miscible with water. Petrographic examination of thin sections of hydrous pyrolyzed shale shows that the liquid product fills wavy fractures that are parallel to and sharp-sided fractures that are perpendicular to the linear fabric of the shale. In some fractures the filling may be traced to the edge of a shale block, where the pyrolyzate continues as a thin film. We observed some of these textural features in shales from cores and outcrops.

Hydrous pyrolysis may prove to be a sophisticated method for correlating crude oils with their source rocks and evaluating the generating capability of a source rock. It should provide more information on the natural oil-generating processes and the dependence of the composition of crude oil on such variables as temperature, pressure, time, and water. It may also help to elucidate the primary migration mechanisms of crude oils in their source rocks.

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Atmospheric Halocarbons, Hydrocarbons, and Sulfur Hexafluoride: Global Distributions, Sources, and Sinks

Abstract. *The global distribution of fluorocarbon-12 and fluorocarbon-11 is used to establish a relatively fast interhemispheric exchange rate of 1 to 1.2 years. Atmospheric residence times of 65 to 70 years for fluorocarbon-12 and 40 to 45 years for fluorocarbon-11 best fit the observational data. These residence times rule out the possibility of any significant missing sinks that may prevent these fluorocarbons from entering the stratosphere. Atmospheric measurements of methyl chloroform support an 8- to 10-year residence time and suggest global average hydroxyl radical (HO) concentrations of* 3×10^5 *to* 4×10^5 *molecules per cubic centimeter. These are a factor of 5 lower than predicted by models. Additionally, methyl chloroform global distribution supports Southern Hemispheric HO levels that are a factor of 1.5 or more larger than the Northern Hemispheric values. The long residence time and the rapid growth of methyl chloroform cause it to be a potentially significant depleter of stratospheric ozone. The oceanic sink for atmospheric carbon tetrachloride is about half as important as the stratospheric sink. A major source of methyl chloride* (3×10^{12} *grams per year), sufficient to account for nearly all the atmospheric methyl chloride, has been identified in the ocean.*

A major uncertainty in the fluorocarbon-ozone theory has been due to insufficient and often conflicting data on the global distribution of halocarbons. Calculation of the residence time of fluorocarbons is critically linked with this distribution and is an essential input into models that attempt to simulate the stratospheric O_3 depletion problem (*1*, *2*). In addition, the budgets and distributions of halocarbons provide a unique means for studying some of the fundamental features of the natural atmosphere. Inert species such as fluorocarbons and SF_6 are tracers that identify and quantify the global circulation, whereas the distribution of the more reactive halocarbons such as methyl chloroform (CH_3CCl_3) offers a unique means for quantifying the role of the hydroxyl radical (HO), a central atmospheric species that cleanses the atmosphere of impurities (*3*, *4*). Because a comprehensive set of global data on the distribution of unreactive and reactive halocarbons has not been available, most estimates have been made from point measurements and the hemispheres have been assumed to be well mixed. We present here extensive global measurements, which substantially alleviate this deficiency and provide an essential means for developing and verifying two-dimensional global photochemical models that are in a state of active development. We also characterize the growth of important atmospheric halocarbons, including several fluorocarbons, on the basis of data collected over a period of 3 years, and we discuss the important role the oceans play in the atmospheric chlorine budget.

We determined the global distributions of a large number of trace constituents between 64°N and 90°S at widely varying longitudes (*5*). We analyzed these background air samples both in situ and by collecting pressurized air samples in specially constructed stainless steel and glass vessels. All the in situ air and seawater analyses were conducted aboard a U.S. Coast Guard vessel, the *Burton Island*, which sailed the Pacific from Oakland, California (37°N), to Wellington, New Zealand (42°S). We took surface seawater samples in the Pacific Ocean from depths of 0 to 300 m at 50-m intervals. We also conducted several short-term field studies in clean remote sites on the west coast of the United States, starting in November 1975. Electron capture and flame ionization gas chromatographic techniques were used to analyze halogenated species and hydrocarbons, respectively. Details of the measurement methods are given in (*6*, *7*).

