VOLVO	SAAB
AUTOMOTIVE	INDUSTRY
EMISSIONS	POLLUTION
SOLVENTS	XYLENE
SAMPLING	ANALYSIS
HEALTH	HAZARDS

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Ambient hydrocarbons from motor-car assembly plants in Scandinavia

Göran Petersson

Hydrocarbon emissions from the automotive industry were major
environmental issues in Sweden during the period 1978 - 1986.
National reports in Swedish include
Kolväten från SAAB
Volvo i Uddevalla

AMBIENT HYDROCARBONS
FROM MOTOR-CAR ASSEMBLY PLANTS
IN SCANDINAVIA

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ABSTRACT

About fifty air-polluting hydrocarbons were determined in immissions from the Volvo and Saab motor-car plants. The sampling technique used was based on the Tenax GC adsorbent. Thermal desorption and glass capillary gas chromatography was used for the analysis.
At a downwind distance of about 1 km, concentrations about 100 times higher than regional levels were recorded. The emissions constitute potential ecological and health hazards and a reduction of quantities and complexity is urgent.

INTRODUCTION

Motor-car plants give rise to large emissions of hydrocarbons originating primarily from solvents used in the painting procedure. Both the hydrocarbons and secondarily formed air pollutants may have harmful effects on health and environment. The present study gives a detailed account of the complex composition of hydrocarbons and also illustrative examples of concentrations and spreading. Ecotoxicological aspects are discussed. In some respects, the report is comparable to a recent study of a large General Motors assembly plant in the Unites States (Sexton and Westberg, 1980).

The Scandinavian motor-car assembly plants of Volvo and Saab are both situated in south-west Sweden. The Volvo plant is located on the West Coast in Göteborg, the second largest Swedish city with about 400 000 inhabitants (Fig. 1). The Saab plant is located between the towns of Vänersborg and Trollhättan, each with about 50 000 inhabitants (Fig. 1). This region lies about 80 km north-east of Göteborg and just south-west of the largest Swedish lake, Vänern.

Rough estimates of the total yearly hydrocarbon emissions are 3000 tons for Volvo and 1500 tons for Saab. Potential health and environmental effects of the emissions from Volvo have lately been the subject of much debate in the region.

