing ratio of 500 pptv \pm 10% [Khalil and Rasmussen, 1984]. The long lifetime allows substantial transport of COS to the stratosphere, where it is believed to sustain the Junge layer with sulfate aerosol particles during volcanically quiescent periods [Engel and Schmidt, 1994; Crutzen, 1976]. These high-altitude aerosols influence the Earth's radiation budget by interacting with incoming solar radiation [Turco *et al.*, 1982] and could partially offset the warming effect of increased greenhouse gases through higher stratospheric optical depths [Turco *et al.*, 1980]. Stratospheric aerosols are also believed to enhance ozone depletion, with the most recent evidence coming from record stratospheric ozone losses over Antarctica following the injection of large amounts of SO₂ from the eruption of Mount Pinatubo [Solomon *et al.*, 1993]. Ozone depletion appears to be a result of heterogeneous reactions of N₂O₅ on sulfuric acid aerosol surfaces, which effectively sequesters active nitrogen and leads to increased levels of ClO, which

reacts to destroy ozone [Fahey *et al.*, 1993; Rodriguez *et al.*, 1991]. These reactions have the potential to influence stratospheric ozone levels on a global scale, since the very low temperatures found only in polar stratospheric clouds are not necessary for removal of N₂O₅. A small secular increase in background stratospheric aerosol mass in the northern mid-latitudes raises the possibility that ozone depletion could be accelerated above populated areas of the northern hemisphere [Hofmann, 1990]. The cause of the aerosol increase remains uncertain, largely as a result of inadequate information on COS sources and sinks.

There has been no detectable change in the average atmospheric concentration of COS since 1977 [Rinsland *et al.*, 1992; Bandy *et al.*, 1992], which implies that sources of COS have been approximately balanced by the sinks. However, most COS budget estimates have sources exceeding sinks by a factor of 2 or more [Khalil and Rasmussen, 1984; Goldan *et al.*, 1988; Chin and Davis, 1993]. Table 1 shows a recent budget estimate [Chin and Davis, 1993], along with our proposed revised budget. The "missing sink," which is often used to bring the budget into balance, is speculated to be COS deposition to land plants. Laboratory studies have shown the uptake resistances for COS and CO₂ to be similar [Goldan *et al.*, 1988]. Limited field measurements, however, have not supported such a large plant sink [Mihalopolous *et al.*, 1989; Berresheim and Vulcan, 1993; Fried *et al.*, 1993; deMello and Hines, 1994], raising the possibility that some COS source terms have been overestimated. Major sources are believed to be emission by soils, the oceans, biomass burning, and tropospheric oxidation of CS₂ [Chin and Davis, 1993]. Additionally, recent laboratory work by Barnes *et al.* [1994] suggests that gas-phase OH-initiated oxidation of dimethyl sulfide (DMS) forms appreciable quantities of COS and may represent a significant global source, leading to an even larger imbalance in the global budget.

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Paper number 95JD01926.
0148-0227/95/95JD-01926\$05.00

Table 1. Global sources and sinks of COS: Previous and Revised Estimates

	Previous Estimate Tg COS per Year	Revised Estimate Tg COS per Year
<i>Sources</i>		
Ocean		
Coastal	0.32 (0.17–0.47)	0.32
Open	0.29 (0.14–0.58)	...
CS ₂ oxidation	0.34 (0.17–0.61)	0.34
Soil and marsh	0.27 (0.14–0.52)	0.27
DMS oxidation	0.17 (0.10–0.28)	0.17
Biomass burning	0.14 (0.04–0.26)	0.14
Anthropogenic	0.05 (0.03–0.07)	0.05
Volcano	0.02 (0.006–0.09)	0.02
Total	1.6 (0.81–3.0)	1.3 (0.67–2.5)
<i>Sinks</i>		
Vegetation uptake	0.43 (0.16–0.91)	0.43
Reaction with OH	0.13 (0.02–0.80)	0.13
Open ocean	...	0.032 (0.010–0.054)
Photolysis	0.029 (0.020–0.040)	0.029
Reaction with O	0.015 (0.009–0.026)	0.015
Total	0.60 (0.19–1.8)	0.63 (0.22–1.9)

Data are from *Chin and Davis* [1993], except for ocean source, which is an average from *Andreae and Ferek* [1992] and *Mihalopolous et al.* [1992], and DMS source, which is from *Barnes et al.* [1994].

The most extensively studied source has been the ocean. COS production is believed to result from photosensitized oxidation of sulfur-containing dissolved organic matter (DOM) in surface seawater [*Ferek and Andreae*, 1984; *Andreae and Ferek*, 1992; *Zepp and Andreae*, 1994]. Coastal and shelf regions, being richer in photosensitizing agents than the open ocean, are thought to make up about 60% of the total ocean flux [*Andreae and Ferek*, 1992], even though by area the coastal ocean accounts for only about 13% of the world's ocean [*Andreae*, 1986]. *Weiss et al.* [1995] have reported that COS photo-production rates are up to an order of magnitude larger in coastal water compared with the open ocean. COS removal from the water column is believed to occur both by sea-air exchange and by reaction with hydroxide ion in the water [*Elliot et al.*, 1989; *Radford-Knoery and Cutter*, 1994], with a rate that depends on temperature and pH. Before measurements of dissolved COS were made, *Johnson* [1981] proposed that the oceans could be a major sink for atmospheric COS based on hydrolysis rate constants determined for fresh water. However, subsequent measurements in selected regions showed that COS was supersaturated with respect to atmospheric equilibrium, leading to the conclusion that the oceans were a major source of COS to the atmosphere [*Rasmussen et al.*, 1982; *Ferek and Andreae*, 1983; *Turner and Liss*, 1985; *Johnson and Harrison*, 1986; *Mihalopolous et al.*, 1992]. On the other hand, data have been sparse from ocean regions that are expected to have the lowest concentrations of dissolved COS (i.e., high latitude, wintertime, or waters with low COS precursor concentrations). In this paper we report the discovery of extensive regions of undersaturation in surface seawaters of the Pacific Ocean. This phenomenon has

not been previously reported, perhaps because the majority of dissolved COS measurements in the past have been carried out either in coastal regions, where production rates are very high, or during spring and summer months in the midlatitude open ocean, where sunlight is abundant and biological activity is high. Previous global ocean fluxes may be overestimated because they do not adequately address the seasonal and spatial variability in seawater COS concentrations, which have been observed to vary by at least 2 orders of magnitude. In particular, coastal and open ocean regions have very different dissolved COS concentrations, yet only two studies [*Mihalopolous et al.*, 1992; *Andreae and Ferek*, 1992] report separate fluxes for these regions. We have collected an extensive open ocean data set of COS concentrations in surface waters and from the overlying marine boundary layer, and the global open ocean flux we present here indicates that the open ocean acts as a weak sink to atmospheric COS. This revision slightly improves the unbalanced budget of global sources and sinks.

