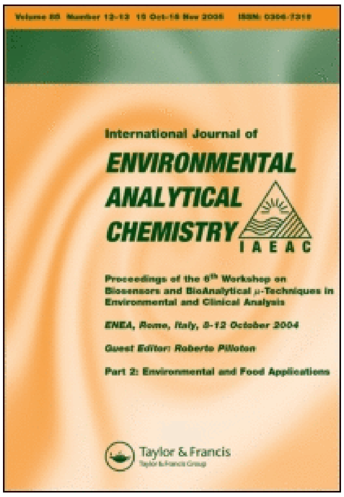

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Sources and Time-Variations of Reactive Hydrocarbon Immissions in the Atmosphere of Different Industrial and Rural Areas

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Sources and Time-Variations of Reactive Hydrocarbon Immissions in the Atmosphere of Different Industrial and Rural Areas†

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The problem of determining the concentration changes of reactive hydrocarbon immissions as a function of time was solved by means of an automatic gas chromatograph which, without enrichment, could record ethylene and acetylene in ppb concentrations. At the same time various other pollutants were covered, so that by a mutual allocation of the individual components it was possible to identify certain emitter groups. The results clearly show that ethylene and acetylene primarily originate from the combustion processes of the automobiles, while the handling and storage of petroleum products and their processing do not exert any influence on the immission of the two components. By way of time series measurements during a summer week in 1976 with very intensive solar radiation it was possible to show indirect secondary photochemical reactions.

KEY WORDS: Reactive hydrocarbons in the atmosphere, ethylene immissions, acetylene immissions, hydrocarbons emission sources, photochemical reactions of air pollutants, air pollution measurements, contributors of air pollutants.

INTRODUCTION

Photochemically reactive hydrocarbons, e.g. olefins and aromatics, contribute to the smog formation process and, not least for this reason, are classified as air pollutants. The special feature of this smog type is the occurrence of new substances, e.g. oxidants, etc.,—in contrast to the well-known London smog, which primarily contains SO_2 and suspended substances. In the presence of other air-alien substances in the atmosphere,

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e.g. nitric oxides, ozone, and under the effect of solar radiation, the reactive hydrocarbons react by way of secondary mechanisms. As a consequence of these photochemical reactions, products are formed and conditions are created which may cause harm to man, fauna and flora. The world literature on such reactions, their stoichiometry, rates and products is numerous and often even contradictory[1-34].

According to the literature the combustion processes especially in automotive engines and firing plants as well as the chemical industry are the main sources of the reactive hydrocarbons (this refers specifically to olefins). Thus, they are largely produced by human activity. In rural areas they are normally not existent in the air or only in very small amounts (5 ppb)[3,5]. While their concentrations in the atmosphere of urban and industrial areas remain within the range of traces, they may increase to hundreds of ppb, however.

REACTIVITY AND OCCURENCE OF INDIVIDUAL HYDROCARBONS IN AIR

The photochemical reactivity of these hydrocarbons primarily depends on the molecular structure and also on type and size.[18,10] Therefore, it is more reasonable to determine individuals and not groups or total classes, as shown in Figure 1. Here the relative reaction rates of the NO photo-oxidation of various hydrocarbon classes as a function of C number are shown.[7,18] The olefins have high reaction rates which depend heavily on the molecular structure and which always substantially exceed that of the paraffins and also that of the aromatics. For the end olefins a clear maximum is observed at carbon numbers around three to four, i.e. in the range of the propylene and the butene. The formation of pollutants such as aldehydes, oxidants and PAN (peroxyacetylnitrates) compunds during these reactions proceeds in a way approximately parallel to that of the curves shown. The most reactive are the middle olefins.

Figure 2 shows the relative reaction velocity for ethylene, propylene and butene with ozone. The reactivity of the ethylene seems to be relatively small, however, in respect of the significance for smog formation, reactivity and concentration in air are decisive. In fact, the concentrations of the ethylene are almost always far higher than those of other olefins.[34] Thus, ethylene gains in importance as one of the most significant initial reactants for the secondary photochemical reactions in air. *Acetylene* is classified as photochemically not reactive[22] together with benzene and the C_1/C_3 paraffins.

