

# Tropospheric formaldehyde concentration at the Mauna Loa Observatory during the Mauna Loa Observatory Photochemistry Experiment 2

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**Abstract.** The concentration of formaldehyde at Mauna Loa Observatory, Hawaii, was determined during four Mauna Loa Observatory Photochemistry Experiment 2 (MLOPEX 2) measurement intensives between September 1991 and August 1992. The observed diurnal variations, 200-900 parts per trillion by volume (pptv) during daytime and 60-200 pptv during nighttime, resulted mainly from the local air circulation pattern whereby island modified marine boundary layer air prevailed during the day and free tropospheric air dominated during the night. A seasonal variation was also observed; the median/mean values of all data points are: 149/196, 129/149, 143/178, and 181/211 pptv for autumn, winter, spring, and summer intensives, respectively. During nighttime downslope flow periods which brought in free tropospheric air to the measurement site, the formaldehyde concentrations (median/mean) were 122/123, 110/112, 120/125, and 140/137 pptv for autumn, winter, spring, and summer, respectively. This seasonal dependence may be attributable to changes in solar insolation and NO concentrations. A simple box model calculation constrained by the experimentally determined concentrations of CH<sub>3</sub>OOH yielded a formaldehyde concentration (without/with heterogeneous removal) for free tropospheric air, at 7°C, of 155/140, 125/115, 210/195, and 220/205 pptv for autumn, winter, spring and summer, respectively. The calculated values are in good agreement with the measured concentrations for winter (within 27/15%, without/with heterogeneous removal) and fall (within 14/5%), but are significantly higher for spring (75/63%) and summer (57/46%).

## Introduction

During the past two decades significant progress has been made in identifying the mechanism governing photochemistry and ozone production in the troposphere. The mechanism that emerged [e.g., Atkinson, 1990], which involves an intricate relationship between hydrocarbon oxidation and ozone formation mediated by NO<sub>x</sub>, is based primarily on laboratory studies and to some degree on modeling results. Consequently, direct field measurements that can determine the temporal and spatial distributions of key atmospheric species at extremely low levels, that is, parts per billion by volume (ppbv) to parts per trillion by volume (pptv) are needed to confirm, constrain, and improve this mechanism. Aply equipped with a suite of sensitive instruments, the Mauna Loa Observatory Photochemistry Experiment (MLOPEX) was conducted for the purpose of characterizing the concentrations of many photochemically relevant species and testing whether these observed values could be adequately

explained by current photochemical models, especially those pertaining to the free troposphere [Ridley and Robinson, 1992]. However, despite the relatively uncomplicated chemistry of the free troposphere, the concentrations of a number of photochemical species, including formaldehyde, methylhydroperoxide and hydrogen peroxide, were found to be in major disagreement with model predictions [Liu *et al.*, 1992]. In the case of formaldehyde, the measured median concentration of the free troposphere ~105 pptv [Heikes, 1992], was significantly lower than the calculated value of 300 pptv.

Since formaldehyde is a major product of the photooxidation of methane and other hydrocarbons [National Research Council (NRC), 1981; Carlier *et al.*, 1986] and, upon photolysis, serves as a free radical source [e.g., NRC, 1991], accurate determination of its atmospheric concentration is needed for gaining insights into the mechanisms by which hydrocarbons are oxidized and photooxidants are produced. The inability to reconcile the difference between the observed and the calculated concentrations of formaldehyde during MLOPEX demands a thorough reexamination of our present capabilities in both modeling and measurement. It may be noted that while the chemistry of the free troposphere is simplified due to the reduced contributions of the nonmethane hydrocarbons (NMHC), the lowered concentrations of many key species also

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make reliable measurements difficult. Subsequently, the discrepancies between the observed concentrations and those calculated for the free troposphere have been thought to arise at least partly as a result of measurement uncertainties [Liu *et al.*, 1992]. However, in their analysis of the MLOPEX data, Liu *et al.* [1992] pointed out a possible deficiency in our understanding of the radical chemistry. Consequently, MLOPEX 2 was designed to collect a more extensive and reliable set of chemical and meteorological data with a greater temporal coverage. Because of the importance of formaldehyde, it was concurrently measured by four different groups using three different techniques to ensure that any measurement inadequacies would be detected. The four teams were from University of Rhode Island, NCAR, Unisearch Associates Inc., and Brookhaven National Laboratory/Washington State University [Heikes *et al.*, this issue]. In this paper, we report the gas phase formaldehyde concentrations measured at Mauna Loa Observatory (MLO) and its diurnal and seasonal variations, and discuss the chemical and transport processes important for formaldehyde in the remote free troposphere.

## Tropospheric Formaldehyde Chemistry

Away from source regions, formaldehyde is produced in the atmosphere from photooxidation of hydrocarbons [NRC, 1981]. In the free troposphere, methane at 1.7 ppmv is the dominant precursor for formaldehyde over NMHC because of their low concentrations: the sum of the reaction rates of NMHC with OH is less than 10% of that of methane in the free tropospheric air [Greenberg *et al.*, 1992; this issue]. In addition, many NMHC-OH reactions do not lead to the formation of formaldehyde, making them less important.

The chemistry of formaldehyde production as related to methane oxidation is shown in Figure 1. Upon reacting with an OH radical, methane produces the CH<sub>3</sub> radical, which rapidly reacts with O<sub>2</sub> to form CH<sub>3</sub>O<sub>2</sub>. CH<sub>3</sub>O<sub>2</sub> radicals react with HO<sub>2</sub> and NO to form CH<sub>3</sub>OOH and CH<sub>3</sub>O, respectively. The latter reacts rapidly to form formaldehyde. The CH<sub>3</sub>OOH molecule is converted to CH<sub>3</sub>O by photolysis and to CH<sub>2</sub>OOH and CH<sub>3</sub>O<sub>2</sub>

by reaction with OH; CH<sub>2</sub>OOH radicals also break down to formaldehyde. The production rate of formaldehyde *P* (in units of molecules per cubic centimeter per second) from these source pathways is given as

$$P = \frac{(k_1 [\text{CH}_4] + k_{4a} [\text{CH}_3\text{OOH}]) [\text{OH}] + k_3 [\text{NO}]}{k_3 [\text{NO}] + k_2 [\text{HO}_2]} + (j_5 + k_{4b} [\text{OH}]) [\text{CH}_3\text{OOH}] \quad (1)$$

where *j* and *k* are photolysis and second-order rate constants, respectively.