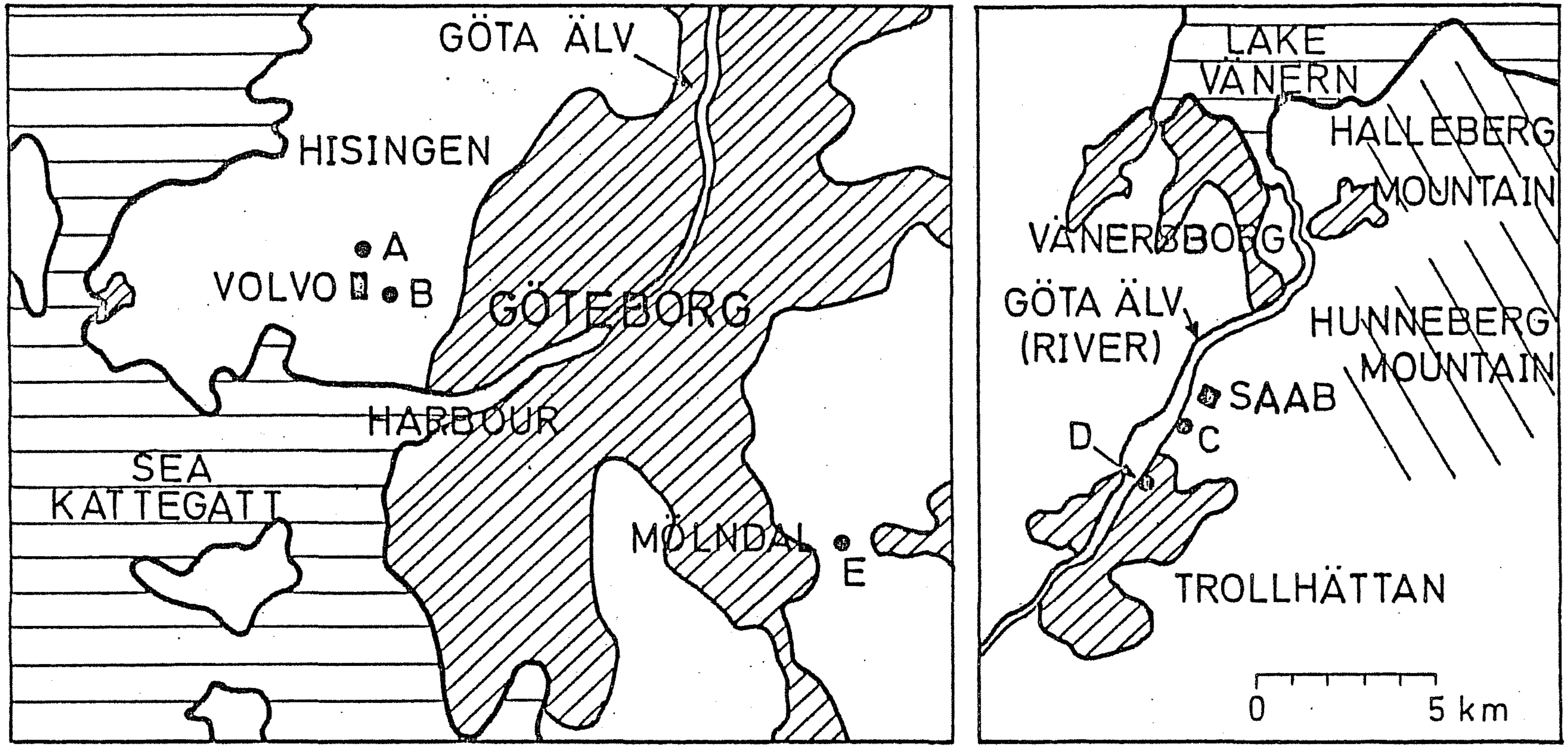

Fig. 1. Location of motor-car plants and sampling points.

METHODS AND MATERIALS

The analytical technique was based on the adsorption of air pollutants at the sampling site and thermal desorption, combined with gas chromatographic analysis in the laboratory.

Adsorption. Sampling was accomplished using a personal monitoring pump (MDA, Accuhaler 808) coupled to a glass tube filled with approximately 0.1 ml of Tenax GC (60-80 mesh). This porous polymer is widely used as an adsorbent (cf. Versino *et al.*, 1976). Normally, accurately determined volumes of between 0.1 and 1 litres were taken, and the air flow was of the order of 10 ml/min. Under these conditions and at the prevailing ambient temperatures, adsorption was quantitative with most C_6 and all C_7 and higher hydrocarbons (Brown & Purnell, 1979). During transport, the adsorbent tubes were doubly enclosed in glass tubes and glass bottles with tight-fitting glass stoppers to prevent undue adsorption. Before sampling, the adsorbent tubes were conditioned for a few minutes at 200°C with helium in the gas chromatograph. First-time conditioning was made at 250°C over night.

Desorption and gas chromatography. A Carlo Erba 2920 gas chromatograph with a flame ionization detector was used for the analyses. The column (RSL, Belgium) was a 50 m x 0.25 mm i.d. glass capillary with OV-101 as stationary phase. The adsorption tubes were original glass liners of the chromatograph, and thermal desorption was achieved by placing them in the injector at 200°C and passing carrier gas (He) through. The oven was kept below zero before and during the first few minutes of desorption by blowing carbon dioxide into it. Linear temperature programming, 2°C/min from 0°C, was applied.

Quantitative and qualitative analyses. A Hewlett-Packard 3380 A integrator was used for recording the chromatograms and for automatic integration. A single response factor was determined by analysing diluted solutions of representative aromatic hydrocarbons. The total analytical error in the reported concentration of a hydrocarbon depends on several factors. Except when the amount adsorbed was very small, it is estimated that very few concentrations given are too high and also that very few are lower than 60-70% of the true values.