Experiment

Air and Water Sampling

Air was sampled from the top of the mast on the flying bridge about 20 meters above the sea surface, by using an Air-Cadet (Cole Parmer) pump and Teflon tubing (1/4" ID), and dried by using a stainless steel loop held at -40°C . COS dissolved in surface water was partitioned continuously by using a Ray Weiss-type (Scripps Oceanographic Institute) equilibrator. Described by *Butler et al.* [1988], the Weiss equilibrator is constructed of clear acrylic and uses a "shower head" to spray seawater through the headspace, maintaining an equilibrator atmosphere that is representative of surface water concentrations. Water from a depth of 5 m was pumped from a forward intake of the ship at a rate of 15–20 L/min. On the basis of results for CO [*Bates et al.*, 1995], another photochemically produced dissolved gas, it was assumed that there was no consistent COS concentration gradient between the surface and the sampling depth of 5 m. The temperature in the equilibrator was continuously monitored by a calibrated thermistor connected to an automated data system, which showed that the water had warmed an average of 0.26°C compared to surface water at the intake. A correction for this warming in the solubility coefficient (H) was made. An estimated gas headspace volume of 20 L was circulated at 4–6 L/min with a pumping system similar to that used for air sampling from the flying bridge. Less than 1% of the headspace volume was removed for each sampling, thus minimizing the amount of ambient air needed to maintain atmospheric pressure inside the equilibrator. The equilibrator and tubing were tested for inertness to COS, and no appreciable losses (or increases) were observed.

Analysis

COS was analyzed by using the electron capture sulfur detector for gas chromatography (ECD-S) described in detail by *Johnson and Lovelock* [1988] and *Johnson and Bates* [1993]. Modifications of the instrument are described by *Weiss et al.* [1995]. The ECD-S has sensitivity down to the femtomole level without sample preconcentration, making it possible to inject 5 mL of sample air directly to the gas chromatograph (GC). COS levels ranged from 0.2 to 4.5 ppb in equilibrated seawater samples where the ECD-S showed a linear response to standards of better than 96%. Standards were made by diluting a 1000-

times ambient level (~500 ppbv) high-pressure gas cylinder standard (Scott Specialty Gases) with COS-free air, to make a continuously flowing secondary standard in the 0.5-ppbv range. The primary tank standard was calibrated from analyses by the manufacturer (Scott) and by using permeation tubes whose weight loss histories were known from bimonthly weighings. The average of all permeation tube calibrations was 504 ± 40 ppbv, which compared well to the Scott calibration of 495 ± 25 ppbv. Over the 2-year period there was no detectable ($>1\sigma$) systematic trend in concentration loss or gain of the high-pressure cylinder. A value of 504 ppb was used for the tank standard calibration for both cruises.

The lower limit of detection, defined as the mixing ratio of COS where signal/noise = 2, was 115 ppt during cruise 1 and 23 ppt during cruise 2. The primary reasons for improvement during cruise 2 were optimization of the fluorination catalyst through occasional conditioning with 1% F_2 in N_2 at 250°C for 1 hour and a reduction of the blank. The majority of the blank during cruise 1 was caused by contamination from the sample injection valve, affecting all injections similarly and canceling out most of the systematic error. About 28 ppt, however, was systematically added to each ambient- and equilibrated-air injection from a valve used to switch between sample dehydration loops, and this amount was subtracted from each of these analyses. During cruise 2 the valve rotors were replaced with a noncontaminating material, and the blank was reduced to about 23 ppt. This residual contamination was a result of incomplete cleanup of ambient air through the zero-air generator (Peak Scientific), making an addition of 23 ppt to each ambient air analysis necessary. The reproducibility of the blanks in both cruises was observed to be about 7%.

The overall accuracy of the measurements, estimated by calculating the root mean square of the standard deviations of the standard calibration and the blank determinations, was 11%. The precision of the measurements was 6–10%, based on the reproducibility of the standard over a 6-hour period.

Results and Discussion

Sea Water Measurements

Measurements of COS in air and seawater were made along two meridional sections (55°N–70°S) (Figure 1) aboard the NOAA ship *Surveyor* from March 20, 1993, to May 7, 1993 (cruise 1), and November 20, 1993, to January 7, 1994 (cruise 2). COS seawater saturation ratios (Figure 2) were calculated from the surface seawater COS partial pressure, P_s , and the atmospheric partial pressure, P_a , and are defined as

$$SR = \frac{P_s}{P_a} \quad (1)$$

where

$$P_s = (P - P_{we}) X_e \frac{H_s}{H_e} \quad (2)$$

and

$$P_a = (P - P_{wa}) X_a \quad (3)$$

where P is the atmospheric pressure at the time of the measurement, P_{wa} is the saturation vapor pressure of seawater at the sea surface temperature and salinity, P_{we} is the saturation vapor pressure of seawater in the equilibrator (calculated from the equilibrator temperature and assuming 100% relative humidity)

