Gezondheidstechniek TNO

The Occurrence of Polynuclear Aromatic Hydrocarbons (PAH) in outdoor air 1)

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Summary

PAH are produced by the inefficient combustion of coal, oil, gasoline, and other organic matter.

Some of these hydrocarbons have carcinogenic properties; so their presence in air may be of importance in relation to the development of lung cancer.

Since December 1964, the PAH content of the atmosphere of the western part of the Netherlands has been determined on a regular basis by the atmospheric pollution division of the Research Institute for Public Health Engineering TNO. From the results of the measurements, it is found that the atmospheric PAH levels have continuously decreased, and that, in cities, the most important source of these compounds is not automobile traffic but, probably, the burning of domestic fuels.

Introduction

Polynuclear aromatic hydrocarbons (PAH) are produced by the inefficient combustion of coal, oil, gasoline, and other organic matter. Research on the occurrence of PAH in outdoor air is of importance because of the fact that several possess carcinogenic properties. Mortality, particularly due to lung cancer, has according to Hueper [1] increased since 1900 by more than 3000%. This is especially true with respect to large cities. The occurrence of PAH in outdoor air is often related to the development of lung cancer.

It should be pointed out, however, that only the potential carcinogenic properties for man of some of the PAH, occurring in outdoor air, have been demonstrated. Epidemiologic research has failed up to now to prove this relationship. A very disturbing factor in this epidemiologic research is the smoking of cigarettes. It has been demonstrated that substances with pronounced carcinogenic effects also occur in cigarette smoke. A list of 34 PAH and their carcinogenic properties is given in Table 1. This table is far from up to date. Many more PAH occur in outdoor air, while regularly new ones are discovered. There is also an indica-

Het voorkomen van polynucleaire aromaten (PNA) in de buitenlucht

Samenvatting

PNA zijn produkten van onvolledige verbranding van kool, olie, benzine en ander organisch materiaal.

Sommige van deze koolwaterstoffen hebben carcinogene eigenschappen zodat het van belang is hun aanwezigheid in de lucht in verband met het ontstaan van longkanker te onderkennen.

Sinds december 1964 wordt door de afdeling Buitenlucht van het Instituut voor Gezondheidstechniek TNO regelmatig het gehalte aan PNA in de buitenlucht in de Randstad Holland bebaald.

Uit de meetresultaten volgt dat de PNA-niveaus in de buitenlucht voortdurend zijn afgenomen en dat de voornaamste bron van de PNA in de steden niet het autoverkeer, maar waarschijnlijk "huisbrand" is.

tion in this table which of the hydrocarbons have been determined on a regular basis by the atmospheric pollution division of the Research Institute for Public Health Engineering TNO since 1964. It can be seen that 9 of these compounds are tested for on a regular basis.

Although only 4 or 5 of these (viz. 1.2-benzanthracene, chrysene, 1.2-benzopyrene, 3.4-benzopyrene and coronene?) have carcinogenic properties, knowledge of their occurrence is useful in attempting to identify the source of pollution.

The results of research have shown that the ratio of some of these PAH in outdoor air depends upon the source.

If the source is automobile exhaust gas, a ratio of 3.4-benzopyrene/coronene of < 0.4-1;

3.4-benzopyrene/1.12-benzoperylene of 0.2-0.6; and pyrene/3.4-benzopyrene of 2-6 is found.

In domestic fuels these ratios are 3.4-benzopyrene/coronene > 1.7 3.4-benzopyrene/1.12-benzoperylene > 0.8 pyrene/3.4-benzopyrene 0.3-0.8.

From these ratios it follows that higher percentages of pyrene 1.12-benzoperylene and coronene are indicative of traffic as the source. This is especially true for the pyrene content.

