

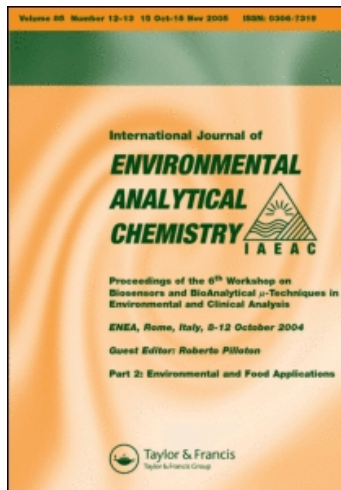
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# Vertical Distributions of Nonmethane Hydrocarbons Over Western Europe: Seasonal Cycles of Mixing Ratios and Source Strengths<sup>†</sup>

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Airborne measurements of the vertical and horizontal distributions of nonmethane hydrocarbons and methyl chloride over western Europe are reported. Annual emission cycles have been calculated from the seasonal variations of mixing ratios using a simple one-dimensional two-box model. They indicate natural sources of ethene, propene, *i*-butane, *i*-pentane, and methyl chloride. Grab samples were analysed by subambient temperature programmed gas chromatography.

**KEY WORDS:** Nonmethane hydrocarbons, methyl chloride, vertical distribution, annual emission cycles, seasonal variations.

## INTRODUCTION

Although nonmethane hydrocarbons play an important role in the chemistry of the unpolluted atmosphere as precursors for nitrogen

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containing oxidants,<sup>1,2</sup> as a source for tropospheric CO formation,<sup>3,4</sup> and as a sink for Cl atoms in the lower stratosphere,<sup>5,6</sup> relatively few measurements of light NMHC outside urban areas are available. Latitudinal distributions of selected NMHC have been reported<sup>7-10</sup> from the Pacific and from the North Atlantic, respectively, besides some measurements of the vertical profiles of light hydrocarbons in the troposphere.<sup>11-14</sup>

We will present additional airborne measurements of light hydrocarbons (ethane, propane, *i*-butane, *n*-butane, *i*-pentane, *n*-pentane, ethene, propene, and ethine) and methyl chloride. They were carried out over the North Atlantic off the coast of Norway, and in the Mediterranean region between September 1981 and September 1982. Since emission cycles rather than seasonal concentration trends should describe the activities of natural and anthropogenic sources, we calculated seasonal variations of the source strengths for the above-mentioned compounds in the Mediterranean area. Conclusions about the origin of the different NMHC are compared with their latitudinal distributions over the Atlantic, measured in April 1982 and in April 1983.

## EXPERIMENTAL

Samples were collected in evacuated stainless steel containers (2 dm<sup>3</sup>) which had been connected to a manifold aboard the airplane. Air was drawn through the manifold from the sample inlet outside the left front window by means of a Venturi tube. After conditioning the system for several minutes, sampling was performed by allowing the containers to fill up to atmospheric pressure.

Gas chromatographic analysis was carried out in the laboratory. From the sample container SC (see Figure 1) the trace gases contained in a known volume of air (calculated from measured temperature, pressure difference, and container volume) were trapped on an absorbent packed enrichment tube ET (15 cm  $\times$   $\frac{1}{8}$ " o.d. stainless steel, 5 cm Spherosil XOA 200, 5 cm Carbosieve B) which was cooled by liquid nitrogen. After thermal desorption by direct electrical heating to 250°C the compounds were transferred to the separation column CC (6 m  $\times$   $\frac{1}{16}$ " o.d. stainless steel, Spherosil XOB 075) by the carrier gas stream (He, 30 cm<sup>3</sup> min<sup>-1</sup>). Water was removed by passing the sample through a drying tube filled with

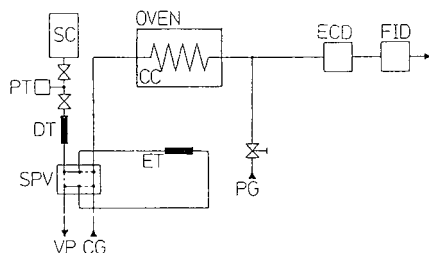


FIGURE 1 Gas chromatographic system. SC sample container, PT pressure transducer, DT drying tube, SPV six-port valve, VP vacuum pump, CG carrier gas, CC chromatographic column, ET enrichment tube, PG purge gas.