For determining the concentration changes as a function of time for some unsaturated hydrocarbons it was necessary to determine the values

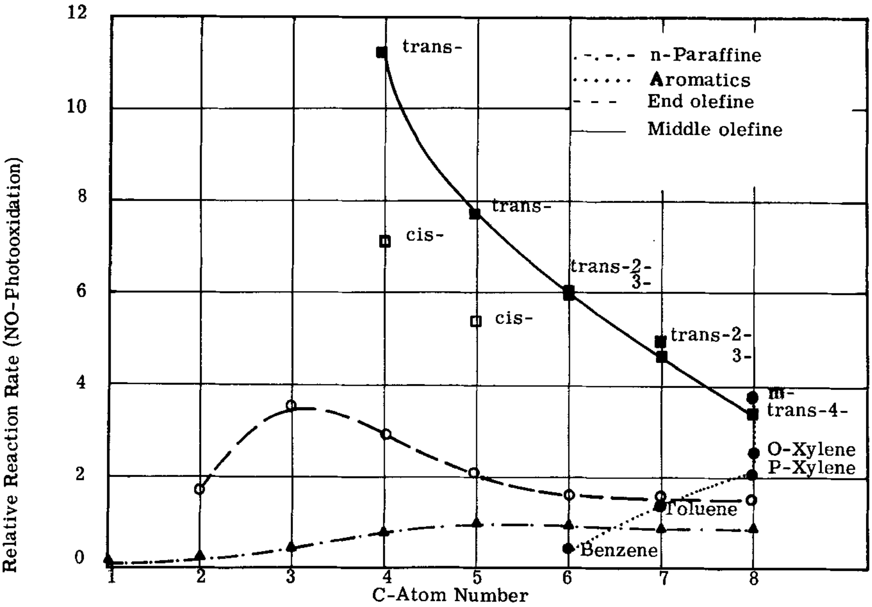

FIGURE 1 Relative reaction rates of hydrocarbons with NO during photooxidation as a function of C-atom-number.

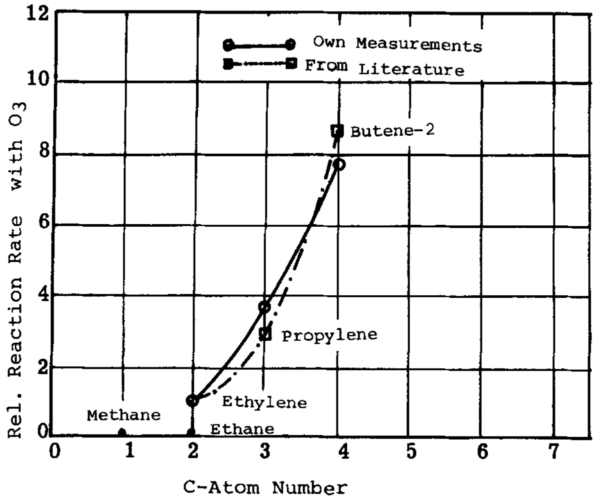

FIGURE 2 Relative reaction rates of the olefins ethylene, propylene and butene-2 with ozone.

in a chronologically close sequence and, if possible, automatically. For this reason the number of the individual hydrocarbons was restricted to 2: ethylene and acetylene, for the reason that both of them occur in such a relatively high concentration in air that no enrichment is necessary.

MEASURING METHOD

For the direct selective immission measurement of hydrocarbon traces in air, the Beckman Air Quality Chromatograph, model 6800 with *F*lame *I*onization *D*etector (FID) was used. For the separation of the individual components, steel columns filled with Porapak Q and N as well as with silica gel were used. The separation and measurement process as well as the analysis sequence are cyclic and automatic. The cycle time for three components (TOC = Total Organic Compounds, CH_4, CO) is 5 minutes and for 5 components (TOC, CH_4, CO, C_2H_4, C_2H_2) 10 minutes. Figure 3 shows a section of a cyclic multi-component chromatogram. Maintainance of cycle time as well as analysis flow is ensured by electronically controlled dosing and column switch valves.

