E 487

Bibliotheek Hoofdkantoor TNO
's-Gravenhage
81 H02684
4 SEP. 1981

IMG-TNO
INSTITUUT VOOR MILIEUHYGIENE
EN GEZONDHEIDSTECHNIEK TNO
Publikatie no. 690
Postbus 214 2600 AE DELFT

POLYCYCLIC AROMATIC HYDROCARBON CONCENTRATIONS IN THE NETHERLANDS

BY

Prof. Ir. L.J. Brasser*

* Head of the Atmospheric Pollution Division of the TNO Research Institute for Environmental Hygiene; Professor of Environmental Chemistry at the University of Technology in Eindhoven.

Publication no. 690 of the TNO Research Institute for Environmental Hygiene, P.O. Box 214, 2600 AE Delft, The Netherlands

TNO
11425

POLYCYCLIC AROMATIC HYDROCARBON CONCENTRATIONS IN THE NETHERLANDS

ABSTRACT

Starting in the winter 1964-1965, the TNO Research Institute for Environmental Hygiene has determined the PAH-concentrations of the atmosphere at several locations in the Netherlands. Long series of data are available for several stations.

The trend in the concentrations is spectacular: the concentrations have fallen from relatively high values to nearly negligible levels. During this period natural gas replaced coal and oil as a fuel for heating buildings. The same, though not complete, changes occurred in the fuels for the production of energy in factories and power stations. The intensity of road traffic has been growing rapidly during the same period. The conclusion can be drawn that modern motor traffic is not a major source of PAH.

The relative proportions of different polycyclic hydrocarbons can give a clue for the detection of the kind of source of the PAH-concentrations. This is illustrated by the results of measurements at different stations.

It is to be expected that in the not too far future, the relative proportions of the fuels used in the Netherlands will change again. This may have some influence on the concentrations of PAH in the atmosphere.

CONTENTS

	Page
1. HISTORICAL BACKGROUND	1
2. MEASURED CONCENTRATIONS OF PAH	3
3. MEASURING TECHNIQUE	5
4. TREND OF THE PAH-CONCENTRATIONS OVER THE YEARS	6
5. RELATIVE PROPORTIONS OF PAH AS AFFECTED BY DIFFERENT TYPES OF POLLUTION	13
6. EXPECTED FUTURE DEVELOPMENTS	21
7. LITERATURE	23
Figures	

POLYCYCLIC AROMATIC HYDROCARBON CONCENTRATIONS IN THE NETHERLANDS

1. HISTORICAL BACKGROUND

Everywhere in the world, firewood was the main fuel in early human settlements. It was used as a fuel for cooking, heating of dwellings and for small industrial activities like brewing. Charcoal from selected firewood was used in metallurgical activities as the production of bronze and iron and steel and in the fabrication of metal tools. The areas that would later form the Netherlands were no exception to this rule. However, Roman reports already mention that the inhabitants of the delta of the Rhine also used another fuel, the peat that covered large areas in most parts of the country was formed into rectangular blocks, dried and used as a fuel. The burning of peat for domestic purposes was still common practice in the first part of the twentieth century.

In the middle ages a new fuel appears. Monks in Limburg were producing coal and lignite in open pit mining. At first this happened only on a small scale but later on, when many woods had been cut down and firewood became more expensive, lignite and coal replaced firewood and charcoal for industrial use.

It will be clear that the quality of the fuels and the inefficient techniques for burning were reasons for producing large quantities of smoke. Though of course no measurements on that subject are available, it can be assumed that the smoke will have contained a relatively high quantity of polycyclic aromatic hydrocarbons (PAH).

In the sixteenth and seventeenth century the smoke concentrations in European towns seem to have been extremely high. Good information can be obtained from the booklet "Fumifugium" written by John Evelyn in 1661 [1] , dealing with complaints about air pollution in London. With some envy, John Evelyn mentions the municipal clean air regulations of Haarlem in Holland (Holland being one of the seven "United Provinces of the Netherlands"). In fact municipal regulations on the quality of

fuels and on the abatement of smoke existed in Haarlem (1608) [2], Breda (1615), Utrecht (1622) and Amsterdam (about 1655). In these regulations the use of firewood was preferred over coal for industrial firing installations.

In the nineteenth century the industrial revolution started in Brabant and Overijssel, later on also in Holland and the other provinces. Energy for the industry was obtained by the burning of coal. From old pictures it is clear that a smoking chimney and prosperity were regarded as being synonymous (which was not true as there was a lot of poverty in the working class). More efficient burning appliances helped to abate the smoke production, though the real intention of the owners of the factories was only to diminish the fuel consumption.

