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Wet and dry removal of tropospheric formaldehyde at a coastal site

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ABSTRACT

Formaldehyde in precipitation and in surface seawater has been measured at Woods Hole, Massachusetts (U.S.A.) a mid-latitude coastal site. From these measurements and a calculation of the diffusion-controlled air-to-sea transfer rate of the compound we estimate the wet and dry flux of H_2CO from the troposphere to nearby coastal waters to be 6.3 $\mu g\ cm^{-2}\ yr^{-1}$ for precipitation and 5.7 $\mu g\ cm^{-2}\ yr^{-1}$ for gaseous diffusion. A comparison of these values with a simple photochemical model shows that these transfers may represent a significant removal mechanism for tropospheric formaldehyde.

The total flux of H_2CO is equivalent to an input of 4.8 $\mu g\ cm^{-2}\ yr^{-1}$ organic carbon, $\geq 1\%$ of estimated total organic carbon air-to-sea transfer. The absence of a detectable amount of formaldehyde in surface seawater suggests that its fate might be biological uptake. This view is supported by the finding that seawater enriched with formaldehyde shows a gradual loss of the compound, whereas the level remains unchanged in sterile seawater under light and dark conditions.

1. Introduction

The heterogeneous transfer of photochemically reactive trace gases from the troposphere to the ocean is of interest for several reasons. First, both wet and dry deposition are important processes in biogeochemical cycling of substances within the environment. They can be considered as sources of key elements (S, C, N) to the ocean (Slinn et al., 1978). From a different point of view, however, the heterogeneous removal of gases which are subject to photochemical transformation may affect the concentration of important trace compounds and radicals in the atmosphere (Crutzen and Fishman, 1977). This is most likely to be the case for moderately long-lived, highly soluble or reactive compounds; then transfer into the oceans by precipitation and dry deposition may compete significantly with photoreaction.

We have investigated formaldehyde as an example of such a gas, using measurements of its concentration in precipitation and surface seawater to estimate wet and dry air-sea transfer and evaluating the total flux as a tropospheric removal mechanism and as a source of organic carbon to local waters.

2. Formaldehyde in precipitation. Wet flux

We measured formaldehyde in precipitation at Woods Hole, Massachusetts, a mid-latitude coastal site (41° 32′N, 70° 40′W), using the analytical methods of Nash (1953) and Belman (1963). Nash's method is colorimetric, involving the formation of the compound diacetyldihydrolutidine, which absorbs strongly at 410 nm and fluoresces at 510 nm. The Nash method is the most formalde-

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hyde-specific of wet aldehyde techniques. It was chosen also because of its high sensitivity, to 10 ppbw in water. Analyses were performed by reacting the Nash reagent in 1:1 or 1:9 mixtures with sample. Absorption and fluorescence spectra were identical to those obtained from standards prepared from reagent formalin. Standard curves (absorbance vs concentration added formaldehyde) from a randomly selected set of precipitation samples followed Beer's law in all cases, but in some of the samples there were negative deviations from the theoretical extinction coefficient, $\varepsilon_{theory} = 7800\ l\ mole^{-1}\ cm^{-1}$. Accordingly, an average extinction coefficient taken from these standard additions was used to compute concentrations for all rainwater samples: $\varepsilon_{rain} = 7360 \pm 770\ l\ mole^{-1}\ cm^{-1}$.

Precipitation was collected in distilled water-rinsed glass and plastic funnels and flasks, which were opened after precipitation had begun to avoid dry deposition and condensation. To obtain samples typical of the general Woods Hole area, sites were selected away from the immediate vicinity of large buildings, the harbor, and roads. One of these was in the village on a lightly populated section of the WHOI campus; the other two collectors were located 2 km NE of the village within a few hundred meters of Vineyard Sound to maximize exposure to offshore winds. It turned out that there were no significant concentration variations among samples collected in parallel at the different locations and in two-thirds of the events only one site was used. Although automatic sequencing was not available, subsampling over the entire range of prolonged storms was always carried out and rainfall, rain rate, temperature, cloud cover, wind speed and direction were recorded periodically. Except for one thundershower all events sampled were frontal storms which were usually accompanied by moderately strong, shifting winds and sharp temperature changes.

