The Role of the Oceans as a Sink for Chlorofluormethanes and similar Compounds

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Model calculations show that the oceans do not represent a global sink for chlorofluoromethanes (CFM 11 and 12) of any significance. The amount absorbed by the oceans consists essentially of three portions: The portion dissolved in the mixing layer; the one that enters the deep sea and the portion which is decomposed or disappears otherwise within the mixing layer by chemical or biological processes. The calculations show that the total amount of CFM which may have entered the oceans up to the present time cannot have exceeded a few percent even if high destruction rates would occur in the oceans. Solubility data in ocean water in conjunction with concentration data in the oceans indicate, however, that the net destruction rate of CFM 11 in the oceans is only of the order of 10^{-7} sec^{-1}.

The problem of a possible reduction of the ozone layer through the chlorofluoromethanes CCl_3F and CCl_2F_2 (CFM 11 and 12) has been discussed for about a year. Rowland and Molina[1] were the first to point out that the CFM's in the atmosphere are evidently only destroyed through photolysis in altitudes above 30 km. The chlorine atoms produced by this process interfere with the natural ozone balance of the stratosphere resulting in a catalytic destruction. The concept developed so far consists essentially of model calculations based on a chemical reaction scheme for the stratosphere as well as on some assumptions which have to be verified by further studies. One of the more important assumptions is that there are no other sinks for CFM 11 and 12 than photolysis in the stratosphere. The total CFM inventory of the atmosphere as well as the total amount of the CFM's so far produced are not sufficiently well known at the present time to exclude the existence of such possible sinks. One obvious possibility is the absorption by and the decomposition within the ocean, and the purpose of this paper is to pursue this question in order to derive a quantitative estimate.

The Model Used for the Calculations

The application of the CFM's produced is such that they are finally released to the atmosphere, in some cases after delay times of years. Estimated figures for the annual global production $q(t)$ were given in[1]. If all the CFM would stay within the atmosphere and if we neglect for the present purpose the slow mixing within the stratosphere, the concentration in air at the earth's surface (c_0) would be

$$c_0(t) = M(t)/A\,H \tag{1}$$

with

$$M(t) \int_{t_0}^{t} q(t)\,\mathrm{d}t\,, \tag{2}$$

A and H being the area of the earth's surface and the scale height of the atmosphere respectively, and t_0 the time CFM production $q(t)$ started.

For the present purpose the ocean can be subdivided with sufficient approximation into two reservoirs: The mixed layer at the surface with an average depth h and the deep sea. The mixed layer receives the CFM's from the atmosphere (flux F_1) and loses them by mixing with the deep sea (F_2) and perhaps by some destruction process, as for instance hydrolysis, uptake by organisms etc. (F_3). The budget equation of the mixed layer is then

$$h\,\frac{\mathrm{d}c_2}{\mathrm{d}t} = F_1 - F_2 - F_3\,. \tag{3}$$

We can assume that the concentration c_2 within the mixed layer is sufficiently uniform due to rapid mixing. F_1 is determined by molecular diffusion through the laminar surface layer of thickness[2] δ.

$$F_1 = \mathrm{D}\,(c_1 - c_2)/\delta \tag{4}$$

with D = diffusion coefficient in water, $c_1 = s \cdot c_0$ the concentration at the ocean air interface in equilibrium with the atmospheric concentration c_0 and s = solubility in water.

