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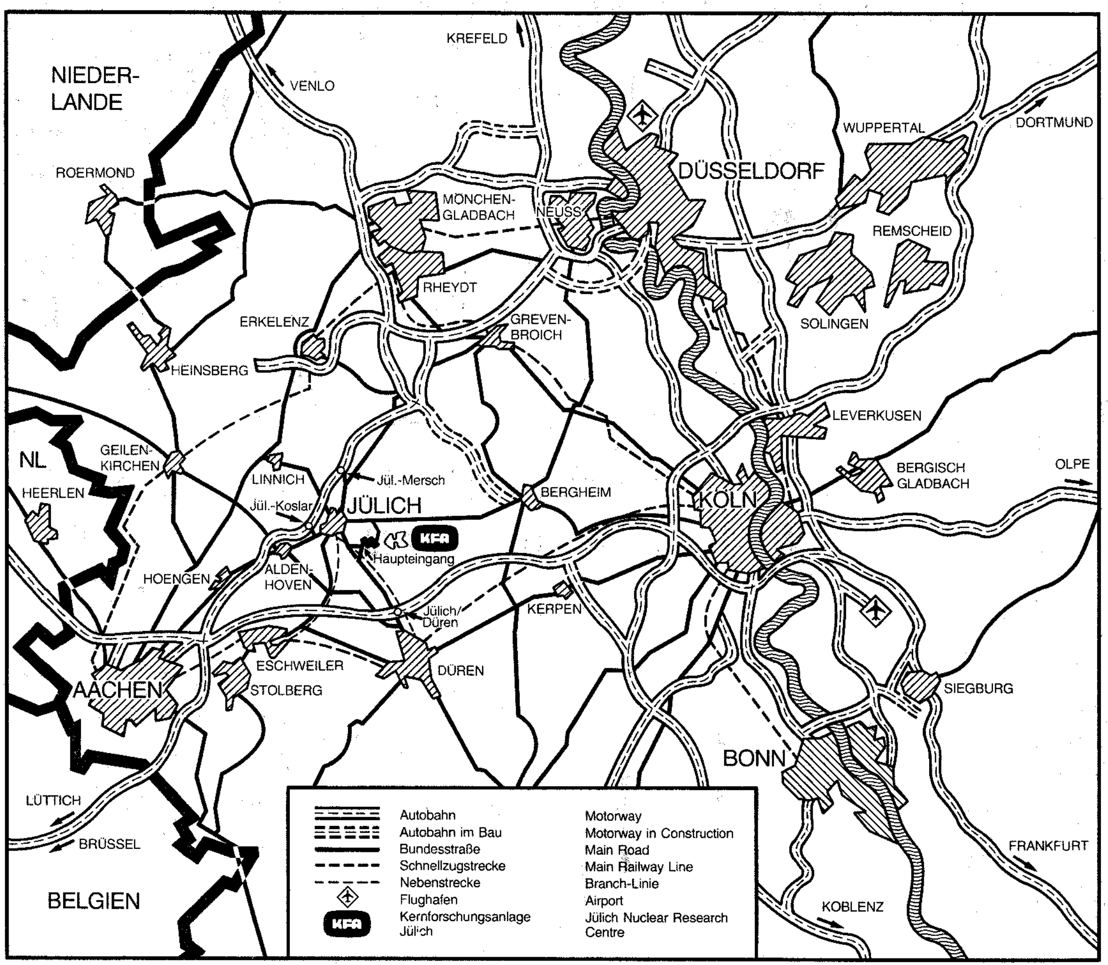

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The Tropospheric Distribution of Formaldehyde

by

D.C. Lowe*, U. Schmidt, D.H. Ehhalt

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Abstract

A new measurement technique for determining the very low formaldehyde (HCHO) concentrations in clean air is described. The method is based on the standard derivatisation of formaldehyde with 2,4-dinitrophenylhydrazine. The derivative, formaldehyde 2,4-dinitrophenylhydrazone, is seperated using high performance liquid chromatography and detected at 254 nm with a conventional UV absorbance detector.

Formaldehyde was sampled using a specially developed battery powered portable apparatus. This equipment proved to be easy and convenient to operate, even in remote clean air locations where the formaldehyde mixing ratio and its natural variations are likely to be of especial interest in air chemistry.

The sampling and analysis technique have been used to measure tropospheric mixing ratios at various places in Europe and New Zealand as well as during a ship cruise in the North and South Atlantic. In addition vertical profiles of the formaldehyde mixing ratio were obtained during several aircraft flights up to 7 km above the Eifel district of the Federal Republic of Germany.

The results of the measurements show that formaldehyde mixing ratios in clean air are very low. At ground level, values are about 0.2 ppbv and decrease with altitude, with values under 0.1 ppbv at 7 km being observed. In clean maritime air no significant difference in the formaldehyde mixing ratio between the hemispheres was observed.

In the mid Atlantic, diurnal variations of the formaldehyde mixing ratio showing weak maxima during the early afternoon were occasionally observed. These variations were attributed to the diurnal behaviour of the photochemical production and destruction of formaldehyde during stable weather conditions.

Measurements in polluted air at Jülich in the Federal Republic of Germany and in the continental boundary layer showed high variable mixing ratios which were undoubtedly due to industrial and vehicular sources of formaldehyde.

Zusammenfassung

Es wird eine neue Meßmethode beschrieben, die die Bestimmung geringer Konzentrationen von Formaldehyd (HCHO) in Reinluft ermöglicht. Das Meßverfahren basiert auf der Sammlung und Anreicherung des Formaldehyd in einer wässrigen Lösung von 2.4-Dinitrophenylhydrazin und dem anschließenden Nachweis des gebildeten 2.4-Dinitrophenylhydrazon mit Hilfe der Hochdruckflüssigkeitschromatographie.

Zur Sammlung wurde ein tragbares, batteriegetriebenes Probenahmegerät entwickelt und gebaut. Es ist einfach zu handhaben und läßt sich deshalb besonders in Reinluftgebieten gut einsetzen, wo der Formaldehydgehalt und seine natürlichen Veränderungen von besonderem Interesse für das Verständnis der atmosphärischen Chemie sind.

Mit diesem Gerät wurden umfangreiche Messungen an verschiedenen Orten in Europa und Neuseeland sowie während einer Schiffsexpedition auf dem Nord- und Südatlantik durchgeführt. Daneben wurden in Flugzeugaufstiegen Vertikalprofile des Mischungsverhältnisses von Formaldehyd bis zu 7 km Höhe über der Eifel, BRD gemessen.

Die Ergebnisse der Messungen zeigen, daß der Formaldehydgehalt in Reinluft sehr gering ist. Das Mischungsverhältnis beträgt etwa 0.2 ppbv am Boden und nimmt mit der Höhe ab. In 7 km Höhe wurden Werte unter 0.1 ppb beobachtet. In maritimer Reinluft wurde kein signifikanter Unterschied des Mischungsverhältnisses in der Nord- und Südhemisphäre beobachtet.

Tagesgänge des Formaldehyd-Mischungsverhältnisses, die im Mittelatlantik gemessen wurden, zeigten manchmal ein schwaches Maximum während des Tages, das durch die Tagesvariation des photochemischen Produktions- und Abbaumechanismus von Formaldehyd in Reinluft erklärt werden kann.

Messungen in verschmutzter Luft in Jülich sowie in der Grenzschicht über dem Kontinent zeigen höhere Werte, die wahrscheinlich durch anthropogene Quellen von Formaldehyd am Boden bedingt sind.

CONTENTS

1.1 Introduction

Formaldehyde, HCHO, is formed as an intermediate product during the oxidation of hydrocarbons in the atmosphere (Levy, 1971, 1972; Wofsy, 1976; Wofsy et al, 1972; Calvert, 1980). It is relatively shortlived, of the order of 8 hours, and its concentration is closely related to the chemical activity of the atmosphere. Provided that variations by transport can be eliminated, measurements of the distribution of HCHO will provide important insight into the destruction processes of atmospheric hydrocarbons.

Over the past 30 to 40 years many measurements of the HCHO concentration in polluted air have been reported. A series of measurements made by Altshuller and McPherson, 1963, show HCHO mixing ratios in Los Angeles air ranging from 5 to 115 ppbv.* More recently Kuwata et al, 1979, found 20 to 35 ppbv in Osaka, Japan. A comprehensive survey of HCHO measurements in polluted regions and the physiological hazards caused by high HCHO concentrations is given by Kitchens et al, 1976.

Relatively few measurements of HCHO in clean air have been published. The first measurements made in clean marine air were reported by Hadamczik, 1947, who found mixing ratios at the Baltic sea coast ranging from 0.5 to 2.0 ppbv. These and other reported measurements of HCHO in clean air are summarised in table 1. The results display a considerable amount of scatter and are difficult to interpret in terms of current photochemical models.

In addition, indirect methods have been used to estimate the HCHO mixing ratio in clean air and these also show large variations. Junge, 1963, first used HCHO measurements made in rain and dew by Dhar and Ram, 1933, to deduce a tropospheric HCHO mixing ratio of 0.75 ppbv. A similar approach was used by McConnel et al., 1971, to estimate a tropospheric HCHO

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*) ppbv - parts per billion by volume ie 1 part of HCHO in 10^9 parts of dry air.

<u>Table 1:</u> Clean air measurements of aldehyde mixing ratios near the ground

Location	RCHO (ppbv)	HCHO (ppbv)	Number of measurements	Reference
Baltic sea coast		0.5-2.0	5	Hadamczik, 1947
Panama	0.9-3.6	-	?	Lodge and Pate, 1966
Irish west coast		0.1-0.4	5	Platt et al., 1979
Eastern Indian ocean		0.8-11.0	63	Fushimi and Miyake, 1980
Central Pacific		0.11-0.57	7	Zafiriou et al., 1980
South Africa		0.2-1.0	5	Neitzert and Seiler, 1981
Irish west coast		0.1-0.42	36	Lowe et al., 1981

mixing ratio of 1.3 ppbv for summer conditions and more recently Warneck et al, 1978, have predicted mixing ratios ranging from 0.12 ppbv to 0.39 ppbv from rain data gathered at the west coast of Ireland by Klippel, 1978.

Various photochemical models have also been used to predict HCHO distributions in the clean troposphere but the computed values are difficult to compare because of the different assumptions used to generate the models. Graedel, 1979, used a kinetic photochemical model to predict HCHO mixing ratios ranging from 0.06 to 0.2 ppbv at the surface in a marine atmosphere. Calvert, 1980, published results from a photochemical model developed by Wuebbles predicting HCHO mixing ratios ranging from 0.45 ppbv at the ground to 0.04 ppbv at 10 km in a clean troposphere at 30 $^{\circ}$N during the solar equinox at noon. More recently Logan et al, 1981, used a tropospheric photochemical model to compute tropospheric HCHO profiles with mixing ratios at the surface ranging from 0.35 ppbv in equatorial regions to 0.10 ppbv at the poles.

1.2 Natural formaldehyde production processes in the troposphere

Formaldehyde is naturally formed in the troposphere during the oxidation of hydrocarbons. These react with OH radicals and ozone to form HCHO and/or other aldehydes as an intermediate in a series of reactions which ultimately lead to CO, H_2, CO_2 and H_2O (Zimmerman et al, 1978; Calvert, 1980).

Of the hydrocarbons found in the clean troposphere methane has the highest concentration of 1.65 ppmv*) in the northern hemisphere. It thus provides the single most important source of HCHO through the following reactions (Levy, 1971).

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*) ppmv - parts per million by volume

$$CH_4 + OH \rightarrow CH_3 + H_2O \qquad (1)$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \qquad (2)$$

$$CH_3O_2 + NO \rightarrow NO_2 + CH_3O \qquad (3)$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2 \qquad (4)$$

Wofsy et al, 1972, considered reaction (3) as unlikely and suggested that methylhydroperoxide, CH_3OOH, could be an intermediate in the reaction series to produce HCHO.

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2 \qquad (5)$$

$$CH_3OOH + h\nu \rightarrow CH_3O + OH \qquad (6)$$

$$CH_3O + O_2 \rightarrow HCHO + HO_2 \qquad (7)$$

These pathways are competitive, but over land areas where NO mixing ratios lie in the range of 20 pptv*) to over 1.0 ppbv (Drummond, 1977), reaction (3) should dominate. Over the oceans where NO mixing ratios are possibly much lower, eg about 4 pptv in the tropical Pacific, (McFarland et al, 1979), CH_3OOH should be important as an intermediate (Logan, 1980).

Because of the relatively long lifetime of CH_3OOH against photolysis (Molina and Arguello, 1979), heterogeneous processes on aerosol surfaces may remove it from the marine troposphere thus interrupting the reaction chain producing HCHO and subsequently reducing the HCHO yield from methane (Logan et al, 1981). However considerable uncertainties exist in NO measurments particularily in marine air and the relative importance of the two HCHO production pathways can therefore not be assessed.

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*) pptv - parts per trillion by volume

For the purpose of estimating a chemical lifetime here, for HCHO in the clean troposphere, reactions (1) to (4) will be assumed with reaction (1) as the rate limiting step. Hence the rate of HCHO production from methane, P, may be written as

$$P = K_1 \, [OH] \cdot [CH_4] \qquad (8)$$

Using $K_1 = 2.4 \times 10^{-12} \, e^{-1710/T}$ (NASA panel for data evaluation, 1979); OH profiles for 45 ^{o}N (Logan, 1980), and a mean tropospheric methane mixing ratio of 1.60 ppmv, equation (5) can be numerically integrated over a 10 km high troposphere to yield an average column HCHO production rate due to methane oxidation of 9×10^{-5} gm/cm^2/yr.

Similar results are obtained using a mean tropospheric OH concentration of 6.5×10^5 molecules/cm^3 (Volz et al, 1981) with a mean methane mixing ratio of 1.60 ppmv giving a column HCHO production in a 10 km high troposphere of 8×10^{-5} gm/cm^2/yr.

This is equivalent to an average world production rate of HCHO from methane of 4.1×10^{14} gm/yr. which greatly exceeds the combined HCHO production rate from all of mans activities.

A large group of non methane hydrocarbons (NMHCs) is also present in the atmosphere but only relatively few of them have so far been identified. They are generally much less abundant than methane with a total concentration of a few ppb or less (Rudolph and Ehhalt, 1981; Eichmann et al, 1979, 1980). NMHCs react much faster with hydroxyl radicals than methane does, and hence the combined production of HCHO from these compounds is as important as the production of HCHO from methane (Hanst et al, 1980). However because of uncertainties in their HCHO yield (Niki et al, 1978, 1981) and in their tropospheric distribution, precise estimates of the HCHO production by NMHCs in the troposphere cannot be made. Gaseous aldehyde formation from high carbon number alkanes is unlikely because the alkylperoxy radicals formed after OH attack are absorbed on aerosol surfaces within a few minutes (Warneck, 1974).

Classes of NMHCs for which large natural sources have been proposed are the terpenes and isoprene. These are emitted by various kinds of foliage, and reaction with the OH radical yields HCHO as an intermediate product (Zimmerman et al, 1978). However since the lifetime of isoprene and terpenes against attack by OH is only of the order of one hour, and HCHO is also relatively short lived this potentially large source of HCHO is only important in the vicinity of vegetation.

1.3 Removal of formaldehyde from the clean troposphere

Various processes contribute to the removal of HCHO from tropospheric air. The action of solar ultraviolet radiation on HCHO results in its photolysis via two channels (Moortgat et al, 1978; Calvert, 1980).

$$HCHO + h\nu \rightarrow H_2 + CO \qquad (9)$$

$$\rightarrow H + HCO \qquad (10)$$

Formaldehyde is also removed from the troposphere by reaction with the OH radical (Stief et al, 1979).

$$HCHO + OH \rightarrow HCO + HO_2 \qquad (11)$$

$$HCO + O_2 \rightarrow HO_2 + CO \qquad (12)$$

Through the reaction series (1) to (4) and reactions (9) to (12), CO and H_2 are produced in the atmosphere via HCHO as an intermediate product. The destruction of one methane molecule leads to the production of approximately one HCHO molecule and ultimately to the production of a CO molecule. The series of reactions also results in a net production of HO_2 radicals, resulting in an overall increase in the chemical reactivity of the atmosphere.

From equations (9), (10) and (11) it follows that the chemical destruction of HCHO, D, is given by

$$D = [HCHO][K_{11}[OH] + J_9 + J_{10}] = \frac{[HCHO]}{\tau} \qquad (13)$$

where K_{11} ist the rate constant of equation (11), J_9 and J_{10} are the photodissociation coefficients for equations (9) and (10) and τ $[sec]^{-1}$ is the chemical lifetime of HCHO in the lower troposphere.

Substituting $J_9 + J_{10} = 2 \times 10^{-5} sec^{-1}$ (mean estimated from Calvert, 1980), $K_{11} = 1.05 \times 10^{-11}$ (Stief et al, 1979) and $[OH] = 1.6 \times 10^6$ molec./cm^3 (mean near the surface estimated from profiles given by Volz et al, 1979) into equation (13) yields an average chemical lifetime for HCHO in the lower troposphere during daylight of 3.8 hours.

Because of the change in UV flux and the OH concentration, the removal rates of HCHO by reaction (9), (10) and (11) vary with altitude (table 2).

Table 2: Comparison of theoretical HCHO removal rates in the troposphere; 1200hr, 30 ^oN, Solar equinox (Calvert, 1980)

Altitude	$K_{11} \cdot [OH]$	J_9	J_{10}
km	Rate of reaction/[HCHO]		(sec^{-1} x 10^{-4})
0	0.93	0.28	0.34
5	0.28	0.36	0.44
10	0.30	0.39	0.49
15	0.40	0.40	0.53

At ground level in the clean atmosphere, reaction with OH is the dominant removal process for HCHO. However in the first few kms of the troposphere above ground level the importance of OH as a removal process decreases with altitude and the photodissociation coefficients J_9 and J_{10} increase in importance.

Formaldehyde is also removed from the troposphere by rainout(1), washout(2) and by deposition(3) at the surface. These processes however can be shown to be of only minor importance in the free troposphere. For example from HCHO measurements made in rainwater collected at an equatorial site in the Pacific, Zafiriou et al, 1980 estimate that rainout is responsible for removing only 1 % of the HCHO produced in the atmosphere by the oxidation of methane.

In addition Warneck et al, 1978, have shown that washout as a removal process for gaseous HCHO in the troposphere is important only in polluted regions and may be neglected in clean air.

Dry deposition at the surface is usually defined by a deposition velocity, v_o(cm/sec), and the flux, f_o, to the surface my be estimated by

$$f_o = v_o \cdot [\mathrm{HCHO}]_o \qquad (15)$$

where $[\mathrm{HCHO}]_o$ is the mean HCHO concentration above the surface.

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1) Rainout refers to the process where gaseous constituents of the atmosphere are absorbed during the formation of cloud droplets.

2) Washout is the process in which falling raindrops scavenge gases, particles and aerosols from the atmosphere.

3) Deposition here refers to the process of absorption of gases and aerosols by the Earth's surface.

The deposition velocity depends on the surface. For example, from measurements made at an equatorial Pacific atoll, Zafiriou et al, 1980, deduced a value for v_o of 0.4 cm/sec. at the ocean surface.

The mean HCHO mixing ratio, $[HCHO]_o$, measured during an oceanographic cruise in the north and south Atlantic, see section 3.4, was 0.22 ppbv corresponding to a concentration of 5.9×10^9 molec./cm^3. With a deposition velocity of 0.4 cm/sec., equation (15) suggests a loss due to deposition at the ocean surface of 2.4×10^9 molec./cm^2/sec. or about 4 % of the column HCHO production from methane oxidation calculated in section 1.2. Although v_o for HCHO is expected to vary with wind velocity, it is unlikely to exceed 1 cm/sec. Hence loss of HCHO from the troposphere due to deposition will be important only near the surface itself.

1.4 Scope of the thesis

Inspection of equations (1) to (11) shows that the production and destruction of HCHO depends on the OH radical concentration and the photon flux. Both of these parameters vary diurnally, seasonally and with latitude and altitude. Hence because of its relatively short chemical lifetime the mixing ratio of HCHO may be expected to show corresponding variations in space and time.

Measurements of these variations in the clean troposphere will place a valuable constraint on models of hydrocarbon oxidation. However, HCHO is also generated by anthropogenic processes leading to large local variations which mask the variations of HCHO caused by natural production and destruction processes. Therefore the measurements must be made in background regions where the hydrocarbon precursors of HCHO are homogeneously distributed and where the effects of transport from polluted areas can be eliminated.

The purpose of this thesis is to develop a technique capable of measuring the low background concentrations of HCHO expected in the clean troposphere (see table 1). The technique will be used to investigate the distribution of HCHO in the lower troposphere with the aim of identifying systematic variations in HCHO mixing ratio which may be used to test the current photochemical theory of hydrocarbon oxidation in the clean troposphere.

2. Development of an analysis technique to measure the HCHO mixing ratio in clean air

Most of the available techniques for HCHO determination have been developed for the measurement of HCHO in urban air and lack the sensitivity required to determine the sub ppb HCHO concentrations expected in clean air. For example the most widely used chemical analysis technique, the chromotropic acid method, has a lower limit of detection of 10 ppb for an air sample size of 60 liters (Altshuller et al, 1961; Bailey and Rankin, 1971). Other commonly used chemical analysis techniques for HCHO are summarised by Kitchens et al, 1976.

Optical techniques approaching the required sensitivity have been used by Platt et al, 1979, and Tuazon et al, 1978. At the present stage of development these techniques are limited to ground based measurements made during conditions of good visibility. Therefore for logistic reasons they cannot be used to obtain latitudinal and vertical profiles of HCHO in the clean atmosphere and other methods must be used.