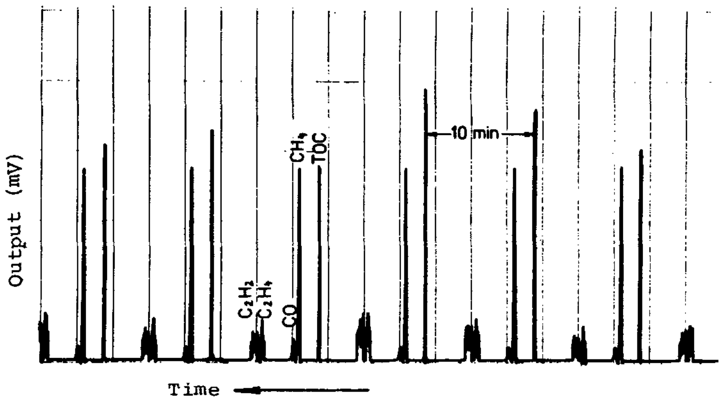

FIGURE 3 Chromatogram of the cyclic analyses of total organic compounds (TOC), CH_4, CO, ethylene and acetylene.

All equipment parts coming in contact with the air sample are of Teflon or stainless steel. The equipment operates isothermally. The oven temperature is thermostated at about 50°C. The lower measuring limit of the Beckman Air Quality GC is stated by the manufacturers as being 5 ppb, which has been confirmed by numerous tests of our own. The required volume flow of the sample gas is pumped by a Teflon diaphragm pump installed in the equipment at a rate of about 5 l/min. The sample volume for separation and identification of the individual components amounts to 1 to 5 ml. The calibration of the equipment is made by way of commercial calibration gas mixtures in the ppm range. Ppb calibration gas concentrations can then be produced by further dilution through gas mixing devices, e.g. Wösthoff pumping and dosing device with rotating cock.

The gas chromatograph together with other measuring instruments for SO_2, NO_x, suspended particles, H_2S, CH_3SH and for the meteorological parameters were installed in a mobile van, which by means of a battery system with converters allowed an independent operation of about 30 hours.

The measuring results were stored in a storage unit before they were called and printed out periodically and automatically. The evaluation was then made either manually or by computer.

RESULTS AND DISCUSSION

A great number of immission measurements have been made since 1973. From the abundant data available we have selected parts representing, in a characteristic form, the concentration changes of ethylene, acetylene and other air pollutants, as function of time.

Figure 4 shows a typical diurnal variation of the immission concentrations in a Hamburg one-way street under heavy bus and passenger car load. Ethylene increases up to a maximum concentration of 150 ppb, acetylene up to 200 ppb. The maxima are typically traffic-dependent because they occurred during the usual rush hours in this street and moreover show a very good correlation with the immissions of CO and total hydrocarbons.

The night concentrations of ethylene and acetylene dropped to values around 10 to 20 ppb, which for the southern part of Hamburg represents a normal concentration in spite of the small traffic volume still existent. The decline in the traffic load is confirmed by a drop in CO immission during the night. With these measurements the influence of home heating and industry has been eliminated, because on the one hand the temperatures were over 20°C and on the other the wind direction was favourable for this purpose.

The diurnal variations of ethylene and acetylene at a large service station (Figure 5) show a similar picture: Definite peaks during rush hours. As the two components in question are not emitted during filling-up of the motor vehicles, the engine combustion is responsible again. In(34) it has been proved that ethylene and acetylene are not present in commercial motor gasoline. The concentrations at the filling station are considerably lower than in a city street, but in comparison to Figure 4 the