F_2 and F_3 can be expressed by

$$F_2 = \varkappa\,h\,c_2 \tag{5}$$

and

$$F_3 = k\,h\,c_2 \tag{6}$$

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with $\varkappa$ = exchange rate of the mixed layer with the deep sea (assuming the concentration in the deep sea to be practically zero) and k = destruction rate in the mixed layer assuming a first order reaction. By putting $\lambda = D/\delta h$ (3) can be written

$$\mathrm{d}c_2/\mathrm{d}t = s\,\lambda\, c_0 - (\lambda + \varkappa + k)\, c_2\,. \qquad (7)$$

There are two ways to obtain numerical results. Using the actual production data $q(t)$ we can calculate $c_0(t)$ and $c_2(t)$ by numerical integration. The other possibility, which shall be adopted in the rest of this chapter, is based on the fact that $q(t)$ and therefore $c_0(t)$ can be fairly well approximated by an exponential function

$$c_0(t) = c_0(t_0)\, e^{\gamma(t-t_0)} \qquad (8)$$

with $c_0(t_0)$ = concentration for t_0, and γ = a positive constant. This results in

$$c_2(t) = \frac{\lambda\, s}{\gamma + \beta}\, c_0(t) \qquad (9)$$

after an adjustment time of the order of β^{-1} after the start of production at t_0 has elapsed with $\beta = \lambda + \varkappa + k$. Even if $k = 0$, β^{-1} is smaller than one year for the numerical data given later, so that (9) is a very good approximation for practically all t values.

For the subsequent discussion we are not interested in $c_2(t)$ but rather in the following important parameters:

1) $$\varphi = c_2/s\, c_0 = \lambda/(\gamma + \beta) \qquad (10)$$

gives the degree of saturation of the mixed layer with respect to c_0; in equilibrium, i. e. for γ, $\varkappa$, $k \equiv 0$, $\varphi = 1$.

2) $$\eta = \frac{\varepsilon\, h\, s}{H}\, \varphi = \varepsilon\, h\, \lambda\, s/H(\gamma + \beta) \qquad (11)$$

is the ratio of the CFM dissolved in the mixed layer, $\varepsilon\, A\, h\, s\, \varphi\, c_0(t)$ and the amount in the atmosphere, $A\, H\, c_0(t)$, with ε = fraction of the oceans at the earth's surface.

3) $$\begin{aligned}\psi &= \varepsilon\, h\, \lambda\, s(\varkappa + k)/(H\,\gamma(\gamma + \beta))\\ &= (\varkappa + k)\,\eta/\gamma \qquad (12)\end{aligned}$$

is the ratio of the amount of CFM which became lost to the deep sea or became decomposed, $\varepsilon\, A \int_{t_0}^{t} (F_2 + F_3)\, \mathrm{d}t$ and again $A\, H\, c_0(t)$.

In this case

$$M(t) = A\, H\, c_0(t)\,(1 + \eta + \psi)$$

and $c_0(t)$ becomes smaller than according to (1). Since η and ψ are rather small, this difference in $c_0(t)$ is small also.

The parameters η and ψ are related to the atmospheric content $A\, H\, c_0(t)$ and not to the total amount $M(t)$. In this latter case the expressions would, however, become more complex and it would be more difficult to understand their dependance on s, k, etc. But since η and ψ are rather small this difference in definition is unimportant for our discussion.

Another useful parameter for our discussion is the time T in which the CFM burden of the atmosphere would drop to e^{-1} after CFM production would be stopped. The available amount of CFM per cm^2 of earth's surface within the atmosphere plus the mixed layer is

$$\Phi = c_0(t)\,(H + \varepsilon\, h\, \varphi\, s)$$

which decreases according to

$$\mathrm{d}\Phi/\mathrm{d}t = -\,\varepsilon\, h\, \varphi\, s(\varkappa + k)\, c_0(t)\,.$$

This gives

4) $$T = (H + \varepsilon\, h\, \varphi\, s)/(\varepsilon\, h\, \varphi\, s(\varkappa + k)) \qquad (13)$$

with

$$\varphi = \lambda/(T^{-1} + \beta) \approx \lambda/(\lambda + k) \qquad (14)$$

as we will see later.

Numerical Values of the Relevant Parameters

In Table I the parameters which enter into the numerical calculations are listed together with the values used in this paper. A few comments are necessary:

1. For the CFMs no values for the molecular diffusion coefficient D are available. A summary for a series of common gases [2] shows that the D-values fluctuate at 10 °C in the range from 0.91×10^{-5} (Radon) to 1.57×10^{-5} (O_2) and that only very small molecules like H_2 and He show considerably higher values. (3.03 and 4.14×10^{-5} respectively.) We have, therefore, chosen the value indicated as a reasonable approximation for an average temperature of 10 °C.