magnesium perchlorate. No change of sample composition could be observed using this drying reagent.<sup>5</sup> During sample desorption (10 min) the separation column was cooled by  $\text{LN}_2$  to  $-80^\circ\text{C}$ . A temperature program (ball. to  $-30^\circ\text{C}$ , hold 5 min,  $5^\circ\text{C min}^{-1}$  to  $60^\circ\text{C}$ , hold 10 min) was applied to separate the compounds. They were detected by flame ionization. Chromatograms were plotted by a strip chart recorder and evaluated by an electronic integrator. The samples from April 1983 have been analysed using a fused silica capillary column ( $60\text{ m} \times 0.32\text{ mm}$ , DB-1) connected to an ECD/FID tandem configuration. Calibration was performed by means of a static dilution system. Detection limits and reproducibilities for the different compounds are listed in Table I.

TABLE I  
Detection limits and reproducibilities for  $1\text{ dm}^3$  (STP) air samples.

Compound	Detection limit (pptv)	Reproducibility ( $\%$ , s.d.)
Ethane	17	0.9
Propane	15	1.6
<i>i</i> -Butane	8	2.1
<i>n</i> -Butane	9	2.3
<i>i</i> -Pentane	5	2.0
<i>n</i> -Pentane	6	1.9
Ethene	57	8.4
Propene	34	3.1
Ethine	75	6.0
Methyl chloride	100	4.4

## RESULTS AND DISCUSSION

Sampling locations are indicated in Figure 2. Vertical profiles are represented by squares, horizontal profiles by solid lines, respectively.

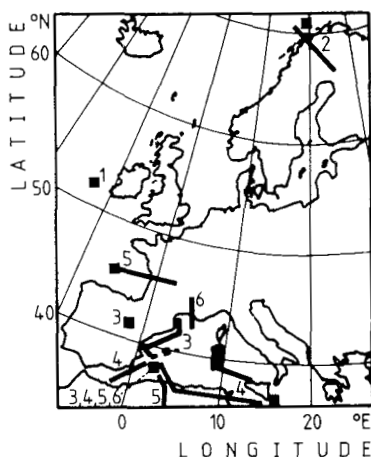


FIGURE 2 Sampling locations.

### Concentration distributions

To demonstrate some aspects concerning the vertical and horizontal distributions of NMHC, two sets of profiles are shown in Figure 3 and Figure 4. The other NMHC profiles will be published elsewhere.<sup>15</sup> Each profile presents data obtained during several flights which were performed within one week at the different sampling sites. Individual values are indicated by circles and rhombs, while the concentration ranges measured during horizontal flights are represented by lines.

The vertical profiles obtained over the Mediterranean area in December 1981 are representative for the distributions observed during our other flights except for the Norwegian ones. As can be seen from Figure 3, mixing ratios generally decrease with height above ground. Assuming the boundary layer to reach an altitude of about 1500 m, mean concentrations within the boundary layer  $c_{IBL}$

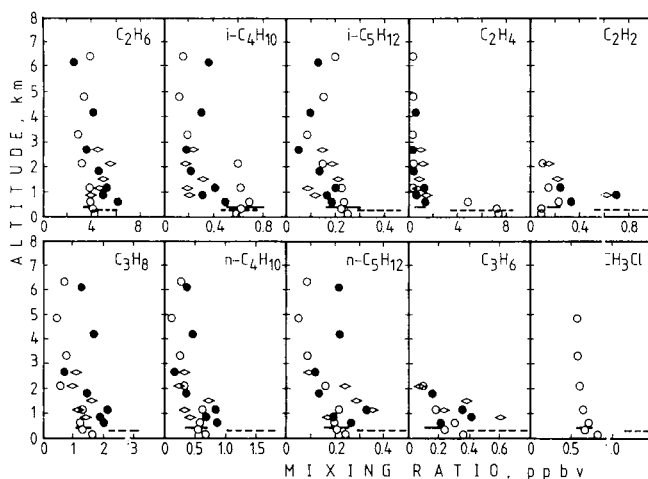


FIGURE 3 Vertical and horizontal distributions of NHMC, Mediterranean region, December 1981.