A total of 87 samples from 24 storms were analyzed between October 1978 and July 1979;

Table 1. *Formaldehyde in precipitation at Woods Hole—Summary of data*

Event no.	Date	Concentration ($\times 10^8$ g F/g RW, $c_i \pm 1\sigma$)	No. samples	Mean temperature (°C)	Rainfall, R_i (cm)	Wind direction, speed*	Mean rainrate (mm/hr)
1	14 Oct 1978	2.91 (±1.09)	5	19	4.2	SE, L	7.6
2	23 Oct 1978	11.6 (±1.06)	2	17	0.6	SW–N, H	2.7
3	27 Oct 1978	18.8 (±6.5)	2	17	0.6	S/SW	7.8
4	17–18 Nov 1978	4.16 (±1.0)	4	16	1.9	E→SW, H	3.4
5	21 Nov 1978	12.0 —	1	3	0.1	N/NE	0.5
6	22 Nov 1978	16.0 —	1	3	0.1	S/SE	0.2
7	27–28 Nov 1978	4.91 (±2.24)	5	4	1.4	E→S, L	2.2
8	29–30 Nov 1978	7.67 (±1.48)	2	7	1.8	SE→NW, M	3.0
9	3–5 Dec 1978	8.92 (±5.14)	5	8	2.6	SE→SW, H	2.4
10	8–10 Dec 1978	5.74 (±5.51)	9	6	4.9	W→NE, L	2.0
11	21 Dec 1978	9.75 (±2.36)	2	3	1.7	SE, L	2.0
12	31 Dec 1978–3 Jan 1979	3.86 (±3.18)	6	6	2.7	SE→SW, M	1.6
13	20–21 Jan 1979	3.70 (±1.36)	5	4	3.9	S/SE, VH	2.3
14	7–8 Jan 1979	1.82 (±1.35)	5	5	1.0	NE, L	0.8
15	21 Feb 1979	7.14 —	1	7	0.6	S/SW, H	2.8
16	24–26 Feb 1979	4.35 (±3.13)	13	3	11.0	SE→NE, H	2.9
17	2 April 1979	13.76 (±6.92)	3	3	1.4	NE→SE, M	1.6
18	4 April 1979	19.08 —	1	4	0.4	E, VH	1.9
19	9 April 1979	5.96 (±4.18)	2	7	1.6	E/SE, H	3.2
20	14 April 1979	5.37 —	1	4	0.3	E/NE, L	0.6
21	27 April 1979	4.51 (±1.58)	6	16	3.9	SE, H	3.2
22	12–14 April 1979	9.81 (±7.46)	3	16	2.9	S/SW	3.8
23	1 July 1979	3.39 —	1	21	2.1	SW→SE, L	9.5
24	27 July 1979	22.8 —	1	21	0.3	S/SE	2.8

* L = Light, M = Moderate, H = High

concentrations ranged from 0.084 to 2.45 × 10^{-7} g F/g rainwater (we use F to signify the equivalent weight of aqueous formaldehyde, which exists mostly as $H_2C(OH)_2$, methylene glycol, MG, at equilibrium: [MG]/[H_2CO] = 2000, Bell and Evans, 1966). These data and a summary of synoptic weather measurements appear in Table 1. Higher formaldehyde levels were often associated with fog, small total rainfall or great turbulence suggesting that in addition to rainout, some washout was occurring. However, washout as indicated by sharp maxima at the beginning of a storm did not seem to be typical since values 2–3 times higher than the event mean were recorded in only three cases. Detailed analysis of concentration variation and meteorological parameters did not reveal any pattern within an event except that in general larger storms with large wind and temperature shifts showed higher variability (σ/c_l). There were also no consistent relationships between concentration and temperature, time of day or year, wind direction or rainfall rate, so that concentration variations among events may be nearly random. Thus, extrapolation to annual rainfall, 107 cm (Ruffner and Bair, 1977) of the total flux from the events analyzed ($\sum_{l=1}^{24} c_l R_l$, where c_l is the mean concentration and R_l is the rainfall in the lth event), gives an estimate for the wet flux to local waters: 6.3 × 10^{-6} g F cm^{-2} yr^{-1}.