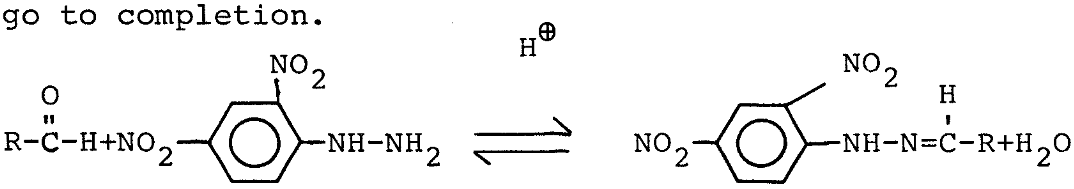
Because HCHO is easily trapped and oxidised on a wide variety of surfaces, direct detection of nanogram quantities of the molecule by standard analytical techniques, for example gas chromatography, is virtually impossible. However one way of overcoming this problem, is to label the HCHO with a marking compound which produces a product both stable and detectable with standard analytical detectors, thus indirectly measuring the original amount of HCHO present.

This method, known as derivatisation, forms the basis of the most sensitive chemical techniques for HCHO analysis. Various derivatives have been used (see Kitchens et al, 1976). The most important of these is based on the reaction of aldehydes and ketones with 2,4-dinitrophenylhydrazine (DNPHzine) to form the corresponding aldehyde or ketone 2,4-dinitrophenylhydrazone (aldehyde or ketone - DNPHzone) as a derivative. These derivatives are very strong absorbers in the near UV, extinction coefficient of the order of 20.000 [liters/mole·cm] and may be used to determine nanogram quantities of aldehydes. For example Papa and Turner, 1972 a, b, have shown that with gas chromatography (GC) or high performance liquid chromatography (HPLC) as a seperation and detection technique, the lower detection limit of the DNPHzine technique for aldehydes is 5ng equivalent to 250 ng/ml when the aldehydes are in solution.

The suitability of this method for the proposed measurements of the thesis was investigated, because its high selectivity for the carbonyl group, and its high sensitivity when used in conjunction with HPLC, indicated that it should be a promising technique for detecting the low HCHO concentrations expected in clean air.

2.1 The reaction of 2,4-dinitrophenylhydrazine with formaldehyde

The reaction of aldehydes and ketones with DNPHzine is one of addition followed by hydration and needs an acid catalyst to go to completion.



It is highly specific for the carbonyl group and the carbonyl-DNPHzone derivatives may be formed by precipitation from aqueous medium or by extraction of the carbonyl compounds into a non aqueous medium containing DNPHzine, (Selim, 1977).

The standard DNPHzine analysis method for aldehydes involves reaction of acidic solutions of DNPHzine with the aldehydes followed by separation of the aldehyde-DNPHzone product with organic solvent extraction techniques (see eg Shriner, 1964).

Following a procedure suggested by Frischkorn, 1978, a preliminary investigation of the suitability of the standard method for the measurement of HCHO in clean air was made by examining the reaction of 0.5 µg/ml aqueous solutions of HCHO with solutions containing 200 µg/ml of DNPHzine in 1.2 %o perchloric acid. After one hour the reaction products were seperated twice with dichloromethane on a seperating funnel and evapourated to dryness under vacuum with a water bath.

The resulting precipitate was dissolved in 2 mls of methanol. The concentration of the HCHO-DNPHzone product in this solution was investigated with a Spectra Physics SP 8000 HPLC equipped with a 254 nm UV detector and a Zorbax reversed phase C 18 column. More details of the HPLC technique used are given in section 2.3. The yield of the product, determined by comparison with standards made by dissolving known weights of the pure solid HCHO-DNPHzone solid compound in methanol, was found to be unacceptably low, less than 2 %, and variable especially when lower HCHO solution concentrations of 100 ng/ml or less were used. If 100 ml of DNPHzine solution are used to collect all the HCHO from 2 m^3 of air having a mixing ratio of 0.2 ppbv, the equivalent HCHO concentration in the solution will be 5.4 ng/ml. This is well below the lower detection limit of the standard technique as reported by Papa and Turner,

1972. Despite considerable efforts, the yield and reproducibility of the method described above could not be improved and it was obvious that the technique needed to be modified considerably to meet the requirements of measuring low HCHO mixing ratios in air.

Trial investigations of the reaction at different pHs, showed that the yield of the HCHO-DNPHzone product could be improved by increasing the pH of the reaction medium. Furthermore it was discovered that the HPLC system used had sufficient sensitivity to enable detection of nanogram quantities of the HCHO-DNPHzone product in the reaction medium itself, thus obviating the need for standard organic solvent extraction and enrichment techniques. This resulted in a dramatic improvement in the reproducibility of the reaction yield. These findings indicated the way in which the standard DNPHzine technique might be modified to enable measurement of HCHO in clean air. However a search of the available literature revealed no published investigations of the DNPHzine reaction with aldehydes in solution at concentrations of a few ng/ml. Investigations of the reaction have been carried out with the reactants at concentrations of µg/ml (Selim, 1977) but because of the proportionately higher risk of contamination these kinetics cannot necessarily be extrapolated to the case where the reactants are present at the ng/ml level.

Therefore to identify the optimum reaction parameters, a systematic investigation of the reaction rate and yield of the HCHO-DNPHzone product at low HCHO concentrations was made at various temperatures, pHs and DNPHzine reagent concentrations. Dilute aqueous solutions of HCHO, 35 ng/ml, were used to test the DNPHzine reaction. Figure 1 shows the reaction rate of DNPHzine with these solutions at different pHs. At low pH the reaction is relatively fast, equilibrium is reached in about one hour, but the HCHO product yield is only 85 % for a DNPHzine concentration of 18 µg/ml. At pH 7 the yield of the HCHO product is 100 %

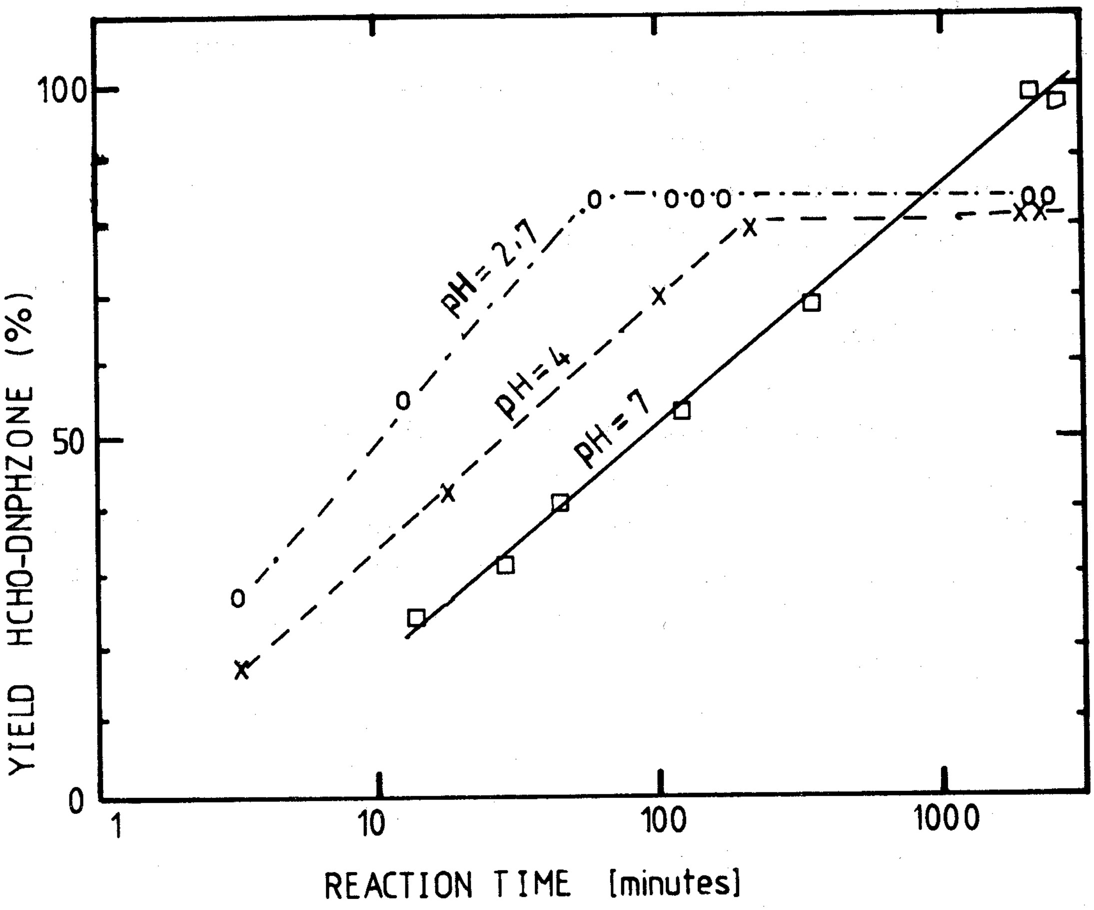


Figure 1 : Yield of HCHO-DNPHzone product as a function of the time since preparation of 35 ng/ml HCHO, 18 µg/ml DNPHzine aqueous solutions at different pHs. The temperature of the solutions is 22 °C.

but the reaction time is much slower, of the order of one day. A reaction time of this length is unsatisfactory because weak HCHO solutions are unstable and decrease in concentration in an unpredictable fashion. Storage experiments with aqueous solutions of HCHO in glass bottles showed that initial HCHO concentrations of about 35 ng/ml could be as low as 20 ng/ml after storage at room temperature for 4 days.

Figure 2 shows the reaction rate of DNPHzine with HCHO at different concentrations of the DNPHzine reagent. When the DNPHzine reagent is present in large excess, greater than 35 µg/ml, the yield of the HCHO-DNPHzone product in solution at pH 3 reaches 100 % in less than one hour. As shown in figure 3 at DNPHzine concentrations of less than 35 ng/ml in solution at pH 3, the yield of the reaction is less than 100 %. The effect of temperature on the reaction is shown in figure 4. Since many airsamples are likely to be collected at temperatures less than 20 °C the effect of warming the sampling solution from 10 °C up to 22 °C was investigated after reaction completion. No effect on the yield of the reaction was found when sampling solutions at pH 3 having a DNPHzine concentration of > 35 µg/ml were tested. However when solutions containing only 18 µg/ml DNPHzine were tested the yield of the HCHO product dropped from 100 % at 10 °C to 85 % at 22 °C (see figure 1).

On the basis of the investigations in this section a sampling solution containing 60 µg/ml of DNPHzine in aqueous solution at pH 3 was adopted for the development of a procedure to sample HCHO in clean air. With sampling solutions of this kind the yield of the reaction was found to be 100 % over a temperature range from 2 °C to 24 °C and the reaction was always complete within an hour.

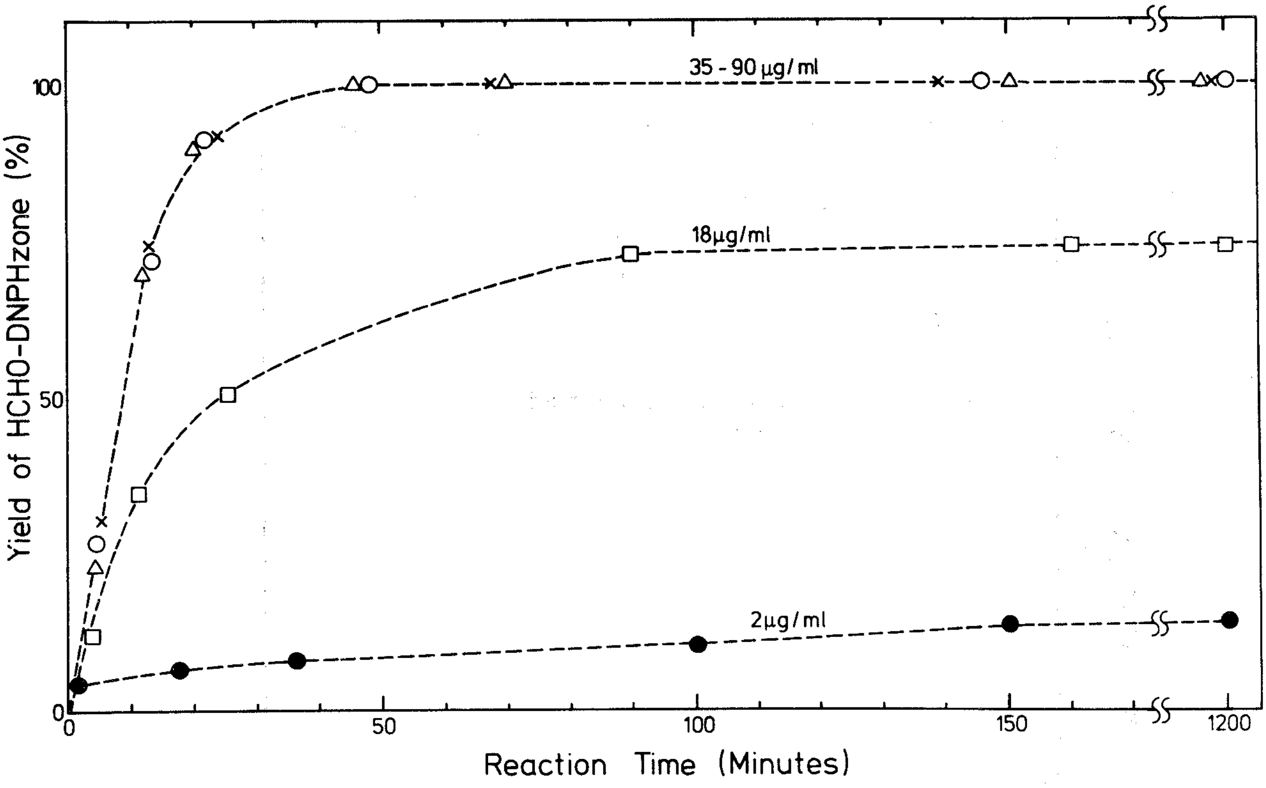


Figure 2 : Yield of HCHO-DNPHzone product as a function of time since the mixing of 35 ng/ml HCHO with DNPHzine solutions of various concentrations at pH3 at 22 °C.

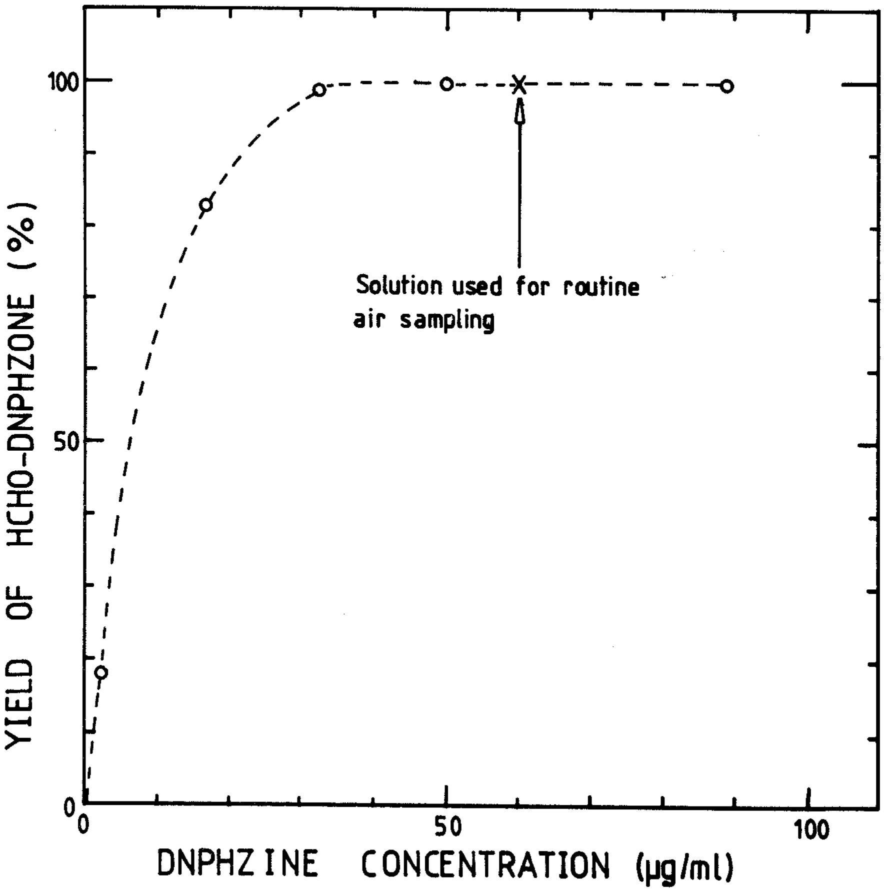


Figure 3: Yield of HCHO-DNPHzone as a function of the concentration of DNPHzine in aqueous solution at pH 3 and 22 °C.

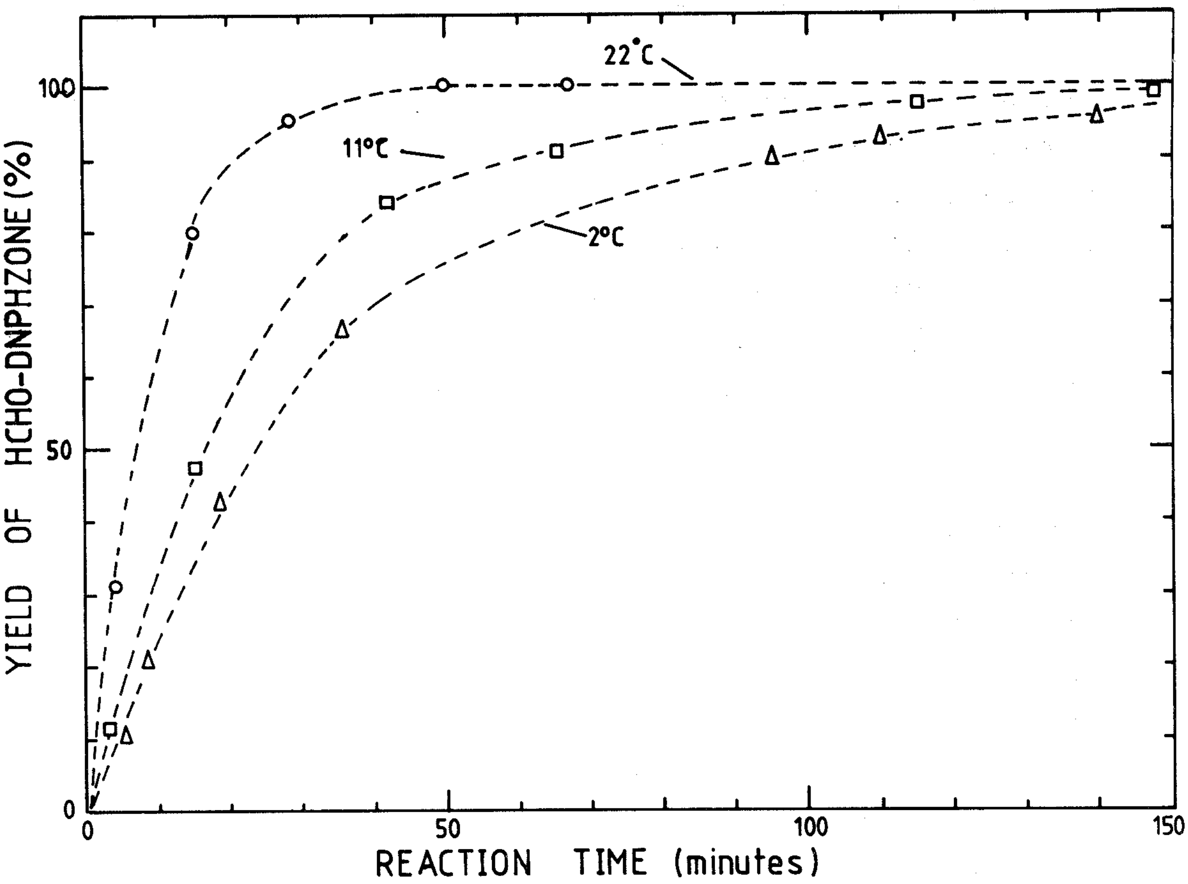


Figure 4: Yield of HCHO-DNPHzone products as a function of time at various temperatures in aqueous solutions, pH 3 and DNPHzine concentration 50 µg/ml.

2.2 Air sampling techniques

The solutions used to develop the air sampling technique were routinely prepared by diluting 200 µl of a concentrated stock solution of DNPHzine with 1 litre of water. The initial stock solutions are made by adding 3 g of the solid DNPHzine reagent (Merck pro analysi, no 3081) to 10 ml of high purity sulfuric acid (Merck, suprapur, no 714). The resulting sampling solution contains about 60 µg of DNPHzine per ml of solution and has a pH of 3.

Obtaining HCHO free water for making the sampling solutions presented considerable difficulties. Attempts to free water of HCHO by slow distillation over potassium permanganate failed as did similar attempts with weak hydrogen peroxide solutions. HPLC water (Baker analyzed HPLC reagent no 4218) was found to have an unacceptably high (for this application) HCHO blank of 20 ng/ml. The technique finally adopted for use during routine sampling was to treat water by passage through a dual ion exchange system followed by a Millipore Milli-Q high purity laboratory water treatment plant. After this treatment the HCHO concentration of the DNPHzine sampling solutions varies between 0.5 and 5 µg/ml. However a careful check on the water quality had to be kept.

Several standard air sampling techniques were tested using the DNPHzine sampling solution. Most standard air sampling techniques for making HCHO measurements in urban areas employ impingers or washing flasks filled with sampling solution. Air is bubbled through the solution at a few liters/minute (see eg Kuwata et al, 1979). However initial tests using these flasks with the DNPHzine sampling solution showed low variable recoveries for HCHO collection especially at flow rates of higher than 10 liters/min. Further tests using a highly efficient, high flow rate glass sampler designed by Münnich and Platt, 1979, were more encouraging. The sampler has been modified and used to sample HCHO from air in the following manner.

The air whose HCHO concentration is to be measured is passed at 40 l/min. through an all glass sampler containing 100 ml of the DNPHzine sampling solution prepared as described above. The sampler used has a volume of 1.5 litre, is 90 mm in diameter and is made of pyrex glass. It contains one liter of 4 mm x 4 mm raschig rings tightly packed to avoid channeling effects which could change the samplers efficiency, and held in place by two glass sieve plates (see figure 7). During sampling the sampler is rotated at about 30 revolutions per minute, ensuring that all the raschig rings are continously bathed in DNPHzine solution. The wet surface area presented to the air flow is very large (1.8 m^2) thus increasing the probability of transfer of a HCHO molecule across the gas-liquid interface even at relatively high airflow rates. However a minimum volume of solution is required to keep all the rings wet, and below this volume the efficiency of the sampler decreases rapidly. The minimum load of sampling solution for the 1.5 litre sampler described above is 40 ml.