With respect to sink processes, formaldehyde is removed from the atmosphere by photolysis and reaction with OH (Figure 1). Its destruction rate, *D* (in units of molecules per cubic centimeter per second), is

$$D = (j_6 + j_7 + k_8 [\text{OH}]) [\text{HCHO}] \quad (2)$$

The change in formaldehyde concentration can be expressed as the difference between the production rate and the destruction rate:

$$d[\text{HCHO}]/dt = P - D \quad (3)$$

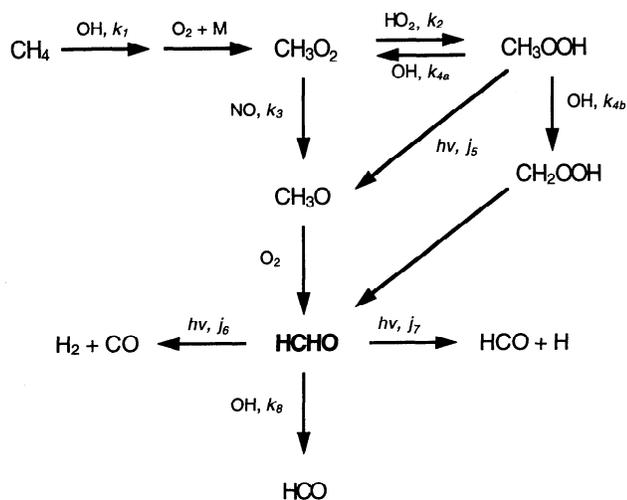
Since photolysis rate constants and concentrations of OH, HO<sub>2</sub>, and NO are functions of sunlight intensity, both the production and destruction rates should exhibit diurnal variations, that is, both reaching maxima around noontime and reaching zero during the night. A simple box model based on the reactions in Figure 1 and (1) - (3) has been constructed, and calculation results are discussed in the steady state calculation section.

## Experimental Section

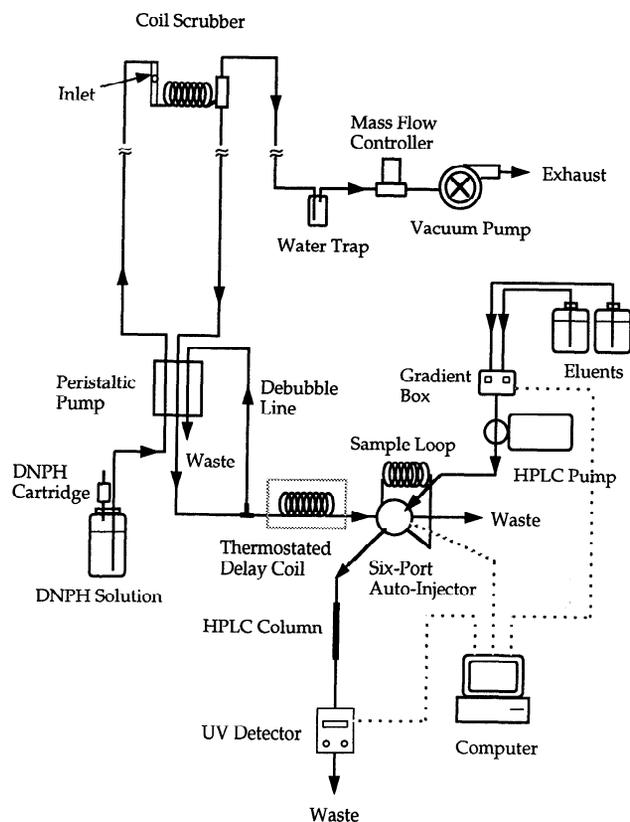
A description of the MLO sampling site has been given previously [Ridley and Robinson, 1992]. The four measurement intensives of the MLOPEX 2 were: 2a, September 15 to October 15, 1991; 2b, January 15-February 15, 1992; 2c, April 15-May 15, 1992; and 2d, July 15 - August 15, 1992. The gas phase concentration of formaldehyde was measured in all of the intensives. Occasionally, glyoxylic acid was also identified.

The method of sampling and analysis was based on a technique recently developed [Lee and Zhou, 1993], which consisted of scrubbing gaseous formaldehyde using a glass coil and subsequent analysis by a high performance liquid chromatography (HPLC) following derivatization with 2,4-dinitrophenylhydrazine (DNPH). The system was automated so that on-line continuous measurements were made about every 20 min. In this configuration, a delay coil was added before the HPLC injection valve to allow for on-line derivatization (~1 hour), and a personal computer was used to perform automatic sample injection, chromatographic analysis, and data storage. The experimental setup is shown in Figure 2.

The glass coil scrubber was installed on the top of a sampling tower at about 10 m above the ground. The sample air was pulled through the coil by a diaphragm pump at 2.0 standard liters per minute (SLM) controlled by a mass flow controller (Sierra, model Sidetrack III). The scrubbing solution, a dilute aqueous DNPH solution, was pumped up to the coil and pulled



**Figure 1.** Methane oxidation mechanism important for formaldehyde chemistry in the troposphere.



**Figure 2.** A schematic diagram of the experimental setup of the formaldehyde detection system. DNPB: 2,4-dinitrophenylhydrazine.

back down to the delay coil through a narrow Teflon tube (I.D. 0.05 cm) by a peristaltic pump (Rainin, model Rabbit Plus). The returning scrubbing solution flowed through the delay coil, and into a 6-port automatic injection valve equipped with a 2-mL sample loop. A debubbler line branched out from the liquid flow just before the delay coil. The sample integration time corresponding to the 2-mL injection volume was  $\sim 10$  min. The liquid flow rate, maintained at  $0.3 \pm 0.03$  mL  $\text{min}^{-1}$ , was measured at least 3 times a day.

The HPLC system consisted of a pump (Eldex Laboratories, Model AA), a C18 reverse phase column (Waters, Radial-Pak cartridge), and a UV-vis detector (Isco, Model V4) equipped with a 10 mm flow cell. The detection wavelength was fixed at 370 nm. The gradient elution and data acquisition were controlled by E-Lab software (Model 2020, OMS Tech) running on an IBM compatible PC. The chromatograms were stored on disks and processed by the E-Lab data system.