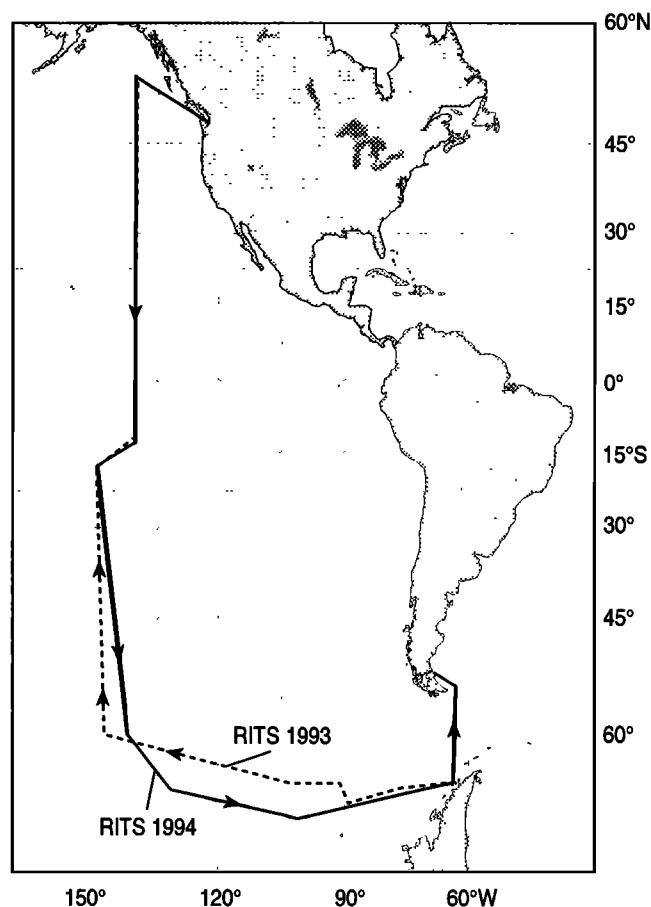


Figure 1. Cruise tracks of the NOAA ship *Surveyor* during the March 20 to May 7, 1993, and November 20, 1993 to January 7, 1994 Radiatively Important Trace Species (RITS) cruises. Cruise 1 (RITS93) began in Punta Arenas, Chile, and cruise 2 (RITS94) began in Seattle, Washington.

[Weiss and Price, 1980], X_a is the measured mixing ratio of COS in dry air, X_e is the measured mixing ratio of COS in the equilibrator headspace air after removal of water vapor, H_s is the Henry's Law solubility constant for COS in seawater at the sea surface temperature, and H_e is the Henry's Law solubility constant for COS at the equilibrator temperature.

The SRs along the cruise track ranged from about 0.2 to 4.5 and were highly variable, especially between low-latitude oligotrophic waters and summertime temperate and polar waters (Figure 2). Such variability reflects changing source and sink strengths in the water column. As was suggested by *Andreae and Ferek* [1992], COS concentrations in seawater are controlled by photochemical production, which depends on both light intensity and COS precursor concentration, and a removal term (hydrolysis) which is of first order with respect to COS concentration. The ocean regions with the highest concentrations of dissolved COS (high latitude, summertime) had abundant sunlight and low water temperatures (slow hydrolysis rates). Although there are no direct measurements, it is likely that COS precursor concentrations were elevated, given the higher photoproduction rates found by *Weiss et al.* [1995] in these regions compared to the rest of the open ocean, as well as the large amounts of biomass in the water reflected by chlorophyll-a measurements. Low-latitude oligotrophic waters had the lowest COS concentrations presumably resulting from relatively warm water temperatures (rapid hydrolysis) and low photoproduction

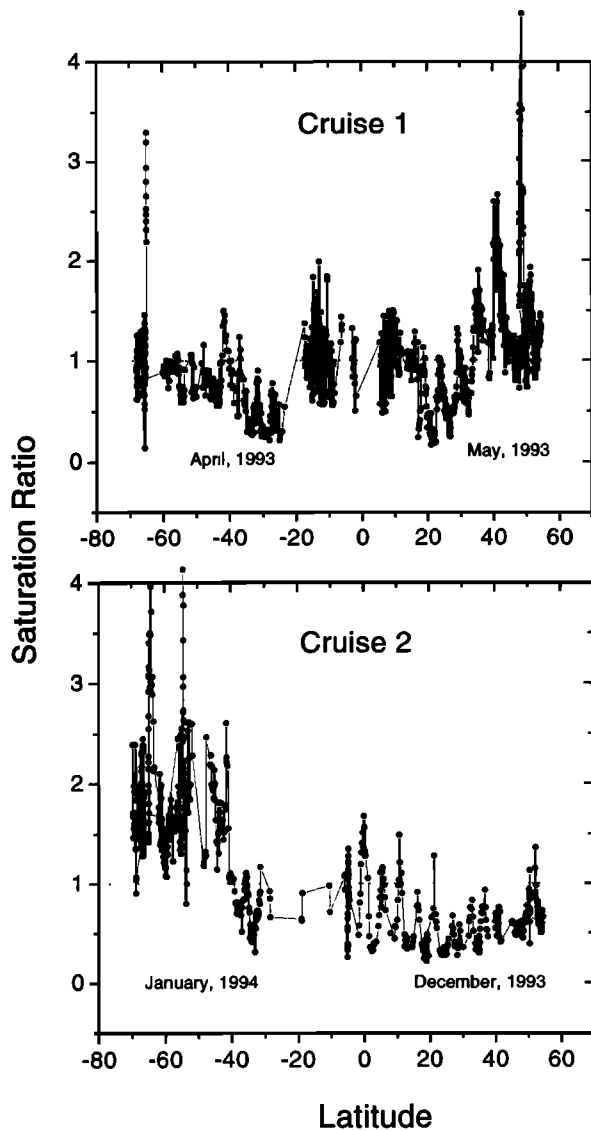


Figure 2. Latitudinal dependence of COS saturation ratios in seawater from both cruises. Horizontal dashed lines indicate a saturation ratio of 1, or seawater in equilibrium with atmospheric COS.

rates [Weiss *et al.*, 1995], in spite of ample solar radiation in these regions.

The importance of season on seawater COS concentration can also be seen in Figure 2. In the temperate and subpolar latitudes (35° – 65°) there is roughly a factor of 2 increase in the average SR between cruise 2 (boreal winter) and cruise 1 (boreal spring), and similarly between austral autumn and summer. The magnitude of this seasonal variation is also consistent with the findings of Mihalopolous *et al.* [1992]. Factors such as changes in available sunlight and precursor concentrations in the surface waters are probable causes of such variability.