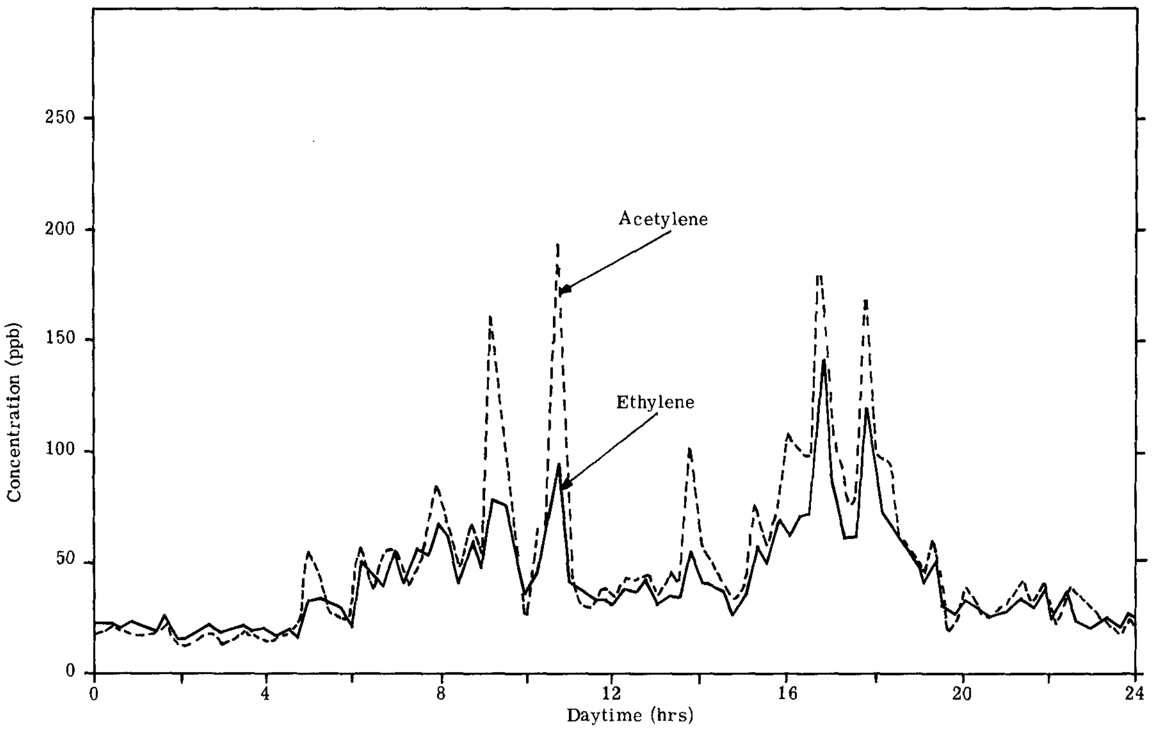

FIGURE 4 Typical diurnal variations of the immissions of ethylene and acetylene at one-way-street in Hamburg-Harburg with high traffic load.

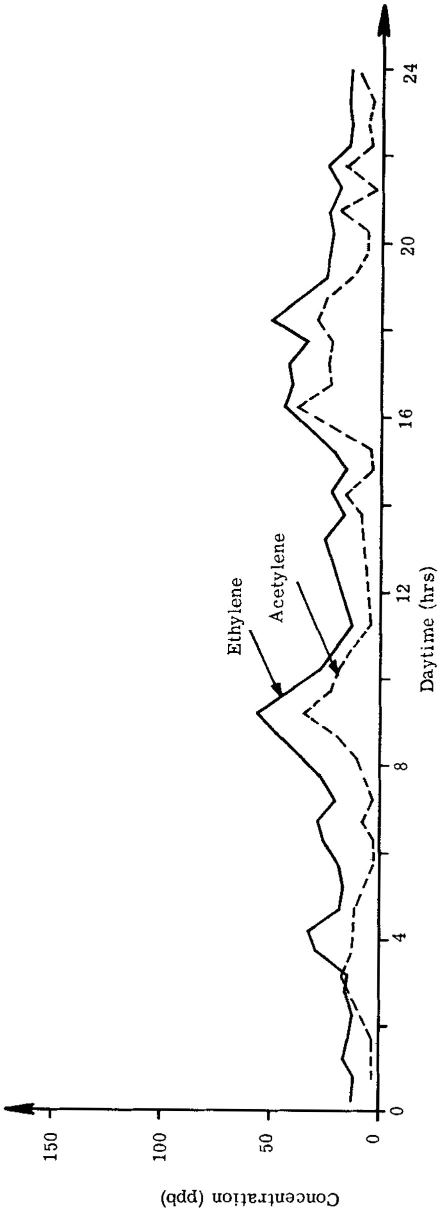

FIGURE 5 Typical immission of ethylene and acetylene as a function of the daytime (self service station in Hamburg).