The mean concentration, $1/24 \sum_{l=1} c_l$, 8.7(±5.8) × 10^{-8} g F/g RW (RW = rainwater) is somewhat higher than the value suggested by total flux because of a weak inverse correlation between concentration and total rainfall and is close to the concentration reported in "maritime" precipitation on the Irish coast by Klippel and Warneck (1978), 1.11 ± 5.9 × 10^{-7} g F/g RW ($n \geq 40$); our range of values is similar to those they measured at several sites in Europe at 50° N from 1974–77. Warneck et al. (1978) also concluded from aerosol measurements that rainout and washout of aerosol-borne formaldehyde is sufficiently small that it can be assumed that the gas phase is responsible for most of the formaldehyde found in marine precipitation. On this basis the gas-phase mixing ratio in equilibrium with rainwater can be evaluated from

$$m = \frac{C_{RW} L}{\beta M_{H_2CO} N_{air}} \qquad (1)$$

where C_{RW} is the mean concentration of formaldehyde in rainwater by weight, L is the density of rainwater in clouds (1 g m^{-3}), M_{H_2CO} is the molecular weight of formaldehyde, N_{air} is the molar volume of air (38 mole m^{-3} at 2 km cloud height), and β is a partition coefficient between the concentration of formaldehyde condensed in raindrops and in the gas phase before condensation (Warneck et al., 1978). Although precipitation at Woods Hole does not usually represent "maritime clean air", since prevailing winds and most storms are from across eastern U.S. coastal waters, we use eq. (1) with the values C_{RW} = 8.7 ± 5.8 × 10^{-8} g F/g rain and β = 0.20 (based on an estimated Henry's Law coefficient for formaldehyde at 10 °C, 0.008 g H_2CO cm^{-3} air/g H_2CO cm^{-3} water; Walker, 1975; Bell and Evans, 1966) to calculate a mixing ratio: 0.38 ± 0.23 ppbv. This is the value for cloud height; a better estimate for ground level, 0.34 ppbv, is obtained from N_{air} = 43, assuming that there is no gradient in the total amount of formaldehyde between 0 and 2 km and that it is all present as H_2CO. Despite the approximations which have gone into the computation of this ground level mixing ratio the value is consistent with recent measurements of tropospheric formaldehyde by long path-length absorption spectroscopy (Platt et al., 1979); Central European background values range from 0.1–6.5 ppbv with a "maritime air" measurement of 0.2 ppbv.

3. Formaldehyde in seawater

We found that the Nash method can be used without modification to analyze formaldehyde in seawater. Surface seawater was sampled from Vineyard Sound in Woods Hole on nine occasions during the period February to June 1979, with temperatures ranging from 1 to 21 °C. At no time was formaldehyde detected; therefore, the concentration must be less than 10^{-8} g F/g SW. Using a different colorimetric method with a similar detection limit, Kamata (1966) found aldehydes in the north Pacific at depths from 50–4000 m but not in surface seawater. Aldehydes were also present in lake water only below 20 m and Kamata demonstrated in the laboratory that formaldehyde added to surface lake water was decomposed microbially. We conducted a similar experiment to determine whether atmospheric H_2CO transferred to local waters might also be consumed biologically.