2. The thickness of the mixing layer h fluctuates between values of less than 50 to ca. 75 – 100 meters. The average value of 50 meters given in Table I may be uncertain by a factor of two if global average conditions are considered.

Table I. Numerical parameters used in the calculations.

D =	Molecular diffusion coefficient of CFM in water at 10 °C estimated to be	10^{-5} cm^2 s^{-1}
h =	Thickness of the mixed ocean layer	5×10^3 cm
H =	Scale height of the atmosphere at the earth's surface	8.0×10^5 cm
s =	Solubility of CFM in ocean water based on Fig. 1 for 10°C CMF 11	1.2×10^{-1}
	CFM 12	4.6×10^{-2}
γ =	Rate of exponential increase of CFM 11	4.3×10^{-9} s^{-1}
	CFM 12	4.1×10^{-9} s^{-1}
δ =	Thickness of the laminar surface layer	7×10^{-3} cm
ε =	Fraction of the ocean's surface	7.1×10^{-1}
$\varkappa$ =	Mixing rate of mixed layer with deep sea	2×10^{-9} s^{-1}
λ =	$D/\delta h$ =	2.86×10^{-7} s^{-1}

3. Until now only sporadic data were available in the literature about the solubility of the CFMs in pure water for certain temperatures [3, 4] as indicated in Figure 1. Measurements were, therefore, made of s for CFM 11 and 12 in sea water and pure water for the temperature range in question [5]. Since CFM 12 is a gas in this temperature range (BP = − 29.8 °C) the solubility could be determined by a static volumetric method. For CFM 11 which is already partly liquid in the temperature range of the measurements (BP = + 23.8 °C) the following method was used: Into the degased water sample liquid degased CFM 11 was condensed up to saturation (appearance of two phases). After shaking for several hours equilibrium was achieved and the respective phases were analyzed. Based on recent measurements of solubilities of H_2 and CO at very low concentrations [6] in sea water, we can now be reasonably confident that also for CFM Henry's law is valid down to very small concentrations. We would like to emphasize this point since in the literature opposite opinions have been expressed for CO [7].

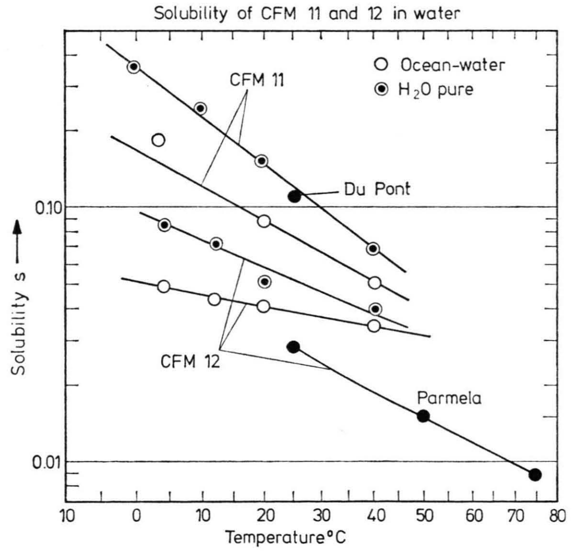

Fig. 1. Measurements of the solubility of CFM 11 and 12 in sea water and pure water by Zeininger, Hoechst A.G. [5]. For comparison the available data by Parmela [3] and Du Pont [4] for pure water are also plotted.

The results are shown in Fig. 1 and compared with the literature data. The new data by Hoechst AG for CFM 12 in pure water are higher than those of Parmela whereas for CFM 11 there is good agreement. The values for sea water are in both cases lower than for pure water which is to be expected as a consequence of the dissolved salt. The figures in Table I are based on an average ocean temperature of 10 °C.