The working scrubbing solution was prepared by diluting a 5-mL DNPB stock solution (1.5 g DNPB in 150 mL 1:4:5 by volume mixture of 6 M  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$ , and  $\text{CH}_3\text{CN}$ ) in 1.5 L water and purified by extracting with three portions of 20 mL HPLC grade  $\text{CCl}_4$  over a 48-hour period. The blank signal for the working DNPB solution was obtained at the beginning and the end of each batch with the system operating normally except with the scrubbing coil bypassed. Calibration was performed using aqueous formaldehyde standards prepared from a concentrated solution ( $\sim 37\%$ , Mallinckrodt) which had been standardized against an  $\text{H}_2\text{O}_2$  solution, which in turn had been standardized by a  $\text{NaHSO}_3$  standard [Intersociety Committee, 1972].

The derivatization of the HCHO standards was made externally using the same working DNPB scrubbing solution for appropriate lengths of time. This solution was then directly injected into the HPLC for the quantitation of formaldehyde signals. The procedure of blank analysis and calibration, which took  $\sim 3$  hours, was usually carried out during the morning hours.

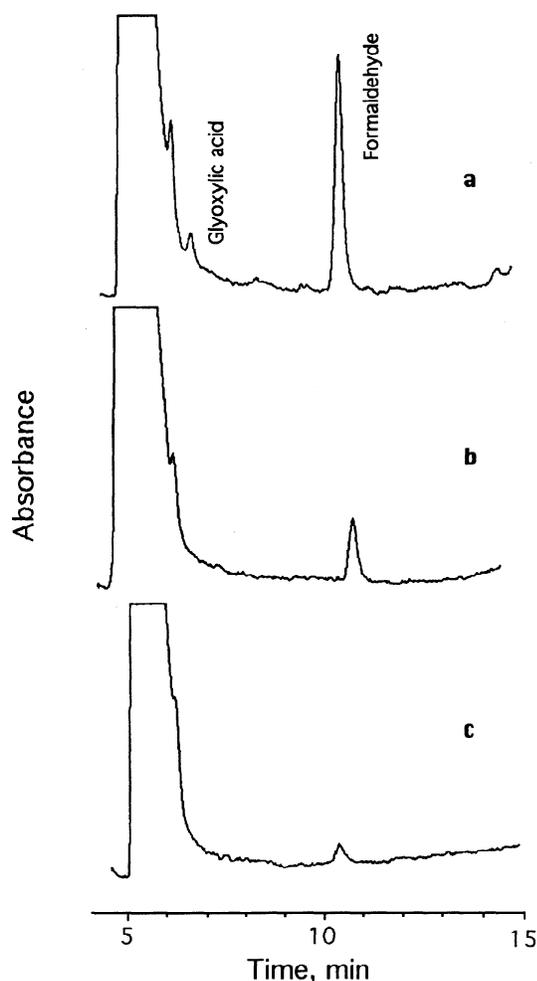
The collection efficiency of the coils was determined in the laboratory using standard formaldehyde gases generated by bubbling ultrahigh purity (UHP)  $\text{N}_2$  through diluted formaldehyde solutions of known concentrations. Under most conditions, two coils were connected in series [Lee and Zhou, 1993]. To determine the effects of ambient pressure on the collection efficiency, the calibration was also carried out in an altitude chamber at  $\sim 680$  mbar. The efficiency was determined as a function of liquid flow rate and gas flow rate.

## Results and Discussion

Typical HPLC chromatograms are shown in Figure 3 for daytime, nighttime, and background samples. The retention time of the formaldehyde peak was slightly retarded in the nighttime because of the lowered temperature in the trailer. The daytime sample exhibited a peak for glyoxylic acid in addition to that for formaldehyde. Since the size of the formaldehyde peak of the blank was typically  $\sim 20\%$  of the nighttime formaldehyde signal (Figure 3), the uncertainty arising from the blank signal was  $\leq 10\%$ . The coil collection efficiencies was  $40 \pm 2\%$  and  $70 \pm 3\%$  for a 10-turn coil sampler (MLOPEX 2a) and a 28-turn (MLOPEX 2b, 2c, and 2d), respectively (Table 1). On the basis of the blank signal and the collection efficiency, the detection limit was estimated to be  $\sim 10$  pptv ( $S/N=3$ ). The major uncertainty in the measurement was due to variations in the liquid flow rate ( $\sim 15\%$ ) which affected not only the liquid volume into which the gas sample was concentrated but also the derivatization time, blanks, and calibration. The overall uncertainty in the formaldehyde determinations taking into account the collection efficiency, the blanks, and the liquid flow rate was estimated as  $\sim (10 \text{ pptv} + 0.2 \times [\text{HCHO}])/[\text{HCHO}] \times 100\%$ , that is, 30% at 100 pptv and 25% at 200 pptv.

The formaldehyde concentrations determined during the four intensives are shown in Figure 4. Although the technique was capable of detecting glycolaldehyde, glyoxylic acid, and pyruvic acid in addition to formaldehyde, only glyoxylic acid was detected at concentrations above the detection limit ( $\sim 10$  pptv) and for only about 10% of the daytime samples. Owing to instrument problems, no data were collected before September 27, 1991 (2a) and between January 27 and February 11, 1992 (2b). Also, the data collected between July 17 and July 19 (2d), after cleaning the liquid plumbing with  $\text{CH}_3\text{CN}$  to remove a clog in the line, exhibited a significant offset compared to the rest of the data collected in the same intensive (Figure 4d). Since a student t-test showed that the data collected during July 18 2200 to July 19 0800 (HST) were significantly different from those collected during other downslope periods (see below for definitions) of this intensive, we excluded these data from the analysis.