Surface seawater samples were enriched with 87

μg/L formaldehyde, and transferred to sterile Pyrex flasks; controls of the same concentration were rendered biologically inactive by sterile filtration and the sterility was confirmed by staining with acridine orange. Solutions were sampled as soon as they were prepared and periodically thereafter using aseptic technique. The "active" flasks were incubated in the dark at two temperatures, 1° and 15° C. One set of controls was also incubated in the dark and a second set was incubated in fluorescent lights which were on 12 hours a day. Only in the non-sterile samples was formaldehyde consumed (Fig. 1). The loss kinetics showed an induction period corresponding to initial growth which was not rapid enough to deplete the nutrient noticeably, consistent with the exponential growth of a bacterial population. Retention of the original formaldehyde concentration in control solutions demonstrates its thermal and photochemical stability. These results are strong qualitative evidence for the biogeochemical cycling of formaldehyde, but the rate of consumption observed in the laboratory cannot be extrapolated to the natural situation in view of the artificially elevated nutrient levels.

4. Exchange rate: Dry flux

The dry flux of formaldehyde to local waters, like any gas exchange between air and sea, can be derived from a two-layer thin-film model in which the transfer is controlled by molecular diffusion through a surface microlayer (Liss and Slater, 1974):

$$\Phi = K_l(C_g/H - C_l) = K_l \Delta C \qquad (2)$$

where Φ is the flux of the gas (mass area^{-1} time^{-1}), C_g is its concentration in surface air, C_l is its concentration in surface water, K_l is the exchange

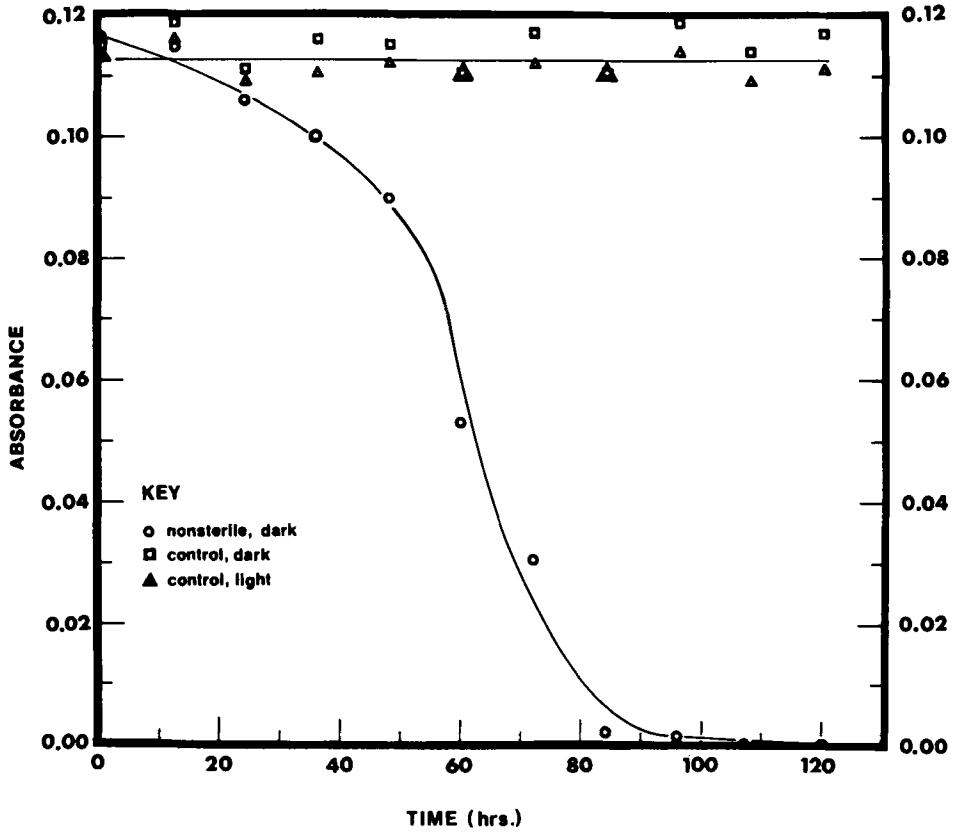

Fig. 1. Microbial consumption of H_2CO in seawater (t = 15°). Non-sterile flasks and controls were prepared in triplicate.

rate or transfer velocity, H is the Henry's law constant (g gas cm^{-3} air/g unassociated or unionized gas cm^{-3} water).