Figure 1 shows the global distribution of five fluorinated species (F stands for fluorocarbon): F12 (CCl_2F_2), F11 (CCl_3F), F113 (CCl_2FCClF_2), F114 ($CClF_2CClF_2$), and SF_6. All these species are man-made, are emitted predominately in the Northern Hemisphere (NH), and are essentially inert in the troposphere. It is clear from Fig. 1 that all five species are well mixed within each hemisphere and that the average concentrations in the Southern Hemisphere (SH) differ only marginally (10 to 15 percent) from the NH values.

Using a simple two-box model (*4*) and the emissions data for F12 and F11 (*8*), we calculate an interhemispheric exchange rate (τ_e) of 1 to 1.2 years. This is in good agreement with estimates by Czeplak and Junge (*9*) but in disagreement with other studies that calculate τ_e values of 2 to 4 years (*9*). Thus, the fluorocarbon data suggest that NH and SH air masses are exchanged in a rela-

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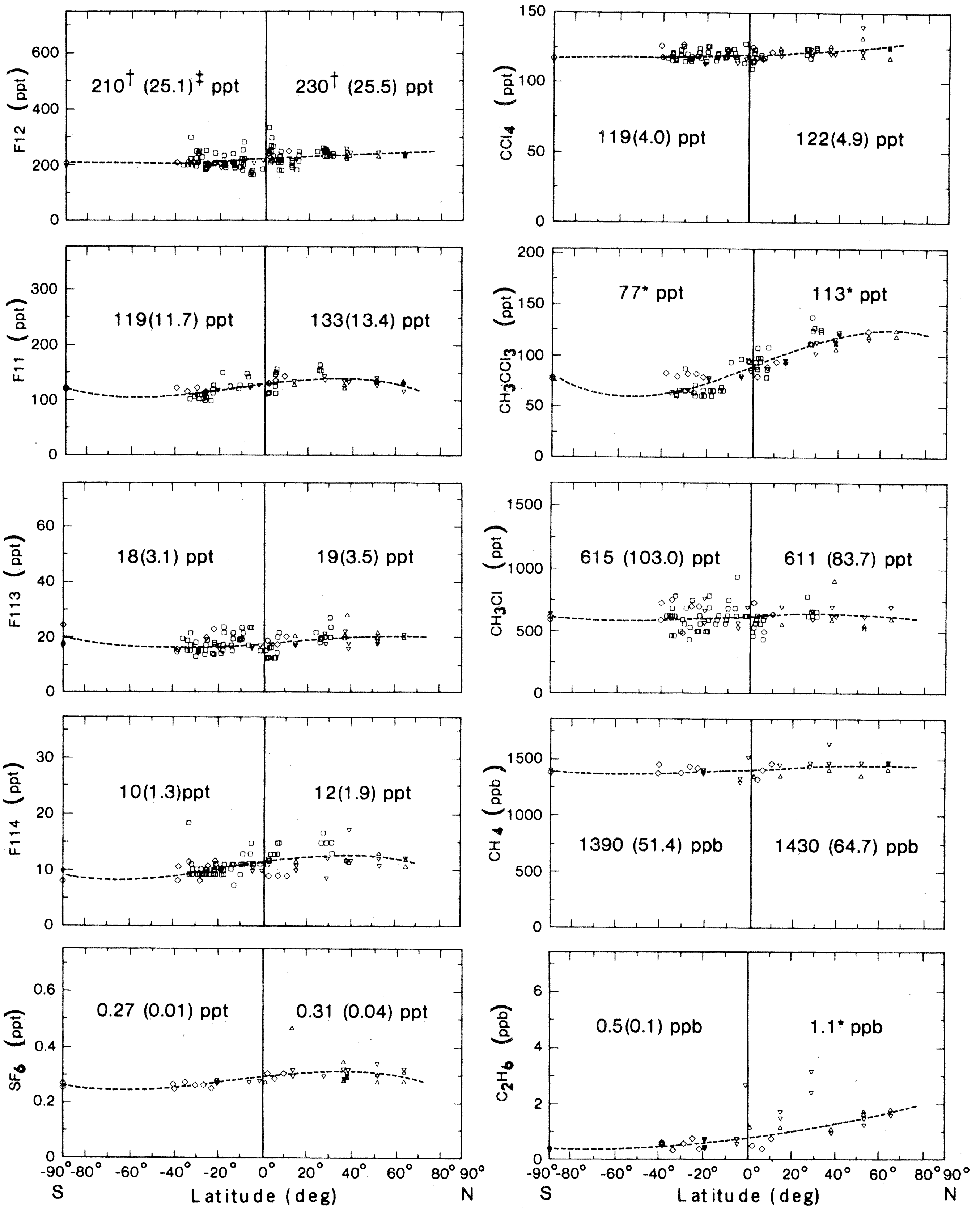