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| NAME | OTHER NAMES IN USE | B.P IN °C | CARCINOGENIC PROPERTIES | FORMULA |
|---------------------------------|---|-------------------|-------------------------|--|
| BENZENE) | (BENZOL), (PHENE) | 80.1 | - | 0 |
| NAPHTHALENE | | 210.8 | - | ∞ |
| NAPHTHACENE | 2.3 - BENZANTHRACENE, TETRACENE | SUBL | 2 | 0000 |
| ACENAPHTHENE | NAPHTHYLENEETHYLENE | 278 | - | H H |
| ACENAPHTHYLENE | | 265-75 (PAR. D) | - | ~~ " & |
| FLUORENE | 2.3-BENZINDENE, DIPHENYLENEMETHANE | 295 | - | S CH₂ |
| PHENANTHRENE | | 336 | - | _ U_ d |
| ANTHRACENE | | 340 COR. 226,5 | - | 000 |
| PYRENE | BENZO [d,c,f] PHENANTHRENE | 393 | - | |
| FLUORANTHENE | INDRYL , 1.2 - BENZACENAPHTHENE | 383 | - | 8 |
| ALKYLPYRENE | | | 2 | |
| 1.2 - BENZOFLUORENE | CHRYSOFLUGRENE | 398 | - | CH ₂ |
| 2.3-BENZOFLUORENE | | | ? | $-\sigma$ |
| 9.10 - BENZOPHENANTHRENE | TRYPHENYLENE, 1.2, 3.4 - DIBENZONAPHTHALENE | 425 | - | -00-0 |
| 1.2 - BENZANTHRACENE | BENZO [a] ANTHRACENE, TETRAPHENE, NAPHTHANTHRACENE, 2.3-BENZOPHENANTHRENE | 437 | + | . 000 |
| CHRYSENE | 1.2-BENZOPHENANTHRENE, 1.2,5.6-DIBENZONAPHTHALENE | 448 | + | 80 |
| PERYLENE | PERI-DINAPHTHYLENE | 350 -400 SUBL: | - | _ v-a |
| 3.4-BENZOPYRENE | BENZO [a] PYRENE | 495 | • | -8 |
| 1.2 - BENZOPYRENE | BENZO [c] PYRENE | 492 | + | -p-6 |
| 2.3-BENZOFLUORANTHENE | 100.000 | | ? | 8 |
| 3.4-BENZOFLUORANTHENE | BENZO [b] FLUORANTHENE | | | |
| 10.11 - BENZOFLUORANTHENE | BENZO [j] FLUORANTHENE | | + | 8 |
| 11.12 - BENZOFLUORANTHENE | BENZO [k] FLUORANTHENE | | ? | |
| 1.12 - BENZOPERYLENE | BENZO [g,h,i] PERYLENE | 503 | | - 85 - W |
| ANTHANTHRENE | | | - T- | |
| CORONENE | 1.12, 6.7 - DIBENZOPERYLENE, HEXABENZOBENZENE | 525 | ? | |
| 1.2,5.6 - DIBENZANTHRACENE | DIBENZO [a,h] ANTHRACENE | | • | - COO |
| INDENO [1.2.3, c.d] PYRENE | | | + | ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~ |
| 1.2 , 3.4 - DIBENZOPYRENE | | | | 0 |
| 1.2, 4.5-DIBENZOPYRENE | | | + | \$ × |
| 3.4 , 8.9-DIBENZOPYRENE | | | + | Q-0-7 |
| NAPHTO [2'.3': 1.2] PYRENE | | | 2 | - com 6 |
| INDENO [1.2.3-c.d] FLUORANTHENE | 4.5- [PERI-PHENYLENE] FLUORANTHENE | | , | ~ & |
| PICENE | DIBENZO [a.i] PHENANTHRENE | 518-520 | 2 | ->> |

LIST OF 34 POLYCYCLIC HYDROCARBONS AND THEIR CARCINOGENIC PROPERTIES

— HYDROCARBONS OF WHICH THE CONCENTRATION IN AIR IS MEASURED BY TNO'S

ATMOSPHERIC POLLUTION DIVISION

According to Sawicky [2] the ratio of pyrene/3.4-benzopyrene in exhaust gas from automobiles varies between 40-60. The explanation for the fact that in the outdoor air ratios of only 2-6 are

usually found is that 3.4-benzopyrene is relatively stable in the atmosphere while pyrene is less so.