The efficiency of the sampler for HCHO collection was tested in the following two ways:

a) An aqueous solution, 100 ml, having a HCHO concentration of about 0.5 µg/ml is used to fill a washing flask that is coupled to the inlet of the sampler to be tested. Before a test is begun, two 20 ml aliquots of the HCHO solution are taken from the washing flask and their initial HCHO concentration is precisely determined by using the DNPHzine technique with HPLC. HCHO free nitrogen is then bubbled through the washing flask at the flow rate to be tested and the sampler collects the outlet vapor and gas from the flask. At the end of the test the HCHO concentration of the solution in the washing flask is redetermined using the DNPHzine technique. From the difference in the concentration and the volume of the solution in the flask the amount of HCHO released to the sampler can be calculated. The difference between this amount and the amount of HCHO actually collected by the sampler indicates the efficiency of the sampler.

b) Two identical samplers were connected in series and the respective amount of HCHO collected by each sampler was measured. If A is the total amount of HCHO [ng] entering the series system and the first sampler collects the amount A_1 ng and the second sampler A_2 [ng], then the efficiency of the samplers for HCHO collection is,

$$\text{Eff (sampler 1)} = \frac{A_1}{A} \cdot 100\ [\%]$$

$$= \text{Eff (sampler 2)}\ [\%]$$

$$= \frac{A_2}{A-A_1} \cdot 100\ [\%]$$

and the efficiency of a sampler can therefore be written as,

$$\text{Eff}\ [\%] = \frac{A_1 - A_2}{A_1} \cdot 100\ [\%].$$

From these experiments the efficiency of the sampler containing one liter of Raschig rings shown in figure 7 was found to be between 95 % and 100 % at sample flow rates up to 50 l/m. Similar tests were also conducted for smaller samplers containing 250 mls and 500 mls of Raschig rings. At 40 l/min these samplers showed efficiencies of 55 % and 80 % respectively (see figure 5). In figure 6 the efficiency of the sampler filled with 500 mls of Raschig rings is shown as a function of the flow rate.

The relationship between the efficiency of a sampler and the volume of homogeneously packed identical raschig rings in the sampler may be examined theoretically. The transfer

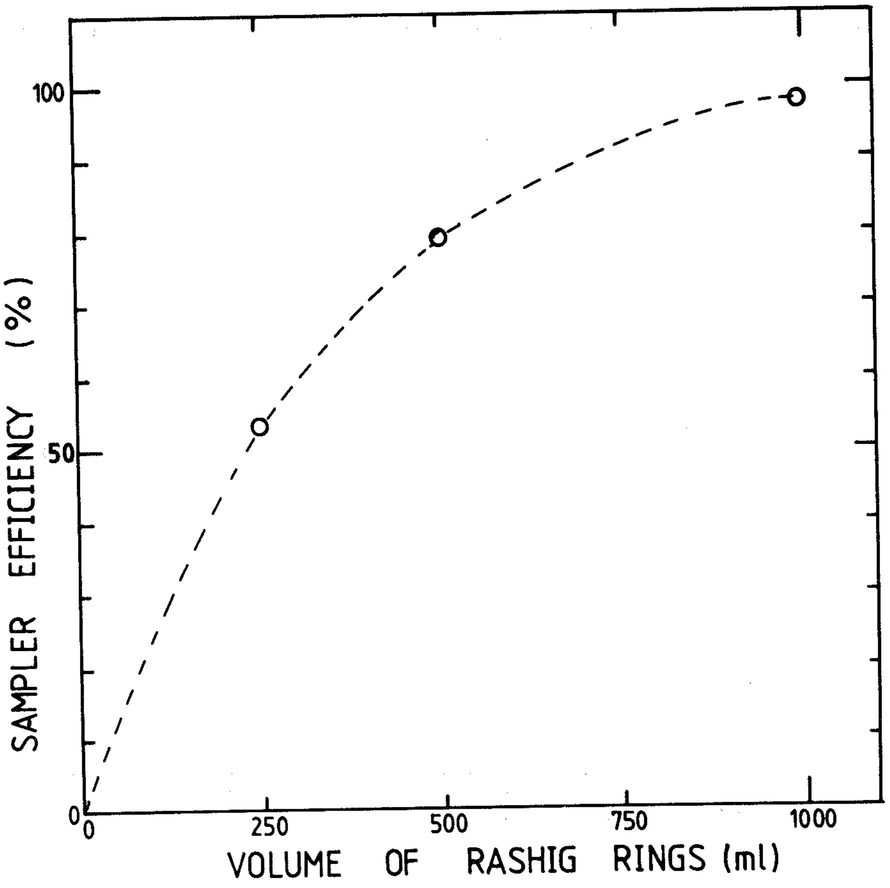


Figure 5 : Sampler efficiency as a function of the volume of Raschig-rings packed in the sampler. All tests at 40 l/min.

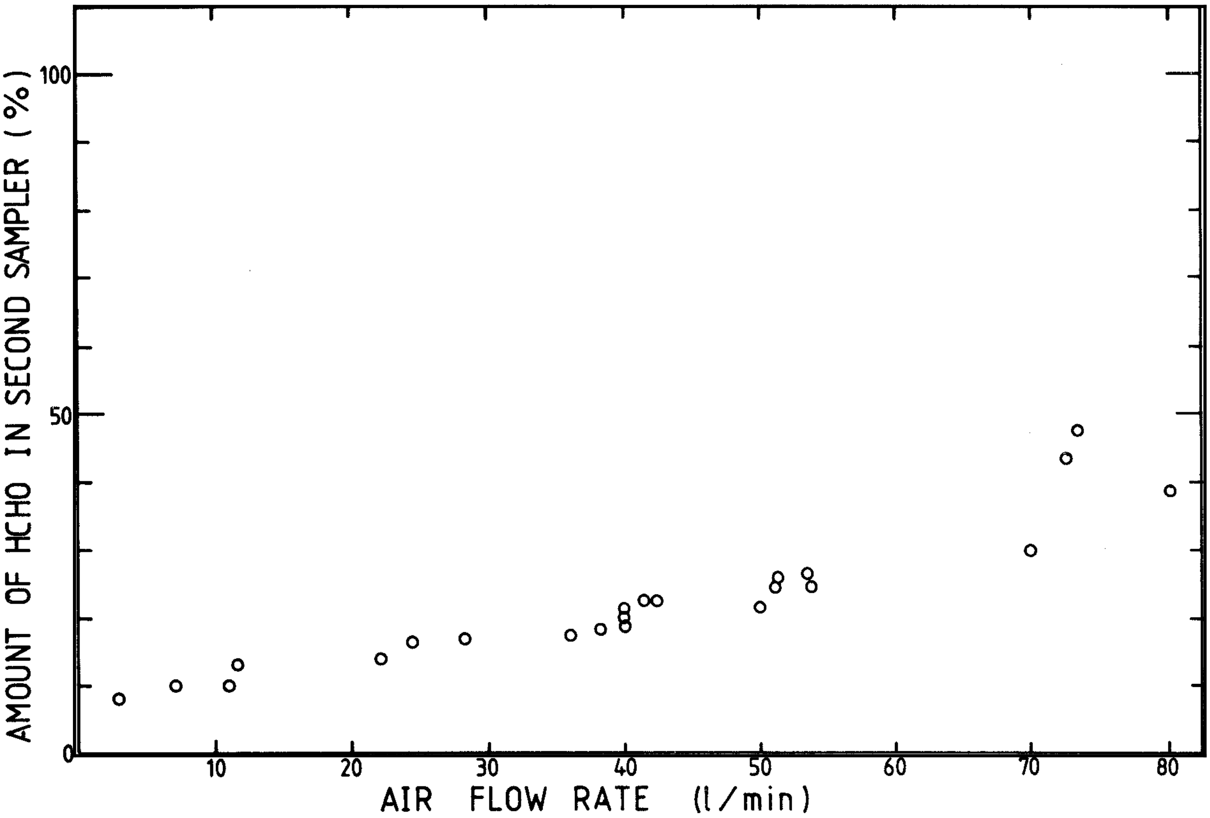


Figure 6 : Ratio of HCHO collected by second sampler to HCHO collected by first sampler when two samplers each containing 500 ml Raschig-rings are run in series at various flow rates.

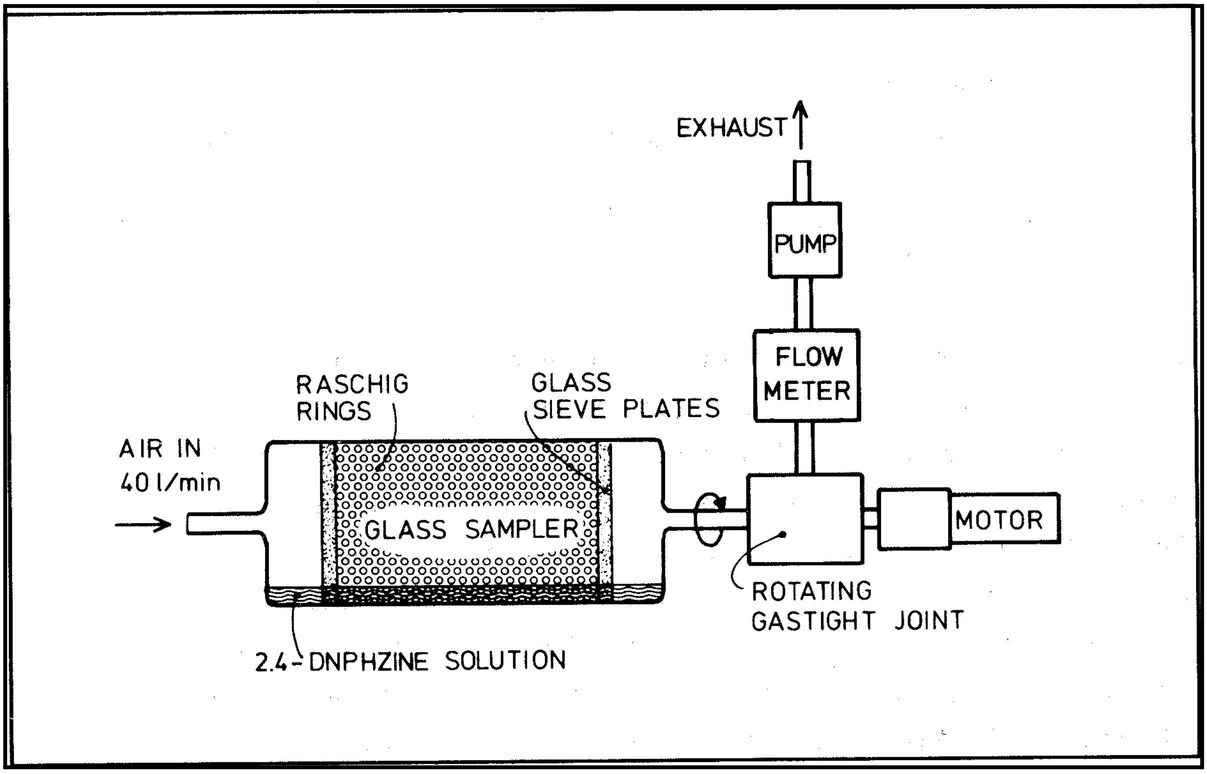


Figure 7: HCHO sampling system (schematic).
The sampling chamber is mounted in a frame with the free end supported by a ball-bearing race and rotated by a motor at about 30 rpm. The motor coupling is combined with a rotating gas tight joint. The glass sampler contains one litre of tightly packed 4 mm x 4 mm Raschig-rings held in place by 2 glass sieve plates. To sample HCHO the sampler is filled with 100 mls of DNPHzine solution and rotated at 30 rpm while air is sucked through it at 40 l/minute.

of HCHO from the gas phase into the sampling solution may be represented by a generalised diffusion equation.

$$\frac{\partial\,[\mathrm{HCHO}]_{g_o}}{\partial t} \simeq -\,C_1\,[\mathrm{HCHO}]_{g_o} \tag{16}$$

or

$$[\mathrm{HCHO}]_{g_o} \simeq [\mathrm{HCHO}]_{g_1}\,e^{-C_1 t} \tag{17}$$

Here C_1 is an exchange constant dependant on many factors, of which the degree of turbulence in the gas and in the liquid, and the chemical reactivity of the gas with the sampling solution are most important (Liss and Slater, 1974), $[\mathrm{HCHO}]_{g_o}$ is the gas phase HCHO concentration after a contact time, t, with the raschig rings and sampling solution, and $[\mathrm{HCHO}]_{g_1}$ is the initial or air HCHO concentration. This equation assumes that at low HCHO concentrations in solution, no back transfer occurs to the gas phase. At low HCHO solution concentrations HCHO reacts rapidly with water to form the monohydrate methylene Glycol and although the HCHO is still available for chemical reactions, eg with DNPHzine, virtually no HCHO is present in the form of individual HCHO molecules (Walker, 1975).

The various samplers tested are homogeneously packed with Raschig rings of identical dimensions, 4 mm x 4 mm, and therefore at constant sample flow rates the contact time, t, of the sample gas with the DNPHzine sampling solution is proportional to the volume of the Raschig rings, v, or

$$t = w.v \tag{18}$$

where w has the units of $[\text{volume flowrate}]^{-1}$. Hence the amount of HCHO collected by a sampler, x, can be written as,

$$x = [\mathrm{HCHO}]_{g_1} - [\mathrm{HCHO}]_{g_1}\,e^{-C_1 .w.v} \tag{19}$$

and the efficiency of the sampler can be expressed as,

$$\mathrm{Eff} = \frac{[\mathrm{HCHO}]_{g_1}\ (1 - e^{-C_1 \cdot w \cdot v}) \cdot 100}{[\mathrm{HCHO}]_{g_1}}\ [\%] \qquad (20)$$

$$= (1 - e^{-C_1 \cdot w \cdot v}) \cdot 100\ [\%]$$

From the results of tests made on samplers filled with 250 mls and 500 mls of raschig ring $C_1 . w$ can be calculated as

$$C_1 . w = 0.0032$$

This leads to an empirical efficiency for the sampler filled with 1 liter of Raschig rings of 96 % showing that the efficiencies of the 3 sizes of samplers tested are mutually consistent.

In practice when two samplers each containing 1 liter of raschig rings were run in series at 40 l/min. no HCHO could be found in the second sampler. Only when the samplers were run for an extended period of time in relatively contaminated air was any HCHO found in the second sampler.

For most of the data reported in this thesis samplers containing one litre of raschig rings were used at air sample flow rates of 40 l/min or less and the efficiency of the samplers was assumed to be 100 %.

Routine sampling for atmospheric HCHO is done in the following manner. Immediately before an air sample is taken, the sampler is thoroughly rinsed with about one litre of fresh DNPHzine sampling solution prepared by the method described above and a 40 ml aliquot of sampling solution is taken from the sampler to serve as the initial HCHO-DNPH-zone blank value for the air sample. Excess DNPHzine solution is then decanted from the sampler until the remaining volume of the solution contained in the sampler is about 100 ml as determined by weight. The sampler is then mounted as shown in figure 8 and run at ~ 40 l/min while rotating at about 30 revolutions per minute.

If the HCHO concentration is expected to be lower than 0.2 ppbv, air is sampled for at least one hour for an air sample volume of about 2 m^3. For polluted areas, where the HCHO concentration is much higher, the air is sampled for a shorter time. After an air sample has been collected 25 ml of the DNPHzine solution is decanted off and stored for analysis as the first air sample. A second air sample may be collected by running the sampler for a further period and storing the remaining solution. The volume of the DNPHzine solution after each sampling is determined by weighing the sampler and solution and subtracting the dry weight of the sampler. From the volume of sampling solution used and its HCHO-DNPHzine concentration the mass of the HCHO collected by the sampler can be calculated, which, with the volume of air sampled, gives the HCHO mixing ratio of the air.

Air sampling solutions may occasionally have to be stored for a few days before they can be analysed. Because of the possibility of introducing contamination and the possibility of the decay of the HCHO-DNPHzone product extensive tests were conducted on various kinds of storage containers. It was found that new pyrex and quartz glass bottles rendered the sampling solution colorless within a few hours indicating that the excess DNPHzine reagent had deteriorated. The effect was reduced by washing the storage bottles with dilute sulfuric acid followed by rinsing with DNPHzine sampling solution. The effect was further reduced by storing samples in the treated glass bottles in the dark in a refrigerator at 4 °C. When polyethylene bottles were tested no decay of the DNPHzine reagent occured but the HCHO-DNPHzone concentration of the samples increased unpredictably with time due to contamination of the samples by HCHO originating from the polyethylene. Other plastic containers showed similar effects to polyethylene.

On the basis of the storage tests pyrex glass containers conditioned as described above were used to store samples. Blank sampling solution was always stored in the bottles and discarded immediately prior to filling the bottles with sampling solution.

Despite these precautions, occasionally sample and blank solutions deteriorate in an unpredictable manner after a few days. Samples which have deteriorated are easily recognised by a change in color and also the appearance of large peaks which mask the original HCHO-DNPHzone peak. However for most routine work close to the laboratory, samples may be analysed within a few hours of collection and the possible deterioration of samples during storage does not pose a problem.

To prevent the possible loss of some samples collected in remote areas, for example, on an oceanographic cruise, or at an isolated coastal site, a portable HPLC as described in section 2.7 is used to enable prompt measurement of the samples.

2.3 Analysis by high performance liquid chromatography, HPLC

A Spectra Physics SP 8000 liquid chromatograph equipped with a SP 8200 detector at 254 nm is used for analysis. The HCHO-DNPHzone is seperated by using a reversed phase column (Du Pont, Zorbax ODS 5 um) and a mobile phase of 65 % methanol and 35 % water at a flow rate of 1 ml/min. The column temperature is 40 ^{o}C. Under these conditions the retention time for the HCHO-DNPHzone product is of the order of 7 minutes. The samples are directly injected onto the column using a relatively large sample loop volume of 300 µl. Injection of the sample using the large loop was found to be more reproducible than evaporative enrichment and two phase seperation followed by injection with a smaller sample loop. A disadvantage of the larger loop is that columns deteriorate more rapidly because of the greater reagent load introduced by each injection. Nevertheless, during normal operation the columns gave good results for at least 400 samples before replacement was required.

A typical chromatogram of a sampling solution used to collect an air sample at Jülich is shown in figure 8. Because of the large excess of DNPHzine used, the chromatogram is dominated by the DNPHzine reagent peaks. Peak 3 is the main DNPHzine peak. Associated with this peak are two other attendant peaks, 4 and 5, whose heights vary in an unpredictable manner with the time since sample collection. In particular peak 5 increases rapidly with time as the sample deteriorates. Peak 6 is the HCHO-DNPHzone peak. The chromatogram also shows the signal for CH_3CHO-DNPHzone, peak 7, which is eluted after about 9 minutes. When the chromatographic parameters listed above are used, peaks 5 and 6 are well resolved and no difficulties are encountered in determining the HCHO-DNPHzone concentration of the sampling solution. However for samples which have deteriorated because of the decay of the DNPHzine reagent, precise determination of the HCHO-DNPHzone is impossible because some of the decay products mask the HCHO-DNPHzone peak.

For air samples taken in a non polluted area, the chromatographic runs were terminated immediately after the elution of the HCHO-DNPHzone peak. However in a polluted area where higher aldehydes and ketones are likely to be present, the run was left for a longer time to allow the respective aldehyde and ketone DNPHzones to be eluted.

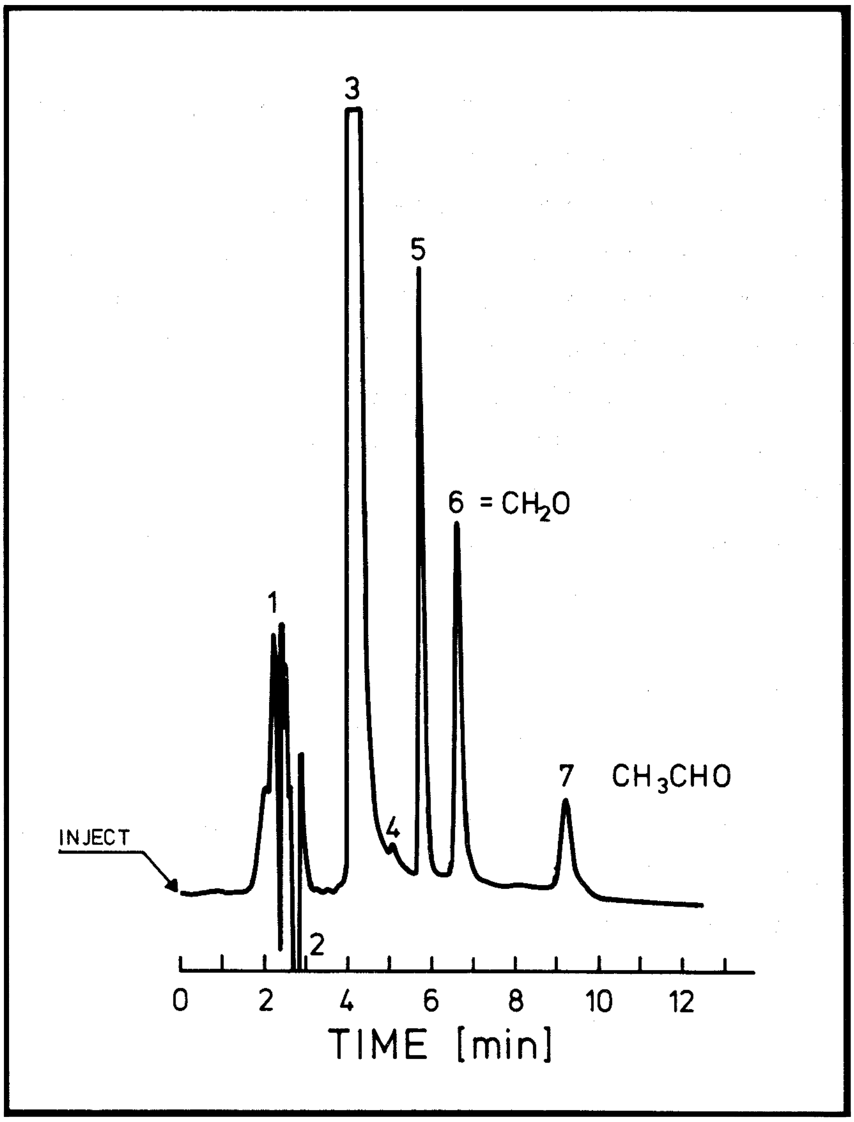


Figure 8 : Typical liquid chromatogram of sampling solution used to collect an air sample at the KFA Jülich. Conditions: mobile phase: 65 % MeOH, 35 % H_2O; pressure: 72 bars; flowrate: 1 ml/min, 1. ion peaks, 2. solvent peak; 3. main DNPHzine peak; 4. and 5. secondary 2.4-DNPH peaks; 6. formaldehyde-DNPHzone; 7. acetaldehyde-DNPHzone. This sample had a HCHO-concentration of 42 ng/ml as HCHO-2.4-dinitrophenylhydrazone.