The data set, which covered 16, 17, 30, and 30 days during the MLOPEX 2a, 2b, 2c, and 2d intensives, respectively, are summarized in Table 1: The median and mean ( $\pm 1\sigma$ ) formaldehyde concentrations were:  $149/196 \pm 108$ ,  $129/149 \pm 61$ ,  $143/178 \pm 101$ ,  $181/211 \pm 104$  pptv, for MLOPEX 2a, 2b, 2c,



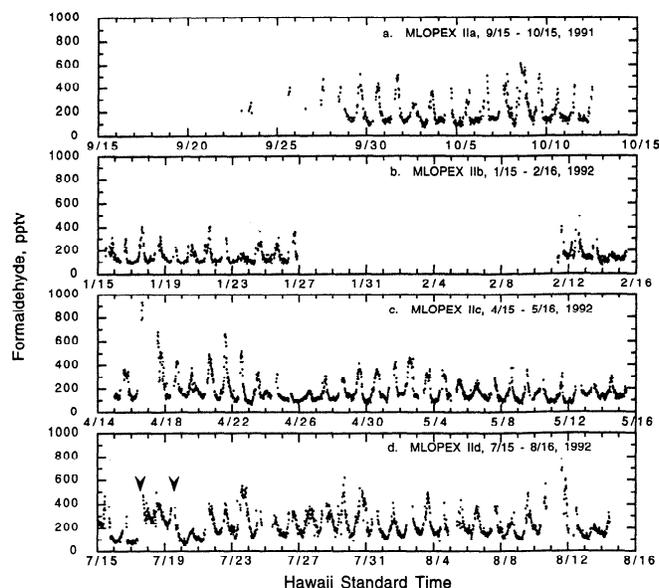
**Figure 3.** Typical chromatograms showing (a) a daytime sample (April 23, 1992, 1515), (b) a nighttime sample (April 23, 1992, 0230), and (c) a blank (April 23, 1992).

and 2d, respectively. These values are in reasonable agreement with those determined by *Heikes et al.* [this issue] during MLOPEX 2 which showed median values of 190, 180, 210 and 180 pptv for the four intensives, respectively. Our mean concentration of the 2c during early spring, that is, 178 pptv, is ~25% greater than the value of 140 pptv determined by *Heikes* [1992] during MLOPEX in the spring of 1988.

**Diurnal variations.** Strong diurnal variations in formaldehyde concentration were observed during all four intensives, as

**Table 1.** Effects of Pressure and Liquid Flow Rate on Formaldehyde Collection Efficiency of the Coil Samplers at Sample Flow Rate = 2 L min<sup>-1</sup> and T = 15 - 30°C

Pressure mbar	Liquid Flow Rate mL min <sup>-1</sup>	Efficiency, Percent ±1σ	
		10-turn coil	28-turn coil
1000	0.24	—	68 ± 4
1000	0.30	41 ± 2	72 ± 3
1000	0.35	—	74 ± 3
680	0.31	40 ± 2	70 ± 3

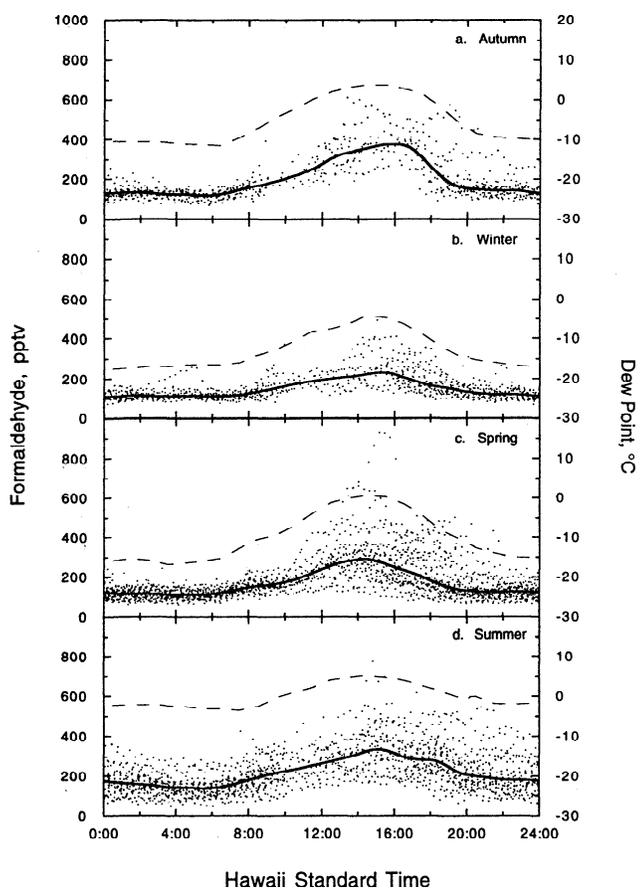


**Figure 4.** Time series of the ambient concentrations of formaldehyde measured during MLOPEX 2. The period marked by two arrows in MLOPEX 2d intensive was not included in the analysis (see text).

can be discerned from Figure 4. This diurnal dependence, shown in Figure 5 as composite diurnal plots, was primarily driven by the local air circulation patterns [*Hahn et al.*, 1992; *Walega et al.*, 1992]. During the daytime the air flows upward to the sampling site resulting from surface warming (upslope air). During the night the air tended to flow downward to the sampling site resulting from cooling of the surface (downslope air). The upslope and downslope flows may therefore bring to the site air masses of completely different origins, that is, from the marine boundary layer (MBL) and the free troposphere, respectively.

The MBL air, when moving upslope over the island, was influenced and modified by both natural and human activities on the island. Consequently, the upslope air was typically marked not only by high relative humidity, but also high concentrations of trace species, including formaldehyde, compared to the downslope air. Similar distributions of formaldehyde concentration and dew point (G. Herbert, personal communication, 1996) is evident in Figure 5. The upslope air masses contained a higher level of NMHC [*Greenberg et al.*, 1992; this issue], whose photooxidation contributes to formaldehyde formation. In addition, higher formaldehyde concentration may be responsible by direct emissions from processes on the island, such as biomass burning around the lava flows of the Kilauea volcano, as indicated by the concurrence of high concentrations of formaldehyde and other trace gases for volcanic activity (see case study section). Consequently, the formaldehyde concentration in the upslope air is expected to be greater and more variable than that in the downslope air (Figure 5).

During nighttime and early morning hours (2200-0800 HST), formaldehyde concentrations were typically between 60 and 200 pptv (Figure 5). In order to identify the downslope air that has a free tropospheric air origin, we adopted a number of criteria: pressure of inversion height  $\geq 680$  mbar, wind speed  $\geq 1$  m s<sup>-1</sup>, and wind direction between 90° and 270° [*Walega et al.*, 1992; B.A. Ridley, personal communication, 1996]. During these



**Figure 5.** Composite diurnal plots of the formaldehyde concentration. The solid lines represent the average values determined with a biweight algorithm which closely approximate the medians. The dashed lines are similarly determined for the dew points.

downslope periods whereby these conditions were met, the air mass was usually representative of the free troposphere at 3400 m [Walega et al., 1992], characterized by dry air and usually low and relatively constant formaldehyde concentrations. The median concentrations of formaldehyde for the four intensives,

between 110 and 140 pptv (Table 2), are somewhat greater than the value of 100 pptv previously reported during MLOPEX in Spring 1988 [Heikes, 1992], and that determined for the free troposphere over Germany [Lowe et al., 1980]. The low formaldehyde concentrations in the free troposphere are expected from the fact that contributions from NMHC are negligible and methane represents the only important precursor. The nighttime air masses that did not meet all of the downslope air definitions are considered to be a mixture of free tropospheric air and MBL air.