ethylene concentrations are higher than those of the acetylene here. This phenomenon can be explained by the fact that in the case of idling and low-lead modes of the engines, the thermodynamic conditions are milder and thus rather favour an ethylene formation. The influence of a nearby main traffic road on these measurements was eliminated by the selection of a suitable wind direction.

Figure 6 shows the immission concentrations of the two components over a week in the industrial area of Minden, a medium-sized town located at a relatively great distance from large agglomeration areas. Although there were no roads with a very high traffic load in the immediate neighbourhood of the measuring point, the peak concentrations in the morning and in the early evening were definite. Since it can be assumed that the industry emits evenly over the whole day, the more distant and the nearby traffic must be responsible. During the night, values around 5 ppb were reached.

Figure 7 shows the concentrations of NO_x, ethylene and acetylene during a week in June 1976 in extremely hot weather. The measurements were made at the western boundary of the Hamburg industrial area. With SW-winds, no industry emissions and only small traffic emissions exerted an influence, while with north to east winds the emission of the industrial area exerted a heavy influence. The increase in atmospheric temperature to over 30°C during this week was combined with very strong solar radiation and weak winds. In spite of this fact the following pollutants remained more or less constant in the course of the week, apart from usual daily variations: acetylene, CO, CH_4, SO_2, TOC (Total Organic Compounds).

However ethylene was different: During the SW-wind situation i.e. rural direction, the concentration remains constant and amounted to about 20 ppb, which can be considered as the glc of the residential and rural areas, while the north-east wind was prevailing, i.e. industrial, city and dense traffic direction, an increase in the ethylene concentration of about 20 ppb was observed.

These 20 ppb can be considered as the direct contribution of a big industrial area and remote traffic to the concentration of ethylene in the atmosphere at distance of about 1 km from emission sources where the measuring station was located.

Home heating cannot have any influence under the measurement conditions. The increase in the NO/NO_x ratio during the week is apparently due to the solar radiation which dissociates NO_2 to NO and O. The O atoms react quickly with the oxygen of the air and thus, by way of the formation of ozone, constitute the beginning of a photochemical reaction chain. It was not possible to determine how much of the ethylene