A minimum concentration gradient for formaldehyde, $\Delta C = 5.0 \times 10^{-11}$ g cm^{-3} is calculated with $C_g = 4.3 \times 10^{-13}$ g cm^{-3} (equivalent to the gas-phase mixing ratio derived from rainwater data) and $C_l = 4 \times 10^{-12}$ g cm^{-3}, the maximum amount of unhydrated H_2CO which could be present in surface seawater in equilibrium with 10^{-8} g F/g seawater (the limit of detection).

Since the temperature of surface seawater at Woods Hole varies from 0 to 25°, Henry's law constant is given the value 0.008, appropriate to 10 °C.

The parameter K_l^{-1} is the inverse of a combined gas- and liquid-phase transfer velocity (see Table 2) and can be thought of as being the overall resistance to gas transfer where r_l and r_g are respectively the inverses of the liquid and gas-phase transfer velocities. In practice the gas-phase exchange velocity k_g is usually taken from the value for water vapor, corrected for the molecular weight of the compound and k_l is taken from the value for CO_2 diffusion, 20 cm hr^{-1}, corrected by an "enhancement factor", α, which is greater than

Table 2. *Evaluation of the diffusion controlled air-sea exchange velocity for formaldehyde*

$$K_l^{-1} = r_l + r_g = \frac{1}{k_{CO_2} \cdot \alpha} + \frac{1}{k_g H} \text{ (Liss and Slater, 1974)}$$

where $k_{CO_2} = 20$ cm hr^{-1} $k_g = 3000$ cm hr^{-1} $\left[\frac{MW_{H_2CO}}{MW_{H_2O}}\right]^{-1/2}$

$H = 0.008$ (Walker, 1975; Bell and Evans, 1966)

Enhancement factor: (Quinn and Otto, 1971), (Hoover and Berkshire, 1969)

$$\alpha = \frac{\tau}{\tau - 1 + \tanh\left[\left(\frac{\langle k\rangle \tau}{D}\right)^{1/2} \frac{D}{k_{CO_2}}\right] \Big/ \left(\frac{\langle k\rangle}{D}\right)^{1/2} \frac{D}{k_{CO_2}}}$$

where k = total hydration constant (sec^{-1})
D = liquid diffusion constant (cm^2 sec^{-1})
τ = ratio of total to ionic forms of dissolved gas

For formaldehyde: $\langle k\rangle = 9$ s^{-1} (Schecker and Schulz, 1969)
$D = 1.6 \times 10^{-5}$ cm^2/sec (Landqvist, 1955)
$\tau = 1$
$\alpha = 2.24$

$$r_g = \frac{1}{k_g H} = 5.38 \times 10^{-2} \text{ hr/cm gas-phase resistance}$$

$$r_l = \frac{1}{k_l \alpha} = 2.23 \times 10^{-2} \text{ hr/cm liquid-phase resistance}$$

$K_l = 13.1$ cm hr^{-1} overall exchange velocity

Note: All parameters used for formaldehyde have been calculated at 10 °C from data on aqueous solutions and can be considered only approximate for seawater.

unity when the dissolved gas reacts in water by forming a hydrate or by an acid-base equilibrium, thereby increasing diffusion through the liquid. The classic case of enhancement by hydration is the exchange of SO_2 for which the factor is close to 2000 and the gas-phase resistance is several hundred times greater than the liquid-phase resistance. For most unreactive and slightly soluble gases, the liquid-phase resistance is greater since the diffusion constant $D = Kz$ (z is the microlayer thickness) is several orders of magnitude lower than it is in the gas phase. For dissolved formaldehyde which would be in equilibrium with a surface air mixing ratio of 0.3 ppbv, formation of the monohydrate methylene glycol will contribute to increased diffusion, but acid-base dissociation of the hydrate and formation of higher order hydrates, which are significant in concentrated formaldehyde solutions, should be negligible in seawater. This simplifies the expression for the enhancement factor (Table 2). The hydration rate, 9 s^{-1}, is such that only a 2.24-fold enhancement over simple H_2CO diffusion results for a thin-film thickness, $D/k_{CO_2} = 30\ \mu m$. However, given the high solubility of formaldehyde, the net result is that gas- and liquid-phase resistances to air-to-sea transfer are comparable. The corresponding transfer velocity K_l is 13.1 cm hr^{-1}.