Fig. 1. Global distributions of atmospheric constituents. Key: ppt = 10^{-12} (volume/volume); ppb = 10^{-9} (volume/volume); (†) is the average concentration in the hemisphere; (‡) is the standard deviation; (*) indicates that for species where a significant gradient within each hemisphere is observed the weighted average concentration is defined to represent the total burden of the species in that hemisphere; ▽, trip 1, stainless steel vessels; △, trip 1, glass vessels; ◇, trip 2, stainless steel vessels; and □, trip 2, in situ air sampling and analysis. The dashed line is a third-order polynomial fitted to the data (*6*). In most cases, individual hemispheres can be treated as well mixed. In the case of CH_3CCl_3 and C_2H_6, where this is not true, the global profile is well represented by the polynomial $89.71 + 0.818\,L + 7.584 \times 10^{-4}\,L^2 - 7.894 \times 10^{-5}\,L^3$ for CH_3CCl_3 and $0.769 + 9.926 \times 10^{-3}\,L + 6.526 \times 10^{-5}\,L^2 + 5.561 \times 10^{-8}\,L^3$ for C_2H_6, where L is the latitude (in degrees) and varies from − 90° to + 64° (NH = 0° to + 90°; SH = 0° to − 90°).

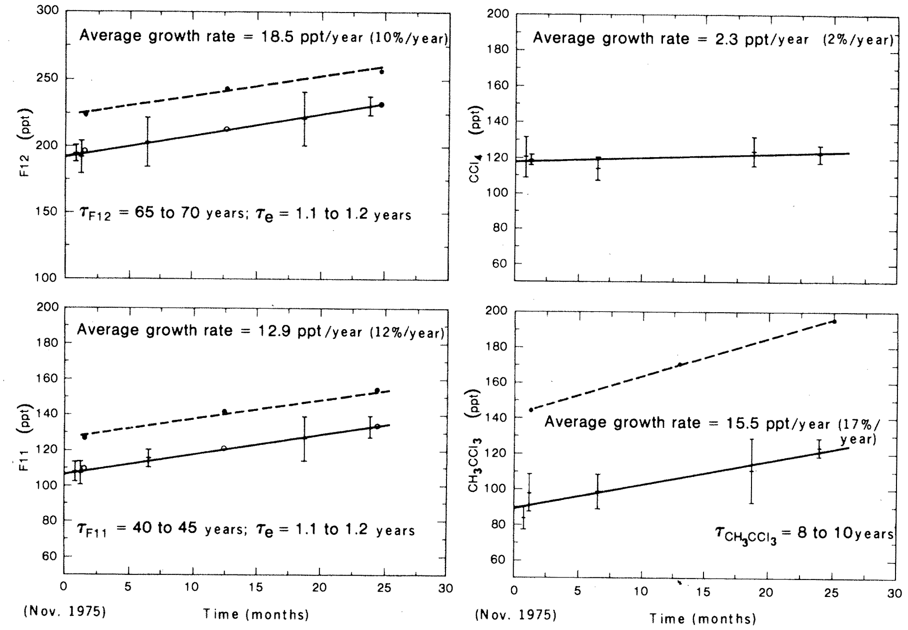

Fig. 2. Atmospheric growth of fluorocarbon-12, fluorocarbon-11, $CC1_4$, and CH_3CC1_3. The solid line shows the average growth based on data measured between 35°N and 65°N, a region of essentially uniform concentration. The dashed line indicates the concentration at 35°N to 65°N that would result if the cumulative emissions were distributed globally according to the distribution shown in Fig. 1. The difference between the dashed and the solid lines is indicative of the amount lost to atmospheric sinks. The circles indicate the predicted concentration in the NH from emissions data and the range of indicated residence times. The interhemispheric exchange rate (τ_e) fits the average north-south distribution of F12 and F11 corresponding to the period and measurements shown in Fig. 1.

tively fast time of less than 1.2 years.