After the second world war the large scale expansion of the industry starts. Especially the chemical and petrochemical industries showed a large growth rate. Also a change over from solid fuels to oil started. In the nineteenseventies the quantity of coal used can be neglected.

Later on, the use of natural gas as a fuel started after the discovery of the very large gasfields of Slochteren in the province of Groningen and of several smaller gasfields. At the moment most of the energy generated in stationary sources in the Netherlands comes from natural gas. As natural gas is a very clean fuel (nearly completely consisting of methane), its use does not produce any important quantity of smoke or PAH.

On the other hand, in about the same period that natural gas came into use as a fuel, motor traffic became to be a major source of air pollution, also containing PAH.

It is a pity that measurements of PAH in the Netherlands were only started on a routine basis in 1964. This means that the measurements give a good cover of the transition period from the use of coal via oil to gas and of the period of the most important growth of the use of motor vehicles, but not of the period in which coal was used as a fuel.

It is not unreasonable to expect that in modern times, the maximum of the PAH-concentrations has occurred in the period of 1950 to 1960. Perhaps another and even higher maximum can have existed locally in industrialised towns between 1900 and 1914 or perhaps even earlier.

2. MEASURED CONCENTRATIONS OF PAH

Starting in December 1964, measurements of PAH were carried out by the TNO Research Institute for Environmental Hygiene. The measurements were made at a large number of stations. Some stations show a continuous series of data from 1965 to the present, others have series covering only several years. A selection was made of some stations having measurements covering long periods of time and showing different local conditions. It should be mentioned that more measurements are available, not only from the files of the TNO Research Institute for Environmental Hygiene, but also from other institutes and from local authorities. However, the stations mentioned here form a good selection from all available data [3].

The selected stations are mentioned in table 1.

Table 1 Measuring stations for PAH selected from the files of the TNO Research Institute for Environmental Hygiene

Station no.	Location	Description of station
V 1	Vlaardingen	Heavily polluted district with many small burning appliances in a middle-sized town near petrochemical industry.
V 2	Vlaardingen	Urban area with small heating appliances in a middle-sized town near petrochemical industry.
W 9	Naaldwijk	Country town in the centre of a large district covered with heated glasshouses.
D 12	Delft	Outskirts of a middle-sized town, near residential areas, industry and university and research institute buildings. Near major motor road.
D 21	The Hague	Residential area in major town.
V 10	Rotterdam	City center in major town.

A second group of data was selected from the files of the TNO Research Institute for Environmental Hygiene covering measurements of short duration at special locations. For instance, measurements were made at border crossings between the Netherlands and Germany on days when, because of the start of holidays, many tourists were passing the border by motorcar. Other extra measurements were made on station D 12 on days with heavy fog and a series of measurements was available near an eel smoking installation.

The first group of data gives a good impression of the fluctuations of the PAH-concentrations over the years, moreover it is possible to study the influence of the changing pattern of sources of PAH on the relative concentrations of the different polycyclic hydrocarbons. The second group of data gives an impression of the relations of the different polycyclic hydrocarbons emitted by sources of different types.

Starting in the winter of 1964-1965 the following polycyclic hydrocarbons were determined at the stations:

pyrene (benzo[d,e,f]phenanthrene)

fluoranthene (indryl)

1,2 benzanthracene (benzo[a]anthracene)

chrysene (1,2 benzophenanthrene)

1,2 benzopyrene (benzo[e]pyrene)

3,4 benzopyrene (benzo[a]pyrene)

1,12 benzoperylene (benzo[g,h,i]perylene)

anthanthrene

coronene (hexabenzobenzene)

Of these polycyclic hydrocarbons, 3,4 benzopyrene is mentioned as having strong carcinogenic properties; 1,2 benzanthracene, chrysene and 1,2 benzopyrene are mentioned to have weak carcinogenic properties.

3. MEASURING TECHNIQUE

As this paper deals with concentrations of PAH and as it is not intended to be a contribution to the study of measuring techniques for PAH, only a short description of the technique used is presented here [4].

The samples are obtained by collection on filterpaper. For the sampling procedure the following apparatus can be used:

a) a volumetric daily SO_2- and smoke sampler;
b) a smoke recorder using filter tape;
c) a high volume air sampler;
d) a special TNO high volume sampler.