To calculate dry deposition of H_2CO to nearby coastal waters, the transfer velocity and $\Delta C = 5 \times 10^{-11}$ g cm^{-3} are substituted into the flux eq. (2): $\Phi = 5.7\ \mu g\ cm^{-2}\ yr^{-1}$. Thus, the gaseous uptake of formaldehyde and the wet flux (6.3 μg cm^{-2} yr^{-1}) are comparable and a reasonable estimate for the total flux of tropospheric H_2CO to coastal waters near Woods Hole, is 1.2×10^{-5} g cm^{-2} yr^{-1}. A similar value can be derived from the maritime rainwater formaldehyde concentration ($C = 1.1 \times 10^{-7}$ g F/g RW) of Warneck et al. (1978) using a mixing ratio of 0.1–0.2 ppbv.

5. Discussion

The generally accepted scheme of tropospheric formaldehyde formation from the photo-oxidation of methane is shown in Table 3 (Levy, 1971, 1972). Its photolysis through the pathways 8–10 is a major source of natural CO (McConnell et al., 1971). Thus every time a molecule of H_2CO is removed by wet or dry deposition one less molecule of CO is formed, interrupting the cycling of the radicals OH and HO_2, Reactions (1) and (11).

Table 3. *Photochemical formation and destruction of tropospheric* H_2CO (Levy, 1971, 1972)

$OH + CH_4$	$\rightarrow CH_3 + H_2O$	(1)
$CH_3 + O_2 + M$	$\rightarrow CH_3O_2 + M$	(2)
$CH_3O_2 + NO$	$\rightarrow NO_2 + CH_3O$	(3)
$CH_3O_2 + NO_2$	$\rightarrow CH_3O_2H + O_2$	(4)
CH_3O_2H	$\xrightarrow{h\nu} CH_3O + OH$	(5)
$CH_3O_2 + CH_3O_2$	$\rightarrow 2CH_3O + O_2$	(6)
$CH_3O + O_2$	$\rightarrow H_2CO + HO_2$	(7)
$H_2CO + OH$	$\rightarrow H_2O + CHO$	(8)
$H_2CO + h\nu$	$\rightarrow H_2 + CO$	(9)
$H_2CO + h\nu$	$\rightarrow H + CHO$	(10)
$CHO + O_2$	$\rightarrow CO + HO_2$	(11)

In order to assess the importance of the heterogeneous removal of tropospheric formaldehyde, consider a one-dimensional transport equation such as that given by Warneck et al. (1978):

$$K_z \frac{\partial}{\partial z} n \frac{\partial m}{\partial z} + P(z) - \bar{J} n m = 0$$

where the first term represents eddy transport, $m(z)$ is the H_2CO mixing ratio, $P(z)$ is the source function, $n(z)$ is the total particle density and $\bar{J}$ is an average photolysis rate. Although the complete set of reactions shown in Table 3 reveals a complex source function for formaldehyde, the rate-determining step in the chain is the reaction of OH and CH_4 ($k = 7 \times 10^{-15}$ cm^3 s^{-1}).

With an assumed OH concentration of 2–5 $\times$ 10^5 molec cm^{-3}, $K_z = 2 \times 10^5$ cm^2 s^{-1} and $\bar{J} = 1.8 \times 10^{-5}$ s^{-1}, the source function of Warneck, et al. cannot support the ground level mixing ratio suggested by our data. This result is not surprising, since the Woods Hole environment does not represent pure maritime air as the model assumes. The imbalance could be removed by methane oxidation with higher OH level or by terrestrial sources of H_2CO, either natural (photo-oxidation of non-methane organics, Zimmerman et al., 1978) or anthropogenic (Cleveland et al., 1977).