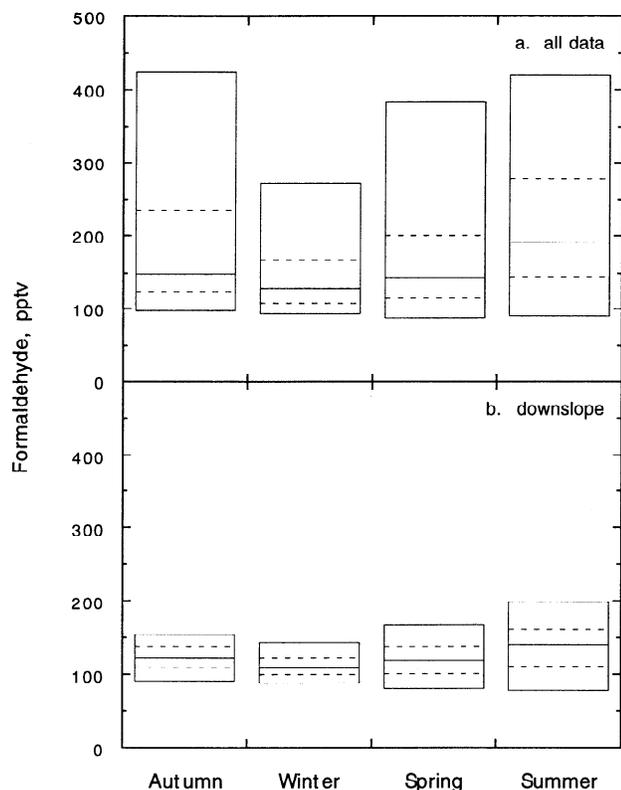
**Seasonal variations.** The seasonal variation of the formaldehyde concentrations measured at the MLO is presented as box plots in Figure 6a for all data points and Figure 6b for downslope condition. The median concentrations (all data) were the highest in summer and lowest in winter, with spring and autumn in between; the increase from winter to summer is ~50% (Figure 6a). This seasonal trend is similar to that exhibited by the dew point (Figure 5) (G. Herbert et al., personal communication, 1996). It may be noted that the spread in the nighttime formaldehyde concentrations is significantly more pronounced in summer than in winter (Figure 5). We believe that this arises mainly from a greater influence of the measurement site by the MBL air during summer as explained in the follows.

The elevation of MLO is ~3400 m (average pressure ~680 mbar), which is often in the transition zone between the two synoptic regimes in this region of the Pacific, that is, easterly trade winds below and westerly tropospheric air above. The average depth of the easterly flow extends from sea level to near 500 mbar in the summer and to only about 700 mbar in the winter, with spring and autumn in between [Hahn et al., 1992]. During nighttime and in early morning in winter, the surface cooling of the mountain slope induces a downslope flow that brings free tropospheric air to the site, which is marked by low humidity. In summer, on the other hand, the trade inversion height frequently sits above the MLO site, resulting in frequent nondownslope events in the same time window. Filtering formaldehyde data by this inversion height criterion, we found ~90% of the nighttime was downslope in winter, and ~80% in spring and autumn; in contrast, only ~55% in summer. For these periods of downslope air, we found that formaldehyde concentrations are less scattered compared to the unfiltered data and that the increase of the median concentration from winter to summer was only ~25% (Table 2, Figure 6b).

**Table 2.** Statistical Summary of the Formaldehyde Concentrations Measured During MLOPEX 2

All Data					Downslope Air				
Range	Median	Mean	$\sigma$	n	Range	Median	Mean	$\sigma$	n
<i>MLOPEX 2a Intensive</i>									
71-611	149	196	108	756	71-170	122	123	20	264
<i>MLOPEX 2b Intensive</i>									
68-491	129	149	61	1020	68-163	110	112	17	435
<i>MLOPEX 2c Intensive</i>									
64-931	143	178	101	2007	64-246	120	125	28	819
<i>MLOPEX 2d Intensive</i>									
49-776	181	211	104	1700	49-227	140	137	35	396

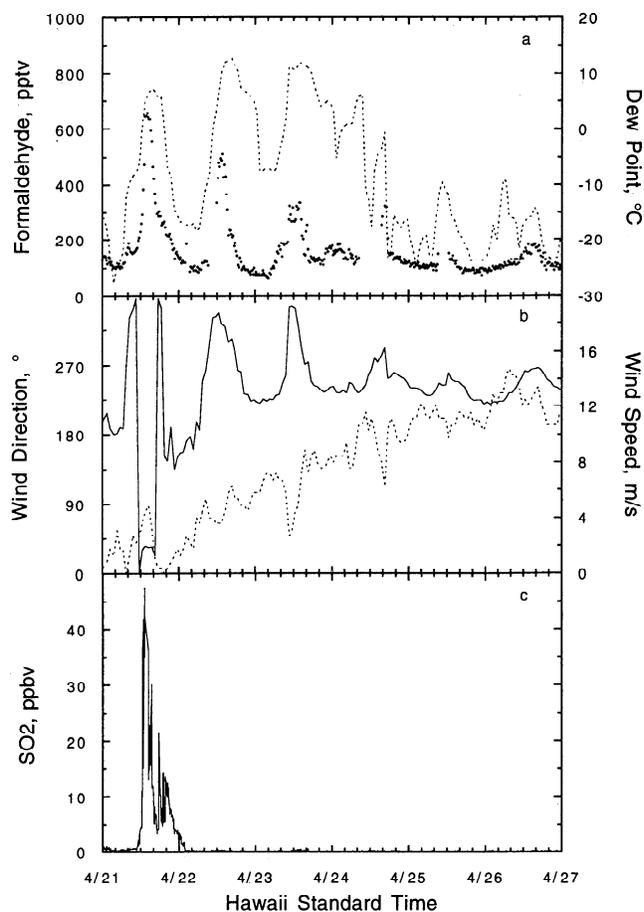
Formaldehyde concentrations in parts per trillion by volume.