Identifications were made by cochromatography with authentic hydrocarbons, by comparisons with literature data, by theoretical considerations of retention data, and by gas chromatography-mass spectrometry of selected hydrocarbon mixtures. Small deviations from methyl silicone retention data were obtained because of deactivation with Carbowax after straightening of column ends before installing the column.

RESULTS AND DISCUSSION

Hydrocarbon composition of immissions. The results given in Table 1 illustrate the composition of C_6-C_{14} hydrocarbons which is fairly similar for the two plants. Variations with time were found to be moderate. The regional sample was taken so as to avoid influence from the motor-car plants and significant contributions from near-by traffic and houses.

The solvents used in the industries are to be almost free of benzene according to work hygienic regulations. Therefore, benzene is likely to originate mainly from the evaporation of petrol and from car exhaust. Cars are present in considerable numbers within and outside both plants. Significant contributions of the same origin are to be expected for the hexanes and toluene.

Toluene, the xylenes including ethylbenzene, and the eight C_9 alkylbenzenes are the quantitatively most prominent components. They originate mainly from the emissions of the spray booths. The characteristic analytical region where these hydrocarbons appear is shown in Fig. 2 for the sample from Volvo. In Fig. 3, the C_9 region and the complex C_{10} region are shown for the sample from Saab.

The aromatic hydrocarbon pattern differs from that of petrol and motor--car exhaust in Scandinavia by a shift towards heavier components. Conspicuous specific differences are the presence of tetrahydronaphtalene and the low concentration of o-xylene. Compared with those of the American study of a large plant (Sexton and Westberg, 1980), the results differ primarily by proportionately higher concentrations of the heavy aromatic hydrocarbons and lower concentrations of toluene.

Table 1. Hydrocarbons from Swedish motor-car assembly plants. Concentrations($\mu g/m^3$) in downwind air compared with regional air.

Aromatic hydrocarbons	*Saab*[a] *nearby*	*Volvo*[b] *1 km (A)*	*Göteborg*[c] *regional (E)*	*Non-aromatic hydrocarbons*	*Saab*[a] *nearby*	*Volvo*[b] *1 km (A)*	*Göteborg*[c] *regional (E)*
Benzene	5·1	3·1	0·93	*n*-Alkanes			
Alkylbenzenes (C_7–C_9)				Hexane	45	2·1	0·34
Toluene	69	11·9	1·22	Heptane	20	1·2	0·16
Ethylbenzene	86	27·8	0·23	Octane	4·3	2·3	0·09
Xylene (*m*,*p*)	264	85·1	0·58	Nonane	9·5	7·2	0·11
Xylene (*o*)	38	11·6	0·21	Decane (8)[d]	13	12·6	0·10
i-Propylbenzene (1)[d]	4·5	0·6	0·02	Undecane (20)	8·8	5·3	0·06
n-Propylbenzene (2)	18	2·6	0·04	Dodecane	4·2	1·3	0·03
1-Ethyl-3-methylbenzene (3)	71	10·3	0·10	Tridecane	1·3	0·7	0·02
1-Ethyl-4-methylbenzene (4)	32	4·3	0·04	Tetradecane	0·6	0·3	0·01
1-Ethyl-2-methylbenzene (6)	30	5·6	0·05	Methylalkanes			
1,3,5-Trimethylbenzene (5)	38	6·1	0·04	2-Methylpentane	19	1·7	0·12
1,2,4-Trimethylbenzene (7)	122	20·4	0·14	3-Methylpentane	18	1·2	0·07
1,2,3-Trimethylbenzene (9)	23	4·9	0·03	2-Methylhexane	39	1·1	0·13
Indane (10)	3·8	0·8	<0·01	3-Methylhexane	30	0·8	0·13
Alkylbenzenes (C_{10})				3-Methylheptane	1·7	0·4	0·05
1,3-Diethylbenzene (11)[d]	3·0	0·9	<0·01	3-Methyloctane	1·9	0·9	0·02
1-Methyl-3-propylbenzene (12)	7·6	2·7	0·02	3-Methylnonane	2·3	1·9	0·02
1-Ethyl-3,5-dimethylbenzene (14)	8·9	2·7	0·01	3-Methyldecane	1·8	0·9	0·02
1-Ethyl-3,4-dimethylbenzene (18)	9·9	2·9	0·01	Cycloalkanes			
1,2,3,5-Tetramethylbenzene (21)	8·7	2·8	0·01	Methylcyclopentane	13	0·5	0·05
Tetrahydronaphthalene (23)	30	4·6	<0·01	Cyclohexane	17	0·5	0·02
Naphthalene (24)	3·7	1·4	0·04	Methylcyclohexane	7·6	0·5	0·03