For the first group of data the instruments mentioned under a) and b) were used. The second group of data was obtained mainly by using the instrument mentioned under d).

For a reliable analysis a large number of daily samples obtained by a volumetric SO_2- and smoke sampler is needed. This means that samples

have to be stored for a considerable period. Due to volatilization, oxidation or decomposition, losses of PAH on the filters might occur if no precautions were taken [5]. No losses occurred if the filters were stored in cyclohexane in a dark place in a refrigerator, even when stored over a period much longer than six months.

The filters are extracted in a soxhlet extractor with cyclohexane. Extraction for 16 hours is necessary to dissolve all PAH (especially coronene dissolves with much difficulty). During extraction, the soxhlet apparatus was screened against light.
Using column chromatography, 24 3 ml fractions are obtained, using cyclohexane with a gradually increasing ether content as an eluting liquid in gradient elution.
The absorption spectra of the fractions are measured in a one cm quartz cuvette in the 270-400 nm region. Using a calibration curve, the amount of PAH in the various fractions is determined.
Interlaboratory tests have shown this method to be reliable. Accidental errors may give rise to differences up to 10% in duplicates. Severe precautions have to be taken against losses during various stages of analysis as these losses can cause systematic errors.

4. TREND OF THE PAH-CONCENTRATIONS OVER THE YEARS

To prevent the printing of endless tables of different PAH-concentrations, only summaries of the data are presented in this paper. The full data are however available (and obtainable) at the TNO Research Institute for Environmental Hygiene.

As anthanthrene and coronene have always showed low concentrations on the stations, their data are omitted here. Pyrene, fluoranthene, and 1,12 benzoperylene, at least in the first years of the measurements, appreciable concentrations. As they are generally considered to have no or only very weak carcinogenic properties, they are also omitted for the study of the trend of PAH-concentrations. For the remaining four polycyclic aromatic hydrocarbons the winter concentrations (that are much higher than the summer concentrations) are presented in table 1A-D

In most cases the period November, December, January, February is considered to be the winter period. However, in several cases the period

December, January, February had to be considered as such as the available data did not allow for other combinations. In some cases one or two months of data are not available.

Table 1 A 1,2 benzanthracene (µg/1000 m^3)

Winter	Station					
	V 1	V 2	W 9	D12	D21	V10
1964-65	32	.	.	.	.	.
1965-66	22	23	8	9	.	20
1966-67	4	.	9	7	.	10
1967-68	12	18	4	9	10	3
1968-69	14	27	19	14	6	13
1969-70	14	23	12	12	6	11
1970-71	10	17	9	9	5	7
1971-72	11	13	11	5	1	6
1972-73	19	18	7	17	11	7
1973-74	n.d.	7	3	n.d.	3	n.d.
1974-75	.	.	.	.	.	2.0
1975-76	.	.	.	.	.	.
1976-77	.	.	3	n.d.	.	2.3
1977-78	.	.	1	1	.	1
1978-79	.	.	2	1	.	n.d.

. means no data available

n.d. means not detectable

Table 1 B chrysene (µg/1000 m^3)

Winter	Station					
	V 1	V 2	W 9	D12	D21	V10
1964-65	.	.	.	.	.	.
1965-66	25	38	8	19	.	25
1966-67	5	.	15	7	.	11
1967-68	.	.	.	.	.	.
1968-69	18	27	22	14	21	20
1969-70	24	33	19	19	10	14
1970-71	14	24	13	15	12	14
1971-72	10	17	20	9	7	14
1972-73	16	17	9	13	10	9
1973-74	n.d.	5	4	18	n.d.	6
1974-75	.	.	.	.	.	6.7
1975-76	.	.	.	.	.	.
1976-77	.	.	8	2	.	5
1977-78	.	.	1	2	.	1
1978-79	.	.	3	n.d.	.	6

Table 1 C 1,2 benzopyrene (µg/1000 m^3)

Winter	Station					
	V 1	V 2	W 9	D12	D21	V10
1964-65	33	.	.	.	.	.
1965-66	22	24	13	18	.	37
1966-67	8	.	15	13	.	22
1967-68	19	17	9	14	15	26
1968-69	22	24	26	22	13	24
1969-70	24	28	17	20	12	25
1970-71	22	28	11	12	17	17
1971-72	21	22	16	10	12	17
1972-73	13	12	8	12	10	16
1973-74	n.d.	8	4	n.d.	2	2.4
1974-75	.	.	.	.	.	3.6
1975-76	.	.	.	.	.	.
1976-77	.	.	4	n.d.	.	3.2
1977-78	.	.	2	n.d.	.	n.d.
1978-79	.	.	n.d.	n.d.	.	1