Figure 2 shows that the atmospheric burden of F12 and F11 increased at an average yearly rate of 10 and 12 percent, respectively; the corresponding emissions data (Fig. 2) increased similarly. In late 1977, the global average concentrations of F12 and F11 were 220 and 126 parts per trillion (ppt), respectively. A comparison of emissions data (*8*) with measured F12 and F11 budgets, with the help of a budget model (*3, 4*), suggests an average F12 residence time (τ_{F12}) of 65 to 70 years and a τ_{F11} of 40 to 45 years. There is good agreement between measurements and calculated values (Fig. 2). These long residence times are consistent with the view that the stratosphere is the only major sink for F12 and F11, and that no other missing sinks of any significance exist.

Jesson *et al.* (*1*) have calculated a τ_{F11} of 10 to 20 years and implied missing sinks for F11. We attribute this difference to the use of SH data as measured by Lovelock *et al.* (*10*) in 1972, in which the SH concentrations of F11 were only half the NH values. Our measurements of the global distribution of five fluorinated species confirm that the SH concentrations of all inert species, including F12 and F11, are only about 10 percent lower than the NH values and, contrary to the findings of Lovelock *et al.* (*10*), no gradients within each hemisphere exist. In addition, analysis of the F11 data (*10*) would suggest a τ_e of more than 2 years. This is not supported by available information (*9*).

The global average concentrations of F113, F114, and SF_6 are 18, 11, and 0.3 ppt, respectively. These values are comparable to the estimated cumulative emissions of these species. An accurate emissions inventory for these species is not available, but their residence times can be expected to be several decades. The stratosphere is expected to be the major sink for F113 and F114. Sulfur hexafluoride (SF_6) is transparent to ultraviolet in both the troposphere and the stratosphere. Continued emissions of, and increases in, SF_6 could result in the deposition of sulfur above 50 km (destruction via electron capture) with unknown effects.

The three most abundant atmospheric chlorocarbons are CCl_4, CH_3CCl_3, and CH_3Cl. Although it was initially suggested that carbon tetrachloride (CCl_4) was of natural origin (*10*), more recent research (*11, 12*) has shown that the budgets and the distribution of CCl_4 are largely consistent with a man-made source. The global background CCl_4 concentration of 120 ppt that we measured (Fig. 1) corresponds to an atmospheric burden of 3.2×10^{12} g. This is somewhat higher than the best available emissions data (*11, 12*) would indicate. Secondary pollution sources of CCl_4 exist, but their quantitative contributions to the atmospheric budget cannot be currently established. No natural sources are known to exist. Figure 1 further shows that, unlike fluorocarbons, CCl_4 is rather uniformly distributed with a NH and SH concentration difference of 2.5 percent. This is not surprising since the emissions of CCl_4 in recent years have been small (*11*). Figure 2 shows a small average growth rate of about 2 percent per year in the atmospheric abundance of CCl_4. We also found that Lisbon CCl_4 concentrations were 180 ppt or about 50 percent higher than the background values. This observation is consistent with our earlier findings that CCl_4 concentrations are 20 to 50 percent higher in urban areas and indicate anthropogenic input (*7*).

Recently, Singh (*3, 4*) reported that the residence time of CH_3CCl_3 in the atmosphere is about 8 years, contrary to all earlier estimates, which placed the residence time between 1 and 2 years. A longer residence time would mean that CH_3CCl_3 could be a potential depleter of stratospheric O_3. This chlorocarbon was also identified as a unique indicator of HO abundance, and we analyzed field data to determine the average HO concentration in the troposphere; this was found to be lower than the earlier estimates by a factor of 5 to 10. Nevertheless, much of the analysis (*3, 4*) was based on point measurements because of the unavailability of data showing the latitudinal variation of CH_3CCl_3.

Figure 1 shows the global distribution of CH_3CCl_3 and a third-order polynomial fitted to it. This compound shows a latitudinal distribution quite different from that of the fluorocarbons. Up to about 30°N, the CH_3CCl_3 is well mixed in the NH with an average concentration of about 123 ppt. A fairly sharp decline seems to occur between 20°N and 20°S, and the concentration of CH_3CCl_3 then levels off to about 75 ppt. This decline cannot be attributed to normal mixing processes, since fluorocarbons do not show this rapid decline. A more plausible explanation of such a phenomenon would be that the HO radical is more abundant around the equator because of the intense sunlight and the high concentration of water vapor in this region.