[a] 13.00–13.30 h, 19 January 1981, around −10 °C.

[b] 15.00–15.30 h, 14 January 1981, around 0 °C, after precipitation.

[c] 21.30–07.50 h, 16–17 February 1981, below 0 °C at night, wind: weak north.

[d] Numbers in parentheses refer to Fig. 3.

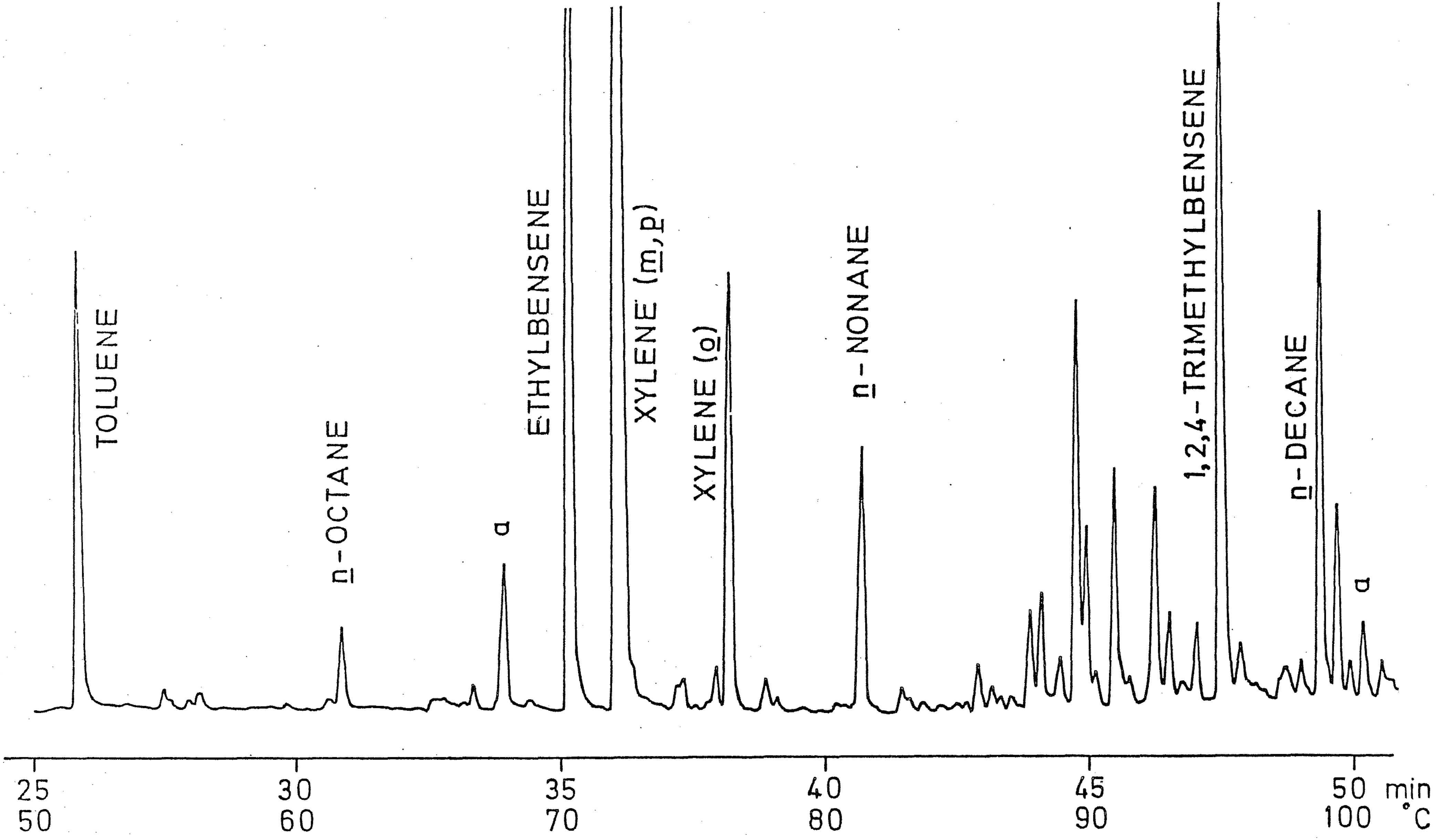

Fig. 2. Characteristic analytical pattern of major hydrocarbons in air polluted by a motor-car plant (Volvo, point A, 1500-1530, 1/14/81, part of the complete gas-chromatographic analyses, cf. Tables 1 and 2, a: analytical artefact).