Table 1 D 3,4 benzopyrene (μg/1000 m^3)

Winter	Station					
	V 1	V 2	W 9	D12	D21	V10
1964-65	28	.	.	.	.	.
1965-66	22	33	14	12	.	26
1966-67	4	.	11	6	.	17
1967-68	18	18	6	8	5	21
1968-69	12	30	19	10	19	22
1969-70	23	27	13	13	6	20
1970-71	14	19	5	13	9	15
1971-72	11	22	14	4	10	20
1972-73	13	20	13	18	18	17
1973-74	10	9	9	10	6	5.3
1974-75	.	.	.	.	.	2.4
1975-76	.	.	.	.	.	3.6
1976-77	.	.	n.d.	n.d.	.	1.3
1977-78	.	.	n.d.	n.d.	.	n.d.
1978-79	.	.	n.d.	n.d.	.	n.d.

The use of fossil fuels and their derivates in furnaces and engines is to be considered as the most probable source of these polycyclic hydrocarbons. To make comparisons possible, the fuel consumption in the Netherlands over the years is presented in table 2 [6]; the number of motor vehicles in the country is presented in table 3 [7].

Table 2

National fuel consumption in the Netherlands. All data are expressed in T cal (10^{12} cal)

Fuel user	year			
	1965	1970	1975	1977
coal				
energy prod.	31900	17500	6300	0
industry	23100	19400	15600	465
others[1)]	38700	11000	2000	678
oil products				
energy prod.	39300	59700	26900	28100
industry	48900	64200	62400	80900
traffic	34100	52200	64800	78000
others[1)]	65000	84800	49200	38100
natural gas				
energy prod.	2100	31900	77300	102000
industry	4200	63600	106200	111000
others[1)]	8000	72600	167300	156000

1) for a major part domestic use for heating.

Table 3

Number of motor vehicles in the Netherlands

thousands of vehicles

Vehicle	year			
	1965	1970	1975	1977
motor cycles	140	72	68	80
passenger cars	1273	2454	3399	3851
buses, lorries, etc.	243	312	342	337
total	1656	2838	3809	4268

Figure 1 and figure 2 give a graphical presentation of the concentrations of 1,2 benzopyrene and 3,4 benzopyrene at station V10 (city center of Rotterdam) in winter. It is clear that during the period of the measurements the concentrations of both PAH's showed a dramatical decrease from relatively high concentrations to nearly negligible levels. This is not only true for the PAH's listed in table 1A-D at the stations listed in paragraph 2, but also at all other stations in the country and for all PAH's studied in this project.

A compilation of the tables 1,2 and 3 makes comparison still simpler.

Table 4
Compilation of tables 1,2 and 3

Subject	year			
	1965	1970	1975	1977
Total coal consumption (T cal)	93700	47900	23900	1143
Total oil consumption (not counting traffic) (T cal)	153200	208700	138500	147100
Total consumption of liquid fuel by traffic (T cal)	34100	52200	64800	78000
Total natural gas consumption (T cal)	14300	168100	350800	369000
Total number of motor vehicles (thousands)	1656	2838	3809	4268
3,4 benzopyreneconcentration at station V10 ($\mu g/1000\ m^3$)	26	15	3.6	n.d.

Though correlations between local PAH-concentrations and national fuel consumptions are not ideal, comparison of these two groups of data is possible. This comparison shows

a) coal consumption and PAH-concentration show a parallel trend
b) there is no parallel between oil consumption and PAH-concentration
c) liquid fuel consumption by traffic and PAH-concentrations show opposite trends
d) natural gas consumption and PAH-concentrations show opposite trends
e) the number of motorcars and PAH-concentrations show opposite trends.

This leads to several conclusions

A) Natural gas consumption does not contribute to an appreciable extent to general PAH-concentrations.
B) Modern motor vehicles do not contribute to an appreciable extent to general PAH-concentrations. It is not yet clear whether motor vehicles had a contribution to PAH-concentrations in the early years of the study.
C) At the end of the study oil consumption does not contribute to an appreciable extent to general PAH-concentrations.
D) The strong parallel between coal consumption and PAH-concentrations indicates a large contribution of the burning of coal to general PAH-concentrations.
E) Local situations can show differences from this general picture (see next paragraph!).