2.4 Calibration

Determination of the HCHO-DNPHzone concentration of the samples is made by comparison against the peak heights of HCHO-DNPHzone standards. These are run frequently during analysis thus positivly identifying the HCHO-DNPHzone peaks by retention time and also monitoring any drift in the sensitivity of the HPLC system. The standards are made by reacting DNPHzine solution, prepared as in 2.1 above, with diluted aqueous HCHO solutions derived from a HCHO stock solution (Merck, pro analysi, no 4003) whose concentration as determined by the absolute Dimedon method (Yoe and Reid, 1941) is 35.8 ± 0.2 % by weight.

Three stages of dilution were used to dilute the stock solution down to the required standard concentration, generally of the order of 30 to 100 ng/ml of HCHO as the HCHO-DNPHzone in solution. The 1 ml syringes used for the dilution were carefully rinsed with blank DNPHzine solution followed by a thorough rinsing with water treated as described in section 2.1. With care and experience the reproducibility of standards made by this method was excellent: for example 4 standards having a HCHO concentration of about 35 ng/ml made independantly by two workers were mutually consistent to within 0.4 %.

The standard solutions are kept in 1 litre pyrex glass flasks stored in a refrigerator. Standards having a HCHO concentration in the range of 30 to 100 ng/ml were made to routinely calibrate the HPLC during the measurement of air samples. The standards were renewed every 2 to 3 months and a constant check on their integrity was kept by comparison with freshly prepared standard solutions. These always agreed to better than 4 % as shown by the following table.

Date standard prepared	Standard concentration (ng/ml)	Discrepancy (%) when compared with previous standard
28 May 1979	100 ± 2	
23 Aug 1979	50 ± 1	+ 1.5
26 Nov 1979	54 ± 1	- 0.6
6 Mar 1980	47 ± 1	- 3.9
16 Apr 1980	37 ± 1	+ 1.2
26 Jun 1980	36 ± 1	- 0.5
27 Aug 1980	39 ± 1	+ 1.6
26 Nov 1980	40 ± 1	- 2.0

An independent cross check on the integrity of the standards made by reaction of HCHO solutions with DNPHzine solutions, was made by comparing them with equivalent standards made by dissolving known weights of the pure solid HCHO-DNPHzone compound in methanol. Peak areas from both standard types agree to better than 5 %.

2.5 Interferences

There are several possible ways in which the yield of the DNPHzine reaction with HCHO may be interfered with, thus leading to erroneous results for the HCHO mixing ratio.

a) Physical interferences
Interference to air sampling solutions may be caused by new glass surfaces. No efforts were made to investigate the cause of the effect. The effect was reduced by conditioning the bottles as explained in section 2.3 which allows storage of air sampling solutions for up to two weeks. However because most of the air sampling solutions reported in this thesis were analysed within a few hours of collection, either by a laboratory based or by a portable HPLC, the storage of samples did not pose a problem.

Precipitation of DNPHzine and HCHO-DNPHzone from the sampling solution can be induced by freezing the samples. When the sampling solutions are warmed back up to room temperature, a fine red precipitate is visible and measurement of the sample by HPLC indicates that the HCHO-DNPHzone concentration of the sample has decreased. For this reason supplementary heating systems are used if the air sampled is below 0 °C, thus preventing freezing of the sampling solutions.

b) Chemical interferences

In polluted air there are many substances which can interfere with the technique by competively reacting with HCHO, inhibiting the DNPHzine reagent, or directly reacting with the DNPHzine reagent.

In clean tropospheric air, however, the number of substances likely to interfere with the reaction is limited. The effect on the reaction by some of the substances which are known to react with HCHO or with DNPHzine has been investigated.

i) Ozone

When a stream of 0.1 % ozone in air is passed through a sampler, the DNPHzine sampling solution rapidly turns colorless. To test for interferences to the reaction at lower ozone concentrations two identical samplers were used to sample the same air stream. However, one sampler had small amounts of ozone added to its inlet. The progress of the reaction was monitored in both samplers. No reduction in the yield of the HCHO-DNPHzone product was observed up to the highest ozone mixing ratios - about 100 ppbv - employed during these tests. In clean tropospheric air, ozone mixing ratios generally do not exceed this level (Oltmans, 1981; Fabian and Pruchniewicz, 1977) and thus the technique will not be affected for samples collected in this region.

ii) Sulfur dioxide

Sulfite reacts quickly with HCHO in solution to form a formaldehyde bisulfite adduct. This reaction has been used as the basis of a standard technique for determining the concentration of HCHO in solution (see for example Walker, 1975). When HCHO is added to a neutral DNPHzine solution containing sodium sulfite the yield of the HCHO-DNPHzone product is reduced. However, when the DNPHzine reagent is made with sulfuric acid (to pH 3) as described above, the yield of the HCHO-DNPHzone product is 100 % despite added sulfite corresponding to a SO_2 mixing ratio in air of 90 ppbv. This is much higher than the SO_2 mixing ratios normally observed at Jülich (Kessler, 1980) and hence SO_2 will not affect the reaction for samples collected in the clean troposphere.

iii) Chloride

In marine air chloride could be carried into the sampling solutions due to salt spray. However, no interferences to the reaction of HCHO with DNPHzine were found when NaCl was added to the sampling solution in quantities far exceeding those expected to accumulate in the sampler during the sampling of marine air.

It is probable that there are other minor reactions with HCHO or with DNPHzine in the sampling solution which have not been considered here. However, the results of HCHO measurements made at Jülich, a moderately polluted area, using the DNPHzine technique are in good agreement with a few parallel HCHO measurements made by a differential optical absorption technique (Platt et al, 1979).

Date	Time	DNPHzine/HPLC technique (ppbv)	Differential technique (ppbv)
18 Jan 1980	17:20-17:50	3.60 ± 0.10	3.8 ± 0.6
22 May 1980	9:10- 9:40	2.02 ± 0.05	1.8 ± 0.4
24 Jun 1980	10:00-11:00	0.68 ± 0.04	0.9 ± 0.4
4 Jul 1980	11:00-11:30	1.96 ± 0.05	1.8 ± 0.4

Hence it is unlikely that the effects of other unconsidered reactions with HCHO of DNPHzine, especially in clean tropospheric air, significantly interfere with the yield of the HCHO-DNPHzone product.

2.6 Error analysis

Both systematic and random errors influence the HCHO mixing ratios determined by the technique.

a) Systematic errors

i) As shown in section 2.1, the one litre sampler used for most of the air sampling described in this thesis collects between 95 % and 100 % of the HCHO entering the sampler. However all the results have been calculated assuming a sampler efficiency of 100 %. Due to this assumption, the results are therefore systematically low by of 0 to 5 %.

ii) In rural continental air, in clean maritime air masses, and in the coastal region of Western Ireland the average HCHO concentrations in the atmospheric aerosol are 40 ng/m^3, $\leq$ 2 ng/m^3 and 5 ng/m^3 respecively (klippel and Warneck, 1980). These concentrations correspond to about 4 %, 1 % and 2 % of the average HCHO mixing ratio in air found for the same kinds of regions.

For technical reasons no filter was used during air sampling and air was sucked directly into the samplers making immediate contact with the Raschig rings and the DNPHzine sampling solution. The results reported here thus make no distinction between gaseous HCHO and the HCHO contained in the atmospheric aerosol. Because of this assumption, the reported HCHO mixing ratios will be systematically high by between 1 % to 4 % depending on the kind of air sampled.

iii) It is possible that a systematic error is present in the HPLC calibration. However because of the good agreement of the few parallel measurements made between the DNPHzine/HPLC technique and the differential absorption technique (see section 2.5), a systematic error in the calibration of the HPLC is not likely to be large.

b) Random errors

i) The volume of the air samples for all samples collected at ground level and on board the ocenanographic ship "Meteor", was measured with an Elster Experementiergaszähler. The precision of the gas meter is quoted at ± 1 % by the manufacturers and is calibrated at a pressure of 760 mms of Hg and at 20 °C. None of the air-sample volume measurements made at ground level were corrected to 760 mm and 20 °C. For example for the measurement at Jülich in cases of exceptionally high, 770 mms Hg, or low 735 mms Hg, atmospheric pressure (Bergs, 1981) the error in the HCHO mixing ratio caused by not correcting to 760 mms is - 1 % and + 3 % respectively. The equivalent largest possible errors caused by not correcting for temperature are - 3 % and + 7 % respectively. However for almost all of the ground level HCHO measurements reported, the temperature was 20 ± 12 °C and the pressure 760 ± 10 mms leading to an average HCHO mixing ratio error of ± 3 %.

The volume of the air samples collected from aircraft was measured with a Tylan devices mass flow meter with a manufacturers specification of ± 1 % full scale accurary and ± 0.3 % full scale precision calibrated at STP. All of the volume measurements made for HCHO samples collected from aircraft thus refer to STP.

ii) The volume of the sampling solution used was determined by an initial weighing of the dry sampler and a subsequent weighing of the sampler filled with approximately 100 mls of sampling solution. The precision of the balance used was ± 0.5 gm leading to a sampling solution weighing error of ± 1 gm or 1 % of a typical sampling solution volume of 100 ml.

On board ship a balance con not be used to determine the volume of the sampling solution. However laboratory tests showed that a sampler, when allowed to drain for ten minutes in an upright position, always drained to a constant weight. Hence for the Meteor HCHO samples, after rinsing, the sampler was allowed to drain for ten minutes before adding a known volume of sampling solution. After sampling the sampler was again allowed to drain for ten minutes and the volume of fluid eluted was measured in a small measuring cylinder. Hence the volume of sampling solution used before and after sampling could be determined. Tests on land with a laboratory balance showed that the typical error in estimating the sampling solution by the 'draining to constant weight' method is about ± 3 %.

iii) The standard deviation of a series of runs made with a solution of 20 ng/ml of HCHO as the HCHO-DNPHzone in a DNPHzine air sampling solution is 0.2 ng/ml or about 1 %. The lower limit of detection is 0.1 ng/ml.

For a typical clean air sample, 2 m^3, with a HCHO mixing ratio of 0.2 ppbv, the amount of HCHO collected by 100 ml of sampling solution is 540 ng. Sampling solutions typically have a blank value of about 3 ± 0.2 ng/ml of HCHO and the resulting HCHO signal is 8.4 ± 0.2 ng/ml. Since the HCHO concentration of the blank has to be subtracted from this signal, the error increases to ± 0.3 ng/ml, or an error of about ± 10 % of the sample HCHO amount. This is the largest single random error in the technique and it could be considerably reduced by lowering the blank HCHO concentration of the sampling solution. However despite several attempts, no method has as yet been found to systematically reduce the blank HCHO concentrations of the sampling solutions below about 3 ng/ml.

The fractional error due to the HPLC measurement decreases with the size of the sample HCHO signal. For example a 2 m^3 air sample with a HCHO mixing ratio of 0.4 ppbv produces a 13.8 ± 0.3 ng/ml HCHO signal in a 100 ml sampling solution with a blank HCHO value of 3 ± 0.2 ng/ml and the resulting error is about 4 % of the sample HCHO amount.

For the land based samples with gas meter measured volumes of about 2 m^3 and a mixing ratio of about 0.2 ppbv, the precision of the method is ± 0.03 or ± 15 %.

For similar samples collected on board ship, the overall precision is ± 17 % with an error for an HCHO mixing ratio of 0.2 ppbv of ± 0.034 ppbv.

For 2 m^3 samples with a mixing ratio of 0.2 ppbv collected from aircraft the overall precision of the method is 11.5 %, a little better than ground samples because of the use of the mass flow meter volume measurements referred to STP.

2.7 Sampling techniques at various locations

The sampling technique described in section 2.1 to 2.5 has been used to make HCHO measurements at various ground sites in Europe and New Zealand and on an oceanographic expedition to the North and South Atlantic. The equipment has also been installed in aircraft and used to measure HCHO in the lower troposphere up to 7 km above the Northern Eifel district of the Federal Rupublic of Germany.

In order to make HCHO measurements at some of these locations, it was necessary to make some modifications to the technique.

For example at remote ground based locations, like exposed coastal sites, a rugged, portable, battery powered sampling unit was used. Power for the sampler pump and rotating drive unit was derived from a 12 volt automobile battery which was capable of running the system for six hours. This meant that the equipment was completely independant of mains power sources and also the problem of possible contamination from the exhaust gases of diesel generators was avoided.

The sampling equipment was also modified for use in aircraft. In a Dornier D-28 propellor aircraft two identical sets of apparatus were installed in 19" racks at the rear of the cabin. Ambient air was sampled through air intakes mounted on top of the fusealage. The air was transferred to the sampling equipment by means of 70 cm long, 25 mm inner diameter glass tubes, which were flushed at very high flow rates (> 600 litres/min(STP)) by the ram pressure of the aircraft. Only 40 litres/min of this flow were passed through to the samplers and the excess draft allowed to go to waste.

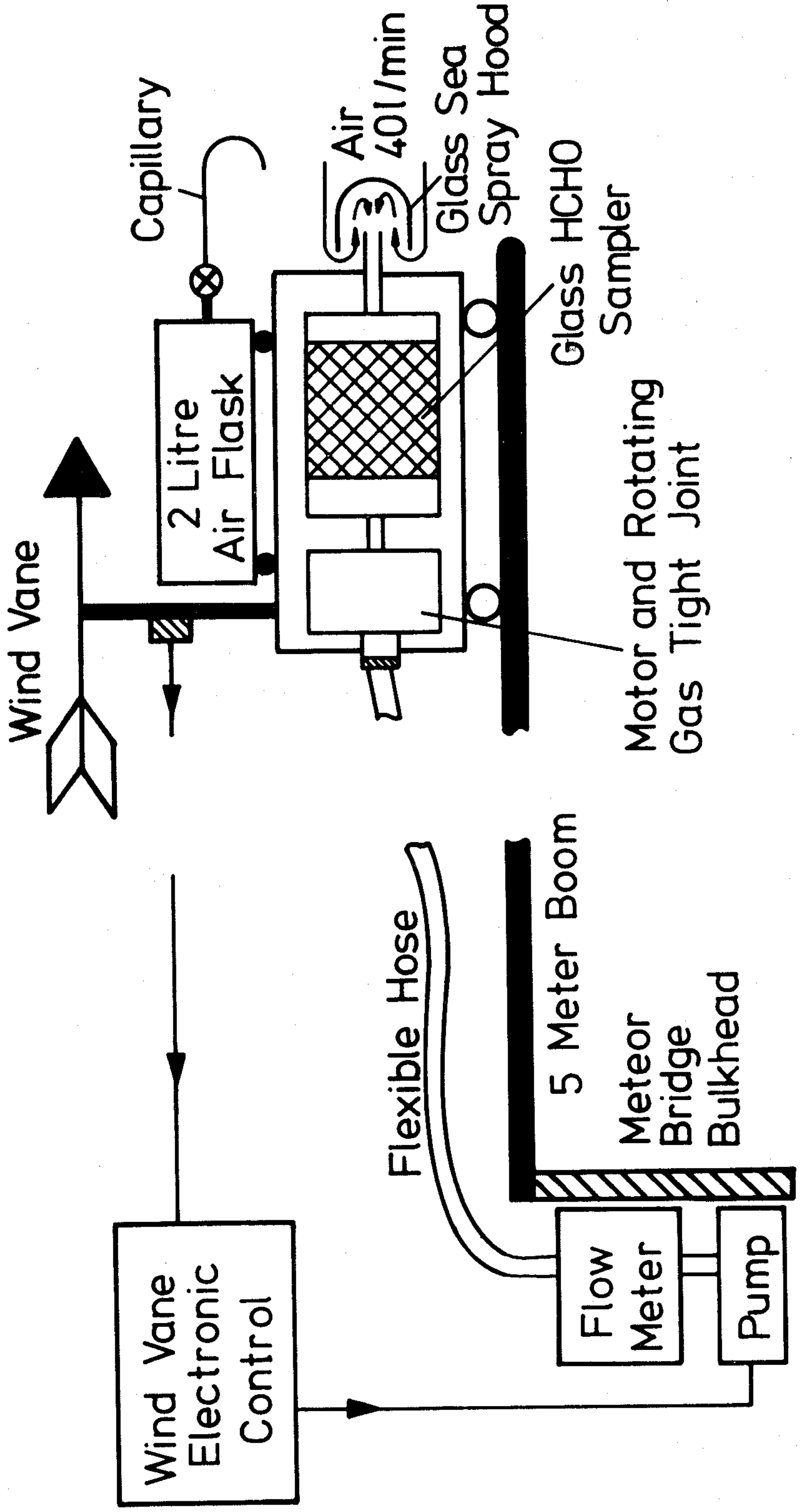
In figure 6 it was shown that a glass sampler filled with 250 mls of Raschig rings and DNPHzine solution collected only 55 % of the available HCHO from a 40 l/min air flow. Also as the available contact time in the dry aircraft inlet line is about a factor of 120 less than in the wet glass sampler, the loss of HCHO from the sample air stream to the walls of the dry inlet tube is considered to be small.

In a twin engined Piper Navajo aircraft ambient air was sampled through a 40 mm diameter glass intake, pointing forward and mounted in a modified window beside the pilots seat in the cockpit of the aircraft. Air was transferred from the intake to the glass HCHO sampler (figure 5) via an 80 cm long, 12 mm inner diameter glass tube flushed at high flow rates by the ram pressure of the aircraft. At 5 km altitude the flow through the inlet line due to the ram pressure of the aircraft is thus still in excess of 100 litres/minute (STP). Approximately 30 litres/min (STP) of this flow was sampled by the HCHO equipment and the remaining draft was allowed to go to waste.

At altitudes of 3 to 7 km depending on the season and weather conditions, the ambient air temperature was often less than - 30 °C, and additional heating had to be provided to prevent the sampling solution from freezing in the samplers. This was achieved by wrapping the air inlet line with electrical heating tape. The inlet air temperature to the sampler was monitored by a thermistor temperature sensor, and raised to a temperature of between 0 °C and 10 °C by applying the required amount of power to the heating tapes.

The sampling and analysis technique was also modified for use on board the German oceanographic vessel, the "F.S. Meteor". Because oceanographic cruises usually last for several weeks, a portable HPLC system was designed so that all samples collected on board ship could be analysed within a few hours of collection. This avoided possible sample contamination and decay problems and had the addi-

Figure 9 : Boom mounted HCHO sampler and two liter air flask. The glass HCHO sampler is contained in a waterproof case on a trolley attached to a five meter long boom perpendicular to a bulkhead above the bridge of the ship. A wind vane and an associated electronics control unit ensures that air is only sampled when the relative wind is from the forward facing sector. Sea spray is prevented from directly entering the HCHO sampler by a glass hood mounted over the inlet to the HCHO sampler. A two litre stainless steel air flask situated immediately above the HCHO sampler is used to collect air samples in parallel with the HCHO samples.


Wind Vane
2 Litre
Air Flask
Capillary
Air
40 l/min
Glass Sea
Spray Hood
Glass HCHO
Sampler
Motor and Rotating
Gas Tight Joint
Flexible Hose
5 Meter Boom
Meteor
Bridge
Bulkhead
Flow
Meter
Pump
Wind Vane
Electronic
Control

tional benefit that subsequent sampling could be planned on the basis of the results already obtained rather than sampling "blind". The HPLC system used comprised of an Orlita high pressure solvent pump (type MF 65); a Dupont Zorbax ODS reversed phase C 18 column kept at a constant temperature of 40 °C; and a Spectra Physics model 8200 254 nm liquid chromatograph detector.

Ships are notorious platforms for the collection of trace gas samples because of the possible contamination problems caused by exhaust gases from the ship's funnel as well as from deck mounted ventilation systems. In an attempt to circumvent these problems the glass sampler and the rotation system (figure 7) were mounted in a waterproof case attached to the end of a 5 meter long boom suspended 6 meters above the foredeck of the Meteor and pointing directly forward (see figure 9). A pulley system with a stainless steel halyard was attached to the boom so that the HCHO sampler could be both sent to the end of the boom for sampling and retrieved after sampling was complete.

To avoid overtaxing the mechanical strength of the boom, the pump and flowmeter of the sampling system were mounted at the base of the boom and connected to the sampler at the end of the boom with a 6 meter length of 40 mm diameter flexible hose (see figure 9).

During stormy weather a large amount of sea spray was encountered at the end of the boom. To prevent sea spray from entering the HCHO sampler, a glass hood was mounted on the sampler intake as shown in figure 9.