In addition to the compounds discussed up to now, other types of organic carcinogens have been demonstrated to occur in outdoor air. These are

polynuclear aza-heterocyclic compounds, such as:

dibenzo 2 (a, h) acridine and dibenzo 2 (a, j) acridine, polynuclear imino-heterocyclic compounds, polynuclear carbonyl compounds, such as: 7H-benzo (d, e) anthracene-7-one, alifatic and olefinic epoxides, organic peroxides and lactones.

Even though it has been proved that these substances are present in the atmosphere, little systematic research has been done on their concentrations and trends in outdoor air. For this reason, these will be ignored in this publication.

There is little information regarding synergistic and antagonistic effects among these organic carcinogens, and these organic carcinogens and other compounds.

It is known, for example, that phenols potentiate and enhance the carcinogenic properties of organic carcinogens. It has also been shown that the carcinogenicity of 3.4-benzopyrene is enhanced if this substance is adsorbed onto certain inert particles—especially iron oxide.

Anti-carcinogenic effects have also been demonstrated amongst PAH. Kotin and Falk [3] have shown that dibenzo (a, h) anthracene, a compound which is carcinogenic, looses its carcinogenicity in the presence of hydro-and hexahydro derivatives of dibenzo (a, h) anthracene as well as benzo (a) antracene and phenanthrene.

Other authors have also pointed out that certain compounds, with little or no carcinogenicity, may diminish the activity of very potent chemically related carcinogenic compounds.

In the light of this information, it follows that the carcinogenicity of complex chemical mixtures (containing carcinogens) cannot be predicted solely on the basis of chemical analyses of the composition of these mixtures.

Of all the PAH occurring in outdoor air, 3.4-benzopyrene possesses the strongest carcinogenic properties.

The yearly emission of 3.4-benzopyrene in the USA from several sources is given in Table 2.

On a country wide basis, the contribution from traffic is low about 5%.

Table 2.

Yearly 3.4-benzopyrene emission in the USA Source: Air Poll. Aspects of Organic Carcinogens (1969) Litton Syst. Inc. Prep. for the APCA

| Heating and generation of electricity | 421.6 ton |
|---------------------------------------|------------|
| Burning of wastes | 20.2 ton |
| Industry | 18.8 ton |
| Traffic | ~ 20.6 ton |
| total | 481.2 ton |

For residential areas and street crossings with a high traffic density, the contribution from this source is higher in the summer.

No correlation, however, has been found between atmosperic levels of 3.4-benzopyrene and the death rate from lung cancer.

In this connection Sawicky [4] states:

"The number and type of carcinogens found in the atmosphere indicate that attempts to correlate carcinogenicity of the mixtures in our chemical environment with concentrations of 3.4benzopyrene are probably naive in most cases and spring from our lack of knowledge of the composition of the mixtures with which we are dealing".

No standards exist for the concentration of PAH in outdoor air. Because of their potential carcinogenicity, the emission into the atmosphere should be kept to an absolute minimum.

Detection and analysis of PAH

Sampling occurs by passing large amounts of air through filter material.

Depending on the concentration in the atmosphere, from 30 to over 300 m³ of air are needed for a valid analysis.

To prevent losses of PAH by oxidation, and decomposition by light, especially UV light, the filters should be stored in cyclohexane in the dark; preferably in a refrigerator.

The analytical techniques most commonly used are chromatographic and spectrophotometric.

The analytical technique which is used in our laboratory may be summarized as follows.

Following collection of the samples, the filters are placed for 16 hours in a soxhlet containing cyclohexane for purposes of extraction.

If necessary, the extract obtained can be purified by shaking it with a mixture consisting of 4 parts methanol and 1 part water.

Following this, most of the cyclohexane is removed by evaporation. The extract can now be separated into fractions by the use of column chromatography.