Diurnal Cycles

In addition to the seasonal and regional variations in COS SRs, the SRs also exhibit a strong diurnal variation. Data from 3 consecutive days in the subtropical gyre region (13° – 29°) of the northern hemisphere are shown in Figure 3. Note that the maximum concentrations each day barely reach saturation, indicating that this region of the ocean was a net sink for

atmospheric COS. Also, the 2- to 4-hour time lag between the maximum light intensity and maximum COS concentrations is consistent with the observations of Andreae and Ferek [1992]. Turnover times of COS in surface waters were calculated by fitting the postsunset concentration decreases to first-order exponential functions and are listed in Table 2. These turnover times show a good agreement to the hydrolysis lifetimes predicted from rate constants from Radford-Knoery and Cutter [1994], indicating that hydrolysis is the dominant removal pathway for seawater COS, as was speculated by Andreae and Ferek [1992]. Predicted lifetimes from Elliot *et al.* [1989] are consistently shorter than our observed turnover times, perhaps indicating that dark production of COS is a significant source in seawater. The rate constants from Elliot *et al.* [1989] were determined in artificial solutions that likely had no dark production, whereas Radford-Knoery and Cutter [1994] used ambient seawater. Dark production, which has been observed previously by Ulshöfer *et al.* [1995] and Weiss *et al.* [1995], would increase the observed turnover time of COS relative to the hydrolysis lifetime. Our results suggest that dark production increases the COS lifetime at the surface by at least 15% under the wind and temperature conditions that prevailed during this study. This is a lower limit, since COS concentrations decrease with depth in the top 100–200 m [Radford-Knoery and Cutter, 1994] and vertical mixing, which would show a decrease in the observed lifetime at the 5-m depth, was not considered here.

A kinetic model for COS diurnal cycles ($SR > 1$) in surface waters can be parameterized:

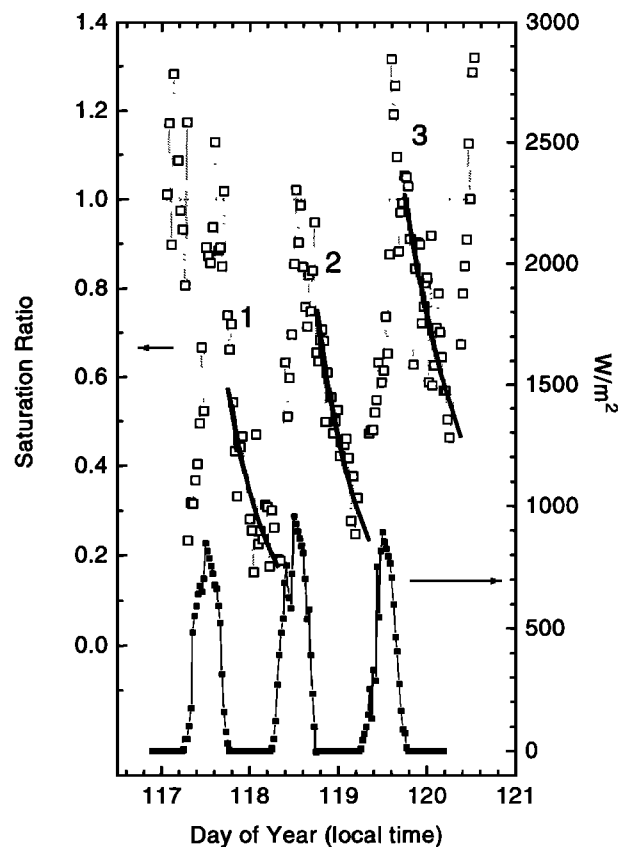


Figure 3. Three consecutive diurnal cycles of dissolved COS concentrations (as saturation ratios) from cruise 1 (13° – 29° N). First-order exponentials have been fitted to the concentration losses each afternoon. Sunlight intensity is also plotted and has a maximum at local noon each day.

Table 2. Comparison of Measured Decay Times of COS Concentration in Seawater With Hydrolysis Lifetimes

Curve Number in Figure 3	Date (Cruise 1, 1993)	Temperature of Equilibrator	τ Hydrolysis, ^a hours	τ Hydrolysis, ^b hours	τ Fit, ^c hours
1	April 27	23.2	10	8	11 ± 3
2	April 28	21.7	12	10	12 ± 2
3	April 29	18.4	17	13	20 ± 4

Hydrolysis lifetimes at specified temperature, and a 3-day averaged pH of 8.17, measured at the same locations during cruise 2 (November 30 to December 2).

^a From *Radford-Knoery and Cutter* [1994].

^b From *Elliot et al.* [1989].

^c Exponential fits to curves in Figure 3, with the error of the fit.

$$\frac{d[\text{COS}]}{dt} = k_1 E(t) [\text{DOS}] + P_{\text{dark}} - k_2 [\text{COS}(t)] - L_{\text{mix}} - L_{\text{vent}} \quad (4)$$

where k_1 is the photoproduction rate, $E(t)$ is proportional to sunlight intensity, $[\text{DOS}]$ is a measure of the COS precursor concentration, P_{dark} is the dark production rate, k_2 is the hydrolysis rate constant, L_{mix} is the loss due to mixing, and L_{vent} is the loss due to gas exchange.

Comparison of the Weiss Equilibrator With Other Sampling Techniques

As a check of the efficiency of the Weiss equilibrator we compared its performance with two other techniques, a bubbling equilibrator and a conventional purge and trap system. The bubbling equilibrator was constructed of glass and is of the same dimensions and design as that used by *Ferek and Andreae* [1983]. This type of equilibrator was originally developed by *Conrad et al.* [1982] for dissolved CO in seawater, and it relies on air bubbled through continuously flowing seawater to obtain equilibrium in the headspace. The headspace is circulated continuously, in similar fashion to the Weiss equilibrator. Having no materials other than glass and Teflon, which are inert to COS, the bubbling equilibrator provided a good check to see whether wall losses were occurring in the Weiss equilibrator (made of acrylic).