**Figure 6.** Box plots of formaldehyde concentrations as a function of season. The solid line represents median value, the upper and lower dashed lines 75 and 25 percentiles, and the upper and lower sides of the box 90 and 10 percentiles: (a) all data, (b) downslope air only.

**Case studies.** A few individual cases are presented below to illustrate how the concentration of formaldehyde may be affected by meteorology. The period of April 21 to April 27, 1992 (MLOPEX 2c) is worthwhile noting in this regard: it experienced a high  $\text{SO}_2$  episode on April 21, a high humidity period during the night of April 23 and the morning of April 24, and strong westerly flows from April 24 through April 27 (Figure 7). The unusually high  $\text{SO}_2$  concentrations on April 21, reaching 45 ppbv around 1400 to 1500 HST (Figure 7c) (G. Hübler, personal communication, 1996) was found to be associated with a high formaldehyde concentration which reached  $\sim 700$  pptv (Figure 7a). Further, high concentrations of condensation nuclei, CN, [Bodhaine, this issue] and  $\text{NO}_x$  (B.A. Ridley, personal communication, 1996) and low concentrations of  $\text{H}_2\text{O}_2$  [Stafflebach *et al.*, this issue; B.G. Heikes, personal communication, 1996] accompanied this  $\text{SO}_2$  episode. The air mass that was responsible for this episode is believed to have been influenced by volcanic activities of Kilauea (elevation 250 m), located about 64 km east-southeast of MLO. Combustion of vegetation from lava flows probably generated a significant amount of formaldehyde as well as aerosol and  $\text{NO}_x$  in the air mass reaching MLO during this period.

On late afternoon of April 23 the upslope northerly flow changed to westerly (Figure 7b) which greatly limited the local influences. This was reflected in a sharp decrease in formaldehyde, from about 350 pptv to about 150 pptv. However, the level of formaldehyde stayed slightly higher, between 150 and 200 pptv, throughout the night and early morning than the



**Figure 7.** Formaldehyde concentration and some other measurements made between April 21 and April 27, 1992. (a) Formaldehyde (solid circles) and dew point (dashed line); (b) Wind direction (solid line) and wind speed (dashed line); (c)  $\text{SO}_2$ .

typical downslope concentration of 120 pptv during the MLOPEX 2c intensive. This level of formaldehyde is thought to be primarily associated with a MBL air, as suggested by a moderately elevated humidity (that is, dew point, Figure 7a) (G. Herbert, personal communication, 1996) and the formaldehyde concentration typical of MBL air masses [Lowe and Schmidt, 1983].

It is interesting to note that the usual daytime maximum in formaldehyde was nearly absent on April 25 and April 26. Between the night of April 24 and the morning of April 26, the site was dominated by westerlies, characterized by high wind (wind speeds  $\geq 10$  m  $\text{s}^{-1}$ ), low humidity (DP  $< -10^\circ\text{C}$ ) (G. Herbert, personal communication, 1996) (Figure 7a,b) and low CN count [Bodhaine, this issue]. Thus the site appeared to be dominated by free tropospheric air, even during the daytime. During this period, the daytime formaldehyde concentration increased only slightly over the nighttime values, reaching about 140 pptv and 170 pptv in the early afternoon of April 25 and April 26, respectively. A plausible explanation could be that the MBL air had been mixed into the westerlies as indicated by an increase in the dew point from  $< -20^\circ\text{C}$  to  $-10^\circ\text{C}$  and a slight shift in wind direction during these daytime periods (Figure 7b).

**Relationship to air mass origin.** Since the air masses that came in contact with the sampling site had different chemical

histories, it is instructive to examine whether they influenced formaldehyde concentrations. Figure 8 shows box plots of formaldehyde concentrations in the downslope air segregated by air mass trajectory origins calculated by Hess et al. [this issue]. The nighttime measurements that were not associated with downslope air masses are pooled together as nondownslope (NDS). For the downslope air, the median values varied narrowly between 115 and 135 pptv. The lower values were mainly associated with air masses from the west/northwest occurring most often during the winter intensive, whereas the higher values were associated with air masses from the east/southeast and of local origin which prevailed during the summer intensive. This small difference may be accounted for by a seasonal dependence of the photochemistry (see below). The lack of appreciable dependence on air mass origin suggests that long-term transport of formaldehyde and its precursors is not important for formaldehyde concentration at this site. On the other hand, the greater and more scattered formaldehyde concentrations observed in the nighttime nondownslope air mass (Figure 8) may have resulted from intrusion of MBL air.

**Steady state calculations.** Since the lifetimes of the reaction products of CH<sub>4</sub> oxidation (Figure 1) are all shorter than ~2 days, steady state concentrations of these species, including formaldehyde, should have been reached in most air masses arriving at the remote MLO site [Liu et al., 1992]. We developed a simple box model based on Figure 1 and (1) - (3) to calculate formaldehyde concentration in the free troposphere at this altitude and latitude. The input parameters are listed in Table 3. Since the median temperature of the nighttime air ranged narrowly between 6° and 8°C (measured on a 40-m tower) for the four intensives, the calculations were made for 7°C (Table 4). It should be pointed out that the majority of the input parameters are independent of season. The exceptions are the photolysis rate constants and the concentrations of OH, HO<sub>2</sub>, NO, and CH<sub>3</sub>OOH. The diurnal *j* values for HCHO and CH<sub>3</sub>OOH were obtained from the radiative transfer model by Madronich [1987]. The OH and HO<sub>2</sub> diurnal concentration patterns were taken from Liu et al. [1992] and Ridley et al.