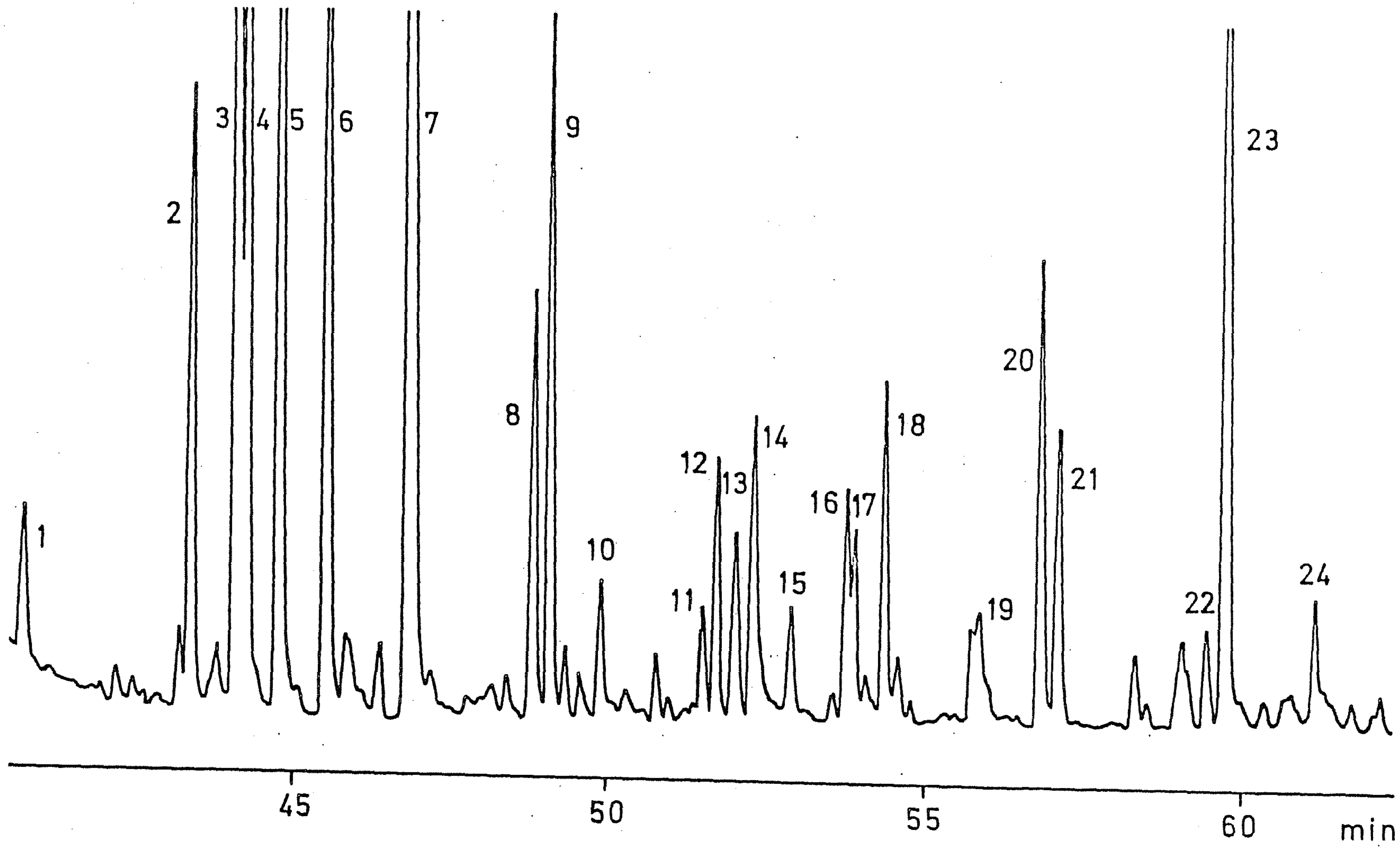

Fig. 3. Characteristic analytical pattern of C_9-C_{10} aromatic hydrocarbons in air polluted by a motor-car plant (Saab, near-by, 1300-1330, 1/19/81, part of complete GC analyses, cf. Table 1 for concentrations and key to numbers, additional compounds: 13, 1-methyl-4-propylbenzene mainly; 15, 1-methyl-2-propylbenzene; 16, 1-ethyl-2,5-dimethylbenzene mainly; 17, 1-ethyl-2,4-dimethylbenzene; 19, 1-ethyl-2,3-dimethylbenzene mainly; 20, 1,2,4,5-tetramethylbenzene and n-undecane; 22, 1,2,3,4-tetramethylbenzene).

The non-aromatic hydrocarbons in Table 1 add up to about 20% of the total reported amount of hydrocarbons. The lower alkanes probably originate partly from light petroleum solvents and the higher alkanes from petroleum fractions used in anti-rust treatments. Although not listed in Table 1, the higher 2- and 4-methylalkanes were recorded in about the same amounts as the corresponding 3-methylalkanes.

This study was focussed on hydrocarbons, but large amounts of polar organic compounds, especially alcohols and esters, are also emitted. The concentrations of ethyl acetate and butyl acetate were estimated to be 850 and 590 $\mu g/m^3$ in the Saab sample, *i.e.