5. RELATIVE PROPORTIONS OF PAH AS AFFECTED BY DIFFERENT TYPES OF POLLUTION

As already mentioned in paragraph 2, short time measurements were made under different conditions on a number of locations. These measurements range from the measurement of pollution generated (nearly) completely by traffic (on border crossings of motorroads, in a tunnel and near a large motorroad) via measurements of mixtures of pollution (in Delft and near a motorroad during low wind velocities on foggy days) to measurements of smoke pollution caused by smouldering wood chips near an eel smoking factory. Nearly always all polycyclic hydrocarbons mentioned in paragraph 2 were measured. As the intention of this part of the study was to find ratios between several PAH's that are specific

for certain types of sources, in this publication only those PAH's used in determining the ratios are mentioned in table 5 (pyrene, 3,4 benzopyrene, 1,12 benzoperylene and coronene)

Table 5
PAH-concentrations during short period measurements (1 or 2 hours) at specific locations

Location	Specific conditions	PAH (µg/1000 m^3)			
		pyrene	3,4 benzopyrene	1,12 benzoperylene	coronene
Denekamp	bordercrossing	48	12	54	32
Bergh	bordercrossing	20	1	27	16
Bergh	bordercrossing	14	1	16	7
Volendam	eel smoking	7	6	6	1
		3	3	2	1
		6	n.d.	n.d.	n.d.
		6	2	4	1
Delft	foggy day, low wind velocity from Rotterdam + motor road	54	49	39	4
		55	56	31	.
		46	54	44	5
Delft	foggy day, low wind velocity from heated glasshouses	27	60	48	6
		12	17	12	3
		13	20	12	3
Delft	foggy day, low wind velocity from Rotterdam + motor road	32	39	31	5
		34	56	37	6
		39	50	39	5
Delft	foggy day, low wind velocity along motorroad	7	6	12	3
Delft	foggy day, low wind velocity from Rotterdam + motor road	33	11	13	3

Delft	foggy day, low wind velocity from The Hague + motor road	214	123	103	21
		312	138	126	19
		220	101	118	18
Delft	foggy day, low wind velocity from Rotterdam + motor road	40	43	31	6
Amsterdam	Coentunnel (motor road)	111	14	16	7
		33	.	4	2
		114	12	11	10
		78	2	10	4
		92	10	8	17
Roelofarendsveen	motor road 2 months measurements	3.2	2.7	2.9	0.8

From the series of measurements as used for determining the trend of the PAH-concentrations some data were selected for studying a possible trend in the ratios between several PAH's. These data are presented in table 6.

Table 6

PAH-concentrations selected from the trend-measurements

Station	Period	PAH (µg/1000 m^3)			
		pyrene	3,4 benzopyrene	1,12 benzoperylene	coronene
V 1	12/64-2/65	29	28	28	3
V 1	12/65-3/66	23	22	11	3
V 2	"	18	33	21	5
W 9	"	11	14	8	2
D12	"	10	12	9	2
V10	"	7	26	17	2
V 1	4/66-8/66	9	n.d.	2	1
V 2	"	4	n.d.	n.d.	1
W 9	"	1	n.d.	n.d.	n.d.
D12	"	2	n.d.	n.d.	n.d.
V10	"	7	n.d.	n.d.	n.d.
V 1	11/69-2/70	13	23	14	3
V 2	"	21	27	17	3
W 9	"	15	13	11	2
D12	"	13	13	16	3
D21	"	5	6	9	1
V10	"	8	20	17	4
V 1	5/70-10/70	2	7	4	n.d.
V 2	"	2	5	4	1
W 9	"	2	3	2	n.d.
D12	"	2	n.d.	2	n.d.
D21	"	2	4	2	n.d.
V10	"	3	3	3	n.d.
V 1	11/72-2/73	4	13	7	1
V 2	"	10	20	9	1
W 9	"	4	13	3	1
D12	"	4	18	9	4
D21	"	4	18	6	1
V10	"	6	17	n.d.	1

Later measurements are too low to produce reliable ratios.

Already in 1961 studies on the ratios between different PAH-concentrations were made in the USA [8, 9].

A study of the literature on this and other material [10], produced the ratios as presented in table 7.