4. The increase in global CFM production as given by Rowland and Molina [1] (Table I) can well be approximated by an exponential function, at least for the period 1960 to 1972. This is the period which is essential for the establishment of conditions in the atmosphere – ocean system preceding the first measurements in the atmosphere which started around 1971 [8]. The values of γ for this time period are given in Table I. They differ slightly for the two CFMs. Since 1973 there is a decline of γ. Both these deviations have very little influence on our conclusions.

5. Fairly reliable values for the thickness of the laminar surface layer were obtained by Broecker and Peng [2] under variable conditions at the sea surface by measuring the escape rate of radon formed in the mixed layer by decay of dissolved radium. They found an average of about 7×10^{-3} cm which apparently does not fluctuate much with respect to time and location.

6. Values for the exchange rate $\varkappa$ of the mixed layer with the deep sea range between 0.1 and 0.02 year^{-1}, corresponding to exchange times of 10 and 50 years. Exchange times of this magnitude are in agreement with the following considerations: The turnover time of the deep sea is estimated to be about 10^3 years which should be equivalent to the time for one complete exchange with the mixed layer. An average depth of the ocean of about 4 km and $h = 50$ meters would thus lead to an exchange time of the mixed layer with the deep sea

of about $1000\times\frac{50}{4000}\approx 13$ years. The $\varkappa$ value in Table I corresponds to an exchange time of 16 years.

7. The values of H and ε are accurately known figures. However, nothing is known about the destruction rate k in the ocean. CFM 11 hydrolyses slowly in pure water ($k\approx 8\times10^{-13}\,\mathrm{s}^{-1}$ at 40 °C)[9]. A 1% solution of Na_2CO_3 at 30 °C results in $k\approx 3\times10^{-9}\,\mathrm{s}^{-1}$ and considerably higher values occur in the presence of sheet metal[10].

Besides hydrolysis other processes may be possible in sea water, for example decomposition by micro-organisms or adsorption by organic debris which drops into the deep sea. The latter process was suggested to be responsible for the relatively fast removal rate of polychlorinated biphenols (PCBs) in North Atlantic surface waters[11], corresponding to $k\approx 3\times10^{-8}\,\mathrm{s}^{-1}$ or about once per year.

Since it is not possible to apply these figures to CFM we treated k as a running parameter in our calculations over the wide range of 10^{-10} to $10^{-1}\,\mathrm{s}^{-1}$. Comparison with observations of CFM 11 concentrations in the ocean surface water suggest a tentative net value of the order of $10^{-7}\,\mathrm{s}^{-1}$, as we will show later.

Discussion and Results

We calculated φ, ψ, η and T in two ways by solving (7) numerically using the actual $q(t)$ values given by Rowland and Molina and also by using the exponential approximation (8) for $c_0(t)$ resulting in the Eqs. (10), (11), (12) and (13). The differences are negligible and do not show up in Figs. 2 and 3. As we see from Fig. 2 φ is almost 1.0 for small values of k, i. e. we have practically solubility equilibrium. The small deviation from $\varphi=1.0$ for $k\to 0$ is due to both $\varkappa$ and γ which are of the same order of magnitude. As k increases, φ decreases rapidly and becomes approximately

$$\varphi(k\to\infty)\approx\lambda/k=D/\delta h\,k \qquad (15)$$

i. e. inversely proportional to k.

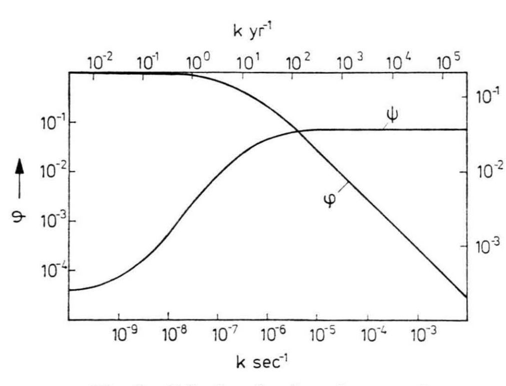

Fig. 2. Calculated values for φ and ψ.