* higher than that of any hydrocarbon. Furthermore, a large variety of non-hydrocarbon organic compounds are formed in and emitted from the paint-drying ovens and other production steps. More than fifty such compounds are reported in the recent application by Volvo for continued production according to the Swedish law of environmental protection.

Influence of sampling position and weather. In Table 2, concentrations of a few key hydrocarbons are given for samples which illustrate the influence of external factors on immissions. The characteristic odour of the immissions was present during all but the last two samplings. The odour was used to assess the position of the downwind plume at ground level.

Table 2. Immissions of representative hydrocarbons (μg/m^3 air) at several ground-level locations.[a]

	Volvo 1 km (A) 1500-1530 1/14/81	Volvo 1 km (A) 1500-1530 1/14/81	Volvo 1 km (B) 1030-1130 4/14/81	Saab near-by 1300-1330 1/19/81	Saab 1 km (C) 1340-1440 1/19/81	Saab near-by 1320-1330 4/30/80	Saab 3 km (D) 1350-1410 4/30/80	Saab 3 km (D) 1220-1240 4/30/80	Göteborg regional (E) 2130-0750 2/16-17/81
toluene	12	12	1.5	69	15	99	3.4	1.1	1.22
ethylbenzene	28	26	9.7	86	12	130	2.6	0.3	0.23
xylene (<u>m</u>,<u>p</u>)	85	80	27	264	37	470	9.2	0.8	0.58
xylene (<u>o</u>)	12	11	4.5	38	5.7	73	1.8	0.2	0.21
1,2,4-trimethylbenzene	20	18	15	122	13	120	3.2	0.2	0.14
<u>n</u>-decane	13	11	3.1	13	12	16	1.7	0.9	0.10