Table 7
Ratios between different PAH-concentrations as measured in practice (data from literature)

Ratio	Motor traffic	Burning of fuels
3,4 benzopyrene / coronene	< 0.4 - 1	> 1.7
3,4 benzopyrene / 1,12 benzoperylene	0.2-0.6	> 0.8
pyrene / 3,4 benzopyrene	2-6	0.3-0.8

These ratios are different from those obtained from measurements in the direct exhaust gases. The reason for this phenomenom is the difference in stability of the specific polycyclic hydrocarbons. For instance, 3,4 benzopyrene is very stable in the atmosphere, pyrene is much less stable. This influences the ratio between these pollutants. As it is clear that PAH can be transported over very large distances [11], especially the ratios between background concentrations will be influenced by this difference in stability.

Another possible effect is a change in the ratio over the years because of changes in the sources of pollution: modern installations and engines may not only produce less pollution, but also give a different ratio between the pollutants than was the case in older installations and engines.

The ratios 3,4 benzopyrene/coronene, 3,4 benzopyrene/1,12 benzoperylene and pyrene/3,4 benzopyrene are calculated for the data mentioned in the tables 5 and 6. The ratios are presented in the tables 8 and 9. It should be kept in mind that ratios derived from low concentrations of PAH may be less accurate.

Table 8

Ratios between PAH-concentrations during short period measurements at specific locations

Location	Source of pollution	Relative proportion PAH		
		3,4 B.P. / COR.	3,4 B.P. / 1,12 B.PER	PYR. / 3,4 B.P.
Denekamp	halting traffic	0.4	0.2	4.0
Bergh	halting traffic	0.1	0.04	20.0
Bergh	halting traffic	0.1	0.1	14.0
Volendam	eel smoking	6.0	1.0	1.1
	"	3.0	1.5	1.0
	"	.	.	≥ 6
	"	2.0	0.5	3.0
Delft	general	12.0	1.3	1.1
	"	.	1.8	1.0
	"	10.8	1.2	0.9
Delft	general + glass-houses	10.0	1.2	0.5
	"	5.7	1.4	0.7
	"	6.7	1.7	0.7
Delft	general	7.8	1.3	0.8
	"	9.3	1.5	0.6
	"	10.0	1.3	0.8
Delft	general + traffic	2.0	0.5	1.2
Delft	general	3.7	0.8	3.0
Delft	general	5.9	1.2	1.7
	"	7.3	1.1	2.3
	"	5.6	0.9	2.2
Delft	general	7.2	1.4	0.9
Amsterdam	traffic in tunnel	2.0	0.9	7.9
	"	.	.	.
	"	1.2	1.1	9.5
	"	0.5	0.2	36.0
	"	0.6	1.3	9.2
Roelofa-rendsveen	traffic on motor road	3.4	0.9	1.2

Table 9

Ratios between PAH-concentrations selected from the trend-measurements

Station	Period	Relative proportion PAH		
		3,4 B.P. / COR.	3,4 B.P. / 1,12 B.PER	PYR. / 3,4 B.P.
V 1	Winter 64-65	9.3	1.0	1.0
V 1	Winter 65-66	7.3	2.0	1.0
V 2	"	6.6	1.4	0.5
W 9	"	7.0	1.8	0.8
D12	"	6.0	1.3	0.8
V10	"	13.0	1.5	0.3
V 1	Summer 66	.	.	≧ 9 *
V 2	"	.	.	≧ 4 *
W 9	"	.	.	≧ 1 *
D12	"	.	.	≧ 2 *
V10	"	.	.	≧ 7 *
V 1	Winter 69-70	7.7	1.6	0.6
V 2	"	9.0	1.6	0.8
W 9	"	6.5	1.2	1.2
D12	"	4.3	0.8	1.0
D21	"	6 *	0.7	0.8
V10	"	5.0	1.2	0.4
V 1	Summer 70	≧ 7 *	1.8	0.3
V 2	"	5 *	1.2	0.4
W 9	"	≧ 3 *	1.5 *	0.7
D12	"	.	.	≧ 2 *
D21	"	≧ 4 *	2.0 *	0.5
V10	"	≧ 3 *	1.0	1.0
V 1	Winter 72-73	13 *	1.9	0.3
V 2	"	20 *	2.2	0.5
W 9	"	13 *	4.3	0.3
D12	"	4.5	2.0	0.2
D21	"	18 *	3.0	0.2
V10	"	17 *	≧ 17 *	0.3

*less accurate because of low concentration

The ratios mentioned in the tables 7, 8 and 9 are graphically presented in the figures 3, 4 and 5. These figures show clearly that the margins mentioned in table 7 are too narrow. In practice the margins for the ratios expected for the different types of pollution can overlap each other. From the data derived from our study we can compose a new version of table 7 with wider margins as is shown in table 10.

