Ref. no. : 89-036
File no. : 8722-17533
Date : January 1989
NP

Title
EMISSIONS INTO THE ATMOSPHERE OF POLYAROMATIC HYDROCARBONS, POLYCHLORINATED BIPHENYLS, LINDANE AND HEXACHLOROBENZENE IN EUROPE

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EXECUTIVE SUMMARY

For the modeling of pollution of the North Sea and the Baltic by aerial pathways some organic substances have been chosen among others. These are: PAH's, PCB's, Lindane and hexachlorobenzene (HCB). Main sources have been selected and emission factors for these have been developed. Surrogate parameters to spatially distribute emissions have been chosen. Emission data, to be expressed as annual averages, have to be representative for the year 1982. They have to be estimated for all European countries.

As was anticipated, only for PAH's sufficient data were available to make emission estimations. The scarce and partially conflicting data for the other substances only allowed order of magnitude values of emissions.

The source types proposed for the model investigation, together with their emission factors, are listed below. It was not possible to give confidential limits, instead, ranges were rougly estimated.

Sources and emission factors

PAH's

Residential combustion;	anthracite	0.5	(0.2-0.8)	$mg.kg^{-1}$ fuel
	bituminous coal	50	(30-70)	"
	coal briquettes, conventional	50	(30-70)*	"
	coal briquettes, smokeless	0.5	(0.2-0.8)*	"
	brown coal briquettes	12	(7-18)	"
	distillate oil	0.5	(0.2-0.8)*	"
	wood (stoves)	100	(10-200)	"
	wood (fireplaces)	25	(10-40)	"
Coke production:	uncontrolled	10	(2-20)	$mg.kg^{-1}$ coke
	controlled	0.2		"
Primary aluminium production;	anode baking	70	(40-120)	$mg.kg^{-1}$ Al
	prebaked anodes	30	(10-50)	"
	Söderberg process	1000	(500-5000)	"
Wood preservation:	carbolineum	200	$g.kg^{-1}$	carbolineum
	creosote	5	$mg.kg^{-1}$	creosote

Mobile sources; gasoline powered vehicles	4	(2-6)	$mg.kg^{-1}$ fuel
diesel powered vehicles	5.3	(3.5-7)	"
Wildfires	10	(5-25)	$kg.km^{-2}$
PCB's			
All sources, except incidental leakages and illegal activities	2	(1-5)	$g.inh.^{-1}.y^{-1}$
Lindane			
Agricultural and veterinary use	5	(3-10)	%**
Other applications	50		%***
Hexachlorobenzene			
Production of tetrachloroethylene	6	(3-10)	$mg.kg^{-1}$
Production of trichloroethylene	3	(1-6)	"
Production of carbon tetrachloride	8	(1-20)	"
Application of pesticides	10	(5-15)	$g.km^{-2}.y^{-1}$ of arable land
Use of pentachlorophenol	15		$mg.inh^{-1}.y^{-1}$

* Assumed

** Fraction of amounts applied according to table 4.9 (per km² of arable land)

*** " " " " " " " (per inhabitant)

Emissions of selected PAH's can be estimated by combining PAH emission factors with appropriate profiles (tables 2.31 or 2.32).

1. INTRODUCTION

Pollution of the sea is a matter of growing concern. Consequently much effort has been put into the study of pollutants. Whereas inputs from surface water and from nagivation and off-shore activities have been given attention for a relatively long time, pollution by deposition from the atmosphere is a more recent object of investigation. Its contribution therefore is still incompletely known.

For a better understanding of the combined effects of these transportways the Umweltbundesamt has launched a study of pollution of marine waters, for which Dornier System GmbH, Friedrichshafen was contracted. The investigation has as receptor areas the North Sea and the Baltic.

Pollutants to be studied were the result of a selection with the purpose of working with a model composition. A selection of heavy metals and organic compounds was made, hence the project's acronym MASH (Metals and Selected Hydrocarbons). The two groups comprised As, Cd, Hg, Pb and Zn respectively PAHs, PCBs, Lindane (γ-hexachlorocyclohexane, HCH) and hexachlorobenzene (HCB). PAHs had to be inventoried as total amounts as well as major single compounds.