[a] All samples, except the regional one, were taken downwind the plants. The first two duplicate samples were taken after precipitation. The temperatures on sampling were, in order, approximately 0, 0, 5, -10, -10, 10, 10, 10 and 0°C.

The two duplicate Volvo samples were taken during wind along the plant buildings. The third sample, taken during wind perpendicular to these long buildings is likely to reflect spray booth emissions better. The samples taken very near to Saab should also correspond closely to spray booth emissions of aromatic hydrocarbons. This is evident from the low proportion of <u>n</u>-decane and from the predominance of aromatic hydrocarbons in the C_9 to C_{11} region (Fig. 3). The proportion of <u>n</u>-decane which represents C_9-C_{14} aliphatic hydrocarbons is higher in the samples taken farther away from Saab. The proportions of various aromatic hydrocarbons are fairly constant, but some fluctuations of emissions with respect to composition occur as demonstrated particularly by the results for short sampling periods. A difference between the Volvo and Saab samples seems to be a higher proportion of toluene from Saab.

The absolute concentrations depend strongly on the distance from the plant. The highest concentrations were obtained near-by Saab in the wind cavity about 50 m downwind from the plant building. The concentrations observed approximately 1 km from the plants were similar for Volvo and Saab and correspond approximately to the United States limit, 160 $\mu g/m^3$, for ambient total non-methane hydrocarbons.

The eighth sample in Table 2 was taken at a location (D) in central Trollhättan with little near-by upwind traffic. The concentrations are similar to those of the regional sample from Göteborg and the pattern of hydrocarbons is similar to that of traffic emissions. The seventh sample was taken at the same position one hour-and-a-half later. This sample exhibits the characteristics of the Saab immissions and the typical smell was noted during sampling. Most likely the presence of the odour can be used to indicate when hydrocarbon immissions from the assembly plants exceed a certain level. At present, this level seems to be about one hundredth of the concentrations recorded near-by Saab.

Wind-speed, mixing height, air turbulence, precipitation and other weather conditions strongly influence ground-level immissions. The samples reported correspond to moderately unfavourable conditions; no efforts to find the most unfavourable weather conditions were made. In the General Motors study (Sexton and Westberg, 1980) it was shown that under conditions of fumigation, ground-level concentrations may remain virtually unchanged several miles downwind from a plant. Moreover, concentrations in the centre of the plume are likely to be much higher than those at ground level.

ECOTOXICOLOGICAL ASPECTS

The results presented demonstrate that ground-level concentrations of a large number of hydrocarbons near the motor-car plants may be about 1000 times higher than regional concentrations. Even at distances larger than 1 km, concentrations more than 100 times higher were recorded. In addition, the observed regional background concentrations are likely to be considerably higher than natural background concentrations. In view of these facts, it is obvious that ecotoxicological consequences of the immissions are to be expected.

Chemical transformations. A discussion of effects cannot be limited to the hydrocarbons themselves, because many other types of organic compounds are formed by chemical transformations in various media. Photochemical reactions in the atmosphere produce a large number of compounds from each hydrocarbon as demonstrated for toluene (Spicer and Jones, 1975). Reactive phenols, aldehydes and peroxides are typical products of aromatic hydrocarbons. Whether and where various products are formed depends on metereological conditions and the reactivity of the hydrocarbon. The reactivity of the alkylbenzenes tends to increase with an increasing number of carbon atoms (Doyle *et al.*, 1975, Bufalini *et al.*, 1976). Complex reactive products from the C_9 and C_{10} hydrocarbons are therefore expected to be formed nearer the plants than products from lighter alkylbenzenes and especially toluene.