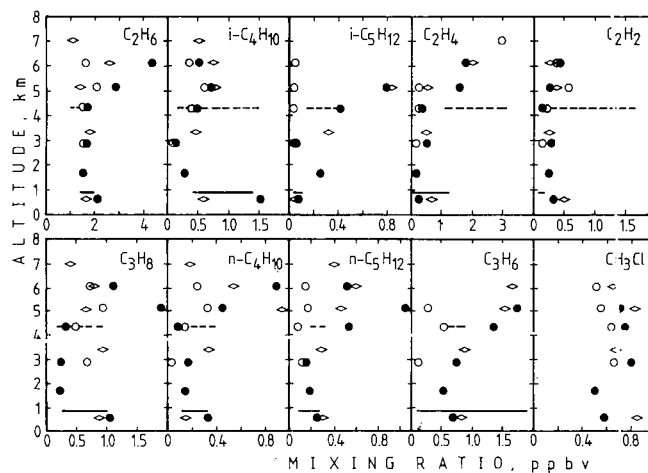


FIGURE 4 Vertical and horizontal distributions of NHMC, Norway, September 1981.

and above the boundary layer  $c_{\text{ABL}}$  can be determined. Whereas the total average of the ratio  $c_{\text{ABL}}/c_{\text{IBL}}$  is  $0.72 \pm 0.26$ , it approaches unity for the longer lived species (ethane, ethine, methyl chloride) and approximately 0.5 for the shorter lived ones. This is consistent with tropospheric residence times and large-scale mixing processes. The Norwegian profiles shown in Figure 4 exhibit a mean  $c_{\text{ABL}}/c_{\text{IBL}}$  ratio of  $1.33 \pm 0.73$ . Assuming that only ground level sources exist, the observed shape of the profiles cannot be assigned to large-scale transport and eddy diffusion only. As the calculated 48 hours backward trajectories showed that the air masses originated from North Atlantic and Greenland regions, direct anthropogenic contamination could be excluded. The observations may be explained however by the presence of a continuous, slightly scattered cumulus cloud layer covering the sampling area during that campaign. Under conditions like this, rapid cumulus cloud transport as suggested by Gidel<sup>16</sup> may be a significant upward mixing process causing the observed distributions.

During horizontal flights no significant trends with respect to geographical parameters have been found. The influence of meteorological conditions however could be observed during the flight along the Spanish Mediterranean coast on December 5, 1981. As depicted in Figure 5, the flight track crossed a cold front near  $41^\circ \text{N}$ . In the north of this point, characterized by a low-pressure area, concentrations were relatively high. This is indicated in Figure 3 by the dashed lines. Proceeding to the high-pressure area in the south of the front, concentrations decreased to values smaller by a factor of 2 to 5, as can be seen from the solid lines in Figure 3. The surface backward trajectories (48 h) calculated for  $41^\circ \text{N}$  (low pressure, circles) and for  $40^\circ 45' \text{N}$  (high pressure, squares) are shown in Figure 5. The northern trajectory crosses highly industrialized regions in France, while the southern one originates from the Atlantic and passes over rural regions in northern Spain. So the observed concentration differences as well as the trajectories confirm the different origins of the two air masses and their sharp separation by the front.

### Seasonal variations

For the discussion of the seasonal variations of concentrations and source strengths only data from the campaigns in the Mediterranean

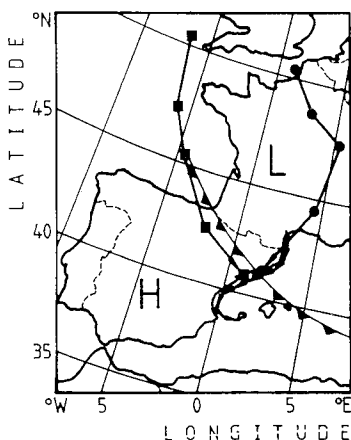


FIGURE 5 Meteorological conditions during the sampling flight on December 5, 1981, and backward trajectories.

area have been used because of the geographical distance to the other sampling sites.

The mean mixing ratios in (full circles) and above the boundary layer (open circles) for December 1981, March, July and September 1982, respectively, are shown in Figure 6. They have been calculated from the data obtained from each campaign. The error bars denote standard deviations.