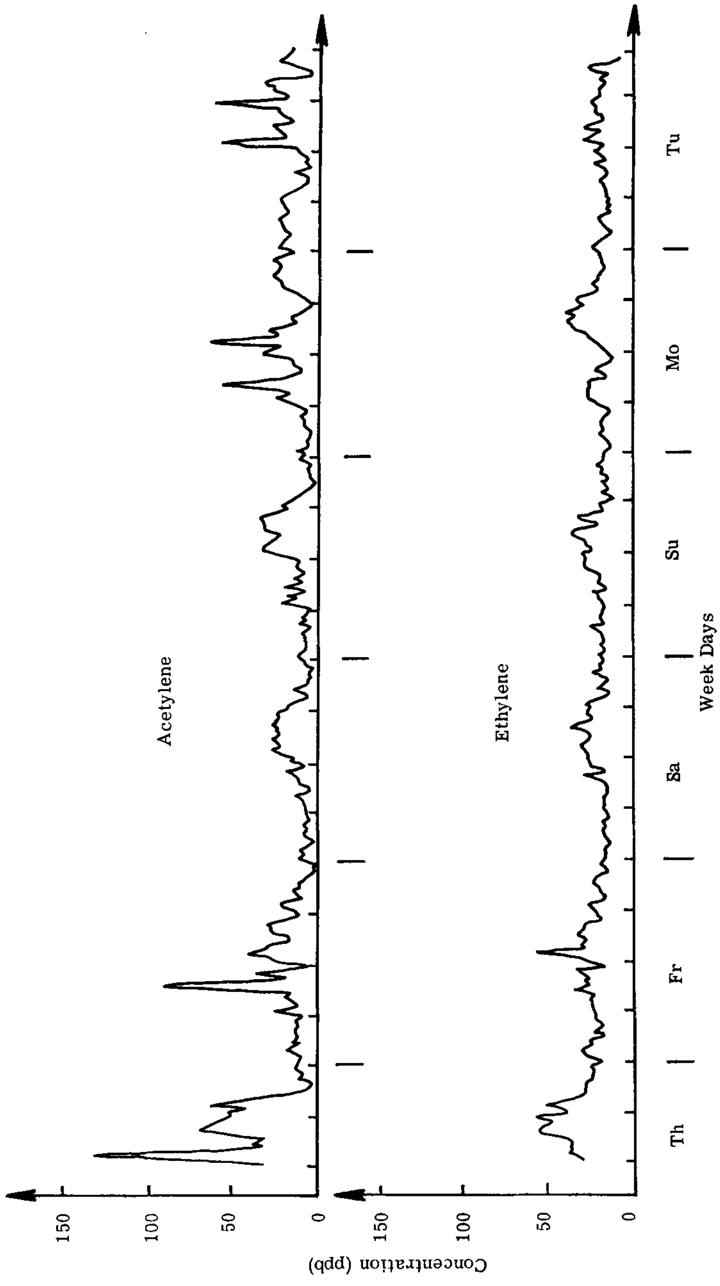

FIGURE 6 Weekly variations of acetylene and ethylene (April 1974) ESSO-Bulk plant in Minden, FRG.