Even during relatively light winds from forward, tests showed that the trajectory of the air reaching the HCHO sampler at the end of the boom, remained well above the bow of the ship and was thus unaffected by exhaust gases from the ship. In order to prevent HCHO samples being taken when the wind came from behind or perpendicular to the ship, an automatic wind vane was fitted to the end of the boom immediately above the HCHO sampler. The wind vane was activated by an electronic control unit which switched the HCHO sampler off as soon as the wind direction veered out of the forward facing 180° sector. If the wind swung back into the forward facing sector the control unit waited 2 minutes before turning the HCHO sampler back on again. This reduced the chances of contamination from the ship during periods of light variable winds.

3. Results and Discussion

3.1 Formaldehyde at Jülich, Federal Republic of Germany

The HCHO sampling and analysis technique described in the previous chapter was first tested by taking routine measurements on a balcony 4 meters above the ground outside the atmospheric chemistry laboratory at the Kernforschungsanlage, KFA, in Jülich. Measurements were made over a one year period from August 1979 to August 1980. Simultaneous observations of meteorological parameters were obtained from the meteorological office at the KFA (see for example Geiß et al, 1980).

Jülich is a moderately polluted area situated only 80 km to the west of the heavily populated and highly industrialised Ruhr valley region of West Germany. Many smaller, towns, industries and coal fired power plants lie within a radius of 50 km of Jülich. Extensive measurements of SO_2 (Kessler, 1980), made at Jülich show mixing ratios well above those expected in clean air. Hence HCHO mixing ratios, due to the considerable anthropogenic activity in the Jülich region, can also be expected to be well above the ambient levels observed in clean marine air.

Figure 10 shows a logarithmic frequency distribution of 174 HCHO samples collected at Jülich over the one year period, August 1979 to August 1980. The distribution approximates a log normal distribution, as shown by the theoretical curve also plotted in figure 10, with a mean and standard deviation of $1.28\,^{+1.32}_{-0.73}$ ppbv.

During periods of light to moderate easterly winds at Jülich the HCHO mixing ratio can be relatively high ranging from 1 to 10 ppv, whereas during westerly winds the HCHO mixing ratio is generally much lower, of the order of 0.2 to 0.9 ppbv. This is demonstrated by figure 11 which shows a frequency distribution for 74 HCHO samples collected at Jülich during conditions of moderate to strong west and

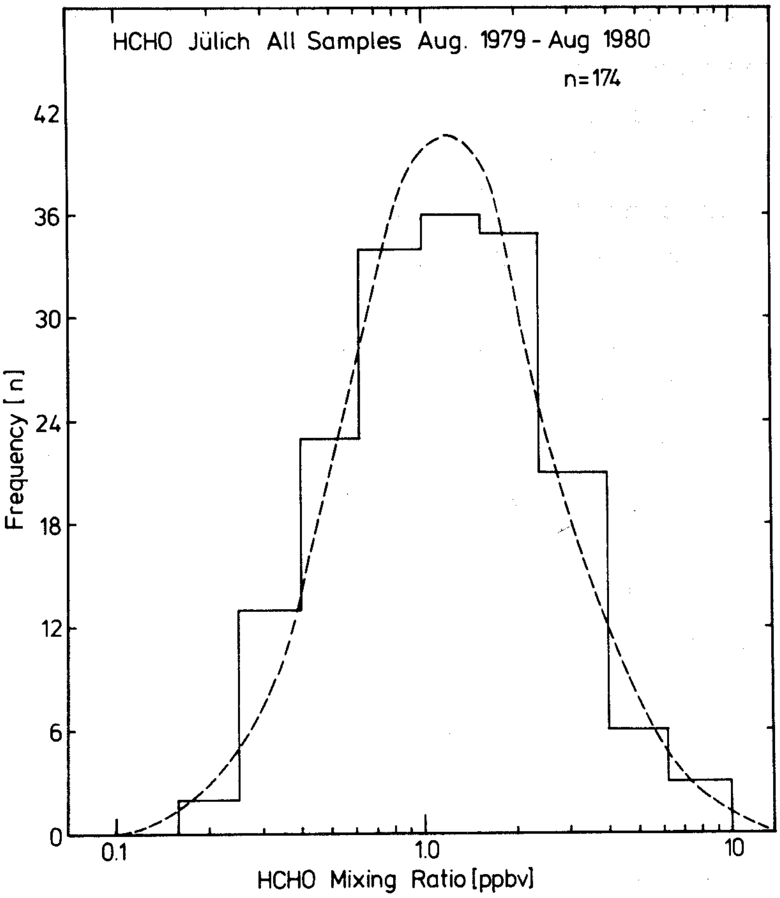


Figure 10: Logarithmic frequency distribution of all HCHO samples collected at Jülich from August 1979 to August 1980. The distribution has been plotted with a frequency interval of constant width on the log scale with X = log m, where m is the HCHO mixing ratio. The smoothed curve is a plot of the logarithmic normal error distribution computed from the experimental data using the function

$$f(X) = \frac{1}{\sqrt{2\pi}} \cdot \frac{1}{X\sigma} \exp\left[-(\ln X - \bar{X})^2 / 2\sigma^2\right]$$

where $\bar{x}$ is the mean of the distribution and σ its standard deviation.

southwest winds. The distribution also approximates a log normal distribution as shown by the associated theoretical curve plotted in figure 11. However the mean and standard deviation of the distribution are $0.73^{+0.52}_{-0.36}$ ppbv, significantly lower than the case of figure 10, indicating that cleaner air may reach Jülich under westerly wind conditions.

During gale force westerly winds at Jülich, dilution of anthropogenic HCHO and of the precursors of HCHO, may cause the HCHO mixing ratios to approach the levels expected in clean air. This is shown in figure 12, where the HCHO mixing ratio measured during a storm on the night of the 31st of January, reached a low value of 0.08 ± 0.01 ppbv, the lowest HCHO mixing ratio ever recorded at Jülich during this work. During the storm 30 consecutive air samples were collected for one hour each, and the resulting HCHO mixing ratios are listed together with concurrent meteorological data in table 3 of the appendix. Heavy rain occurred several times during air sampling on the 31st of January and the 1st of February 1980. When possible, rain samples were collected over the same hourly integration periods as the air samples. The HCHO concentrations of the rainwater samples are also listed in table 3.

During the storm a trough of low pressure passed over Jülich at about 20:00 on the night of the 31st of January. The HCHO mixing ratio steadily decreased until this time when the wind direction began to veer further towards the West because the low pressure region had moved further to the East. At this stage it is likely that the effluent plume of a large browncoal power plant located at Weisweiler, 10 km to the southwest, passed over the KFA sampling site. Despite the large dilution caused by the high wind velocities, ≥ 10 m/sec, the plume would still have led to an increase in the HCHO mixing ratios observed at the KFA site. Kessler, 1980, has observed similar increases in SO_2 mixing ratio at the KFA which are directly correlated with wind direction and the trajectory of the

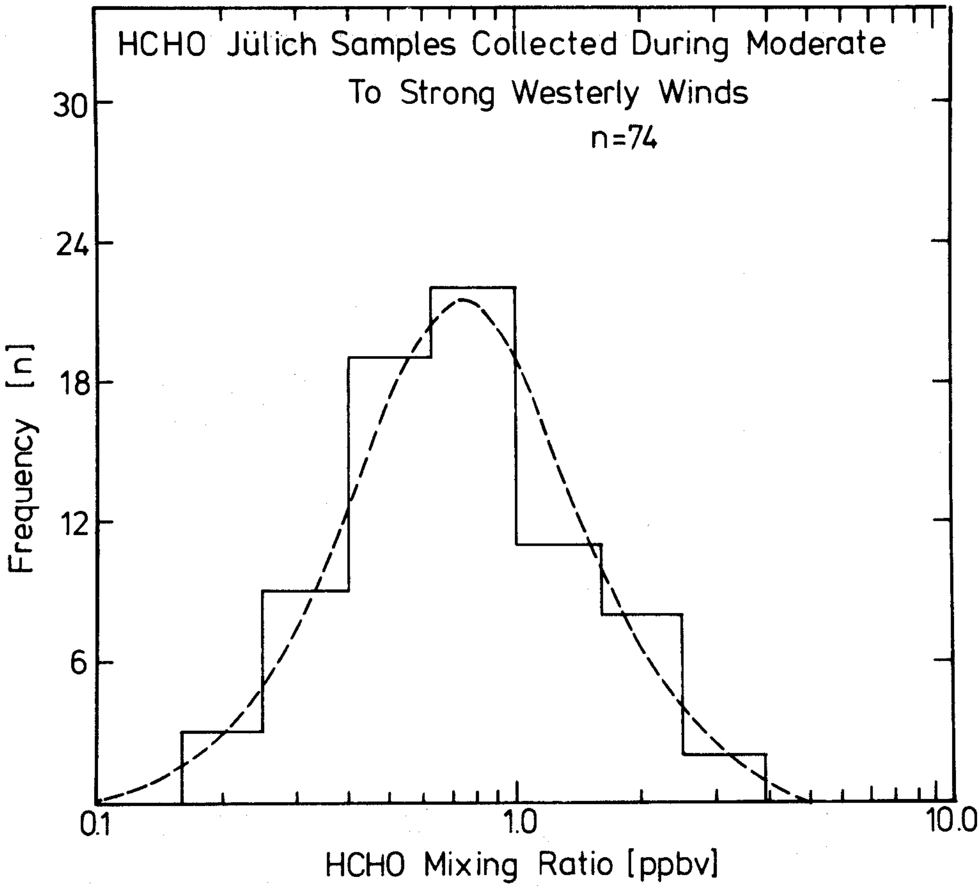


Figure 11: Logarithmic frequency distribution of 74 HCHO samples collected at Jülich from August 1979 to August 1980 during moderate to strong westerly winds. The distribution is plotted in the same manner as figure 10 and the smoothed curve represents the log normal error function pertaining to the distribution.

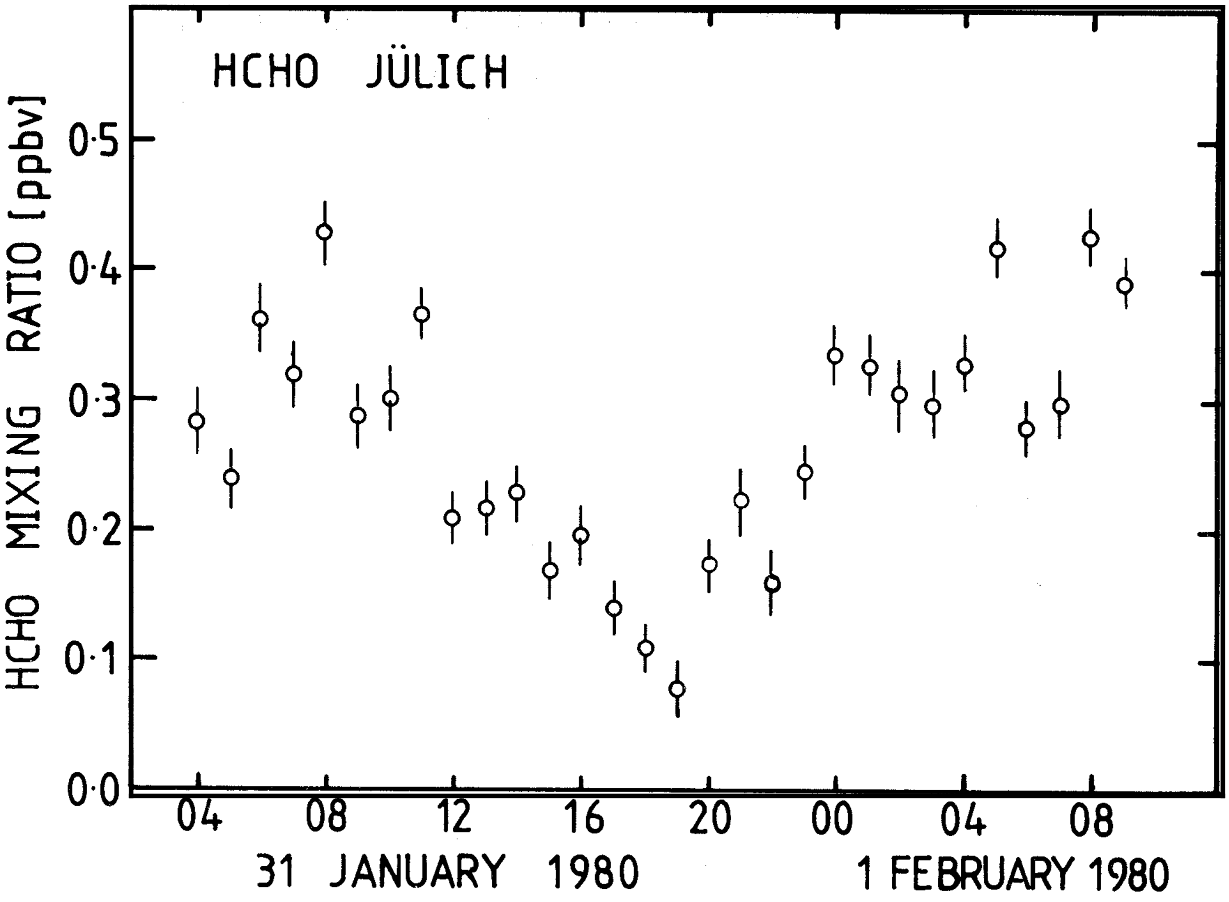


Figure 12: Thirty consecutive hourly HCHO samples collected during a westerly storm on 31 January and 1 February 1980. The vertical error bars indicate the experimental error associated with each sample.

Weisweiler powerplant plume.

Unfortunately not enough rain data were collected to allow systematic investigation for a relationship between the HCHO concentration in the rainwater and the HCHO mixing ratio of the air. The few rain data collected, show a large variability in concentration with a similar range of concentrations to those found by Thompson, 1980 at a coastal site in the USA and Warneck and Klippel, 1978 at Deuselbach in the FRG. Klippel and Warneck, 1978, have demonstrated that HCHO from the gas phase is responsible for most of the HCHO found in precipitation. On this basis Warneck et al, 1978 have shown that the HCHO gas phase mixing ratio, m, in equilibrium with rain water may be evaluated from

$$m = \frac{C_{rw} \cdot L}{\beta \cdot M_{HCHO} N_{air}} \qquad (15)$$

where C_{rw} is the mean concentration of HCHO in rainwater by weight, L is the density of rainwater in clouds (1 g/m^3), M_{HCHO} is the molecular weight of HCHO, N_{air} is the molar volume of air (38 mole/m^3 at 2 km cloud height)and β=0.245 is a partition coefficient between the concentration of HCHO condensed in raindrops and in the gas phase before condensation. The mean HCHO concentration of the rainwater samples collected during the storm at Jülich is 47 ± 26 ng/ml which when substituted into equation (15) yields a HCHO mixing ratio in air at cloud height of 0.18 ± 0.10 ppbv. This is in agreement, within the error bars, with the observed mean HCHO mixing ratio at the surface of 0.27 ± 0.09 ppbv.

In an attempt to find a seasonal variation in the HCHO mixing ratio at Jülich all of the data collected during periods of strong to moderate westerly winds over the period August 1979 to August 1980 are plotted in figure 13. The points represent the means of the westerly wind selected data averaged for samples collected during two weekly periods and the vertical bars represent ± standard deviation about this mean. The points without error bars indicate periods during which less than 5 samples matching the wind

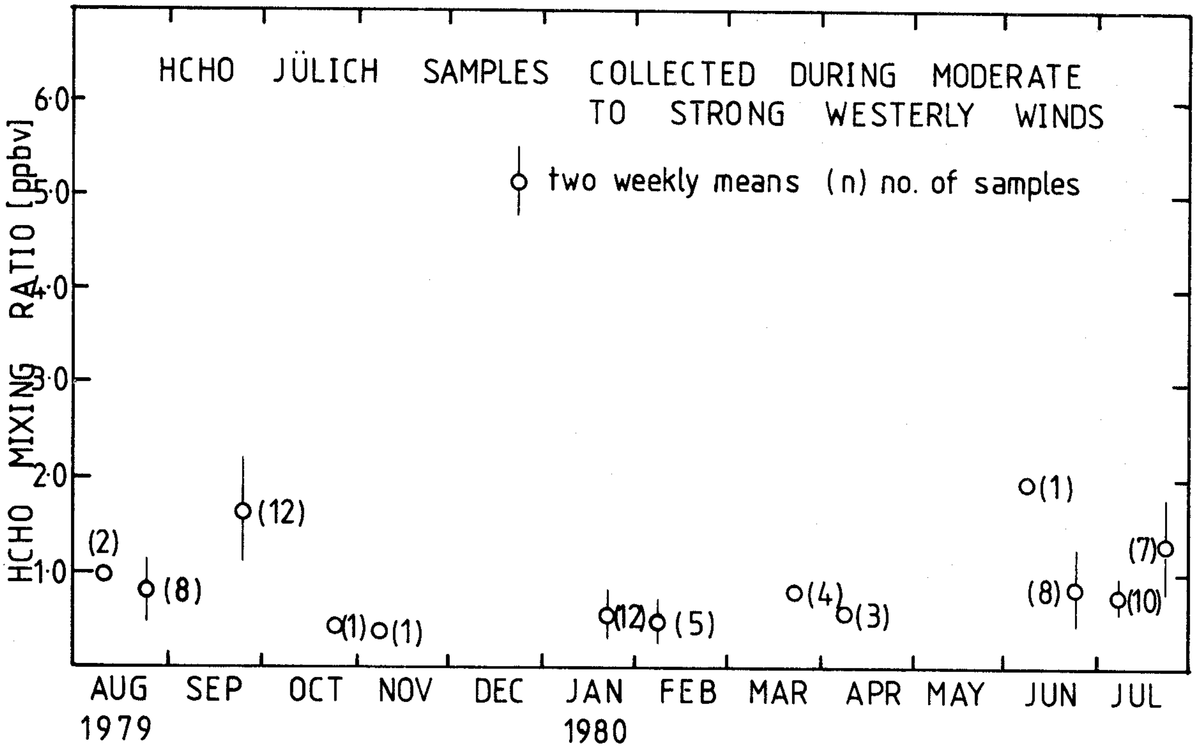


Figure 13: Two weekly means of HCHO samples collected at Jülich from August 1979 to August 1980 during periods of moderate to strong westerly winds. The numbers in brackets indicate the number of samples used to calculate the mean with the vertical bars indicating ±1 standard deviation about the mean when the number of samples in a two weekly period is 5 or more. Because of a prevalence of easterly winds many two weekly periods contain no samples at all.

selection criteria were collected. In several of the two weekly periods, because of a prevalence of easterly winds, no HCHO samples fitting the wind selection criteria were collected.

In the summer months the photochemical sources of HCHO increase at a slightly greater rate than the photochemical sinks and the mean HCHO mixing ratio should be higher than in the winter months. However because of the small amount and large scatter of the data collected it is impossible to deduce an annual variation of the HCHO mixing ratio at Jülich from the data of figure 13.

3.2 Formaldehyde at the Irish west coast, April 1980

In order to test the suitability of the method for the detection and analysis of HCHO in clean marine air, a test sampling project was carried out in April 1980 at the west coast of Ireland. The main sampling site, at which 36 air samples of 2 m^3 volume were collected, was located at the brink of a 100 meter high cliff overlooking the Atlantic ocean about 2 km south of Kilkee (53 ^{o}N). A further 6 samples were collected in a similar location near Loop Head lighthouse.

Within a few hours of collection, the sampling solutions were stored in a refrigerator. During transport from Ireland to the laboratory in Jülich, the samples warmed up to room temperature for two days before they could be returned to a refrigerator in the laboratory.

All of the samples were analysed within 10 days of collection but 5 of the 42 samples collected were lost due to deterioration of the excess DNPHzine reagent used in the sampling solutions. These samples were easily recognised and rejected from further consideration by the method described in section 2.3. The results of the remaining 37 samples, together with a summary of the sampling and weather conditions are listed in table 4 of the appendix.

Figure 14 shows a logarithmic frequency distribution of these samples. The experimental distribution approximates a log normal distribution as shown by the theoretical parent distribution also plotted in the figure. The mean and standard deviation of the experimental distribution is $0.20 ^{+0.13}_{-0.08}$ ppbv, much lower than observed in Jülich indicating that the Irish data have not been influenced by anthropogenic sources of HCHO to the same extent as the Jülich data. However a few of the data collected on the 29 April 1980 were influenced by anthropogenic activities because of variable winds during sampling. For example a few measurements made before and just after sunrise when the wind was light and variable from the land, show the influence of anthropogenic pollution, probably due to the burning of turf fires.

On the 27th of April 1980 the wind was strong and consistently onshore from the north and northwest. Over the period 10:00 to 24:00, 11 consecutive HCHO samples were collected in an attempt to measure a diurnal variation in the HCHO mixing ratio (see table 4). During the daylight hours fine conditions prevailed although the sky clouded over occasionally. No diurnal variation in the HCHO mixing ratio was seen and no correlation of the HCHO mixing ratio with cloud cover was evident. The mean of these samples was 0.16 ppbv with a standard deviation of only 0.03 ppbv demonstrating that for stable weather conditions at clean air sites in mid latitudes, only relatively minor variation in the HCHO mixing ratio occur.