Purge and trap analysis has been the most common technique for sampling dissolved COS, and the apparatus used here is described by *Weiss et al.* [1995]. Table 3 presents the results of the intercomparisons. The uncertainty values represent 1 σ of the mean for the number of measurements (N). Comparisons were made in a variety of water types with different ambient levels of dissolved COS, usually at night to minimize diurnal variability. The measurements with the Weiss equilibrator fall within the uncertainty ranges of the other techniques, indicating that there are no systematic differences among the three techniques. The advantage in using the Weiss equilibrator over the other methods is that an automated system is much easier to set up and maintain. The bubbling equilibrator is sensitive to losses of headspace gas through bubbles escaping into the seawater drain, which cause the water level to slowly rise. For the purge and trap system, manual injections make this technique very labor intensive and the hardest to automate.

Saturation Ratio Comparisons With Other Studies

Where open ocean measurements from this work overlap with previous studies in region and season the agreement is usually

within measurement uncertainties. For example, our average springtime SR from the temperate North Pacific (cruise 1) is 1.2, compared to the results of *Andreae and Ferek* [1992], who report an SR of 1.9 from the North Atlantic, and of *Rasmussen et al.* [1982], who report an SR of 1.4 from the North Pacific. *Staubes and Georgii* [1993] report SRs of 3–6 in the South Atlantic (50°–70°S) during the austral summer solstice, compared to our SRs of 1–4 from cruise 2. The only previously reported wintertime open ocean data come from the Sargasso Sea during November [*Andreae and Ferek*, 1992]. *Andreae and Ferek* report an average SR of 1.5, which is 2–3 times larger than our findings in the Pacific but may reflect the higher productivity of the Sargasso Sea in winter compared to the subtropical Pacific. Coastal ocean SRs from this work (from off the Washington/Oregon coast and the eastern side of Tierra del Fuego) average 2.6, which is on the low end of the range from other studies from temperate coastal regions (SR = 2–20) [*Mihalopolous et al.*, 1992]. Such a discrepancy could originate from the types of coastal areas studied, since COS concentrations are likely to be higher in bays and inlets, rich in terrigenous runoff, than off rocky coastlines, where most of our coastal measurements were taken. Consequently, we have chosen to separate our data into open ocean and coastal/shelf (<400-m depth) categories and calculate an open ocean flux of COS to compare with previous studies.

Table 3. Comparison of Weiss Equilibrator With Bubbling Equilibrator and Purge and Trap

Location	Weiss Equilibrator		Bubbling Equilibrator	
	N	Headspace Concentration, ppt	N	Headspace Concentration, ppt
55°N, 140°W	7	580 ± 54	5	631 ± 61
20°N, 140°W	10	276 ± 53	12	297 ± 59
44°S, 144°W	15	826 ± 85	14	823 ± 82
Location	Weiss Equilibrator		Purge and Trap	
	N	Seawater Concentration, pmole / L	N	Seawater Concentration, pmole / L
7°S, 140°W	15	5.8 ± 1.0	23	5.3 ± 1.2
21°S, 149°W	3	4.6 ± 1.0	5	3.5 ± 1.7
64°S, 134°W	50	31.7 ± 6.7	11	29.7 ± 7.3

Air-Sea Flux Calculations

The oceanic flux of COS can be estimated by using the model of *Liss and Slater* [1974]:

$$F = K_w \left(C_w - \frac{C_a}{H_d} \right) \quad (5)$$

where C_w and C_a are the COS concentrations in seawater and air, respectively, K_w is the sea-air transfer velocity, and H_d is the dimensionless Henry's Law solubility constant from *Johnson and Harrison* [1986]. Expression (5) can be also written

$$F = K_w \left(\frac{P_a}{H_p} \right) (SR - 1) \quad (6)$$

where P_a is the atmospheric partial pressure of COS and H_p is the Henry's Law solubility constant in units of L atm mole⁻¹ ($H_p = H_d RT$). K_w is a function of wind speed and the Schmidt number, which is the ratio of seawater viscosity to COS molecular diffusivity, both being functions of temperature.

Two methods for calculating the transfer velocity were used in the subsequent data analyses. The first is based on the equations developed by *Liss and Merlivat* [1986], which are linear fits of wind speed to transfer velocities determined by tracer experiments under three different wind speed regimes [*Mihalopolous et al.*, 1992]:

$$K = 0.17 (A(\theta))^{-2/3} u \quad u < 3.6 \text{ m s}^{-1} \quad (7)$$

$$K = 0.17(A(\theta))^{-2/3} u + 2.68(A(\theta))^{-1/2}(u - 3.6) \quad (8)$$

$$3.6 < u < 13 \text{ m s}^{-1}$$

$$K = 0.17(A(\theta))^{-2/3} u + 2.68(A(\theta))^{-1/2}(u - 3.6) \quad (9)$$

$$+ 3.05(A(\theta))^{-1/2}(u - 13) \quad u > 13 \text{ m s}^{-1}$$

where K is the transfer velocity in centimeters per hour, u is wind speed in meters per second, $A(\theta)$ is the ratio $Sc(\theta)/Sc(20)$, where $Sc(\theta)$ is the Schmidt number of COS and $Sc(20)$ is the Schmidt number of CO₂ in seawater at 20°C, equal to 595 [*Mihalopolous et al.*, 1992].

The second method for calculating the transfer velocity comes from *Wanninkhof* [1992] and is a quadratic fit of climatological wind speeds to transfer velocities determined from ¹⁴C disequilibria in the ocean:

$$K = 0.39 u^2 (A(\theta))^{-1/2} \quad (10)$$

where K , u , and $A(\theta)$ are defined above except that $Sc(20) = 660$ [*Wanninkhof*, 1992]. The factor 0.39 is used for climatological winds, as opposed to 0.31, which is appropriate for instantaneous (ship's) winds. Since there is no current consensus over which relationship (*Wanninkhof* versus *Liss and Merlivat*) provides the more accurate values for transfer velocity, we use the two relationships to bound the range of potential values.