Table 10

Ratios between different PAH-concentrations as measured in practice (this study)

Ratio	Motor traffic	General pollution
$\frac{\text{3,4 benzopyrene}}{\text{coronene}}$	< 3.5	> 3.5
$\frac{\text{3,4 benzopyrene}}{\text{1,12 benzoperylene}}$	< 1.5	> 0.5
$\frac{\text{pyrene}}{\text{3,4 benzopyrene}}$	> 3.5 (1 exception)	< 3.5

From the data the following conclusions can be drawn:

Conclusion 1 The ratios between different PAH-concentrations can give clues for detecting the source of the pollution. Especially the ratio $\frac{\text{3,4 benzopyrene}}{\text{coronene}}$ looks promising.

Conclusion 2 Mixtures of different types of pollution will show ratios between PAH-concentrations that do not fit into the margins mentioned in table 10.

Conclusion 3 Special types of pollution, for instance eel smoking or specific industrial sources may give ratios different from those in table 10, but specific for that special source.

Conclusion 4 It is to be expected that flowing traffic and halting traffic will show different ratios between their PAH-concentrations. We are under the impression that halting traffic (measurements at border crossings) gives lower ratios for $\frac{\text{3,4 benzopyrene}}{\text{coronene}}$ and for $\frac{\text{3,4 benzopyrene}}{\text{1,12 benzoperylene}}$ than does flowing traffic.

Conclusion 5 The ratio $\frac{\text{pyrene}}{\text{3,4 benzopyrene}}$ gives very wide ranges for traffic pollution in which no influences of halting versus flowing traffic seem to be visible.

Conclusion 6 It was to be expected that with lower concentrations of general air pollution, the influence of traffic air pollution on the ratios would become visible. This was not the case, perhaps with the exception of the summervalues of 1966. Other summers (including those not shown in table 9) did, however, not show the same phenomenon as 1966.

Conclusion 7 The data for traffic under specific conditions (halting, flowing) and for special sources of pollution need extra information.

6. EXPECTED FUTURE DEVELOPMENTS

It is to be expected that in the Netherlands the next few years will show a new development in the trend of energy production. For domestic heating natural gas will be the only important source of energy as it is now already. For larger installations, however, gas will be replaced by oil and/or coal and for the very large units as for instance power stations coal will be the most probable fuel for new units. For the emission of PAH, these changes will not be of much importance, as all smaller furnaces will still use the clean burning natural gas, only larger installations will go back to coal. There will be no production of PAH in these large, modern and well-run furnaces. The changes do mean that the downward trend in PAH-concentrations will stop. Concentrations arising from furnaces and boilers will be constant (and still low) from now on.

A further growth of the intensity of the motor traffic will not change the total picture to an important degree. Local development of traffic jams in situations where the traffic is now flowing well can, however, result in local problems.

It is difficult to foresee future developments in industrial processes. In practice local problems can exist near special industrial installations. In the farther-away future when coal mining and coal gasification

will come into the picture again, problems may arise if there would be taken no sufficient precautions against the production of PAH. The 3,4 benzopyrene emission data for the USA [12] show that coal production, processing and burning are the most important sources of 3,4 benzopyrene in the USA. Of the 1260 tons of 3,4 benzopyrene produced per year, 953 tons arise from these sources (however nearly half of that amount escapes out of domestic heating flues; this will not be the case in the Netherlands where domestic heating will still be using natural gas for the next few decades).

Another source shown in (7.12) is the burning of refuse. Especially refuse from agriculture and forestry is important. The burning of wood (as refuse or in open fires for heating) can be a local source of PAH, comparable to eel smoking as described in this study.

Summarising these remarks leads to the conclusion that PAH-concentrations in the Netherlands will be low and more or less constant in the near future. Local problems can exist or develop because of motor traffic exhaust or industrial operations. Monitoring the general concentrations on a limited scale can be useful to keep an eye on the trend. Study of special sources (industry, refuse burning, traffic jams, aeroports) will be necessary. It would be welcome if more information on agricultural refuse burning, garden bonfires and wood burning open fires for heating could be made available.

Further study on ratios between the different PAH-concentrations can give better information on the relative importance of the different sources of pollution in the total pattern of PAH-concentration. International comparison of data with other countries where trends in the PAH-concentrations exist [13] will provide extra evidence of the importance of abatement of PAH-pollution.