During the sampling period,7 whole air samples were collected in parallel with the HCHO samples and measured in the GC laboratory at the KFA Jülich for CO, CH_4, and C_2 to C_5 alkanes and alkenes. The mean CO and CH_4 mixing ratios determined were 189 ± 17 ppbv and 1.67 ± 0.01 ppmv respectively, and the alkenes and alkanes measured showed low values indicate of clean marine air (Rudolph, 1981). Hence the value of 0.16 ± 0.03 ppbv obtained for the HCHO mixing

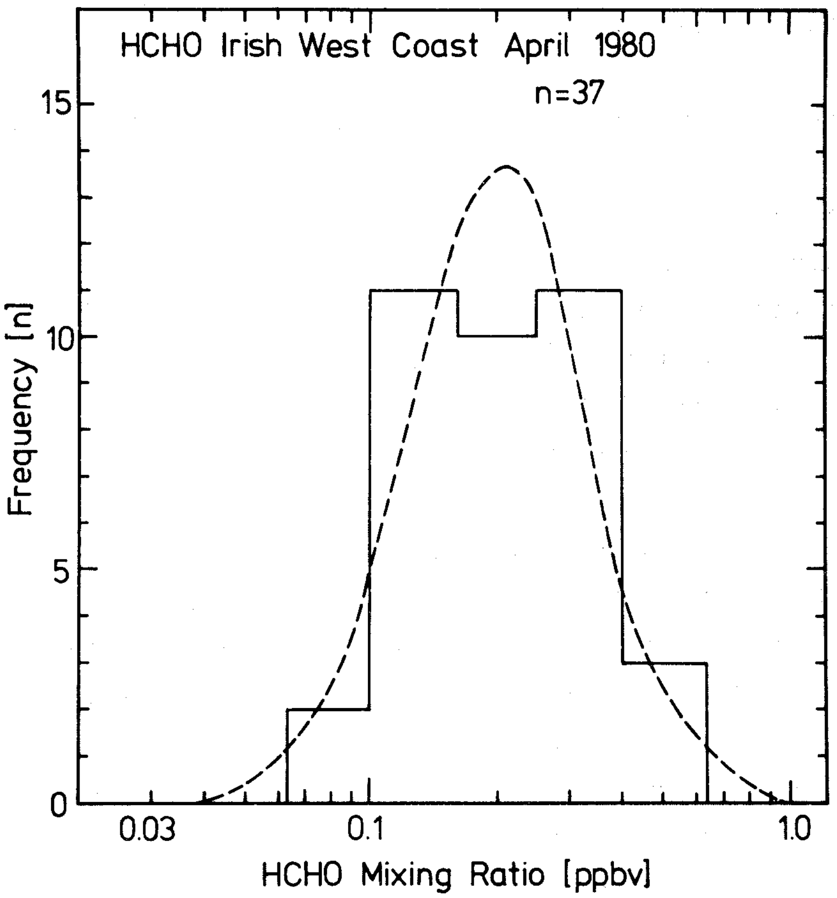


Figure 14: Logarithmic frequency distribution of 37 HCHO samples collected at the west coast of Ireland in April 1980. The distribution is plotted in the same manner as figure 10 and the dashed curve represents the log normal error function of the distribution.

ratio during this period is probably representative of clean tropospheric air at the surface at 53 °N in April.

3.3 Formaldehyde at Wellington, New Zealand, January 1981

Additional HCHO samples were collected in New Zealand at mid latitudes in the southern hemisphere. Twelve samples were collected during galeforce northwest winds in Petone, a suburb of Wellington (42 °S). A further 14 were collected at the New Zealand DSIR clean air station at Baring Head on a south easterly facing penisula of the North Island of New Zealand (42 °S). Baring Head is located at the brink of an 80 meter high cliff directly exposed to winds from the south western Pacific ocean. All samples were analysed within a few hours of collection with a Spectra Physics SP 8000 HPLC at a DSIR laboratory in Lower Hutt, New Zealand using the procedures and chromatographic parameters described in section 2. The results of the measurements with associated weather and sampling information are listed in table 5 of the appendix.

A logarithmic frequency distribution of all of the data collected in New Zealand is shown in figure 15. The means and standard deviation of the distribution are $0.28 \begin{smallmatrix} + 0.26 \\ - 0.15 \end{smallmatrix}$ ppbv, higher than observed in Ireland, but still lower than for the HCHO data observed in Jülich. The parent log normal distribution shows poor correlation, probably due to the limited number of data collected. The data were sampled under a variety of wind conditions including down wind from an urban area and the relatively high and variable HCHO mixing ratios observed are indicative of contamination from anthropogenic sources of HCHO.

However 3 samples collected at Baring Head during a strong onshore south east wind, showed HCHO mixing ratios of 0.19, 0.18 and 0.23 ppbv. Lowe et al, 1979, have shown on the basis of CO_2 measurements, that air sampled at this site during onshore southeast wind conditions is representative

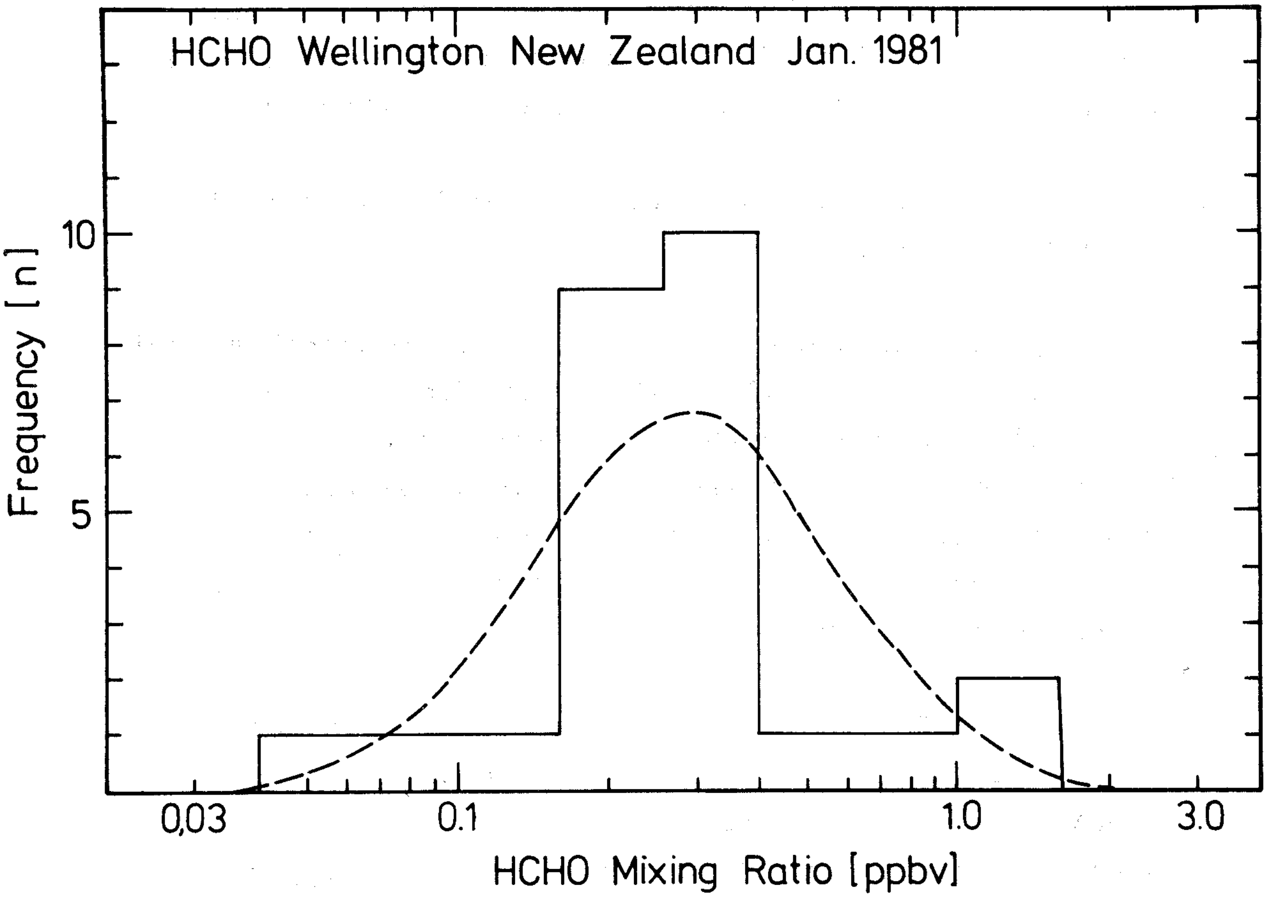


Figure 15: Logarithmic frequency distribution of 26 HCHO samples collected at Petone and Baring Head, New Zealand, January 1981. The distribution is plotted in the same manner as figure 10 and the dashed curve represents the log normal error function of the distribution.

of a large area of the south western Pacific ocean. The 3 HCHO samples collected under these conditions are therefore thought to be representative of clean maritime air.

3.4 Formaldehyde measurements from "Meteor" cruise 56/1 October - November 1980

Participation in a cruise of the German research vessel F.S. Meteor in the fall of 1980 provided an excellent opportunity to measure the HCHO mixing ratio over the Atlantic Ocean. The cruise track during section 56/1 is shown in figure 16 and covers the English Channel and the Atlantic Ocean from 54 ^{o}C at Hamburg, F.R.G., to 35 ^{o}S at Montevideo in Uruguay.

A total of 175 HCHO air samples were collected aboard the Meteor. Of these 15 were rejected because of various mechanical and electrical failures experienced with the sampling equipment or because the wind velocity during sampling was under 2 m/sec. The remaining samples are plotted in figure 17 as a function of latitude with the exception of 2 samples collected in Rio harbour whose mixing ratios were too high to be conveniently included in the figure.

On oceanographic stations the Meteor was held stationary while casts were lowered overboard and deep seawater samples were collected. Under these conditions wind velocities at the end of the boom fluctuated considerably and the sampler was constantly turned on and off by the electronic wind vane switching unit (see figure 9). A few HCHO samples collected on the first two oceanographic stations of the voyage are included because a careful check was made to ensure that the wind was always from forward and more than 2 m/sec during the entire sampling time. However because of the greater chances of contamination due to variable winds, HCHO sampling during the remaining oceanographic stations of the voyage was discontinued.

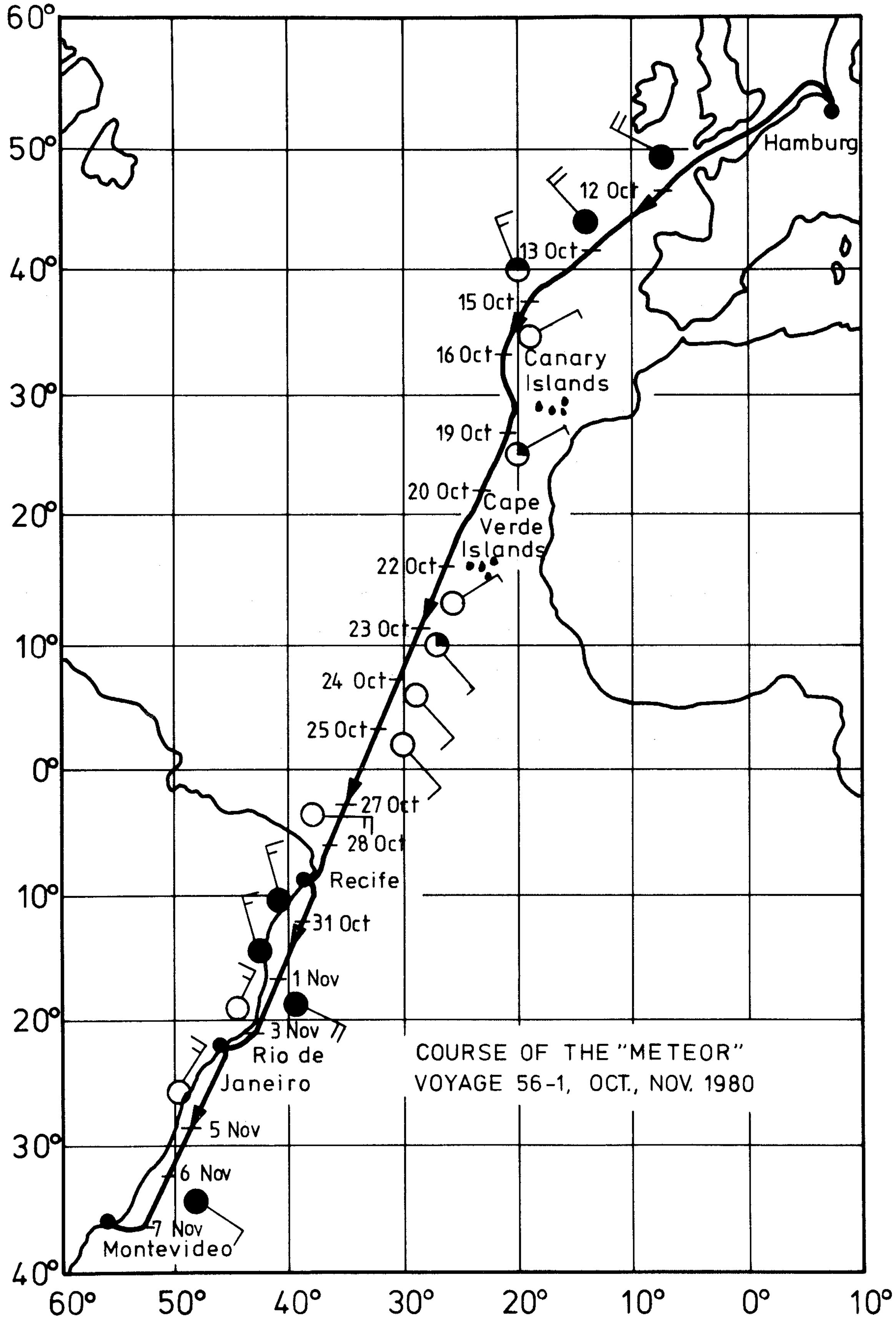
The scatter of the data plotted in figure 17 is almost certainly due to real variations in the HCHO mixing ratio rather than to variations in sampling and analysis technique. This is borne out by the fact that measurements of HCHO mixing ratio made within an hour of each other and during stable weather conditions are usually reproducible to within 0.03 ppbv.

Some of the scatter in the data is probably due to the transport of HCHO and its precursors from sources on land. For example as shown in figure 16, the course of the Meteor followed the South American coastline from 10 °S to 35 °S. Because of the proximity of the course to the coast, favourable offshore winds could have transported anthropogenic HCHO or NMHCs some distance from the coast, especially during cloudy conditions or at night when the chemical lifetime of the compounds is increased due to a decrease in the OH radical mixing ratio.

Fires are widely used in agricultural practices in Brazil. During October and November, large fires are used to remove sugarcane plants after harvesting in regions both to the north and south of Recife. Smoke from these fires could often be seen from the Meteor. Also from a commercial aircraft flying at an altitude of 11 km at night about 300 km southwest of Recife in November 1980, 50 to 60 large fires could be seen burning at any one time. Fires are large sources of NMHCs (U.S. Environmental Protection Agency, 1977) as well of HCHO itself (Morikawa, 1976) and considerable scatter can thus be expected in HCHO measured in air downwind from them.

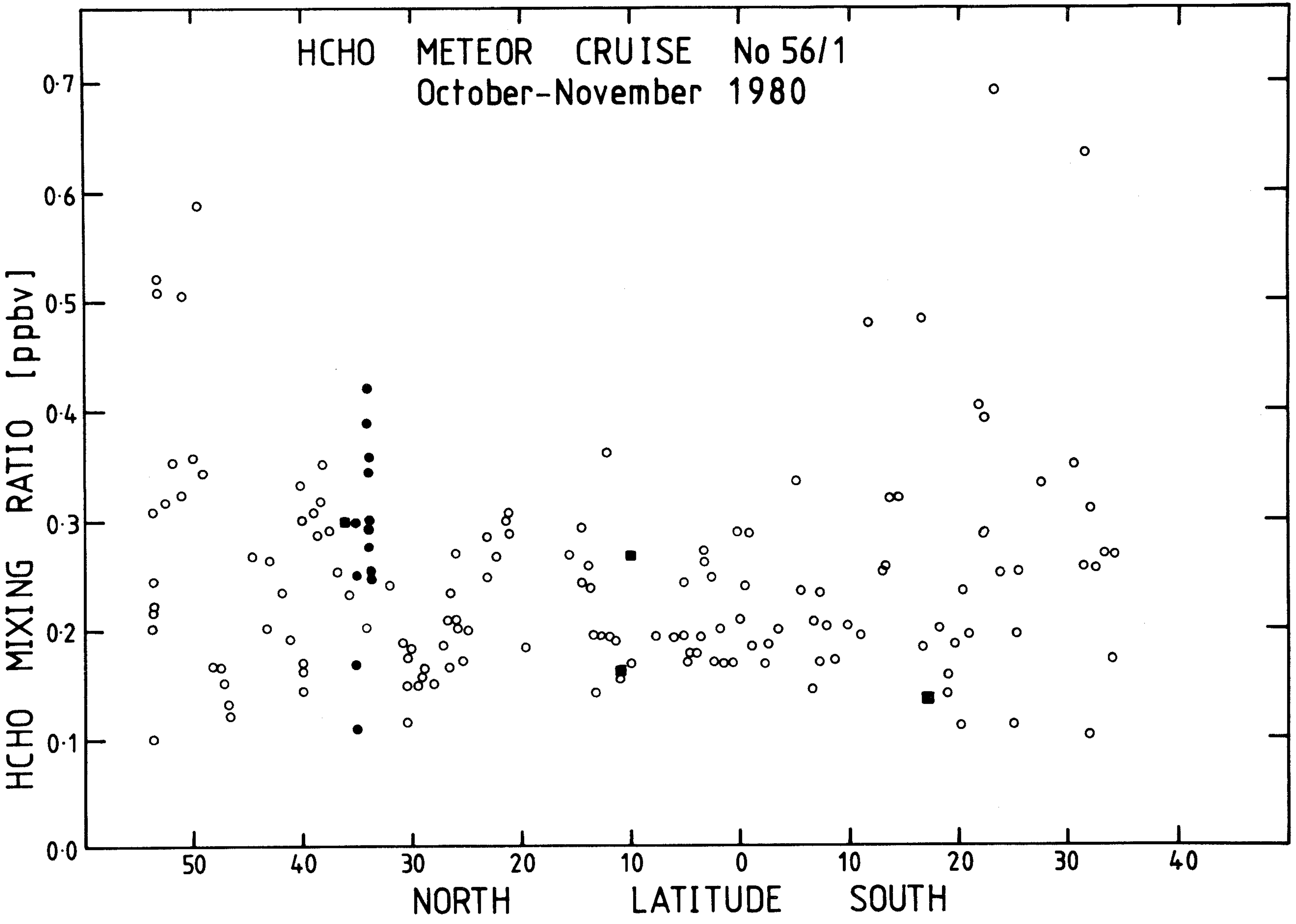
In order to interpret the data of figure 17 in terms of clean tropospheric photochemistry, it will be necessary to remove data which have been influenced by anthropogenic activities. This may be done on the basis of wind direction, if the measurements were close to a coastline, as well as on the basis of parallel measurements of other trace gases,

Figure 16: Course of the F.S. Meteor during Antarctic cruise 56/1, October/November 1980. Ports of call were Recife, Rio de Janeiro and Montevideo. The dates shown mark the ships position at midday. The symbols shown indicate approximate wind direction, wind speed and cloudiness according to the following scheme: wind direction is shown by the alignment of the symbol. Wind speed is shown by the strokes on the tail of the symbol - one long stroke represents 10 knots, one short stroke 5 knots. The circle at the base of the symbol represents the approximate cloudiness in units of 1/4 of total cloud cover.



COURSE OF THE "METEOR"
VOYAGE 56-1, OCT., NOV. 1980

Figure 17: All HCHO data collected during the Meteor cruise 56/1 with the exception of data collected in Rio harbour or when the sampling equipment failed. The full circles represent samples collected on stations and the squares represent samples collected during rain.


HCHO METEOR CRUISE No 56/1
October-November 1980
HCHO MIXING RATIO [ppbv]
0·0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
50
40
30
20
10
0
10
20
30
40
NORTH LATITUDE SOUTH

for example CO, which are sensitive indicators of anthropogenic pollution. A limited series of two liter whole air samples, which were taken in parallel with some of the HCHO measurements, can be used for this purpose.

Examination of the meteorological records taken during the cruise shows that on several occasions the wind blew strongly from offshore, for example in the latitude range from 11 °S to 16 °S. The seven samples collected in this range show a mean HCHO mixing ratio of 0.33 ± 0.11 ppbv compared to the mean mixing ratio of 0.17 ± 0.04 ppbv collected in the region from 16 ° 30' S to 22 °S where the wind blew strongly onshore from the southeast (see figure 16).

Whole air samples collected from 22 °S to 31 °S during northeast winds clearly showed the effects of anthropogenic activities with higher CO and C_2 to C_5 alkene and alkane mixing ratios (Rudolph, 1981). Formaldehyde samples collected in the same latitude range also showed relatively high mixing ratios, especially samples collected immediately downwind from Rio de Janeiro and in Rio harbour with values as high as 1.66 ppbv.

Because of heavy shipping traffic and the proximity of highly industrialised continent and UK, the English Channel is also likely to be a contaminated area. The mean of 15 samples collected in this region was 0.34 ± 0.15 ppbv. Simultaneously measured CO values by Seiler, 1980 showed values slightly higher than expected for clean air.

In the latitude range 35 °N to 15 °N, when the Meteor was an average distance of about 400 km from the African coast and close to the Canary and Cape Verde islands, light variable winds were encountered. Under these conditions transport of anthropogenic HCHO and its precursors from land may have been possible. However examination of whole air samples collected in parallel with the HCHO samples did not show high values of CO and C_2 to C_5 alkenes which could be attributed to anthropogenic influences. The measurements made in the latitude range 35 ^{o}N to 15 ^{o}N are therefore considered to be representative of the clean marine troposphere.