The weighted average of CH_3CCl_3 concentrations of about 113 ppt in the NH and 77 ppt in the SH best describes the burden of CH_3CCl_3 in each hemisphere. When used in a two-box model together with available emissions data (*4*), this hemispheric distribution indicates a higher average HO concentration in the SH than in the NH ($[HO]_{SH}$/

Table 1. Concentrations of halocarbons in Pacific seawater.

Date (1977)	Latitude	Longitude	Water temperature (°C)	Concentration (ng/liter)				
				F12	F11	CCl_4	CH_3Cl	$CHCl_3$
11/25	19°02′N	137°48′W	24.3	0.40				
11/26	15°43′N	140°05′W	25.5	0.32				
11/27	11°52′N	142°25′W	25.4	0.32				
11/28	06°35′N	145°14′W	28.4	0.47				
11/29	02°35′N	145°14′W	26.5	0.07				
11/30	01°26′S	150°10′W	27.6	0.35				
12/1	06°07′S	153°13′W	28.1	0.14				
12/2	09°07′S	155°75′W	28.8	0.07	0.15	0.41	34.5	< 0.05
12/4	18°24′S	161°42′W	26.7	0.14	0.24	0.45	85.8	< 0.05
12/6	25°40′S	167°33′W	23.2	0.25	0.07	0.35	21.2	< 0.05
12/7	30°14′S	171°18′W	21.5	0.40	0.10	0.38	1.4	< 0.05
12/8	33°40′S	173°50′W	18.5	0.19	0.10	0.40	12.5	< 0.05
12/11	39°05′S	179°13′W	16.9	0.53				< 0.05
Average surface concentration (0 to 2 m)				0.28+ 0.15	0.13 ± 0.06	0.40 ± 0.03	26.8 ± 31.2	< 0.05
Average 300-m concentration				0.21	0.06	0.15	3.3	< 0.05

$[HO]_{NH} \geq 1.5$). The asymmetric HO distribution can be attributed to carbon monoxide which is an important atmospheric sink for HO and is three times more abundant in the NH when compared to SH. Should the excess carbon monoxide in the NH be due to man-made causes, as is currently believed, additional depletion of HO in the NH can be expected in the future. The depletion of HO would have the effect of reducing the scavenging ability of the atmosphere. This would allow an increasing amount of pollutants to enter the stratosphere. In addition, the tropospheric reservoir of many natural and man-made species would increase. Two-dimensional global models would be required to simulate the global distribution of CH_3CCl_3 and HO more precisely. Budget considerations, which are insensitive to the CH_3CCl_3 distribution, support a $\tau_{CH_3CCl_3}$ of about 8 to 10 years, corresponding to a seasonally averaged global HO value of 3×10^5 to 4×10^5 molecules per cubic centimeter. Figure 2 shows that the average growth rate of CH_3CCl_3 at the north temperate latitudes has been 15.5 ppt per year (≈17 percent). Available emissions data for CH_3CCl_3 suggest an increase of about 25 percent per year during the same period.

An 8- to 10-year $\tau_{CH_3CCl_3}$ allows an estimated 15 to 20 percent of all CH_3CCl_3 to enter the stratosphere. The long tropospheric residence time, when coupled with the rapidly increasing emissions, suggests that CH_3CCl_3 may be a potential depleter of stratospheric O_3 in the decades ahead. Worldwide release of CH_3CCl_3 to the atmosphere currently approaches 7×10^{11} g $year^{-1}$ and is increasing at a rate of 15 to 20 percent per year. Continued uncontrolled release of CH_3CCl_3 to the atmosphere should be a matter of future concern.

Methyl chloride (CH_3Cl) has been measured in the NH by a number of researchers (*13*), but no SH data have been available. Figure 1 shows an essentially uniform global distribution, with an average global concentration of 615 ppt. The relatively short lifetime of CH_3Cl (2 to 3 years) and its uniform global distribution support the idea of a large natural source. The primary man-made emissions of CH_3Cl have been thought to be negligible. Contrary to this belief, we found in Lisbon CH_3Cl concentrations of nearly 2200 ppt. Our studies near Los Angeles (Riverside) showed an average CH_3Cl concentration of 1500 ± 700 ppt (maximum of 3800 ppt), about 2.5 times the background concentrations measured (*7*). Thus, a significant urban source of CH_3Cl exists. The possibility that automobile exhaust may be such a source should be investigated.