Besides ethine and methyl chloride the hydrocarbons develop significant seasonal cycles of their mixing ratios. Different reasons for the seasonal variations of hydrocarbon concentrations in the troposphere have been proposed. Singh and Salas<sup>8</sup> pointed out, that the seasonal trend in propane and *n*-butane abundance they had measured is not inconsistent with OH seasonal gradients predicted by current models. The summer minimum and autumn to winter maximum Graedel and McRay<sup>17</sup> detected monitoring total organic carbon were proposed to be predominantly due to higher emissions in autumn by the decay of organic matter. Yet it is not possible to decide about the role of either process without dividing into the influence of emissions and of atmospheric removal mechanisms, respectively. Based on data on the seasonal OH and ozone variability,<sup>18</sup> on reported kinetic data,<sup>19-24</sup> and on our measurements we therefore



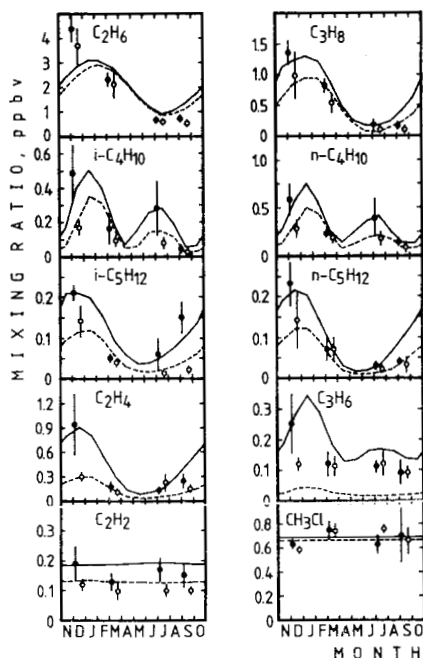


FIGURE 6 Seasonal cycles of mixing ratios in and above the boundary layer.

tried to estimate the seasonal variations of the source strengths of the different compounds for the latitude belt from  $35^{\circ}\text{N}$  to  $50^{\circ}\text{N}$ .

We employed a simple one-dimensional two-box model to represent the troposphere in and above the boundary layer. It is assumed that only ground level sources exist, and that there are no effective sinks other than reactions of NMHC with OH radicals and ozone. The model is given by the equations

$$\frac{dc_{\text{IBL}}}{dt} = S \frac{ART_{\text{IBL}}}{MV_{\text{IBL}}P_{\text{IBL}}} + \eta c_{\text{ABL}} - \left( \eta + \frac{1}{\tau} \right) c_{\text{IBL}} \quad (1)$$

$$\frac{dc_{\text{ABL}}}{dt} = \eta c_{\text{IBL}} - \left( \eta + \frac{1}{2\tau} \right) c_{\text{ABL}} \quad (2)$$

where  $c_{\text{IBL}}$  and  $c_{\text{ABL}}$  are the observed mixing ratios,  $\eta$  is a coefficient

determining the transport between the two boxes, and  $\tau$  stands for the season depending lifetime of the compounds according to

$$\tau = (k_{\text{OH}}c_{\text{OH}} + k_{\text{ozone}}c_{\text{ozone}})^{-1} \quad (3)$$

$S$  is the source strength in  $\text{g m}^{-2} \text{h}^{-1}$ ,  $M$  is the molecular weight, and  $R$  is the universal gas constant. The dimensions of the model boundary layer are given by a surface area  $A = 1 \text{ m}^2$  and a geometric volume  $V_{\text{IBL}} = 1500 \text{ m}^3$ . Physical conditions are fixed by a mean temperature  $T_{\text{IBL}} = 283 \text{ K}$  and a mean atmospheric pressure  $p_{\text{IBL}} = 930 \text{ hPa}$ . With respect to lower temperature and reactant concentrations the residence time above the boundary layer has been chosen to be twice the residence time within the boundary layer. For steady-state conditions the system can be solved for the source strength  $S$ .