Another source of uncertainty in transfer velocity calculations is in choosing values for wind speed. Two wind fields were compared in this study: winds measured aboard the ship at a height of 18 m above sea level and 40-year climatological winds obtained from the Comprehensive Ocean-Atmosphere Data Set

(COADS), which are monthly averages on a 2° × 2° latitude-longitude grid. Ship winds gave larger transfer velocities using the *Liss and Merlivat* relationship by nearly a factor of 2 because of high wind speeds associated with particular storm events and the nonlinearity of the transfer velocity expressions. Transfer velocities calculated by using the shipboard winds provide the best estimate of the instantaneous flux, although these calculations are not necessarily representative of the zonal average flux. Additionally, we have observed no significant anticorrelation between ship's wind speed and our measured seawater COS concentrations, indicating that COS concentrations in the mixed layer are not very sensitive to rapid changes in wind speed. This is not surprising, since the venting of COS to the atmosphere is a minor loss term in the cycling of dissolved COS in the mixed layer. Thus, for the purposes of estimating a regional and seasonal flux we have chosen to use the COADS winds. It should be noted that there is no standard observational height for COADS winds. However, by assuming a height of 10 m, we estimate (using a drag coefficient of 1.5×10^{-3} [*Liss and Merlivat*, 1986] an added uncertainty to the transfer coefficients of only 2%.

Using equation (6), we calculated a local flux at each SR measurement location. Local fluxes were then averaged into six latitude bands for the open ocean and three seasons: summer, winter, and equinox. Separating the data into three seasons was based on the fact that the first cruise was entirely during the spring/fall seasons and the second cruise was entirely during the winter/summer seasons, for northern and southern hemispheres, respectively. These seasons were defined so that their midpoints coincide with the equinox (for fall/spring) or the solstice (for winter/summer), corresponding to the midpoint in the solar cycle for a particular season. Since COS production is a strong function of available sunlight, this redefinition of seasons seems justified. A summary of the flux calculations based on seasons and regions is given in Table 4. Note that the regionally averaged values for K , P_a , H , and SR were not used for the regionally averaged flux calculation, but instead the local values for these parameters were used to obtain a local flux, which was then averaged into regions. Thus a regionally averaged SR of 1.0 does not necessarily give a regionally averaged flux of 0. The total open ocean flux of COS to the atmosphere is -0.022 Tg/yr, using monthly averaged winds from COADS and transfer velocity relationships from *Liss and Merlivat* [1986]. If the *Wanninkhof* [1992] transfer velocity relationship is used, the result is a flux of -0.041 Tg COS/yr. Thus we have chosen to report our open ocean flux as -0.032 Tg/yr, the average of the two extremes. Figure 4 shows a comparison of the regionally and seasonally averaged fluxes calculated by using the two different expressions for transfer velocity. *Wanninkhof* [1992] fluxes are consistently larger in each season, in both the positive and negative direction. It is also interesting to note that no amount of uncertainty in K can change the fact that the wintertime open ocean is a sink for atmospheric COS. Including the uncertainties in the SRs, P_a , K , and H in the flux by calculating the root mean square of the percent errors in each parameter gives a range of fluxes from -0.010 to -0.054 Tg COS/yr.

With regard to the atmospheric budget of COS, designating the open ocean as a sink rather than a source makes the sum of the sources only ~50% larger than the sum of the sinks (Table 1). However, even if this revised budget were accurate, atmospheric COS would still be increasing by about 11%/yr, given a global atmospheric burden of 4.6 Tg. This is directly contradictory to the findings of *Rinsland et al.* [1992] and *Bandy et al.*

Table 4. Calculation of Seasonal, Regional, and Global COS Sea-Air Flux

Region	Latitude, deg.	Area, ^a m ²	Schmidt Number	Wind Speed, m/s	<i>K</i> , m/day	<i>P_a</i> , natm	H	SR	Flux, ^b Gg COS/yr
<i>Equinox</i>									
Polar	65–80	9.50E+12	2,665	7.2	1.3	0.445	1.0	1.0	–0.3
Subpolar	50–65	9.50E+12	1,862	8.5	2.1	0.451	1.3	1.2	0.9
Temperate	35–50	2.40E+13	1,360	8.0	2.2	0.466	1.6	1.2	2.4
Subtropical	20–35	3.35E+13	825	6.8	2.1	0.472	2.3	0.6	–5.4
Tropical	5–20	3.85E+13	610	6.7	2.3	0.481	3.0	1.0	–0.4
Equatorial	0–5	4.60E+13	569	5.3	1.4	0.430	3.1	0.9	–0.5
Total									–3.4
<i>Summer</i>									
Polar	65–80	9.50E+12	2,886	6.7	1.1	0.443	0.9	1.7	3.2
Subpolar	50–65	2.40E+13	2,285	7.6	1.6	0.444	1.1	1.9	10.0
Temperate	35–50	3.35E+13	1,205	7.1	1.9	0.435	1.7	1.4	6.1
Subtropical	20–35	3.85E+13	882	6.5	1.8	0.408	2.2	0.7	–4.4
Tropical	5–20	4.60E+13	597	6.5	2.2	0.394	3.0	0.9	–1.9
Equatorial	0–5	1.60E+13	622	7.0	2.6	0.391	2.9	0.9	–0.7
Total									12.3
<i>Winter</i>									
Polar ^c	65–80
Subpolar	50–65	9.50E+12	1,511	10.2	3.0	0.488	1.4	0.7	–2.6
Temperate	35–50	2.40E+13	1,139	10.0	3.4	0.414	1.8	0.6	–8.3
Subtropical	20–35	3.35E+13	822	7.6	2.6	0.424	2.3	0.5	–8.2
Tropical	5–20	3.85E+13	624	7.9	3.2	0.429	2.9	0.6	–7.3
Equatorial	0–5	4.60E+13	618	6.9	2.5	0.427	2.9	0.7	–4.3
Total									–30.7
Total									–21.8

Parameters used are climatological winds, transfer velocities (*K*) [from *Liss and Merlivat*, 1986], and *H* [from *Johnson and Harrison*, 1986]. Seasons are defined as follows: equinox, February 5 to May 7 and August 5 to November 7; summer, May 8 to August 4 (northern hemisphere); winter, November 8 to February 4 (northern hemisphere).

^a Areas from *Bates et al.* [1987]. E is exponential, e.g., 9.50E + 12 = 9.5 × 10¹².