We measured the concentrations of other species, but detailed latitudinal profiles could not be developed because of contamination problems or lack of air samples. The best data obtained suggested background concentrations in the NH of 14 ± 7, 44 ± 14, 16 ± 8, 40 ± 12, 7 ± 1, and 5 ± 1 ppt for $CHCl_3$, CH_2Cl_2, C_2HCl_3, C_2Cl_4, C_2Cl_6, and CH_2BrCH_2Br, respectively. The SH background concentrations were very low: 3, 20 ± 4, < 3, and 12 ± 3 ppt for $CHCl_3$, CH_2Cl_2, C_2HCl_3, and C_2Cl_4, respectively. The $CHCl_3$ concentrations in the SH were between 2 and 3 ppt. No SH data for C_2Cl_6 and CH_2BrCH_2Br were collected. Limited CH_3Br measurements in the NH indicated a ground-level background concentration of 5 ppt or less, with concentrations as high as 20 ppt in the clean marine environment. Similarly, CH_3I had an average concentration of 5 ± 3 ppt in the marine boundary layer, but it essentially disappeared over continental air masses. Fluorocarbon-21 ($CHFCl_2$) was also measured in the NH and SH at concentrations of 5 ± 3 and 4 ± 1 ppt, respectively. We do not know if F21 is a true atmospheric constituent or an unknown artifact. It must be emphasized that these averages are based on a limited amount of data and do not adequately take into account intrahemispheric variabilities and gradients.

Methane is a critical stratospheric and tropospheric trace constituent. The global distribution of CH_4 is nearly uniform, with a north-south concentration difference of about 3 percent (Fig. 1). The average global concentration is measured to be 1410 parts per billion (ppb). Although CH_4 is known to be of a predominantly natural origin, significant anthropogenic sources exist. The nearly uniform distribution of CH_4 suggests that an atmospheric residence time as high as 20 years cannot be ruled out.

With the finding that the atmospheric HO concentrations are probably significantly lower than formerly believed (*3, 4*), it becomes feasible that hydrocarbons other than CH_4 may play an important role in the lower and upper atmospheric chemistry. Our search suggests that ethane (C_2H_6) is the second most ubiquitous hydrocarbon. Figure 1 shows its highly nonuniform global distribution. In the SH, the concentration of C_2H_6 is relatively uniform, averaging about 0.5 ppb. In the NH, however, the concentration approaches 2 ppb at northern mid-latitudes but drops off to about 1 ppb near the equator. The weighted average concentration of C_2H_6 that represents its burden in the NH is calculated to be 1.1 ppb. In continental air masses over the United States, C_2H_6 concentrations were between 3 to 5 ppb. Assuming that reaction with HO is the major removal mechanism, we estimate a global C_2H_6 source strength of 3×10^{12} to 5×10^{12} g $year^{-1}$.

We also measured halocarbons in Pacific seawater, primarily to determine the ability of the ocean to act as a source or a sink for them. The average concentrations of individual species at 0 and 300 m are given in Table 1. The average measured surface water concentrations of F12, F11, CCl_4, CH_3Cl, and $CHCl_3$ were 0.28, 0.13, 0.40, 26.8, and < 0.05 ng $liter^{-1}$, respectively. With the surface water concentrations of halocarbons known, a simple film diffusion model of the flux of halocarbons into or out of the ocean can be determined (*6, 14*)

$$F = \frac{D}{Z}(C^{w} - C^{w}_{eq}) \qquad (1)$$

where F is the flux from ocean to air, D is the diffusion coefficient, Z is the film thickness, C^{w} is the concentration of the species in water, and C^{w}_{eq} is the concentration in equilibrium with the burden in air.

Solubility data for F12 and F11 (*14*) suggest that, if the surface water is in equilibrium with the atmospheric burden, the concentrations of F12 and F11 in water should be about 0.05 and 0.06 ng liter^{-1}, respectively. These concentrations are lower than the measured average concentrations of 0.28 and 0.13 ng liter^{-1}, so it appears that ocean water is supersaturated with F12 and F11. This means that either the solubility data are inaccurate or the water samples were inadvertently contaminated. It is also possible that the ocean surface waters have been contaminated by man-made activities on a global scale. The lowest concentration of F12 and F11 measured, 0.07 ng liter^{-1}, is about what one would expect if the surface water were saturated with F12 and F11. If the surface water were saturated, the ocean would be a relatively ineffective sink for F12 and F11 but could act as a reservoir containing less than 0.5 percent of the atmospheric burden of F12 and F11 in a steady-state situation.