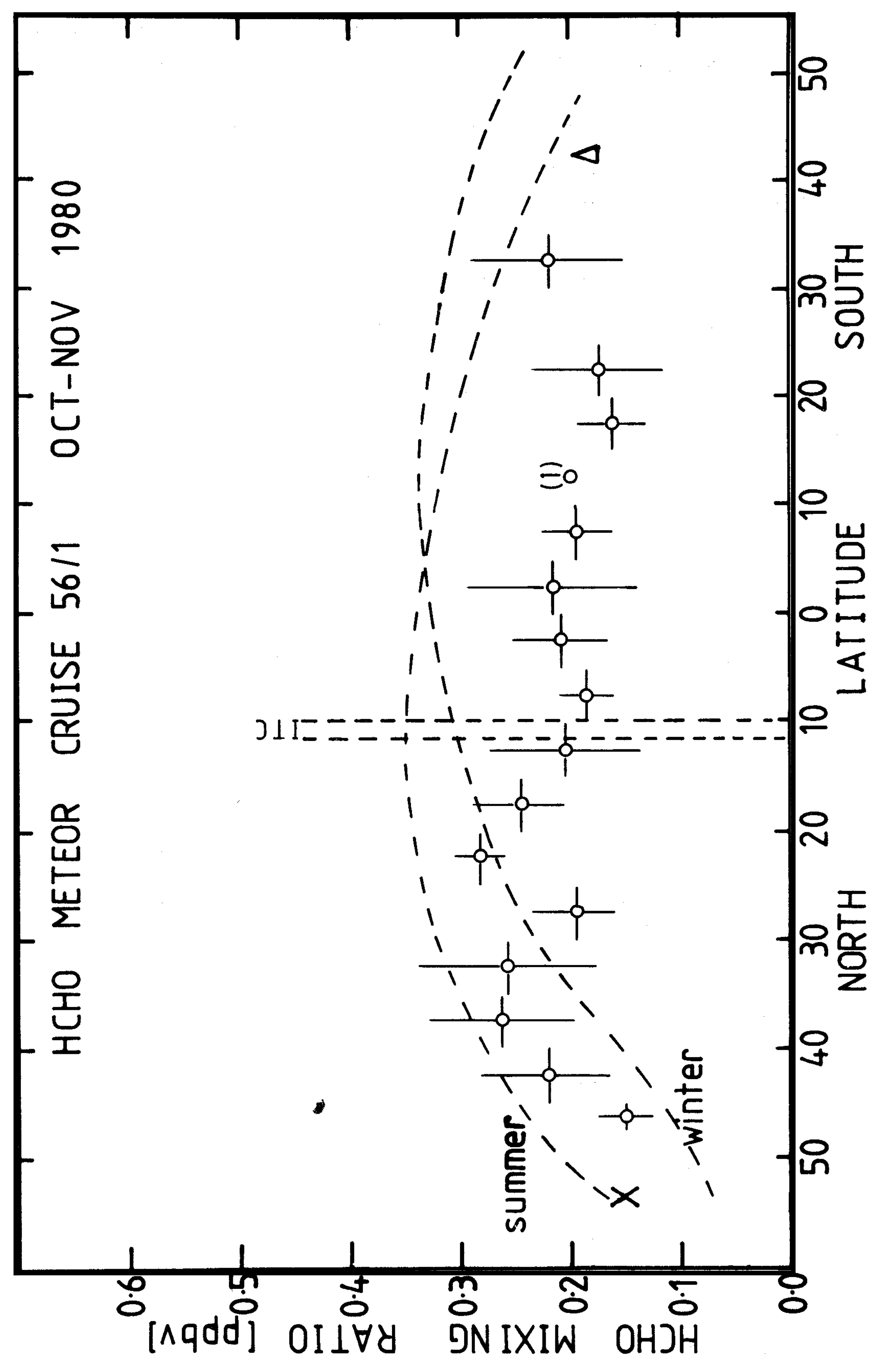
When the HCHO data collected during offshore winds near the South American coast, and the data collected in the English Channel region are removed, the scatter of the data in figure 17 is greatly reduced. In figure 18 the remaining data considered to be representative of the clean troposphere, have been reduced to means of samples collected every 5^{o} of latitude and the error bars represent the standard deviation about this mean. Also shown for comparison in the figure, are the means of data collected during strong offshore winds at the west coast of Ireland in April 1980, and at Baring Head, New Zealand in January 1981. The dashed curves shown in the figure represent latitudinal model profiles of the HCHO mixing ratio for winter and summer conditions as computed by Logan et al, 1981.

The experimental data show a relatively uniform HCHO mixing ratio in the southern hemisphere. In the northern hemisphere, the mixing ratio is more variable with a decrease towards mid latitudes which is also predicted by the model curves. However the assumed conditions for which the model curves were generated, differ from those under which the HCHO data were sampled in the following important ways.

i) The Meteor data were taken in the northern fall and the southern spring in October and early November, whereas the model curves are calculated for mid summer and winter.

ii) The model curves represent the HCHO mixing ratio at noon, which is close to the time of the predicted daily maximum in HCHO mixing ratio, whereas the observational data are the means of data collected during day and night.

Figure 18: Latitudinal means of the HCHO mixing ratio measured in the Atlantic aboard the Meteor, October and November 1980. The circles represent the means of data collected in each 5° latitudinal region when the data collected during offshore winds near the S. American coast and in the English channel are not considered. The vertical error bars show ±1 standard deviation about these means except the region from 10 °S to 15 °S where only one measurement during onshore winds near the S. American coast was made. The X and the Δ represent means of the HCHO mixing ratio measured during strong onshore winds at the west coast of Ireland in April 1980 (53 °N) and at Baring Head, New Zealand in January 1981 (42 °S). The dashed curves represent latitudinal profiles of the HCHO mixing ratio at the surface for winter and summer conditions from a model developed by Logan et al. (1981).


HCHO METEOR CRUISE 56/1 OCT-NOV 1980
HCHO MIXING RATIO [ppbv]
0·0
0·1
0·2
0·3
0·4
0·5
0·6
LATITUDE
NORTH
SOUTH
50
40
30
20
10
0
10
20
30
40
50
ITC
summer
winter
X
Δ
(!)

iii) The model assumes cloudless conditions. The HCHO observations however, were made under a variety of cloud conditions ranging from totally overcast to cloudless.

iv) The model assumes HCHO production from methane only. As indicated in chapter 1, the oxidation of NMHCs are also an important source of HCHO.

Because the voyage was made in the northern fall and the southern spring a composite of the two model curves would probably be a better representation of the sampling time and conditions. This would tend to reduce the predicted gradient between the hemispheres and would thus show better agreement with the experimental data. Also as will be shown later the HCHO mixing ratio at noon is close to the maximum at 14:00. The mean daily HCHO mixing ratio estimated from a diurnal HCHO model, Wuebbles, 1980, is about 30 % lower than the HCHO mixing ratio at noon. For comparison with the experimental profile, the model profiles should therefore also be reduced by a factor of about 30 % which would bring them into closer overall agreement with the observations.

The effect of cloudiness on the model profiles cannot be assessed in terms of current photochemical models. Also because of uncertainties in the distribution and yield of HCHO from NMHCs, no reasonable estimate of their contribution to the HCHO mixing ratio can be made. Because of these uncertainties as well as the problem of comparing the conditions used to develop the model with the conditions encountered during the measurements, precise comparisons between the experimental and model latitudinal profiles shown in figure 18 can not be made.

During fine conditions in the mid Atlantic, several attempts were made to measure a diurnal variation of the HCHO mixing ratio. On the 18th and 19th of October 1980, 18 consecutive HCHO samples were collected. The measurements were carried out from 31 $^{\circ}$N to 27 $^{\circ}$N with clear cloudless conditions

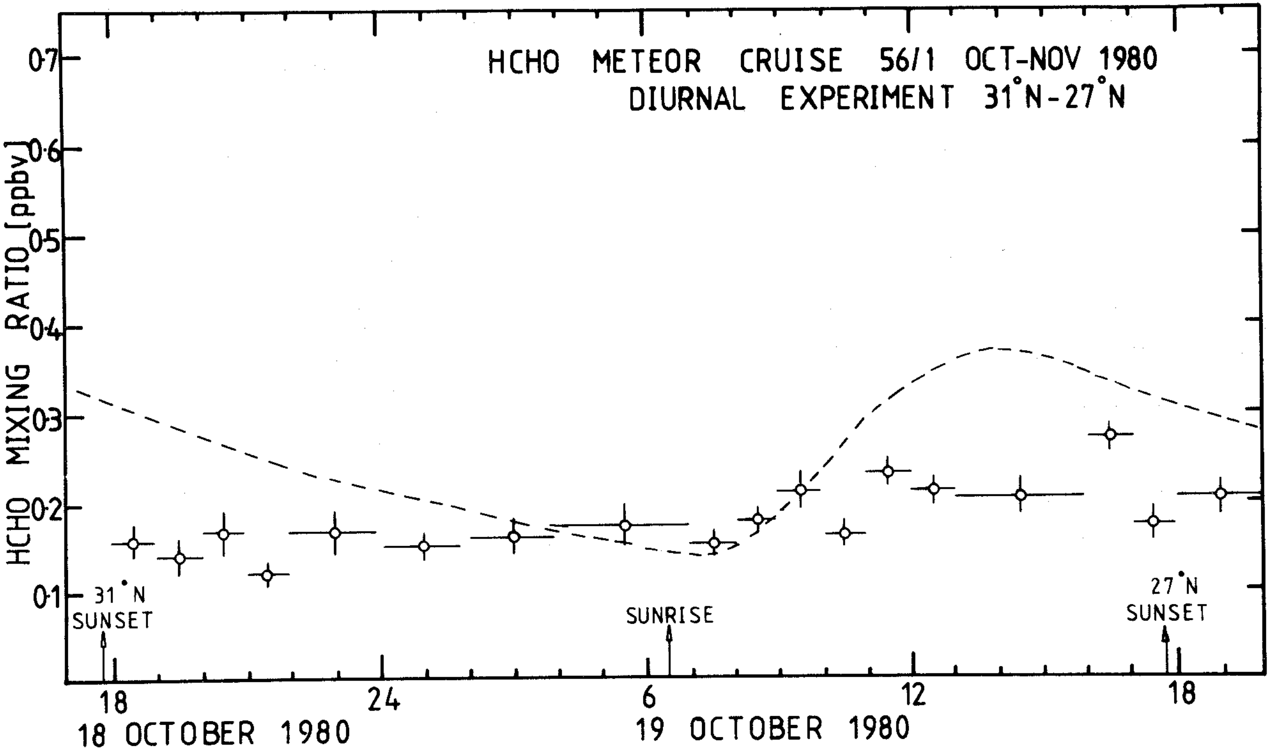


Figure 19: Measured and model diurnal variation of HCHO mixing ratio from 31 °N to 27 °N in the mid Atlantic. The circles represent HCHO measurements with the vertical bars showing the experimental error of each measurement and the horizontal bars the duration of each measurement. The dashed curve shows a diurnal model developed by Wuebbles, 1980, for the HCHO mixing ratio at the surface at 30 °N, solar equinox and with methane as the only source gas.

day and night when winds from forward at 10 to 15 knots prevailed, and the results are plotted in figure 19 as a function of local time. The vertical bars represent the analysis error range of ± 0.03 to 0.04 ppbv depending on sample volume and the horizontal bars represent the time over which the HCHO sample was collected. Also plotted in figure 19, as the dashed curve, is a diurnal model profile of the HCHO mixing ratio at the surface for cloudless equinoctial conditions at 30 $^{\circ}$N with methane as the only source gas (Wuebbles, 1980). Apart from the non-inclusion of NMHCs as source gases for HCHO, the conditions used to develop the model are in good accord with the actual conditions encountered during the observations. The experimental data show a small diurnal variation only, with a slight increase in mixing ratio during the daylight hours, whereas the model predicts a relatively large diurnal variation with a maximum at 14:00 and a higher mean HCHO mixing ratio.

To identify the possible cause of the discrepancy, it will be necessary to investigate the relative importance of the sources and sinks of HCHO in the marine troposphere. In figure 20, the production and destruction rates for the chemical and physical processes determining the HCHO mixing ratio at the surface are plotted as a function of time. The curve for the production of HCHO from methane, P_{CH_4}, and its removal by OH, D_{OH}, are calculated using equations (1) and (11) with the diurnal variations of HCHO and the OH mixing ratios at the surface given by Wuebbles, 1980. The curve representing the removal of HCHO by photolysis, $D_{h\nu}$, is calculated from data for the photolysis coefficients, J_9 and J_{10}, given by Calvert, 1980, which are also derived from the model of Wuebbles, 1980. Removal by dry deposition, D_{dep}, and by rainout and washout, D_{rain}, are given by

$$D_{dep} = \frac{1}{\tau_{dep}} \cdot [HCHO]_o \; [molec \cdot cm^{-3} \cdot sec^{-1}] \qquad (21)$$

$$D_{rain} = \frac{1}{\tau_{rain}} \cdot [HCHO]_o \; [molec \cdot cm^{-3} \cdot sec^{-1}] \qquad (22)$$

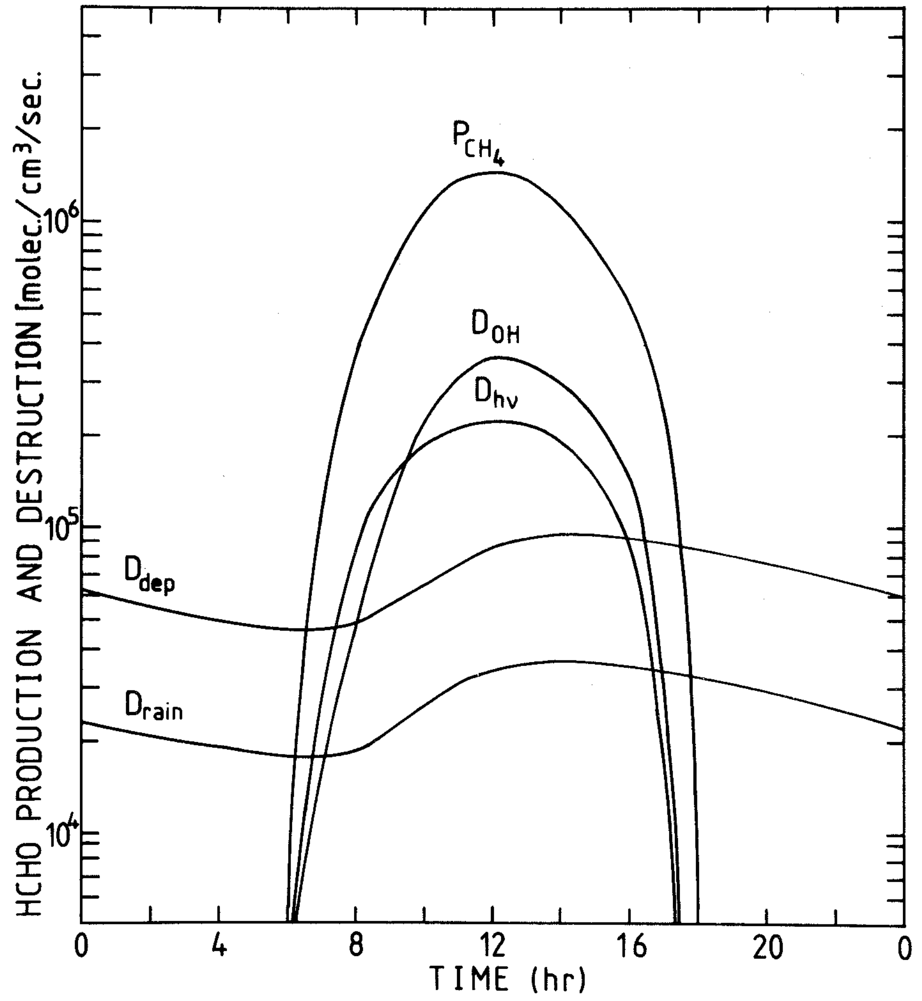


Figure 20: Absolute production and removal rates of HCHO at the surface in a marine troposphere. P_{CH4} is the production of HCHO from methane and D_{OH}, $D_{h\nu}$, D_{dep} and D_{rain} represent the removal of HCHO by the OH radical, photolysis, dry deposition and rainout and washout respectively.

where τ_{dep} = 27.8 hours and τ_{rain} = 71.9 hours are dry deposition and wet removal lifetime assumed in the HCHO diurnal model of Wuebbles, 1980, and $[HCHO]_o$ is the HCHO mixing ratio at the surface.

As shown in figure 20, the only active processes at night are dry deposition, rainout and washout. Without these processes, the HCHO mixing ratio would show little diurnal variation, because the steady state HCHO mixing ratio achieved during daylight would remain constant over night. Hence the intensity of a diurnal variation in the HCHO mixing ratio is a function of the strength of the deposition, rainout and washout processes removing HCHO from the troposphere. If the terms D_{dep} and D_{rain} are reduced, then the amplitude of the diurnal variation in the model shown in figure 19 decreases. However, the mean HCHO mixing ratio increases slightly moving the curve further away from the experimental data. Thus it seems unlikely that a false estimate of deposition or rainout and washout are the only causes of the discrepancy between the model curve and the experimental data shown in figure 19.

The mean HCHO mixing ratio is also sensitive to a change in the value of the OH radical mixing ratio. For example, an increase in the OH radical mixing ratio will at first lead to a net increase of the HCHO mixing ratio because the absolute difference between the production of HCHO from methane and the removal of HCHO by the terms shown in figure 20 increases. Because all the removal processes, including D_{dep} and D_{rain}, are of first order, decreasing the OH radical mixing ratio will also decrease the amplitude of a diurnal variation in the HCHO mixing ratio. A reduction in the OH radical mixing ratio used in the diurnal model will thus reduce both the mean HCHO mixing ratio and the amplitude of the diurnal variation, bringing the model curve and the experimental data shown in figure 19 into closer agreement. A false estimate of the OH radical mixing ratio used in the model therefore seems likely to be part of the cause of the discrepancy between the model and data shown in figure 19.

A further series of diurnal measurements of the HCHO mixing ratio were made in the vicinity of the equator from the 24th to the 28th of October 1980. The data are plotted as a function of time and latitude in figure 21. The samples were collected under clear cloudless conditions, except for a 3 hour period on the 26th of October when the Meteor sailed under a localised heavy bank of stratocumulus clouds (8/8 cover). The relative wind at the end of the boom was consistently from forward and averaged 20 knots. Also shown in the figure as the dashed curve is the same diurnal model shown in figure 19.

The data show rather irregular but persistant maxima during daylight which are better resolved than the case at 30 $^{\circ}$N. Because of the higher solar zenith angle and the liklehood of higher OH mixing ratios near the equator in October, the data of figure 19 could be expected to show bigger diurnal variations than the observations at 30 $^{\circ}$N. The correlation of the experimental data with the model is poor, but the prediction of higher HCHO mixing ratios during daylight is confirmed, thus demonstrating that the sources of HCHO in the clean troposphere are indeed photochemical in nature.

3.5 Vertical profiles of formaldehyde above the northern Eifel, F.R.G.

On four days in October and November 1979, two identical sets of sampling apparatus were installed in a Dornier D-28 aircraft. Three flights up to an altitude of 5 km were made above the northern Eifel district of the F.R.G. and one flight at an altitude of about 500 meters between Düsseldorf and Cuxhaven in northern F.R.G.

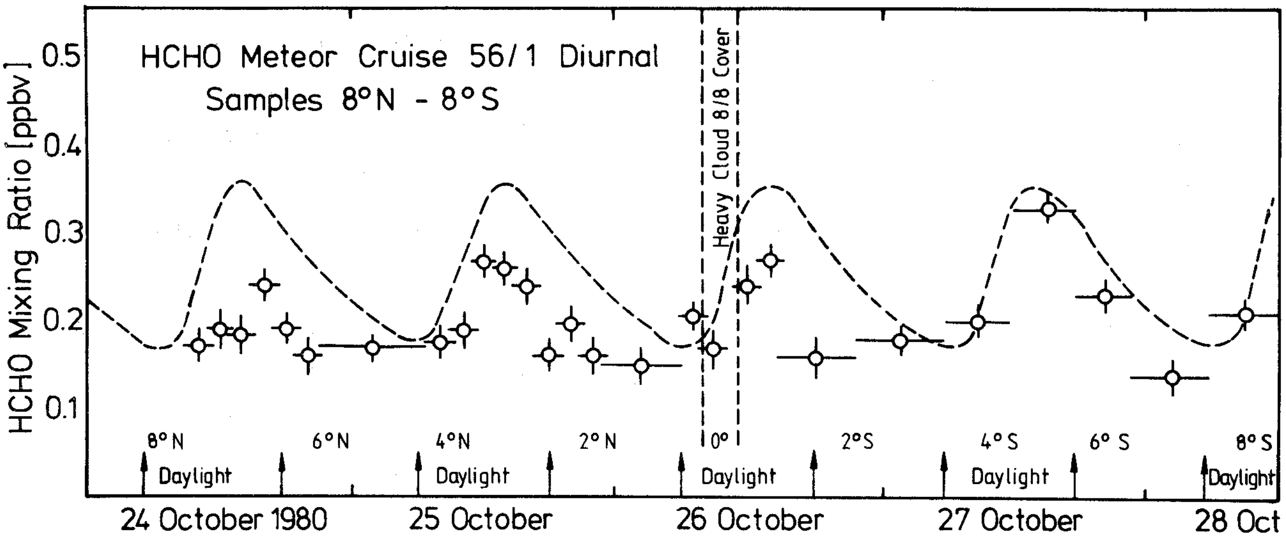


Figure 21: Measured and model diurnal variations of HCHO mixing ratio from 8 ^{o}N to 8 ^{o}S in the Atlantic, October 1980. The circles represent HCHO measurements with the vertical bars showing the experiment error of each measurement and the horizontal bars the duration of the measurements. The dashed curve shows predicted diurnal variations of the HCHO mixing ratio from a model developed by Wuebbles, 1980, for HCHO at the surface at 30 ^{o}N, solar equinox and with methane as the only source gas. Daylight conditions were bright sunshine except for a three hour period on the 26 October when the Meteor passed under a bank of heavy cloud as shown by the vertical dashed lines. Nighttime conditions were cloudless.

Each HCHO sample was collected over a one hour period and a total of 14 samples were collected including four sets of parallel samples. The results of the measurements and appropriate weather information are listed in table 6 of the appendix and plotted in figure 22.

At the time of these measurements the HCHO sampling and measurement technique was in an early stage of development and the error of the individual measurements was relatively high, of the order of ± 0.1 ppbv. In August 1980 two flights were made over the northern Eifel district at altitudes of up to 7 km using improved sampling equipment installed in a Piper Navajo aircraft as described in section 2.5. The results of the measurements and weather information are listed in table 7 of the appendix.