A fraction of each hydrocarbon reaches the biosphere unchanged. This fraction is chemically transformed in a very different way by metabolic reactions of microorganisms and higher organisms. In man, a number of transformations are known (Toftgård and Gustafsson, 1980). Consequently, effects of an emitted hydrocarbon on an organism may be caused by the hydrocarbon itself, by the complex mixture of abiotic decomposition products of the compound, and by metabolic products of both the hydrocarbon itself and its abiotic decomposition products. In the case of motor-car plants, the non-hydrocarbon compounds emitted as solvents or formed in various production processes add further to the complexity of the problem.

Health hazards. The results presented indicate that health hazards due to emitted hydrocarbons are a potential problem primarily within and in the immediate vicinity of the plants. Farther away, significant immissions of the hydrocarbons are obtained only in the downwind direction, and concentrations normally decrease rapidly with distance.

A nonresidential zone of 2-3 km radius around the Volvo plant is being discussed. For the vast majority of people outside this zone, exposure to xylene and most other hydrocarbons studied is due mainly to petrol and car exhaust. The dependence of exposure on distance for other hazardous compounds is less clear, however.

Within the plant buildings, problems may arise both by direct exposure and by exposure to pollutants re-entering through air intakes. Hygienic standards are normally set presuming exposure to a single compound. Obviously such standards are inadequate in the present case.

Growing evidence is presented of significant differences in organ distribution (Bergman, 1979) and metobolic effects (Toftgård and Gustafsson 1980), even between the structurally closely related alkylbenzenes. Therefore, it is essential that light hydrocarbons are regarded individually just as polycyclic aromatic hydrocarbons and most other air pollutants. Because of potential synergistic effects, it is important to reduce the number of compounds as much as possible. Smoking and exposure to other industrial pollutants and traffic exhaust are likely to increase health hazards by additive and synergistic effects.

Ecological hazards. Up till now, the great ecological and health concern about large hydrocarbon emissions has been the regional formation of ozone and other oxidants. Effects on growth of conifers and various crops have been demonstrated, not only in the United States but also in Scandinavia (Eastmond and Skärby, 1979).

The ozone-forming capacity and the rate of ozone formation is very different for different hydrocarbons (Bufalini *et al.*, 1976). The higher alkylbenzenes emitted from the motor-car industry have a high ozone-forming capacity and high reaction rates. The complexity of the mixture of reactive and hazardous products formed on photochemical degradation (Cox and Derwent, 1980) also increases with increased number and structural complexity of the hydrocarbons.

In the biosphere, the lipophilic hydrocarbons tend to enrich in nerve tissues (Bergman, 1979) and might be expected to have ethological effects. The more hydrophilic decomposition products have toxic effects of various kinds. The over-all effects are likely to be extremely complex. Effects on Scandinavian ecosystems may well be aggravated because homeostatic mechanisms operate inadequately due to the alarming acidification of waters and soils.

CONCLUSIONS

At present, the exposure of people within and near-by the motor-car plants is a matter of concern. Regional ecotoxicological effects of the present emissions are very complex and may be serious.

Potential health and environmental effects depend strongly on the chemical composition of emissions. Consequently, environmental protection regulations based on the total emitted amount of hydrocarbons are insufficient. A reduction of the number of chemical species used in the production is essential. The components of solvents and paints should be selected not only from technical and economic considerations, but also from a consideration of their impact on health and environment. Around the plants, the required non-residential area can be made smaller if appropriate measures leading to reduced and less hazardous emissions are taken.

Technical measures to reduce the large emissions from the spray booths and the complex emissions from the paint-drying ovens are urgently needed. The choice of paint and procedures for its application must be governed to a larger extent by environmental considerations and less by the latest fashion. It is hoped that the present study will promote measures and planning which can decrease harmful effects on man and environment of the motor-car industry.

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