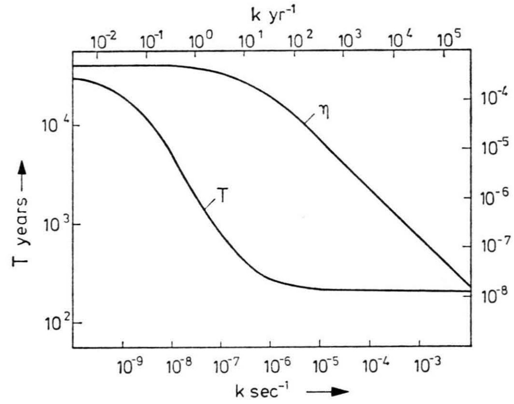

Fig. 3. Calculated values for η and T.

ψ starts with very small values and reaches a plateau of 3.5×10^{-2} for $k>10^{-6}$. This value corresponds to

$$\psi(k\to\infty)=\frac{\varepsilon\,h\,\lambda\,s}{H\,\gamma}=\frac{\varepsilon\,D\,s}{H\,\gamma\,\delta}=0.035 \qquad (16)$$

which is proportional to s and inverse proportional to γ. This is an interesting and important result. It shows that even for high destruction rates in the oceans the total amount of CFM 11 destroyed and removed to the deep sea cannot be larger than a few percent. The reason for this is the fact that the concentration of CFM which controlls the destruction decreases inversely with k as indicated by φ. Since ε, δ, H and to a large extent also D are independent of the characteristics of the substance ψ in (16) is practically only controlled by s and γ. Our conclusion, therefore, would hold for all gaseous pollutants with s smaller and γ larger than those for CFM 11. For CFM 12, for instance $\psi(k\to\infty)=0.014$.

In Figure 3 η remains always below the value

$$\eta(k\to 0)\approx\frac{\varepsilon\,h\,s\,\lambda}{H(\gamma+\lambda+\varkappa)}\approx\frac{\varepsilon\,h\,s}{H}=5.2\times10^{-4} \qquad (17)$$

since γ and $\varkappa\ll\lambda$. The maximum amount dissolved in the mixed layer, controlled by s, remains therefore completely negligible for both CFMs.

The calculation of T according to (13) can be simplified by neglecting T^{-1} in Eq. (14) which is justified by the fact that T calculated with this approximation is always larger than 200 years for all k-values, corresponding to $T^{-1} < 1.6 \times 10^{-10}\ \mathrm{sec}^{-1}$. This value is smaller by one order of magnitude than $\varkappa$ and three orders of magnitude than λ (Table 1), hence, vor all practical purposes $\varphi = \lambda/(\lambda + k)$.

The T values in Fig. 3 decrease with rising k from 3×10^4 years to a constant value

$$T(k \to \infty) = H/(\varepsilon\,\lambda\,s\,h) = (H\,\delta/\varepsilon\,D\,s) = 208\ \text{years}. \tag{18}$$

As expected the ocean could barely contribute to any recovery of the atmosphere – ocean system.

The conclusion from these results is that up to now and also for the foreseeable future the ocean can be neglected as a sink for CFM 11. The Eqs. (16), (17), and (18) show that this is even more true for CFM 12 because of the lower solubility.