The donor area was chosen to be Europe, i.e. the EMEP area. An inventory with annual average emission rates for the year 1982 was decided upon. It had to have the PHOXA data base structure, that is, all activities that emit one or more of the model pollutants and are not in the PHOXA data base had to be added to it.

The Norwegian Institute for Air Research (NILU) was subcontracted for the inventory of the heavy metals. The Dutch Organization for Applied Scientific Research (TNO) was subcontracted for the inventory of the organic substances and data base elements.

Investigation of the organic substances implied selection of emitting activities and the development of appropriate emission factors, since for these pollutants no adequate history of air pollution inventorying exists (with the exception, more or less, of PAH's).

This report deals with this investigation. Characteristics of the selected substances, selection of emitting activities and the development of air pollutant emission factors for these activities are

reported. PAH emission factors are reported together with composition profiles containing a selection of major polyaromatic hydrocarbons.

2. SOURCES OF POLYCYCLIC AROMATIC HYDROCARBONS AND THEIR EMISSION FACTORS

2.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are compounds consisting of two or more fused aromatic carbon five or six rings. Many of them are regarded as, or suspected to be carcinogenic or mutagenic. Therefore intake by inhalation of air or by consumption of food or water which is polluted by these compounds may be hazardous. The concentrations with which PAHs are present in air, water or food depend largely on the rate with which PAHs are emitted by sources into these media. Most of the PAHs which are formed and emitted are the result of combustion processes and are directly released into the air. Part of the PAHs may subsequently, sometimes after long times and over large distances, be deposited on soil or on water.

2.2 Selection of PAH compounds

In combustion and industrial processes many PAHs are formed and released into the atmosphere. In emissions from combustion processes about 70 PAHs have been identified, half of which are biologically active (Junk and Ford, 1980). Lists of PAHs with indications referring to their carcinogenity and/or mutagenity have been given by several authors. This information is summarized in Table 2.1. Apart from these PAHs there are some heterocyclic compounds (azo-compounds) of which carcinogenity has been established, e.g. dibenz(a,h)acridine and dibenz(a,j)acridine.
The large amount of PAHs necessitates a selection procedure for which abundancy and biological activity can be used as criteria. Another reason for considering only a limited number of compounds is that in investigating PAH emissions already selections are made because of analytical constraints. On comparison, unfortunately, these selections often appear not to be consistent. It can be concluded from measurements that, generally, the lower molecular PAHs show the larger emissions. Opposite to this is their relativily low toxicity. Generally, emission data of the low molecular PAHs are limited to three-ringed PAHs, in

Table 2.1 Biological activity of Polycyclic Aromatic Hydrocarbons

PAH	Carcinogenity 1)	Carcinogenity 2)	Mutagenity 2)
Fluorene	-		
Phenanthrene	-		
Anthracene	-		
Fluoranthene	-		-/+
Pyrene	-	-	-
Cyclopenta(cd)pyrene		+/++	+++
Chrysene	-/+		
Benzo(c)phenanthrene	++++	++	++
Benzo(a)anthracene	+		
1-methylchrysene		-	+
2-methylchrysene		+	+
3-methylchrysene		+	+
4-methylchrysene		+	+/++
5-methylchrysene		+++	++/+++
6-methylchrysene		+	+
1-methylbenzo(a)anthracene		-/+	+
Cholanthrene	+++		
Benzo(b)fluoranthene	+++	++/+++	++
Benzo(j)fluoranthene	+++	++/+++	++/+++
Benzo(k)fluoranthene	-	+	++
Perylene	-	-	
Benzo(a)pyrene	++++	++++	++++
Benzo(e)pyrene	-	-	+
7,12-dimethylbenzo(a)anthracene	++++		
Dibenzo(a,c)fluorene			
Dibenzo(a,g)fluorene	++		
Dibenzo(a,h)fluorene	-/+		
3-methylcholanthrene	++++		
Indeno(1,2,3-cd)pyrene	++	++	++
Benzo(ghi)perylene	++	-/+	+
Anthanthrene	-	+/++	+
Benzo(c)chrysene		++	
Dibenzo(a,c)anthracene	++	-/+	+++
Dibenzo(a,h)anthracene	++++	+++/++++	++/+++
Dibenzo(a,j)anthracene	++	++	+
Coronene	-		
Dibenzo(a,e)pyrene		++/+++	++
Dibenzo(a,h)pyrene	++++	++++	++++
Dibenzo(a,i)pyrene	++++		
Dibenzo(a,l)pyrene	-/+		

- inactive, -/+ uncertain or weak, + weak, ++ moderate, +++ strong, ++++ very strong activity

1) National Research Council, Committee on Biological Effects of Atmospheric Pollutants (1972).