The source strength of Warneck et al., which is 5–12 $\times$ 10^4 molec H_2CO cm^{-3} s^{-1} at ground level, is sufficient to sustain a marine air mixing ratio of 0.1–0.2 ppbv, provided that no oceanic sink exists. Extending the ground level production rate throughout a 5 km atmospheric mixed layer (thus, ignoring vertical gradients) gives an upper limit to

the production rate: 8–18 × 10^{-5} g cm^2 yr^{-1}. Hence, an air-to-sea flux of formaldehyde of 1.2 × 10^{-5} g cm^{-2} yr^{-1}, is on the order of 7–15% of the source strength provided by methane oxidation. This suggests that heterogeneous removal should be included in the photochemical transport equation for proper balance.

The total flux of formaldehyde to coastal waters represents a source of 4.8 × 10^{-6} g cm^{-2} yr^{-1} organic carbon. This is approximately 1% of the estimated maximum total organic carbon input from the atmosphere (Duce and Duursma, 1977). However, most of the formaldehyde which has been found in subsurface seawater is probably of biological origin.

6. Summary

Formaldehyde has been measured in precipitation at a mid-latitude coastal site to give a value for wet flux, and the surface level gas-phase concentration of H_2CO, C_g, has been estimated from the average value in precipitation, assuming that formaldehyde on aerosol makes a negligible contribution to the measured total. Analysis of formaldehyde in surface seawater allows an upper limit to be placed on the concentration of the dissolved gas, C_l and the dry flux of H_2CO is evaluated from the difference $(C_g/H - C_l)$ using an overall exchange velocity made up of comparable liquid- and gas-phase components. The total flux of H_2CO represents a transfer of 4.8 × 10^{-6} g cm^{-2} yr^{-1} organic carbon from atmosphere to ocean, and enrichment experiments show that this formaldehyde could be consumed biologically.

We realize that the flux we calculate as applicable to a coastal environment, 1.2 × 10^{-5} g H_2CO cm^{-2} yr^{-1}, is derived from limited data and a number of approximations. This is especially true for the estimate of dry deposition. Thus, although it appears that the air-to-sea transfer of formaldehyde may represent a significant sink for this tropospheric gas, more data are needed to substantiate this interpretation. These data should include not only further measurements of formaldehyde fluxes, but also more accurate determinations of its photochemical source strength and photolytic lifetime under natural conditions (Moortgat et al., 1978; Calvert et al., 1972), since ultimately the importance of an oceanic sink depends on the relative magnitudes of homogeneous and heterogeneous removal.

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МОКРОЕ И СУХОЕ УДАЛЕНИЕ ТРОПОСФЕРНОГО ФОРМАЛЬДЕГИДА В БЕРЕГОВОМ МЕСТЕ

Формальдегид, содержанный и в осадках и в поверхностной морской воде, измерялся в середине широты в береговом месте Вудс-Холя, Массачусемса (США). По этим измерениям и вычислению класса "воздух-море" управляемой на рассеяния скорости перемещения для соединения оцениваем мокрое и сухое течение H_2CO от тропосферы до соседних береговых вод в 6,3 μг см$^{-2}$ год$^{-1}$ за осадки, а в 5,7 μг см$^{-2}$ год$^{-1}$ за газообразное рассеяние. Если с простой фотохимической моделью сравнить эти величины, то кажется, что эти перемещения являются значительным механизмом удаления для тропосферного формальдегида.

Общее течение H_2CO равняется подводу 4,8 μг см$^{-2}$ года$^{-1}$ органического углерода, $\geqslant 1\%$ общего оценённого органического углеродного класса "воздух-море" перемещения. Отсутствие заметного количества формальдегида в поверхностной морской воде значит о том, что вышла бы его судьба из биологического поднятия. Это мнение подтверхдается том, что обогащённая формальдегидом морская вода показывает постепенную убыль соединения, тогда как при световых и тёмных условиях в чистой морской воде остаётся уровень неизменяем.