In Figure 7 the calculated seasonal emission patterns are presented. Based on these cycles we will try to decide about the origin of the

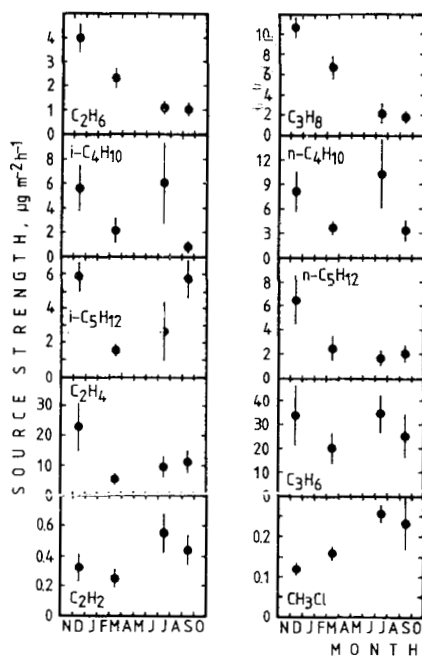


FIGURE 7 Seasonal cycles of source strengths.

individual trace gases, and we will check the results against the latitudinal distributions of the different compounds, shown in Figure 8.

According to sunlight intensity and temperature trend, compounds originating from biogenic processes should develop maximum emissions during summer. This holds for methyl chloride which is known to be emitted mainly from the oceans.<sup>10,25</sup> Though ethine shows a very similar seasonal variation, its summer maximum has to be assigned to a higher amount of automobile exhaust, since incomplete combustion is its only identified source.<sup>26</sup> These conclusions agree with the latitudinal distributions of the two compounds. Ethane, propane, and *n*-pentane develop winter maxima indicating enhanced release, probably due to fossil fuel burning. Latitudinal distributions also argue for sources within the northern hemisphere.

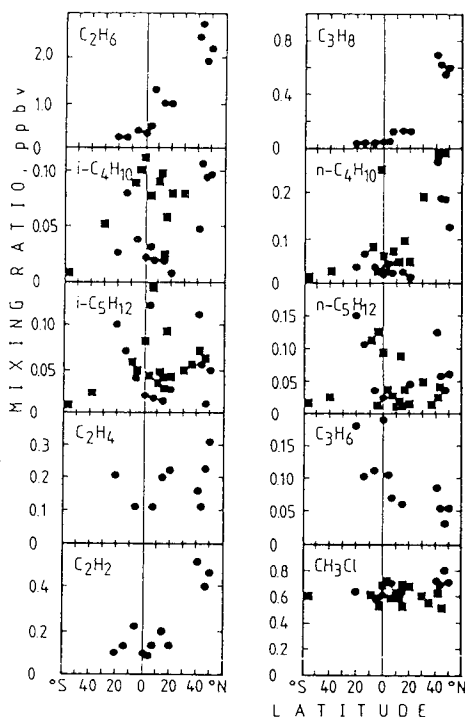


FIGURE 8 Latitudinal distributions of NMHC over the Atlantic.

The production of ethene and *i*-pentane begins to increase in early autumn already. An additional source appears to be suggested by this phenomenon, and we will shortly discuss the probability that it may be caused by a biogenic process.

Ethene is known to be released from foliage.<sup>27,28</sup> While its production from plants normally covers a range of approximately 0.6 to 6 ng g<sup>-1</sup> h<sup>-1</sup>, it increases to about 120 ng g<sup>-1</sup> h<sup>-1</sup> during ripening of fruits and during senescence and abscission of leaves.<sup>29</sup> Considering a foliage density of 400 g m<sup>-2</sup> in midlatitudinal deciduous forests,<sup>30</sup> source strengths of 0.2 to 2.3 μg m<sup>-2</sup> h<sup>-1</sup> can be estimated for summer. When vegetation dies in autumn, emission rates of up to 50 μg m<sup>-2</sup> h<sup>-1</sup> are not unlikely. Despite the large uncertainties inherent in the preceding considerations they show that there is evidence for significant natural contributions to the atmospheric ethene budget, reaching a maximum in autumn. The small north-to-south gradient, together with the relatively short residence time of ethene, confirm the existence of tropical, and, most probably, natural sources.