Table 3. PAH content in $\mu g/1000 \ m^3$; 24 Oct. 1956 - 10 Apr. 1957

| | Conway Valley (Caernarion) | Liverpool (Princess Road) |
|--------------------|-------------------------------|------------------------------|
| Pyrene | 2 | 50 |
| Fluoranthene | 5 | 67 |
| 3.4-Benzopyrene | 1 | 166 |
| 1.12-Benzoperylene | 1 | 68 |

The PAH content of the fractions is then determined by spectrophotometric measurement at wave lengths between 270-400 nm. The concentrations of the different components are expressed as $\mu g/1000 \text{ m}^3$ of air.

The occurrence of PAH

Extensive research in America has shown that PAH are present in outdoor air almost everywhere. The concentrations in the big cities are much higher than in suburban areas. The average concentration of 3.4-benzopyrene in the cities during the year 1966 was 3 μ g/1000 m³, while in the areas outside the cities this value was only 0.3 μ g/1000 m³. Commins [5] also points to the great difference in concentration in these areas (see Table 3).

In addition to these differences, seasonal variations in concentrations in outdoor air have been shown

During the summer months much lower concentrations are found than in the winter months.

Because of these seasonal variations, our laboratory has decided to determine the PAH concentration as averages over the months of

January + February

March + April

May - October and

November + December.

The highest concentrations are found over the months of November + December, and the lowest in the months May — October.

The results of some investigations which were conducted by our Institute in the western part of the Netherlands are presented in Table 4.

Because the highest concentrations are found during fog periods in winter we have included in the table data obtained from measurements during one of the notorious smog episodes in London.

From the data presented for the Dutch cities, it is quite apparent that much higher concentrations are found during the winter season than in the summer. This is an indication that the seasonal

Table 4. PAH concentrations measured in outdoor air (µg/1000 m³)

| | | De | lft (T1 | NO ar | ea) | | The I | Hague | | , | Vlaarc | lingen | | | Amste | erdam | | | Rotte | rdam | |
|--------------------|---|------|---------|-------|------|------|-------|-------|------|------|--------|--------|------|-----|-------|-------|------|------|-------|------|------|
| | | '68 | '69 | '70 | '71 | '68 | '69 | '70 | '71 | '68 | '69 | '70 | '71 | '68 | '69 | '70 | '71 | '68 | '69 | '70 | '71 |
| Pyrene | S | 1 | 3 | 2 | 5 | | 3 | 2 | 2 | 4 | 3 | 2 | 2 | | 4 | 1 | 2 | 2 | 1 | 3 | 2 |
| | W | 15 | 16 | 5 | 1 | 14 | 6 | 2 | 4 | 22 | 24 | 11 | 8 | 22 | 19 | 8 | 4 | 10 | 10 | 3 | 5 |
| Fluoranthene | S | n.d. | 5 | 4 | 7 | | 3 | 1 | 2 | 3 | 4 | 3 | 1 | | 3 | 2 | 2 | 1 | 1 | 2 | 2 |
| | W | 13 | 17 | 6 | 1 | 11 | 6 | 4 | 3 | 27 | 25 | 10 | 4 | 2.5 | 18 | 9 | 1 | 8 | 8 | 3 | 4 |
| 1.2-Benzanthracene | S | 2 | 1 | 1 | 2 | | <1 | <1 | 1 | 3 | 1 | 3 | 3 | | n.d. | 1 | 1 | 1 | 1 | 7 | _ 1 |
| | W | 16 | 10 | 8 | 4 | 6 | 7 | 4 | 2 | 29 | 25 | 19 | 14 | 20 | 11 | 7 | 4 | 17 | 12 | 6 | 5 |
| Chrysene | S | | | 2 | 4 | | | 1 | 2 | | | 5 | 4 | | | 2 | 2 | | | 3 | 5 |
| | W | 15 | 20 | 10 | 6 | 21 | 14 | 7 | 4 | 28 | 38 | 16 | 13 | 26 | 17 | 4 | 8 | 21 | 18 | 11 | 18 |
| 1.2-Benzopyrene | S | n.d. | 2 | 2 | 5 | | 2 | 1 | 2 | 3 | 4 | 5 | 6 | | | 2 | 1 | 4 | 2 | 3 | 3 |
| | w | 28 | 23 | 13 | 5 | 14 | 23 | | 9 | 31 | 31 | 22 | 20 | 21 | 17 | 10 | 6 | 25 | 24 | 14 | 14 |
| 3.4-Benzopyrene | S | n.d. | 3 | 1 | 3 | | 4 | 4 | n.d. | 3 | 4 | 5 | 9 | | 2 | 2 | n.d. | 3 | 1 | 3 | 2 |
| | w | 20 | 18 | 12 | 6 | 23 | 12 | • | 13 | 35 | 32 | 13 | 16 | 22 | 18 | 5 | 8 | 15 | 23 | 19 | 23 |
| 1.12-Benzoperylene | S | n.d. | 1 | 2 | 2 | | 2 | 2 | 2 | 1 | 3 | 4 | n.d. | | n.d. | 2 | 1 | 2 | 3 | 3 | 2 |
| | w | 20 | 17 | 7 | 6 | 12 | 8 | | 2 | 20 | 15 | 11 | 14 | 17 | 12 | | 7 | 23 | 18 | 13 | 6 |
| Anthanthrene | S | n.d. | <1 | | 1 | - | <1 | <1 | <1 | n.d. | <1 | <1 | n.d. | | n.d. | <1 | n.d. | n.d. | <1 | <1 | n.d. |
| | W | n.d. | 1 | <1 | n.d. | n.d. | 1 | | n.d. | 4 | 3 | 2 | 1 | 2 | | | <1 | 2 | 3 | 2 | 1 |
| Coronene | S | 1 | 1 | | 2 | | <1 | <1 | 1 | 1 | 1 | 1 | n.d. | | n.d. | <1 | n.d. | n.d. | 1 | <1 | 1 |
| | w | n.d. | 2 | 1 | n.d. | n.d. | 1 | | n.d. | 2 | 3 | 2 | 2 | 2 | 2 | 2 | 1 | 4 | 3 | 2 | 2 |