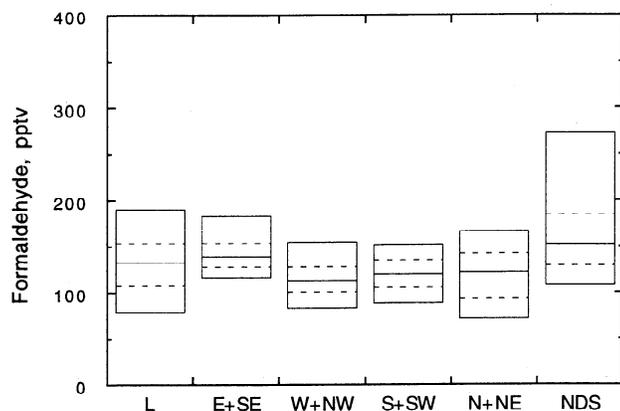
**Table 3.** Values of the Input Parameters Used in Simple Box Model Calculation Based on Figure 1

Constants				
	Values	References		
[CH <sub>4</sub> ]	3.0 × 10 <sup>13</sup>	Greenberg et al. [1992]		
<i>k</i> <sub>1</sub>	4.4 × 10 <sup>-15</sup>	Vaghjiani and Ravishankara [1991]		
<i>k</i> <sub>2</sub>	6.9 × 10 <sup>-12</sup>	Lightfoot et al. [1992]		
<i>k</i> <sub>3</sub>	7.8 × 10 <sup>-12</sup>	Lightfoot et al. [1992]		
<i>k</i> <sub>4a</sub>	3.9 × 10 <sup>-12</sup>	Vaghjiani and Ravishankara [1989]		
<i>k</i> <sub>4b</sub>	1.9 × 10 <sup>-12</sup>	Vaghjiani and Ravishankara [1989]		
<i>k</i> <sub>8</sub>	1.1 × 10 <sup>-11</sup>	Atkinson [1990]		
<i>k</i> <sub>hr</sub>	2.3 × 10 <sup>-6</sup>	Liu et al. [1992]		
Seasonal Dependent				
	Autumn	Winter	Spring	Summer
<i>J</i> <sub>5max</sub>	7.8 × 10 <sup>-6</sup>	6.8 × 10 <sup>-6</sup>	8.2 × 10 <sup>-6</sup>	8.4 × 10 <sup>-6</sup>
<i>J</i> <sub>6max</sub>	4.5 × 10 <sup>-5</sup>	4.0 × 10 <sup>-5</sup>	4.7 × 10 <sup>-5</sup>	4.8 × 10 <sup>-5</sup>
<i>J</i> <sub>7max</sub>	3.2 × 10 <sup>-5</sup>	2.8 × 10 <sup>-5</sup>	3.4 × 10 <sup>-5</sup>	3.5 × 10 <sup>-5</sup>
[NO] <sub>max</sub>	6.8 × 10 <sup>7</sup>	7.1 × 10 <sup>7</sup>	10.4 × 10 <sup>7</sup>	9.1 × 10 <sup>7</sup>
[CH <sub>3</sub> OOH]	6.9 × 10 <sup>9</sup>	3.7 × 10 <sup>9</sup>	7.2 × 10 <sup>9</sup>	9.0 × 10 <sup>9</sup>
[OH] <sub>max</sub>	3.5 × 10 <sup>6</sup>	2.7 × 10 <sup>6</sup>	4.1 × 10 <sup>6</sup>	4.5 × 10 <sup>6</sup>
[HO <sub>2</sub> ] <sub>max</sub>	3.8 × 10 <sup>8</sup>	3.6 × 10 <sup>8</sup>	4.8 × 10 <sup>8</sup>	4.8 × 10 <sup>8</sup>

Photolysis rates and concentrations of OH, HO<sub>2</sub>, and NO are listed for their daytime maxima, but their diel values are used in the calculation. The *j* values are obtained from a radiative transfer model of Madronich [1987] for MLO on Oct. 1, Feb. 1, May 1, and Aug. 1. Units are per second for *j*; cubic centimeter per molecule per second for *k*; molecules per cubic centimeter for concentrations.

[1992]. The summer midday maximum concentrations were 4.5 × 10<sup>6</sup> and 4.8 × 10<sup>8</sup> molecules cm<sup>-3</sup> for OH and HO<sub>2</sub>, respectively. The spring, fall, and winter OH concentrations were adjusted by factors of 0.9, 0.78, and 0.61, respectively, from that used for the summer, according to a model-predicted seasonal variations of OH for 20°N and 700 mbar [Spivakovsky et al., 1990]. Smaller seasonal adjustments were made for [HO<sub>2</sub>], that is, factors of 1.0, 0.8, and 0.75 for spring, fall, and winter, respectively, as estimated from H<sub>2</sub>O<sub>2</sub> seasonal variations observed by Heikes et al. [1993]. NO diurnal values were derived from the observed downslope NO<sub>x</sub> [Ridley et al., personal communication] multiplied by the NO/NO<sub>x</sub> ratio [Ridley et al., 1992]. Seasonal variation of the NO/NO<sub>x</sub> ratio was estimated from NO<sub>2</sub> photolysis rates from the radiative transfer model [Madronich, 1987].

An example of the model results is shown in Figure 9 for the spring. The predicted free tropospheric formaldehyde concen-

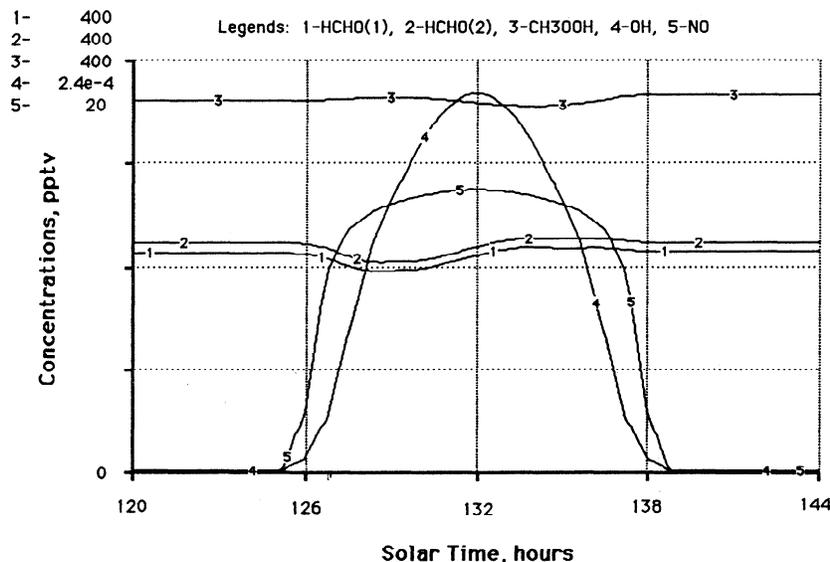


**Figure 8.** Box plots of nighttime formaldehyde concentrations as a function of the direction the air masses originated from. The solid line represents median value, the upper and lower dashed lines 75 and 25 percentiles, and the upper and lower solid lines of the box 90 and 10 percentiles. Symbols: L, local; E + SE, east and southeast; W + NW, west and northwest; S + SW, south and southwest; N + NE, north and northeast; NDS, nondownslope.