The average surface water concentration for CCl_4 was 0.40 ng liter^{-1}. The flux of CCl_4 into the ocean can be calculated from Eq. 1 with $D = 10^{-5}$ cm^2 sec^{-1}, $Z = 90$ μm, and $S_{CCl_4} = 0.85$. The solubility, S, in seawater is defined as the ratio of the species concentration at the air-sea interface (C^{w}_{eq}) to the atmospheric concentration at standard temperature and pressure. A high Z is used because CCl_4 is rapidly absorbed in fatty tissues and may be biologically active. For such species the upper limit of the stagnant film thickness calculated from radon data (63 ± 30 μm) is more appropriate. Using Eq. 1, we can calculate a CCl_4 flux into the ocean of 2.8×10^{-16} g cm^{-2} sec^{-1}. If we assume this flux to be typical of all oceans, we obtain an exchange rate of 3.2×10^{10} g year^{-1}. The atmospheric burden of CCl_4 from our measurements is calculated as 3.2×10^{12} g. Thus the ocean is a sink for CCl_4 that can provide a turnover rate of 100 years ($\tau_{CCl_4} = 3.2 \times 10^{12}/3.2 \times 10^{10}$). Our measurements thus indicate that the oceanic sink for CCl_4 is about half as effective as the stratospheric sink.

The surface concentration of CH_3Cl in the Pacific is quite variable (Table 1), with values somewhat higher near the equator. The average surface concentration found was 26.8 ng liter^{-1}. Using an S_{CH_3Cl} of 2.65 (*15*) and other parameters as defined earlier, we estimate a CH_3Cl flux from the ocean to the atmosphere of 2.6×10^{-14} g cm^{-2} sec^{-1}. Extending this to the world ocean body gives an exchange rate of 3.0×10^{12} g year^{-1}. From our measurements, the atmospheric burden of CH_3Cl can be estimated to be 5.5×10^{12} g. Thus, on the basis of our limited data, the ocean appears to be a significant source of CH_3Cl, which can provide an atmospheric turnover rate of about 2 years. This is in reasonable agreement with the estimated CH_3Cl residence time of about 2 to 3 years, due to HO attack (HO = 3×10^5 to 5×10^5 molecules per cubic centimeter).

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Minor Planets: The Discovery of Minor Satellites

Abstract. *The recent confirmation of the discovery of a satellite of the minor planet 532 Herculina indicates that other similar anomalous sightings are probably also due to satellites, which must therefore be numerous and commonplace. There are now 23 candidate satellites for eight minor planets, and no one of these minor planets occulting a star has failed to show evidence of at least one secondary event. Such companions are gravitationally stable but apparently have rapid tidal evolution rates.*

The discovery which led to general recognition of the minor satellite phenomenon (the self-descriptive operational title "minor satellites" is adopted to refer to orbiting satellites of the minor bodies, predominantly the minor planets, in the solar system) was that of J. H. McMahon of 7 June 1978. McMahon responded to a last-minute prediction correction calculated by D. W. Dunham based on astrometric data obtained by W. Penhallow which showed that the path of the occultation of the star SAO (Smithsonian Astrophysical Observatory) 120774 by the minor planet 532 Herculina would cross the western United States. McMahon successfully observed a 20.6-second occultation of the star by Herculina, but he also timed and reported six additional events with durations of 0.5 to 4.0 seconds occurring within 2 minutes before and after the main event (*1*). These secondary events were certainly not atmospheric because the light reduction in each true occultation was nearly four magnitudes.

Table 1. Status of minor satellite observations as of October 1978.

Minor planet	Number of minor satellites		
	Confirmed	Probable	Suggested
2 Pallas		2	2
3 Juno		1	
6 Hebe		1	
9 Metis			1
12 Victoria			1
129 Antigone		1	
433 Eros		2	2
532 Herculina	1	5	4
Total	1	12	10

Accepting McMahon's observations at face value, Dunham prompted other ob-