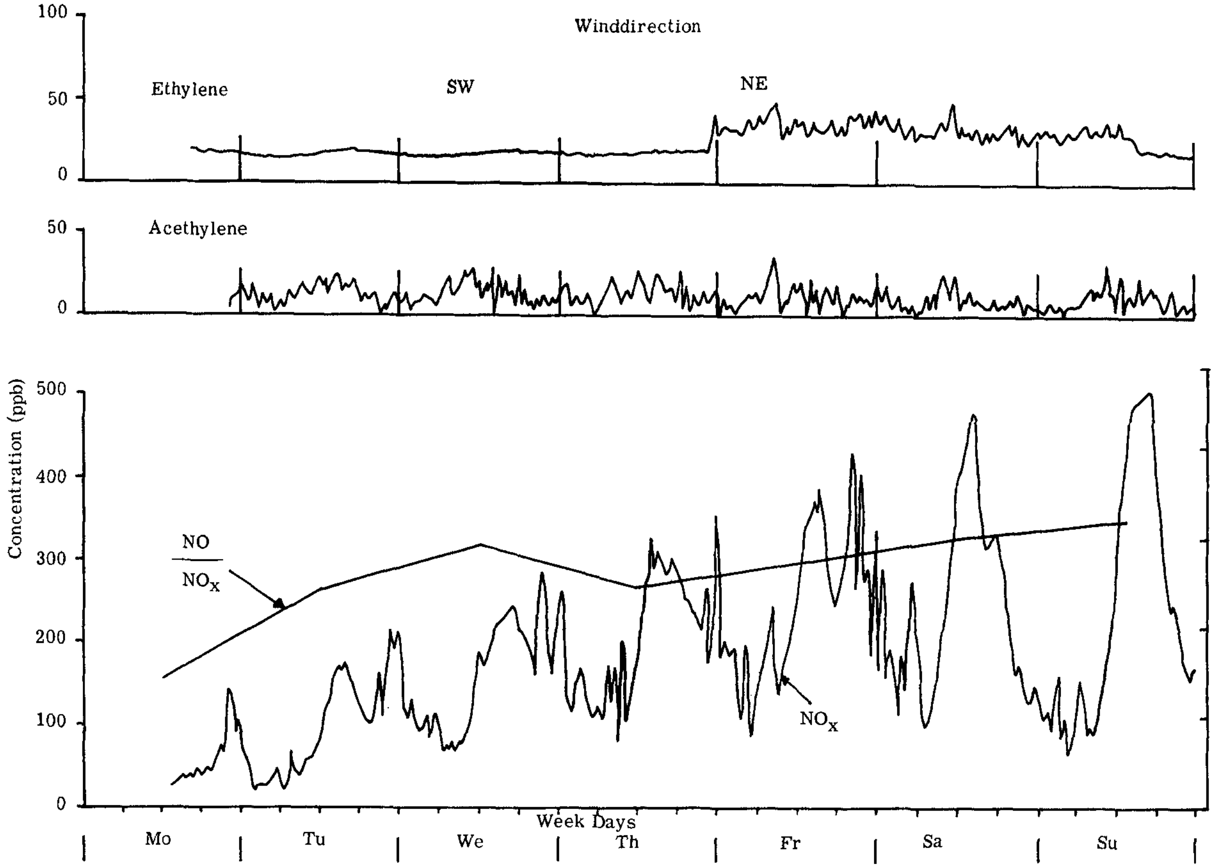

FIGURE 7 Weekly variations of the immissions of C_2H_2, C_2H_4 and NO_x during extremely hot weather with high radiation intensity (Summer 1976). Industrial area of Hamburg and Hamburg refinery.