IMG-TNO-Abu
1979-09-07
GD/DV

7. LITERATURE

1. Evelyn, John. 1661
   Fumifugium or the Inconvenience of the Aer and Smoake of London dissipated. Reprint 1933, 42 p. National Smoke Abatement Society, Manchester (now National Society for Clean Air, Brighton).
2. Biersteker, K.
   Luchtverontreiniging in Haarlem in 1608.
   Ned. Tijdschrift voor Geneeskunde, 1968, jaargang 112, nr. 1.

3. Several measuring reports of the TNO Research Institute for Environmental Hygiene, covering the period of 1965 - present.
   IMG-TNO, Delft.
4. Kommers, F.J.W.
   Polycyclic hydrocarbons.
   Report G 689 of the TNO Research Institute for Environmental Hygiene.
   IMG-TNO, Delft, January 1976.

5. De Graaf, H.
   Annual report of the Laboratory of the Food Inspection, Rotterdam, 1964.
   Keuringsdienst van Waren (KvW) Rotterdam 1965.
6. Statistisch Zakboek.
   Editions 1976 and 1978.
   Centraal Bureau voor de Statistiek (CBS) The Hague 1976,1978.

7. Several editions of Statistisch Zakboek.
   Centraal Bureau voor de Statistiek (CBS) The Hague.
8. Sawicki, E.
   Analysis for airborne particulate hydrocarbons: their relative proportions as affected by different types of pollution.
   Symposium: Analysis of carcinogenic air pollutants, Cincinnati August 1961, National Cancer Institute Monograph No. 9, p. 201 - 220.

9. Lyons, M.J.
   Comparison of aromatic polycyclic hydrocarbons from gasoline engine and diesel engine exhausts, general atmospheric dust, and cigarette-smoke condensate.
   Symposium: Analysis of carcinogenic air pollutants, Cincinnati August 1961, National Cancer Institute Monograph No. 9, p. 193 - 199.

10. Blokzijl, P.J.
Kankerverwekkende stoffen in de buitenlucht.
Natuur en techniek, 41e jaargang nr. 4, 1973., p. 1 - 13.

11. Björseth, A., Lunde, G., Lindskog, A.
Long-range transport of polycyclic aromatic hydrocarbons.
Atmospheric Environment vol. 13 p. 45-53, 1979.

12. Grimmer, G.
Messtechnische Erfassung von PAH durch Profil-Analyse.
Umwelt 2/79, p. 123 - 125.

13. Commins, B.T., Hampton, L.
Changing pattern in concentrations of polycyclic aromatic hydrocarbons in the air of Central London.
Atmospheric Environment vol. 10 p. 561-562, 1976.

FIGURES

Figure 1 Concentration of 1,2 Benzopyrene in winter Station V 10 (Rotterdam city center)

Figure 2 Concentration of 3,4 Benzopyrene in winter Station V 10 (Rotterdam city center)

Figure 3 Ratios between PAH-concentrations $\frac{\text{3,4 B.P.}}{\text{COR.}}$

Figure 4 Ratios between PAH-concentrations $\frac{\text{3,4 B.P.}}{\text{1,12 B.PER.}}$

Figure 5 Ratios between PAH-concentrations $\frac{\text{PYR.}}{\text{3,4 B.P.}}$

Figure 1 CONCENTRATION OF 1,2 BENZOPYRENE IN WINTER STATION V 10 (ROTTERDAM CITY CENTER)

Figure 2 CONCENTRATION OF 3,4 BENZOPYRENE IN WINTER STATION V 10 (ROTTERDAM CITY CENTER)

3,4 B.P.
COR.
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
Table 7
Table 9
General
Table 8
General,
Traffic
Table 8
EEL smoking
General pollution
Traffic pollution
EEL smoking
Mixture of general and traffic pollution
RATIOS BETWEEN
PAH-CONCENTR.
3,4 B.P.
COR.

Figure 3

3,4 B.P.
1,12 B.PER
5
4
3
2
1
0
Table 7
Table 9
General
Table 8
General,
Traffic
Table 8
EEL smoking
General pollution
Traffic pollution
EEL smoking
Mixture of
general and
traffic pollution
RATIOS BETWEEN
PAH-CONCENTR.
3,4 B.P.
1,12 B.PER

Figure 4

PYR.
3,4 B.P.
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
20
36
Table 8
General,
Traffic
Table 7
Table 8
EEL smoking
Table 9
General
RATIOS BETWEEN
PAH-CONCENTR.
PYR.
3,4 B.P.
General pollution
Traffic pollution
EEL smoking
Mixture of
general and
traffic pollution

Figure 5