^b Regional fluxes were obtained from the average of local fluxes in that region, calculated from local SR, *H*, *K*, and *P_a* values, not from the regionally averaged parameters listed.

^c Wintertime polar ocean is assumed to be ice-covered.

[1992], who have observed that atmospheric COS has changed by less than 1%/yr since 1977. Other sources must be investigated with the possibility that they are overestimated. One possibility is the proposed soil source. *Castro and Galloway* [1991] found that the enclosure technique used to generate previous data may have produced artificially high COS fluxes as a result of using sulfur-free purge gas. Recent work by *de Mello and Hines* [1994] also suggests that the magnitude of COS fluxes from soils and wetlands depends on whether a static or dynamic enclosure system is employed. Most budgets also have CS₂ conversion as a major source of COS, while knowledge of sources and sinks of CS₂ is even more limited than that of COS. Finally, the magnitude of the coastal ocean flux should be the focus of future COS measurements in the marine environment. Table 5 shows a comparison of average SRs for coastal regions, including our work, which is significantly lower. The discrepancy is probably a result of different measurement locations, as mentioned earlier, indicating that more measurements need to be made in various coastal environments in order to better resolve the spatial and seasonal variations.

Atmospheric COS Concentrations

Ambient atmospheric measurements from both cruises are shown in Figure 5 averaged in 5° bins as a function of latitude. Averages by hemisphere and cruise are shown in Table 6. Linear fits to the concentration data from each cruise show an inter-hemispheric gradient that changes direction between the two cruises. Interhemispheric ratios shown in Table 6 are less than the standard deviation of the average concentrations from each hemisphere; however, these trends are statistically significant at the 95% confidence level based on a *t* test. Average concentrations in the northern hemisphere appeared to change by about 10% between cruises compared to only a 5% change in the southern hemisphere. Although the magnitude of the seasonal changes observed in this work is less than the overall measurement accuracy, estimated at 11%, the data trends suggest that the northern hemisphere experiences a more pronounced seasonal cycle of atmospheric COS than the southern hemisphere. *Mihalopolous et al.* [1991] have observed a seasonal cycle of similar magnitude in the southern hemisphere (<5.4%). An increase in northern hemisphere COS concentrations on the

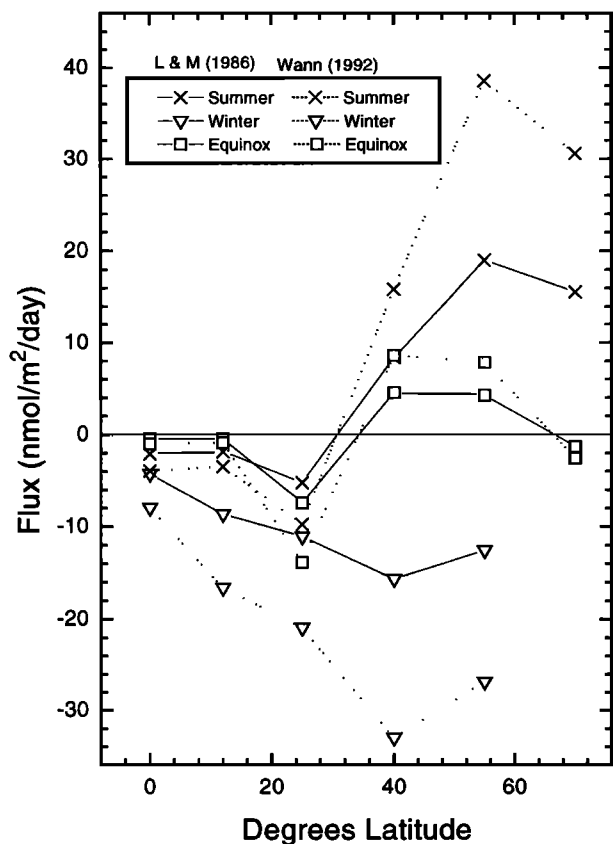


Figure 4. Regional and seasonal distribution of COS sea-air flux in both northern and southern hemispheres. Solid lines are fluxes calculated by using transfer velocity-wind speed relationships from *Liss and Merlivat* [1986] (L & M), and dotted lines are fluxes using transfer velocity-wind speed relationships from *Wanninkhof* [1992] (Wann). Symbols represent the midpoint of each region defined in Table 4. Seasons are also defined in Table 4.

order of 5–10% in the spring/summer months has also been observed by *Rinsland et al.* [1992], using total column infrared spectroscopy from two temperate northern hemisphere sites. Some of their seasonal signal was attributed to seasonal changes in tropopause height, although by accounting for this correction they still report a seasonality of about 5%, with a distinct maximum during late summer. The magnitude of this seasonality is in general agreement with our findings. Our lack of northern hemisphere data during the summer and autumn months makes a complete comparison impossible.

The magnitude of the interhemispheric gradients from each cruise is less than 5%, which is in agreement with past measurements over the Pacific [*Torres et al.*, 1980; *Johnson and Harrison*, 1986]. This distribution suggests that the COS lifetime is greater than the interhemispheric mixing time (~1 year) or that the sources and sinks are nearly the same in the two hemispheres. The Pacific data are not consistent with the large interhemispheric gradients (15–25%, north > south) observed by *Bingemer et al.* [1990] and *Johnson et al.* [1993] over the Atlantic in the boreal spring and summer. Given the long lifetime of COS, the interhemispheric gradient of COS over the Atlantic should be similar to that of the Pacific during the same season. *Bingemer et al.* [1990] suggest that their gradient and correlations with CO and CH₄ concentrations are evidence for anthropogenic sources of COS from Europe and North America,

Table 5. Observed Coastal Ocean Saturation Ratios

Reference	SR
This work	2.6 ± 0.8 ($R = 45$)
<i>Mihalopolous et al.</i> [1992]	9
<i>Andreae and Ferek</i> [1992]	9
<i>Johnson</i> [1985]	4
<i>Turner and Liss</i> [1985]	4.6
<i>Rasmussen et al.</i> [1982]	4.2

which may be increasing owing to a worldwide increase in industrialization. This is not consistent, however, with the upper limit of 0.2%/yr global increase in COS set by *Rinsland et al.* [1992]. More high-precision measurements of atmospheric COS are needed to help resolve this discrepancy.