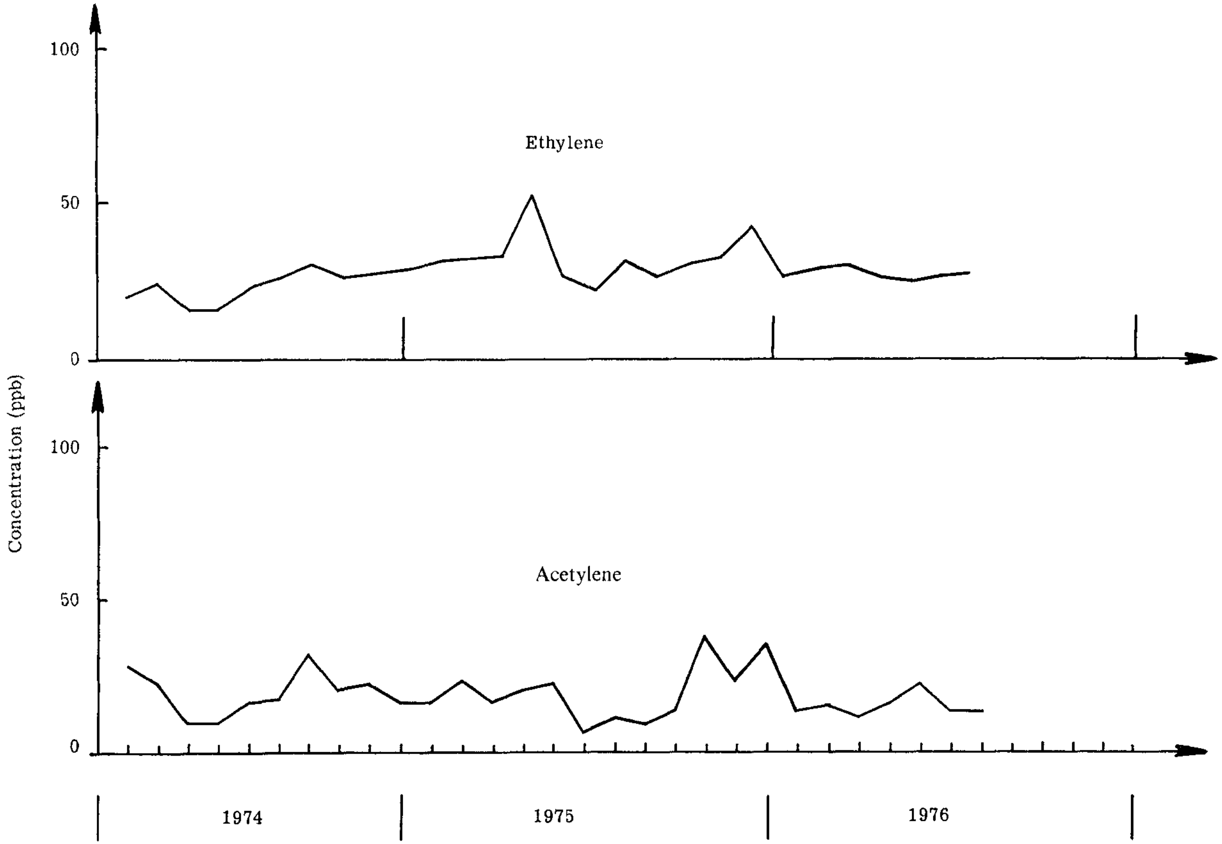

FIGURE 8 Monthly means of ethylene and acetylene over 3 years. Industrial area of Hamburg and Hamburg refinery.

TABLE I

Ethylene concentrations in the atmosphere of different areas

Location	Ethylene concentrations ppb		Date of Measurement	Reference
	Means	*Max. Values*		
Los Angeles	60	125	9–11/1961	(23)
Saarbrücken	440	—	1972	(24)
Den Haag (Holland)	17–21	—	1973/1974	(25)
Delft (Holland)	15–22	—	,,	,,
Los Angeles	54	77	1967	(26)
Los Angeles	102	>180 ($C_2H_4+C_2H_6$)	1967	,,
Azuza (Los Angeles Basin)	20	21	1967	,,
Gelsenkirchen-Buer (FRG)	112	–($C_2H_4+C_2H_6$)	1975	(27)
Hüls (Marl) (FRG)	88	131 ($C_2H_4+C_2H_6$)	1970/1971	(28)
Los Angeles	52	122	1967	(29)
St. Louis Area (USA)	68	–(background 6,4 ppb)	1972	(30)
Los Angeles	60	—	1965	(31)
	Mean Value of 216 Samples			
California	18	66	1968	(32)
Swansea area (South Wales, England)				
(a) Near domestic housing	280	410	1973	(33)
(b) On or near main roads	280	320	,,	,,
(c) On hillsides	200	220	,,	,,
Los Angeles	54	165	1973	(34)
Washington	39	100	1973	(3)

TABLE II

Ethylene concentrations in the atmosphere of different areas (EAG's measurements)

Location	Ethylene concentration (+) ppb Mean value	 Max. value	Date of Measurement
Hamburg-Harburg (Upwind of the industrial area)	19	21	June 1976
Hamburg-Harburg (Downwind of the industrial area)	33	50	June 1976
Hamburg-Harburg (City center)	41	141	Feb./Mar. 1974
Ingolstadt (Refinery area)	19	42	May/June 1976
Karlsruhe (Refinery area)	21	39	May/June 1976
Osterwald-Emsland (Crudeoil fields)	20	41	June 1976
Minden (Bulkplant area)	25	44	April 1974
Rendsburg (Bulkplant area)	25	45	August 1974
Wilhelmshaven (Tanker terminal)	34	65	February 1976

(+) These results are averages of longterm measurements, based on 1/2 h-mean values.

could have photochemically reacted in the time between emission and measurement. Further clarification can only be obtained by way of detailed measurements of the reaction products, such as ozone, aldehydes and PAN.

Figure 8 shows monthly mean values of ethylene and acetylene during a 3-year period at the same Hamburg measuring point at the SW-boundary of the industrial area. A slight seasonal variation can be observed: In summer both components have a minimum—an indication of a possible conversion through photochemical reactions. Any influence of home heating must be denied, however, because the maxima do not fall in the winter time. The SO_2 concentration, which is not shown here, indicates a clear increase in winter which cannot be explained by unfavourable spreading conditions in winter.

Figure 8 shows further that the concentration of ethylene and acetylene has remained constant over the last three years although a considerable part of the emitters in this area is constituted by petroleum and other chemical industries. At the same time it can be seen that the values are definitely low compared with values from the literature (Table I) and measurements of our own at other points, e.g. city centers and main roads (Table II).

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