S = Summer (May-October)

W = Winter (November-December)

trend is due mainly to fuel consumption for home heating rather than automobile exhausts.

This is further substantiated by the data presented in Figure 1. From this figure, it can be seen that data from cities in and outside the Netherlands (except for Los Angeles) give ratios of 3.4-benzo-pyrene/coronene, pyrene/3.4-benzopyrene and 3.4-benzopyrene/1.12-benzoperylene which are clearly in accord with those obtained when domestic fuels rather than automobile exhausts are the source.

For tunnels, border-crossings, and a city such as Los Angeles, the opposite is, understandably, the case.

It is remarkable that, during the smog episode of September 1971 in Rotterdam, ratios were found which indicated that automobile traffic was the primary source of PAH contamination. At that time, however, the maximum temperature ranged from 21°C to 25°C. Under these conditions, it can be assumed that there was very little need for home heating.

In Table 5, the 3.4-benzopyrene content for several localities in Europe and in America is given.

Traffic as a source of PAH

In recent years, opposition has arisen to the addi-

tion of lead compounds to gasoline in order to obtain the desired octane rating. Reduction in the lead content of gasoline is desirable for the following reasons:

- (a) to minimize environmental contamination by the added lead which is known to be a cumulative poison;
- (b) to make feasible the use of catalytic afterburners for other toxic components in automobile exhaust gas.

Such after-burners are readily "poisoned" in the presence of lead. Although raising the aromatic content of gasoline (instead of the use of lead additives) is not the only possibility for obtaining the required octane rating, it is the only method which could be used on short notice. Experiments have shown that raising the concentration of aromatics in gasoline leads to an increase in the concentration of PAH in exhaust gas. In view of the carcinogenic potentialities of these compounds, this would not be a desirable procedure. It should again be pointed out, however, that not traffic, but other combustion processes, such as the burning of bituminous coal for heating purposes, are the most important sources of PAH in outdoor air. Diesel-