It is of interest to compare the calculated φ-values with measurements in the ocean made by Lovelock et al.[8]. These authors have measured the concentration of CFM 11 in air and water simultaneously in the North and South Atlantic. We will base this comparison on their South Atlantic data because they show almost no variation with latitude and little scatter. The data published for the water concentration c_2^* are those which adjust themselves in a 10 ml volume of air in equilibrium with a 100 ml sample of ocean water. The amount of CFM 11 in a volume V of water at temperature T_1 (original temperature of the sample) is $c_0\,\varphi\,V\,s_{T_1}$ with c_0 the concentration in air. After equilibration at temperature T_2 the concentration c_0^* in the air volume $V/10$ is determined by

$$c_0\,\varphi\,s_{T_1} = c_0^*/10 + c_0^*\,s_{T_2}$$

resulting in

$$\varphi = \frac{c_2^*}{c_0}\,\frac{0.1 + s_{T_2}}{s_{T_1}}. \tag{19}$$

The data c_0 and c_2^* are given in Fig. 1 of reference[8]. No data were given for T_1 and T_2. If we consider latitudes south of 50° T may be as low as 0 °C and T_2 could range between 0 °C and 25 °C (laboratory). The observed ratio c_0^*/c_0 is 22/41. This corresponds to the range $0.55 \leqq \varphi \leqq 0.83$. According to Fig. 2 we should expect k to fall into the range $4.5 \times 10^{-8} \leqq k \leqq 2.0 \times 10^{-7}\ \mathrm{s}^{-1}$ or $1.4 \leqq k \leqq 6.5\ \mathrm{yr}^{-1}$. This does not sound unreasonable and would indicate some active removal process of the same order as that found by Harvey et al.[11] for PCBs.

It may be useful to show how sensitive the values of φ, ψ, η and T are with respect to variations in the values of those parameters given in Table I which are not too well known, i. e. D, h, δ and $\varkappa$. In Table II we calculated the variation of φ, ψ, η and T assuming $k = 10^{-7}\ \mathrm{s}^{-1}$ if each of these parameters would vary by a factor of two up and down, using Eqs. (10), (11), (12) and (13). We see that ψ does not rise above 1.5×10^{-3} which confirms our conclusion about the inefficiency of the ocean sink. Because $\varkappa$ is so small its variations have no effect at all. But even uncertainties in D, h and δ do not have much effect except in the case of h for ψ and η. Table II therefore shows that even considerable uncertainties in the crucial parameters of our model can not alter our conclusions.

There is one final point which we like to mention here. A small amuont of CFM 11 and CFM 12 is introduced into the oceans by rainfall due to the fact that the solubility in pure water, $s_p = a\,s$, is higher by a factor of a than in sea water (Fig. 1). If p is the global average rainfall rate per year which is close to 1000 cm and p^* the corresponding value per second, the influx F_4 into the mixed ocean layer due to rainfall is

$$F_4 = p^*\,c_0(s_p - s) = p^*\,c(a - 1). \tag{20}$$

This results into the ratio

$$\frac{F_4}{F_1} = \frac{p^*\,\delta(a = 1)}{D(1 - \varphi)}. \tag{21}$$

Table II. Variation of φ, ψ, η, and T if D, h, δ, and $\varkappa$ are varied by a factor of 2 up and down. k is assumed $= 10^{-7}\ \mathrm{s}^{-1}$.

	unmodified value	D	h	δ	$\varkappa$
φ	0.73	0.84/0.57	0.57/0.84	0.57/0.84	0.73/0.73
ψ	9.2×10^{-3}	$11/7.3 \times 10^{-3}$	$15/5.3 \times 10^{-3}$	$7.3/11 \times 10^{-3}$	$9.4/9.4 \times 10^{-3}$
η	3.9×10^{-4}	$4.5/3.1 \times 10^{-4}$	$6.1/2.2 \times 10^{-4}$	$3.1/4.5 \times 10^{-4}$	$3.9/3.9 \times 10^{-4}$
T	800	690/1020	510/1380	1020/690	790/810

For $k = 10^{-7}\,\mathrm{sec}^{-1}$, $\varphi = 0.73$ and with $a \approx 2$ for both CFM 11 and 12 at 0 °C, we have

$$F_4/F_1 \approx 1 \times 10^{-3},$$

so that for our considerations F_4 can be neglected. Only for $k \to 0$, F_4 becomes about equal to F_1.

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