With respect to *i*-pentane the situation is even less clear. Since we do not know of considerable emissions from vegetation<sup>31</sup> or from soils,<sup>32</sup> its autumn increase may be regarded as an indication for the release of *i*-pentane during the decay of organic matter, especially leaves. Their annual amount in midlatitudinal forests can be estimated to reach about 4000 Tg yr<sup>-1</sup>.<sup>30</sup> Among the many organic compounds contained in leaves there are substances suitable as precursors for *i*-pentane. From zeatine, isopentyladenine, dihydrozeatine, and methylthiozeatine, compounds belonging to the class of cytokinines, it is known that the first step in their enzymatic decomposition is the elimination of their isopentyl side chain from the exocyclic amino group of the adenine system.<sup>29</sup> Probably there are other compounds present in biomass, that may yield *i*-pentane during degradation. One may think of the terpenes in this context. It should be emphasized that these considerations are highly speculative, but the latitudinal distribution of *i*-pentane does not at all rule out natural sources. They show up the necessity to determine the emissions of decaying organic matter in different natural environments.

The seasonal emission cycles of propene, *i*-butane, and *n*-butane show two maxima and can hardly be interpreted without further

background information. From their latitudinal distributions predominantly northern sources can be deduced for *n*-butane, while *i*-butane seems to be emitted more equally. For propene major sources in the tropics are to be supposed.

Another possibility to derive an estimation about the distribution of NMHC sources is to compare published values for global emissions to calculated annual emission rates for the latitude belt from 35–50° N. The results are shown in Table II. Despite large uncertainties in calculations and emission inventories the mainly anthropogenic origin of at least *n*-butane and *n*-pentane seems to be confirmed.

TABLE II  
Contributions from the latitude belt 35–50° N to global NMHC emissions.

Compound	Source strength ( $\mu\text{g m}^{-2} \text{h}^{-1}$ )	Emissions 35–50° N ( $\text{Tg yr}^{-1}$ )	Global emissions ( $\text{Tg yr}^{-1}$ )	Contributions from 35–50° N (%)
Ethane	2.3	1.0	5.0 <sup>a</sup>	20
Propane	5.9	2.5	4.0 <sup>b</sup>	63
<i>i</i> -Butane	3.9	1.7	—	—
<i>n</i> -Butane	6.5	2.8	2.4 <sup>b</sup>	117
<i>i</i> -Pentane	3.8	1.6	2.5 <sup>b</sup>	64
<i>n</i> -Pentane	3.4	1.4	1.4 <sup>b</sup>	100
Ethene	12.4	5.3	18.6 <sup>b</sup>	28
Propene	28.6	12.1	100.0 <sup>a</sup>	12
Ethine	0.4	0.2	1.0 <sup>a</sup>	20
Methyl chloride	0.2	0.1	1.9 <sup>c</sup>	19

<sup>a</sup>Penkett (1982).

<sup>b</sup>Ehhalt and Rudolph (1984).

<sup>c</sup>Crutzen and Gidel (1983).

In the course of source strength calculations the transport coefficient  $\eta$  had been eliminated as an unknown quantity. We determined a mean value of  $3.2 \times 10^{-3} \text{h}^{-1}$  for  $\eta$ , which yields a mean mixing time of 13 days for ground-level pollutants up to 5 km altitude. This is consistent with a widely used value of  $10^5 \text{cm}^2 \text{s}^{-1}$  for the vertical eddy diffusion coefficient.<sup>18</sup> To test the model,  $\eta$  has been introduced into Eqs. (1) and (2) together with time dependent loss and

production terms, which were approximated by sine functions. The model was then solved numerically with respect to  $c_{\text{IBL}}$  and  $c_{\text{ABL}}$ . The results are indicated in Figure 6 by the solid (IBL) and the dashed (ABL) lines and are in agreement with the measured values. The only exception is the propene abundance above the boundary layer. The reason for this may be the fact that the model does not include diurnal cycles, while the lifetime of propene is well within this time scale.

## CONCLUSION

Using a very simple model for production, loss, and transport mechanisms, respectively, it could be shown that there is evidence for the natural production of ethene, *i*-pentane, and methyl chloride at mid-northern latitudes. Natural sources cannot be ruled out for *i*-butane and propene. Based on measurements during four months within one year, these results can be considered as gross approximations only. The uncertainties show, however, that considerable effort is required to improve our knowledge of the biogeochemical cycles of hydrocarbons.

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