Conclusions

With the global budget of COS greatly out of balance, the magnitude of the open ocean source was reevaluated on the basis of measurements in many ocean regions and in seasons not previously sampled. COS concentrations were measured in surface waters of the Pacific and the overlying boundary layer between 55°N and 70°S on two cruises covering three seasons. Seawater COS concentrations were observed to be dependent on water type, time of day, and season. Highest concentrations (saturation ratios of 1–4.5) were observed in coastal waters and

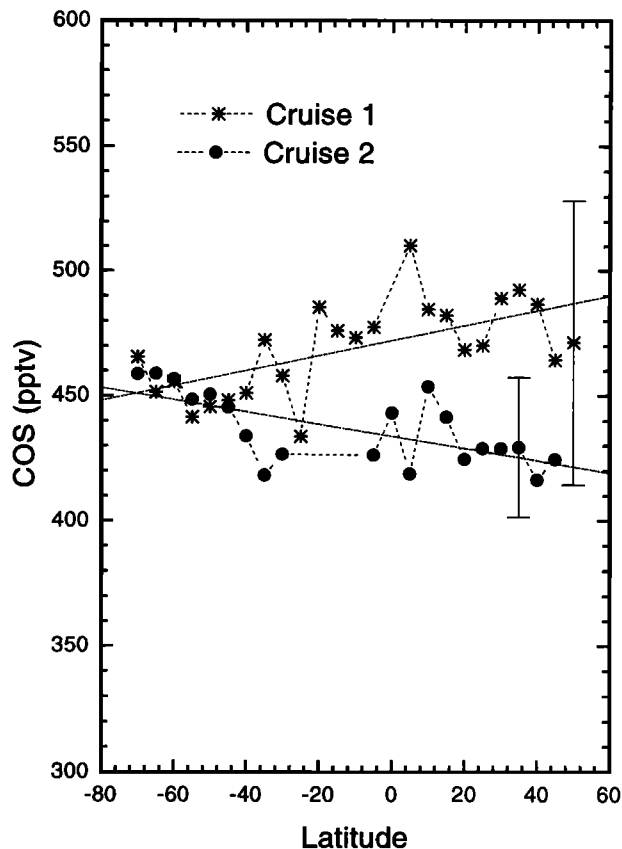


Figure 5. Ambient atmospheric measurements of COS mixing ratio, in parts-per-trillion by volume (pptv), presented as 5° averages. Linear fits to the data sets are also shown. The error bars indicate the average of the standard deviations from each latitude bin.

Table 6. Ambient Atmospheric Data From Both Cruises

	Cruise 1	Cruise 2
<i>Northern Hemisphere</i>		
Mean, ppt	477	431
σ , ppt	40	37
σ /mean	0.08	0.08
<i>N</i>	382	185
$\sigma/N^{1/2}$, ppt	2	3
<i>Southern Hemisphere</i>		
Mean, ppt	463	448
σ , ppt	67	25
σ /mean	0.14	0.06
<i>N</i>	360	353
$\sigma/N^{1/2}$, ppt	4	1
<i>Total</i>		
Mean, ppt	470	442
σ , ppt	55	31
σ /mean	0.12	0.07
Gradient, ppt/ $^{\circ}$ latitude	0.30	-0.24
IHR, ^a %	3.0	-3.8

^a IHR, Interhemispheric gradient, equal to (northern average minus southern average) / southern average.

in polar and subpolar waters that had continuous sunlight. Dissolved COS concentrations were lowest (saturation ratios of 0.2–1.5) in subtropical gyre regions of low biomass (determined by chlorophyll fluorescence) and limited sunlight (subpolar, wintertime waters). Extensive regions of the open ocean were observed to be undersaturated with respect to atmospheric equilibrium of COS and thus to act as a sink for atmospheric COS. First-order decay times of dissolved COS concentrations in surface seawater agreed with predicted hydrolysis lifetimes from seawater solutions. This finding suggests that hydrolysis was the dominant sink mechanism under the wind and temperature conditions that prevailed during this study. Dark production may have played a significant role in lengthening the observed lifetime of COS at the surface relative to laboratory measurements of hydrolysis lifetimes on artificial solutions.

A global open ocean flux for COS, calculated by using monthly averaged wind speeds and the *Liss and Merlivat* [1986] expressions for transfer velocity, gave a net sink of 0.022 Tg COS/yr. The open ocean COS sink, calculated by using the *Wanninkhof* [1992] expression for transfer velocity, was significantly larger, 0.041 Tg COS/yr. Averaging the two, we report an average sink of 0.032 Tg COS/yr (0.010–0.054), which includes uncertainties due to the transfer velocity relationships, wind fields, atmospheric mixing ratio measurements, Henry's constants, and regionally averaged saturation ratios. These results indicate that the open oceans are a relatively unimportant factor in the global COS budget. Furthermore, there is considerable uncertainty in the global flux from the coastal ocean, which could very likely be overestimated. Future COS measurements in the marine environment should focus on coastal/shelf regions, where understanding of mechanisms of COS photoproduction is still limited. Also, since all of the above observations have been done in the Pacific Ocean, data from other oceanic regions, especially in wintertime, are clearly needed.

Atmospheric COS mixing ratios appeared to increase from south to north during the equinox cruise and decrease from south to north during the summer/winter cruise. This reversal in gradient direction implies a seasonal cycle on the order of 10% in the northern hemisphere, with a maximum during the boreal springtime. The difference in average COS mixing ratios between hemispheres was less than 5%, in agreement with previous measurements, but inconsistent with measurements over the Atlantic Ocean during similar seasons.

Acknowledgments. We appreciate the support of the officers and crew of the NOAA ship *Surveyor* and the help of Jerry Davison and Steve Hankin with the COADS wind data. P.S.W. is supported by the U.S. DOE Graduate Fellowship for Global Change administered by ORISE. We thank the Radiatively Important Trace Species (RITS) and Aerosol and Climate Components of the NOAA Climate and Global Change Program for general support. This is contribution number 1611 for NOAA/PMEL and 305 for JISAO.

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(Received January 2, 1995; revised June 14, 1995; accepted June 16, 1995.)