| Delft fog 7-12-'66 | Delft fog 11-2-'69 | Delft fog 12-12-'69 | R'dam foga 31-12-'64 | London ^b 1956 | 3-12-'57 | Denekamp June '65 | Beek Nov. '69 | Beek July '69 | |
|-----------------------|-----------------------|------------------------|-------------------------|-----------------------------|----------|----------------------|------------------|------------------|--------------------|
| 29 | 33 | 312 | 420 | 10 25 | 3170 | 48 | 61 | 20 | Pyrene |
| 28 | 37 | 377 | 725 | 10 25 | 4070 | 23 | 43 | 8 | Fluoranthene |
| - 22 | 11 | 104 | 240 | | .,, | <1 | 17 | 7 | 1.2-Benzanthracene |
| 72 | 23 | 209 | 325 | | | •. | | 3 | Chrysene |
| 64 | 14 | 175 | 200 | 8 20 | 740 | 13 | 15 | 7 | 1.2-Benzopyrene |
| 55 | 11 | 138 | 190 | 12 50 | 2220 | 13 | 14 | <1 | 3.4-Benzopyrene |
| 23 | 13 | 126 | 145 | 8 25 | 1060 | 49 | 11 | 27 | 1.12-Benzoperylene |
| 3 | n.d. | 11 | 14 | 2 5 | 380 | 10 | 2 | 2 | Anthanthrene |
| 6 | 3 | 19 | 35 | 4 10 | 280 | 28 | 5 | 16 | Coronene |

a) Report Keuringsdienst van Waren, Rotterdam

b) Royal Soc. Health Journal, 76 (1957) p. 776

Table 5. 3.4-benzopyrene content (µg/1000 m³)

| Locality | Date | Concentration | Date | Concentration |
|-------------------------------|----------------------|--|------------------------------|---------------|
| Delft | winter '68 | 20 | summer '68 | n.d. |
| | winter '69 | 18 | summer '69 | 3 |
| | winter '70 | 12 | summer '70 | 1 |
| | winter '71 | 6 | summer '71 | 3 |
| Vlaardingen | winter '68 | 35 | summer '68 | 3 |
| | winter '69 | 32 | summer '69 | 4 |
| | winter '70 | 13 | summer '70 | 5 |
| | winter '71 | 16 | summer '71 | 9 |
| Rotterdam | winter '68 | 15 | summer '68 | 3 |
| | winter '69 | 23 | summer '69 | 1 |
| | winter '70 | 19 | summer '70 | 3 |
| | winter '71 | 23 | summer '71 | 2 |
| Oslo (a) | winter '56 | 15 | summer '56 | 1 |
| Copenhagen (b) | winter '56 | 17 | summer '56 | 5.4 |
| ondon (c) | winter '56 | 50 | summer '56 | 12 |
| Liege (d) | winteraverage '58/62 | 113 | summeraverage '58/62 | 14.5 |
| Liverpool (e) | 24.10.'56-10.4.'57 | 166 | summer '56 | 33 |
| Hamburg (f) | winteraverage '61/63 | 183 | summeraverage '61/63 | 17 |
| Milan (h) | winter '58 | 198 | summer '59 | 1 |
| Paris (i) (rue de Dantzig) | winter '58 | 300-500 (48 results of the measurements) | summer '58 | |
| Düsseldorf | winter '63 | 75 | summer '63 | 3.5 |
| Detroit (Michigan) (g) | winter '59 | 31 | summer '59 | 3.4 |
| Chatanooga (Tennessee) | winter '59 | 31 | average over the year '60 | 8.3 |
| Hammond (Indiana) | winter '59 | 39 | average over the year '60 | 3.9 |
| Charlotte (N. Carolina) | winter '59 | 39 | average over the year '60 | 5.7 |
| Richwood (Virginia) | winter '59 | 45 | | |
| St. Louis (Missouri) | winter '59 | 54 | average over the year '60 | 5.3 |
| Nashville (Tennessee) | winter '59 | 55 | summer '59 | 1.4 |
| Altoona (Pennsylvania) | winter '59 | 61 | | |
| Birmingham (Alabama) | winter '59 | 74 | summer '59 | 1.6 |