Over continental areas a temperature inversion above the ground may prevent penetration of contaminated air into the middle and upper troposphere. Hence HCHO measurements made above such an inversion can provide mixing ratios representative of relatively clean air above continental regions.
Figures 22 and 23 show the data listed in tables 6 and 7 from HCHO measurements made from the aircraft flights above the northern Eifel.
In figure 22 the HCHO mixing ratios measured below the inversion are higher than predicted by models. Whole air samples collected in parallel with these HCHO samples showed elevated values of CO, CO_2 and CH_4 indicating that the HCHO measurements had probably been affected by anthropogenic sources of HCHO. However above the inversion layer the HCHO mixing ratio was much lower at about 0.1 ppbv or less. Whole air samples collected in parallel with the HCHO samples above the inversion layer showed low values of CO, CO_2 and CH_4 indicative of relatively clean air.

In figure 23 the flight made on the 25th August 1980 shows a relatively constant HCHO mixing ratio of 0.1 ppbv from 4 km to 7 km altitude above a strong temperature inversion at 1.2 km. For comparison, a model prediction of the HCHO

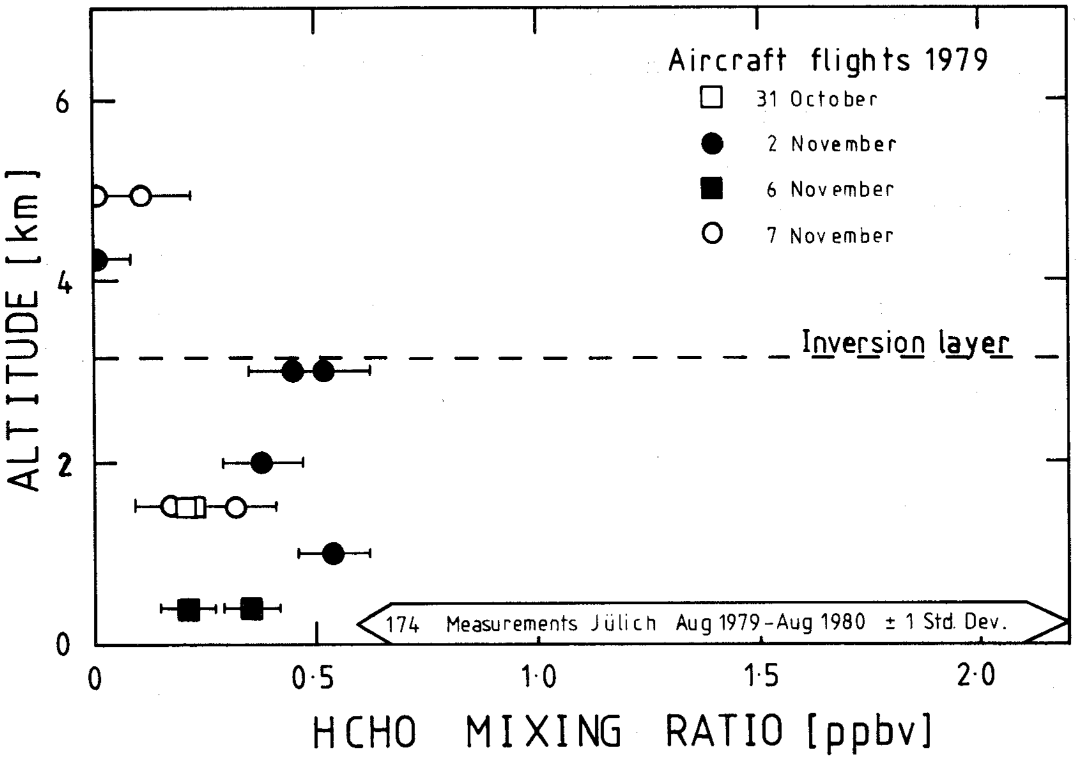


Figure 22: HCHO measurements in the lower troposphere during aircraft flights, 1979. The dashed line shows the height of the inversion layer on the 2nd and 7th of November 1979. For comparison the range of the HCHO measurements made outside the KFA laboratory is shown at the bottom of the figure.

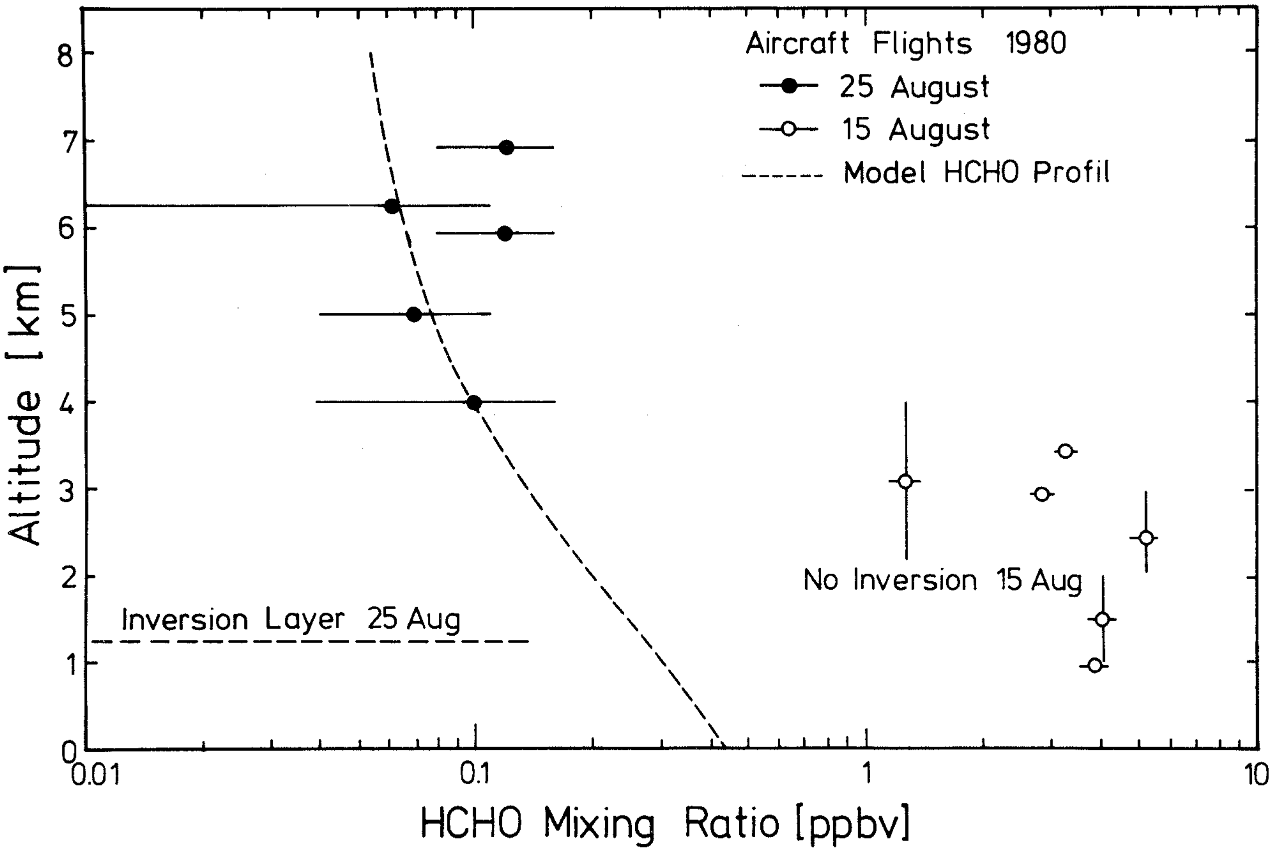


Figure 23: HCHO measurements in the troposphere above the northern Eifel district of the F.R.G., 1980. The dashed line shows the height of the inversion layer on the 25 August 1980 and the vertical dashed curve is a model profile of the HCHO mixing ratio from Wuebbles, 1980.

mixing ratio as a function of altitude at 30 °N, solar equinox at 12:00 (noon) with methane as the only source gas is also shown in the figure (Wuebbles, 1980). The agreement between the model and the experimental data is suprisingly good for the samples collected at lower altitudes but shows a discrepancy of about a factor of two at 7 km.

The discrepancy is probably caused by HCHO sources above the boundary layer which have not been included in the model. These sources are likely to include NMHCs. Rudolph et al, 1981, have found that alkenes and alkanes up to carbon number 5 may reach relatively high mixing ratios at 5 km in continental air, for example ethylene at 0.2 ppbv, despite the existance of a strong temperature inversion. At 5 km assuming an OH radical mixing ratio of 1 x 10^6 molecules $\cdot cm^{-3}$, oxidation of 0.2 ppbv of ethylene may lead to a source strength of 4.4 x 10^4 HCHO molecules$\cdot cm^{-3} \cdot sec$. This is about half of the source strength provided by methane oxidation at 5 km and demonstrates that NMHCs must be taken into consideration for any photochemical models predicting the HCHO mixing ratio over continental areas.

Also shown in figure 23 are the results of HCHO measurements made above the northern Eifel on the 15th August 1980 when no temperature inversion was present. Under these conditions vertical transport can move HCHO and its precursors generated by industry and combustion processes at the surface, into the middle troposphere. The results of the 15th of August flight show that relatively high HCHO mixing ratios may be found in the middle troposphere, for example 3.3 ppbv at 4 kms.

The processes determining the HCHO mixing ratio in the troposphere above a continent are obviously complex and model calculations must take tropospheric transport processes as well as the photochemistry of NMHC compounds into account. The two profiles shown in figure 23 demonstrate that the HCHO mixing ratio is very dependant on local conditions and sensitive to transport processes. Hence to determine the impact of NMHC compounds as a source of HCHO in the continental troposphere for example, simultaneous measurements of HCHO and NMHC mixing ratios, photon fluxes, NO_x and meteorological parameters must be made.

4. Conclusion

The sampling and analysis technique developed in this thesis has been found to be suitable for measuring the low mixing ratios and variations of HCHO in the clean troposphere. Adaptions of the technique have enabled measurements to be made at remote coastal sites as well as on board ship and aircraft.

A principle criterion has been to design and develop the technique so that it allows reproducible and efficient stripping of HCHO from about 2 m^3 of air into an aqueous sampling solution where the derivatisation with DNPHzine to produce the HCHO-DNPHzone product occurs directly.

A further criterion of the method has been to reduce chemical and physical handling of the sampling solutions to a minimum between the collection and analysis of the sample. This has been achieved by using the high efficiency glass sampler described in section 2.3., which removes HCHO from large volumes of air in a relatively short time. The resulting concentration of the HCHO-DNPHzine product in the sampling solution is thus high enough to allow direct injection of the sampling solution onto a HPLC column without further chemical or physical treatment of the solution. This has circumvented the problems of low variable recoveries and increased risk of sample contamination experienced after seperation by organic solvents and standard enrichment techniques at low sample HCHO concentrations.

Considering the current limitations of photochemical models, the surface measurements made using the technique show good agreement with the predicted HCHO mixing ratios in clean air. In particular when account is taken of probable uncertainties in values of the OH mixing ratio, diurnal measurements of the HCHO mixing ratio made in the mid Atlantic show good agreement with model calculations.

The limited number of vertical profiles made above the continental boundary layer, show that HCHO mixing ratios lower than 0.1 ppbv may be encountered. However the shape of predicted profiles of the available models is not confirmed by the experimental results, probably because of additional sources of HCHO not included in the models.

In order to better understand the significance of HCHO as an intermediate compound in the photooxidation schemes proposed for methane and NMHCs, other parameters need to be measured in parallel with HCHO. These include simultaneous measurements of NMHCs, methane, OH, NO_x, photon flux and meteorological parameters. In particular because of the probable important role of NMHCs in the troposphere, the most abundant and reactive species need to be identified and a study of their degradation schemes made.

Measurements of these parameters with the support of the HCHO measurements made by the technique developed in this thesis will help to provide a general understanding of hydrocarbon cycles in the troposphere.

APPENDIX

Formaldehyde results from Jülich, west coast of Ireland, New Zealand and above the northern Eifel district F.R.G. Tables 3 to 7

Table 3: Hourly average HCHO mixing ratio at Jülich, 31 January and 1 February 1980

Time C.E.T. (31. Jan. 1980)	HCHO in air (ppbv)	HCHO in rain (ng/ml)	Air temperature (^{o}C)	Wind direction (^{o})	Wind speed (m/sec)
04	0.28±0.02	40.4±0.5	6.0	120	4.0
05	0.24±0.02	30.3±0.5	5.5	115	4.5
06	0.36±0.02	45.1±0.5	5.0	160	2.5
07	0.32±0.02	60.0±0.5	5.5	210	7.0
08	0.43±0.03	12.2±0.5	9.0	215	8.0
09	0.29±0.02	25.2±0.5	10.0	215	7.0
10	0.30±0.02	-	10.0	215	7.5
11	0.37±0.02	-	10.5	215	7.0
12	0.21±0.02	-	11.0	215	7.5
13	0.22±0.02	14.7±0.5	11.0	220	7.5
14	0.23±0.02	-	7.5	215	6.5
15	0.17±0.02	-	8.5	210	5.0
16	0.20±0.02	-	8.5	195	6.5
17	0.14±0.01	-	9.0	195	5.5
18	0.11±0.01	35.5±0.5	8.5	195	7.5
19	0.08±0.01	-	8.5	200	8.5
20	0.18±0.02	-	8.0	210	9.0
21	0.23±0.02	-	8.0	215	10.0
22	0.16±0.02	-	7.5	220	10.5
23	0.25±0.02	45.4±0.5	7.5	230	11.0

Table 3: continued

Time C.E.T. (1 February 1980)	HCHO in air (ppbv)	HCHO in rain (ng/ml)	Air temperature (^{O}C)	Wind direction (^{O})	Wind speed (m/sec)
00	0.34±0.02	38.4±0.5	7.0	250	8.5
01	0.33±0.02	106.0±1.0	6.0	245	5.5
02	0.31±0.02	-	6.0	255	7.0
03	0.30±0.02	-	5.0	255	7.0
04	0.33±0.02	73.7±1.0	4.0	270	7.5
05	0.42±0.02	79.1±1.0	2.5	310	8.5
06	0.28±0.02	-	0.0	300	8.0
07	0.30±0.02	-	0.5	295	6.5
08	0.43±0.03	-	0.5	290	6.5
09	0.39±0.03	47.4±0.5 (snow)	-0.5	295	5.5

Table 4: HCHO mixing ratio at the west coast of Ireland, April 1980

Time G.M.T.	HCHO (ppbv)	Air Temp. (^{o}C)	Wind	Remarks
(25.4.80)				
13:25-14:25	0.28±0.02	14.0	light SW	Squall over the atlantic
14:30-15:30	0.26±0.02	14.0	"	
15:34-16:32	0.40±0.03	11.5	light NW	Showers over the atlantic
16:37-17:30	0.16±0.02	11.4	"	
17:31-18:22	0.28±0.02	10.8	"	Bright sunshine over sea and land
18:28-19:18	0.23±0.02	10.8	"	"
(26.4.80)				
12:34-13:32	0.21±0.02	11.0	"	Scattered cloud
13:36-14:30	0.27±0.02	11.0	"	"
14:32-15:28	0.32±0.02	11.2	light W	~ 4/8 Cumulus, sun visible
15:32-16:24	0.24±0.02	11.2	"	"
16:25-17:24	0.32±0.02	10.4	light NW	"
17:31-18:32	0.12±0.01	10.2	strong NW	light misty rain
(27.4.80)				
10:05-11:00	0.22±0.02	10.2	strong NW	~ 7/8 stratocumulus
11:05-12:01	0.16±0.02	10.2	"	"
12:03-12:58	0.13±0.01	10.4	mod. NW	bright sunshine
13:05-13:56	0.18±0.02	10.3	"	"

Table 4: continued

Time	HCHO (ppbv)	Air Temp. (^{o}C)	Wind	Remarks
(27.4.80)				
13:57-14:55	0.12±0.01	10.6	mod. NW	bright sunshine
15:00-15:55	0.14±0.01	10.2	"	"
15:57-16:58	0.15±0.02	10.6	"	~ 6/8 Cirrus
17:05-17:57	0.17±0.02	10.6	mod. NNW	"
20:10-21:11	0.18±0.02	9.8	strong NNW	sunset at 21:00
21:18-22:10	0.16±0.02	9.8	strong N	dark stormy weather, no rain
22:29-23:59	0.10±0.01	9.8	strong NNW	clear starry night, no clouds
(28.4.80)				
11:06-12:00	0.12±0.01	9.8	mod. N	~ 3/8 Cumulus, bright sunshine
12:06-13:02	0.09±0.01	9.8	"	"
13:03-14:00	0.11±0.01	10.0	"	"
14:07-15:00	0.14±0.01	10.0	"	"
(29.4.80)				
05:30-06:30	0.33±0.02	4.8	light SE	sunrise 06:25, clear sky
06:34-07:30	0.26±0.02	6.2	"	~ 1/8 Cumulus on western horizon
07:31-08:30	0.32±0.02	7.2	light NE	"
08:35-09:30	0.18±0.02	8.2	mod. NW	wind swung to NW at 08:10
09:31-10:50	0.23±0.02	9.0	"	cloud cover increases to full

Table 4: continued

Time	HCHO (ppbv)	Air Temp. (°C)	Wind	Remarks
(29.4.80)				
10:53-11:59	0.20±0.02	9.0	mod. N	~ 3/8 Cumulus
14:01-15:00	0.42±0.03	11.2	mod. NW	~ 1/8 Cumulus, bright sunshine
15:08-16:00	0.30±0.03	10.8	"	"
(30.4.80)				
10:50-11:35	0.45±0.03	10.6	light NW	~ 5/8 stratocumulus
11:40-12:35	0.52±0.04	11.4	"	"

Table 5: HCHO mixing ratio, Petone New Zealand, January 1981

Time	HCHO (ppbv)	Air Temp. (^{o}C)	Wind	Remarks
(7.1.1981)				
08:00-09:00	0.24±0.02	23	gale NW	~ Cumulus, bright sunshine
09:05-09:30	0.21±0.02	23	"	"
15:00-16:00	0.05±0.01	20	"	"
16:00-17:00	0.13±0.01	20	"	"
17:00-18:00	1.23±0.07	17	"	bright sunshine, smell of smoke
18:00-19:00	0.33±0.03	15	"	bright sunshine, wind gusts up to 40kts
19:00-21:00	0.23±0.02	16	"	"
21:00-23:30	0.35±0.03	15	"	sunset 20:45, clear starry night
(8.1.1981)				
06:00-08:15	0.38±0.03	16	"	bright sunshine, sunrise 05:30
08:15-10:50	0.19±0.02	18	"	"
10:55-12:00	0.22±0.02	23	strong NW	"
12:00-13:30	0.21±0.02	24	"	"

Table 5: HCHO mixing ratio, Baring Head light house, New Zealand, January 1981

Time	HCHO (ppbv)	Air Temp. (°C)	Wind	Remarks
(11.1.1981)				
16:00-18:00	0.10±0.01	23	mod. NW	bright sunshine
18:00-20:00	0.27±0.02	22	"	"
20:00-22:00	0.35±0.03	20	strong NW	sunset 20:45, dark starry night
22:00-23:59	0.35±0.03	16	"	clear night, no clouds
(12.1.1981)				
00:00-01:00	0.46±0.04	17	"	"
01:00-02:00	0.40±0.03	17	"	"
05:00-06:30	0.34±0.03	18	mod. NW	bright sunshine, sunrise 05:30
06:30-07:15	0.36±0.03	19	"	"
07:15-08:20	0.31±0.02	20	"	"
08:20-09:30	1.08±0.07	21	"	"
09:30-10:40	0.80±0.06	22	"	bright sunshine, wind to west at 10:00
10:40-12:00	0.19±0.02	22	mod. SE	bright sunshine
12:00-13:00	0.18±0.02	22	"	"
13:00-15:35	0.23±0.02	21	"	"

Table 6: HCHO mixing ratios, measured for aircraft samples collected over the Eifel, West Germany

Date and Time (1979)	Altitude (meters ASL)	Temperature (°C)	HCHO (ppbv)	Weather conditions
31 Oct. 15:30-16:45+)	1520	+ 4.0	0.23±0.11	Flight in light cloud
15:30-16:45	1520	+ 4.0	0.21±0.11	"
2 Nov. 13:20-14:10	1006	+ 2.5	0.54±0.08	Below cloud ceiling
14:20-15:25	2013	- 2.0	0.38±0.09	"
15:20-16:10+)	3020	- 4.5	0.45±0.10	Flight in cloud tops
15:20-16:10	3020	- 4.5	0.52±0.10	"
16:20-17:22+)	4240	- 10.5	0.01±0.07	Bright sunshine
16:20-17:22	4240	- 10.5	below det.	"
6 Nov. 10:45-11:40	380	+ 2.5	0.22±0.06	Cloudy, turbulent
12:20-13:10	410	+ 2.5	0.36±0.07	"
7 Nov. 11:20-12:10+)	1525	- 0.5	0.18±0.09	Bright sunshine
11:20-12:10	1525	- 0.5	0.32±0.09	"
13:00-13:40+)	4880	- 10.0	0.01±0.09	"
13:00-13:40	4880	- 10.0	0.11±0.11	"

+) two HCHO samples taken in parallel over the same time period

Table 7: HCHO mixing ratios measured for aircraft samples collected over Eifel, F.R.G.

Time	Altitude (meters)	HCHO (ppbv)	Air Temp. (°C)	Remarks
(15.8.1980)				
10:15-10ß28	915	3.94±0.15	+ 17	Clear sky above, brown haze on horizon
10:30-10:45	915-1980	4.03±0.16	+ 17 to + 12	" "
10:47-11:04	1980-2900	5.28±0.20	+ 12 to 0	" "
11:05-11:24	2900	2.83±0.11	+ 6	" "
11:30-12:00	3960	3.30±0.13	0	" "
12:02-12:23	3960-2130	1.27±0.05	0 to - 11	" "
(25.8.1980)				
12:50-13:15	3960	0.10±0.06	- 4	Flight well above haze in bright sunshine
13:22-14:08	4970	0.07±0.03	- 8	" "
14:13-14:58	5870	0.12±0.04	- 16	" "
15:02-15:50	6830	0.12±0.04	- 22	" "
15:54-16:23	6270	0.06±0.05	- 20	" "

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