**Table 4.** The Steady State Concentration of Formaldehyde Calculated Using a Simple Box Model Based on Figure 1 and the Input Parameters Listed in Table 3

Intensives	A	B
2a, autumn	155	140
2b, winter	125	115
2c, spring	210	195
2d, summer	220	205

Values in column A are calculated without heterogeneous removal, and column B with a heterogeneous removal rate of 2.3 × 10<sup>-6</sup> s<sup>-1</sup>. Concentration of formaldehyde is in parts per trillion by volume.



**Figure 9.** A simple box model calculation for the free tropospheric conditions representative of MLO during the spring season. The time window is between day 5 and day 6 after initiation of the calculation. Initial formaldehyde concentration is zero. HCHO (1) is the formaldehyde trace without a constant  $\text{CH}_3\text{OOH}$  constraint, in which the steady state  $\text{CH}_3\text{OOH}$  is 370 pptv. HCHO(2) is the formaldehyde concentration trace with an observed  $\text{CH}_3\text{OOH}$  concentration of 400 pptv as a constraint. Concentrations of OH and NO are input parameters and are identical for both calculations with and without the observed  $\text{CH}_3\text{OOH}$  concentration as a constraint.

trations for the four seasons are summarized in Table 4. When constrained by measured  $\text{CH}_3\text{OOH}$  concentrations, the calculated HCHO concentrations are 155, 125, 210, and 220 pptv for fall, winter, spring, and summer, respectively. Compared to the median measured formaldehyde concentrations of 122, 110, 120, and 140 pptv for the four seasons (Table 2), respectively, the calculated values are in good agreement for fall and winter, within 27 and 14%, but are significantly higher for spring and summer, by 75, and 57%. With a heterogeneous removal pathway added to the sink process [Liu *et al.*, 1992], the differences for the corresponding seasons are reduced to 15, 5, 63, and 46%. Since formaldehyde may be subject to dry deposition, the measured concentration at 10 m height could have underestimated its concentration in the free troposphere. Using the average deposition velocity determined for  $\text{HNO}_3$  at MLO [Lee *et al.*, 1993], we estimate that a decrease in formaldehyde concentration up to 12% could have resulted from dry deposition. Taking this into consideration, the agreement between the observed and calculated concentrations is further improved.

The uncertainties in these calculations are mainly governed by uncertainties in the rate constants and the measured concentrations. For example, a sensitivity test showed that a  $\pm 30\%$  variation in  $j_6 + j_7$ , [OH], [NO]/[HO<sub>2</sub>] and [CH<sub>3</sub>OOH] resulted in corresponding variations of  $\sim \pm 27\%$ ,  $\sim \pm 20\%$ ,  $\sim \pm 13\%$  and  $\sim \pm 14\%$ , respectively, in the calculated values. The overall uncertainty of the calculated value is estimated to be  $\sim \pm 50\%$ . In view of the uncertainties associated with the measured ( $\sim \pm 30\%$ ) and the calculated concentrations ( $\sim \pm 50\%$ ) and the fact that the measured values may exhibit a negative bias due to dry deposition, we consider the agreement to be reasonable even for spring and summer. However, although the model predicts a similar seasonal variation pattern,

the magnitude of the increase from winter to summer is significantly greater in the calculated values than in the measured values, that is, 75 versus 25%.

It should be pointed out that the calculated formaldehyde concentration of 210 pptv for spring (without heterogeneous removal) is about half way between the measured median value of 120 pptv and the value of 300 pptv calculated by Liu *et al.* [1992]. To examine whether the difference in the two model predictions might have resulted from intrinsic model structure, we also ran our model with  $\text{CH}_3\text{OOH}$  being calculated as a dependent variable, similar to the earlier report [Liu *et al.*, 1992]. The steady state concentrations of HCHO and  $\text{CH}_3\text{OOH}$  thus determined are 205 and 370 pptv, respectively (Figure 9). It is interesting to note that  $\text{CH}_3\text{OOH}$  concentration is nearly identical to the measured value of 400 pptv [Heikes *et al.*, 1993; Stafflebach, this issue], but significantly lower than the 700 pptv calculated by Liu *et al.* [1992]. The concentration of 400 pptv measured for  $\text{CH}_3\text{OOH}$  during MLOPEX 2 spring intensive was significantly higher than that of 140 pptv measured during MLOPEX [Heikes, 1992]. Finally, we ran our model at 15°C and obtained the predicted concentrations of HCHO and  $\text{CH}_3\text{OOH}$  of 270 pptv and 500 pptv, respectively, in good agreement with the results of Liu *et al.* [1992]. This suggests that the input parameters used in present model are largely consistent with those employed by Liu *et al.* [1992].

## Summary

The concentration of formaldehyde at Mauna Loa Observatory, Hawaii, was determined by a liquid scrubbing sampling system coupled to an HPLC analysis technique during

four MLOPEX 2 intensives. Strong diurnal variations were observed throughout the MLOPEX 2, typically, 60-200 pptv during 2200-0800 HST and 200-900 pptv during daytime. These variations were mainly caused by local air circulation patterns. The formaldehyde concentrations also exhibited a seasonal variation, the median/mean (all data points) being: 149/196, 129/149, 143/178, and 181/211 pptv for autumn, winter, spring, and summer intensives, respectively, reflecting the seasonal variation in the degrees of influence by marine boundary layer air on the sampling site. For downslope air periods when the air masses were thought to be of free tropospheric origin, the formaldehyde concentrations (median/mean) were 122/123, 110/112, 120/125, and 140/137 pptv for autumn, winter, spring, and summer, respectively, slightly greater than that measured at the same site during MLOPEX, that is, ~100 pptv. The slight seasonal dependence, highest in summer and lowest in winter, may have been caused by variations in solar insolation and NO concentrations. The origin of the air masses during downslope periods had no appreciable effect on the formaldehyde concentrations, reflecting the fact that the free tropospheric air at this site contained little precursors for formaldehyde other than methane and that steady state is obtained relatively quickly. A diel steady state calculation, constrained by the measured CH<sub>3</sub>OOH concentrations, yielded a formaldehyde concentration (without/with heterogeneous removal) for the free tropospheric air, at 7°C, of 155/140, 125/115, 210/195, and 220/205 pptv for autumn, winter, spring, and summer, respectively. These values are in reasonable agreement with those observed, especially for winter and fall, considering the uncertainties of ~± 50% and ± 30% for the calculated and the measured values, respectively, and the possible negative bias in the measured values due to surface deposition.

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