n.d. = not detectable

a) Brit. J. of Cancer. 10/4201 (Sept. 1956)
b) Danish Med. Bull. 3/205 (Nov. 1956)
c) Roy. Soc. Hlth. J., 76 (1956) p. 677
d) Arch. Belg. Med. Soc., 9/10 (1963) p. 578
e) Int. J. of Air Poll., 1 (1958) p. 14
f) Int. J. of Air and Wat. Poll., 8 (1964) p. 185
g) Air Poll. Aspects of Organic Care. (1969) I

g) Air Poll. Aspects of Organic Carc. (1969) Litton Syst. Inc. Prep. for the APCA h) Centro per Lo Studio Sugli Ing. Atm. (1958) i) Revue Poll. Atmosph., 7 (1956) p. 316

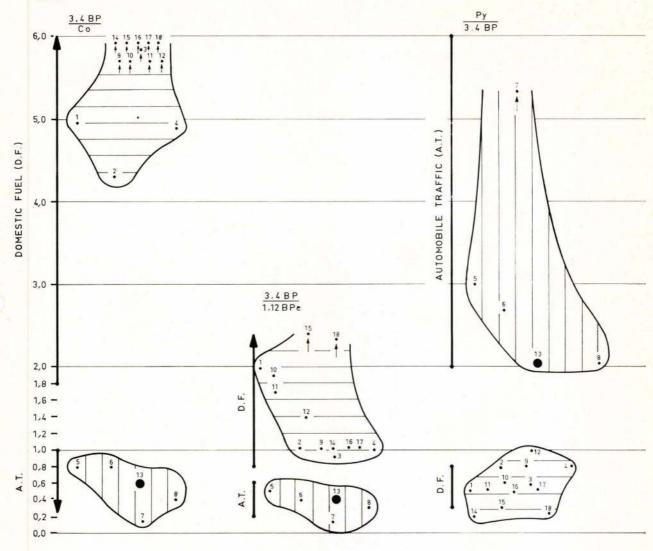


Fig. 1. PAH ratio for several localities

| 0 | 2000년 전 1000년 1월 1일 1일 전 1일 전 1일 전 1일 | | |
|-----|---|---|--|
| 1. | London, 1956 Source: | Roy. Soc. Hlth. J., 76 (1957) p. 776 | |
| 2. | Liege, 1958/1962 | Arch. Belg. Med. Soc. No. 960 (1963) p. 578 | |
| 3. | Rotterdam-W, 1968/1969 | IG-TNO data | |
| 4. | Detroit, 1959 | Am. Ind. Hyg. Ass. J., 23 (1962) p. 137 | |
| 5. | Blackwall tunnel 1960 | Brit. J. of Ind. Med., 18 (1961) p. 250 | |
| 6. | Denekamp, 1965 | IG-TNO data | |
| 7. | Beek, 1969 | IG-TNO data | |
| 8. | Los Angeles, 1959 | Am. Ind. Hyg. Ass. J., 23 (1962) p. 137 | |
| 9. | Delft-W, 1968/1969 | IG-TNO data | |
| 10. | Vlaardingen-W, 1968/1969 | IG-TNO data | |
| 11. | The Hague-W, 1968/1969 | IG-TNO data | |
| | Amsterdam-W, 1968/1969 | IG-TNO data | |
| 13. | Rotterdam Smogepisode 1971 | Rep. of the Keuringsdienst van Waren, Rotterdam, 1971 | |
| | Delft-W, 1971 | IG-TNO data | |
| 15. | The Hague-W, 1971 | IG-TNO data | |
| 16. | Vlaardingen-W, 1971 | IG-TNO data | |
| 17. | Amsterdam-W, 1971 | IG-TNO data | |
| 18. | Rotterdam-W, 1971 | IG-TNO data | |
| | | | |

W = Winter season

| C | Diesel | ratio for equal | |
|--------------------|----------|-----------------|--|
| Component | Gasoline | | |
| Pyrene | 0.12 | 1111 | |
| Fluoranthene | 1.7 | | |
| 1.2-Benzanthracene | 0.79 | | |
| Chrysene | 0.07 | | |
| 3.4-Benzopyrene | 4.2 | | |
| 1.2-Benzopyrene | 3.9 | | |
| 1.12-Benzoperylene | 3.8 | | |
| Coronene | 2.9 | | |

Data from J. L. Sullivan and G. J. Cleary, Brit. J. Ind. Med. 21 (1964) p. 117.

powered engines are also more important in this respect than are those using gasoline. This is illustrated by the data contained in Table 6. It gives the ratios obtained for PAH content when equal volumes of exhaust gas from the two sources are analyzed.

From Table 7 it can be seen that, since 1960, the 3.4-benzopyrene content of the air in Rotterdam has consistently decreased despite an increase in traffic density. The concentration of 1.12-benzoperylene, which is relatively abundant in automobile exhausts, has also decreased since 1964.

The emission of PAH by gasoline powered motors can be decreased by:

- (a) better maintenance of the motor and provision for more complete combustion of the fuel,
- (b) after-burning (catalytic) of the exhaust gas,
- (c) a change in the composition of the fuel (aromatics are less favorable than highly branched aliphatic compounds; LPG is a favorable fuel).

The emission from diesel-powered engines may be reduced by:

(a) improved maintenance and better adjustment of the motor,

Table 7.

| 37 | 3.4-be | nzopyrene | 1.12-benzoperylene |
|------|-----------|-----------|--------------------|
| Year | 1 + 4 qu. | 2 + 3 qu. | 1 + 4 qu. |
| 1960 | 56 | 341 | |
| 61 | 27 | 7 | |
| 62 | 46 | 4 | |
| 63 | 25 | 3 | |
| 64 | 26 | 6 | 32 |
| 65 | 19 | 2 | 34 |
| 66 | 6 | 0.5 | |
| 67 | 8 | 0.6 | 20 |
| 68 | 5 | 0.7 | |
| 69 | 3 | 0.4 | 5 |
| 70 | 2 | n.d. | 5 |
| 1971 | 2.5 | 0.3 | 7 |

Data from annual reports of the Keuringsdienst van Waren, Rotterdam.

(b) less strain on the motor, i.e. not overloading.

Furthermore, it has been demonstrated that the highest PAH emissions occur in the stationary, accelerating, and decelerating phases of the driving cycle. A more efficient traffic control system which would assure a free-flowing traffic pattern (synchronized traffic lights, for example) might improve the situation with respect to PAH emission.

Standards

Data from America show that the hydrocarbon content, indicated as C_xH_y , in exhaust gas from the 1970 model cars is $60^{\circ}/_{\circ}$ lower than was the case for models prior to 1966, when standards were established. The PAH content is $30^{\circ}/_{\circ}$ lower. The very stringent California standard for 1972 is about 1.5 g C_x H_y/km . Recent legislation provides that the whole of America will have standards which are even more severe by 1975 (for hydrocarbon emissions 0.29 g/km). Let us now examine the situation for Europe. A British survey has shown that, on the average, each automobile of the total British car population produces 2.6 g C_yH_x/km , based on the European testing cycle.

In the common market countries, standards for production models are 3.2 g C_xH_y/km for automobiles in the weight class of 1250-1470 kg; and, 2.7 g C_xH_y/km for those in the 750-850 kg range. It can be seen that these figures are, on the average, 2 times higher than those already established for California.

If one really wants to tackle the problem of pollution by automobiles, a first consideration should be the setting of standards for automobile exhaust gas (of which lead is only one of the toxic components) which are far more stringent than those now recommended by the European Economic Community. If we accept such standards for hydrocarbon emissions, a decrease in the lead content of gasoline with an accompanying increase in the aromatic content, will not necessarily affect the aromatic and PAH content of exhaust gas.

Older cars, which cannot meet the more severe standards, should be fitted with catalytic after-burners. If the proposed reduction in lead additives is effected, the danger of "poisoning" for these after-burners will be negligible. In addition to this, it is of interest to note that on a relative basis, the catalytic after-burners lower the PAH content more so than they do the total hydrocarbons.

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