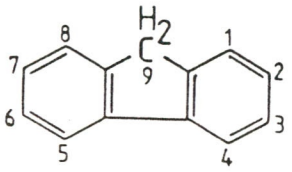
2) Jacob et al. (1984).

other words, naphtalene and its derivates are not considered to be PAHs. Again, only a few authors report measurements of the three-ringed compounds acenaphtene and acenaphtylene, probably because of their instability in an oxidizing atmosphere. Therefore these compounds have been left also out of consideration, although their total emission may sometimes be of the same order of magnitude as the total PAH emissions included in this study.

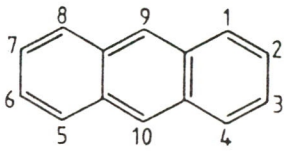
Since it is the aim of the study to create tools to estimate a more or less complete emission picture of PAHs, only those will be considered about which sufficient emission data are available from literature. It was found that the emission data in the literature frequently regard ca. 20 PAHs, whereas information on other PAHs is found only incidentally. Emission data on benzofluoranthenes and on dibenzoanthracenes often refer to these substances together. Therefore the emission factors given here also will refer to the grouped compounds.

Based on these considerations the following PAHs have been selected (Table 2.2):

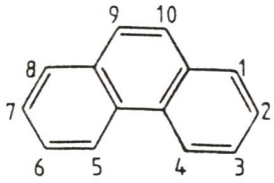
Table 2.2 PAHs selected for the MASH study



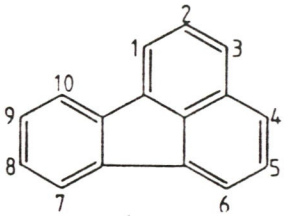
fluorene



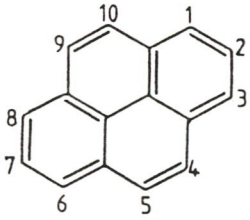
anthracene



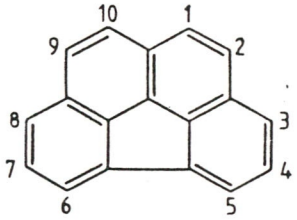
phenanthrene



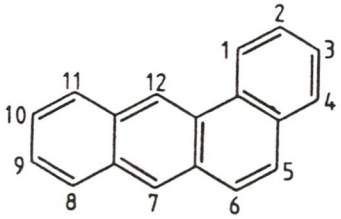
fluoranthene



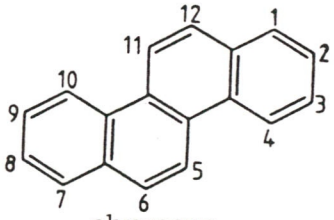
pyrene



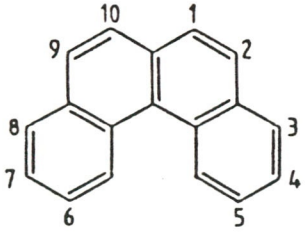
cyclopenta(cd)pyrene



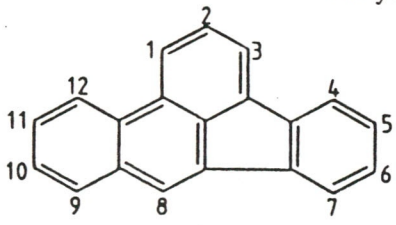
benzo(a)anthracene



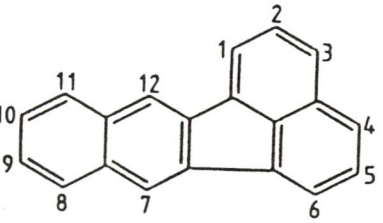
chrysene



benzo(c)phenanthrene

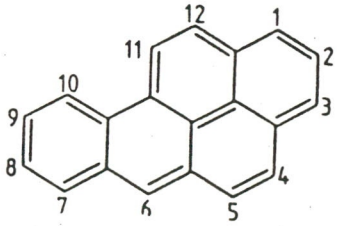


(b)

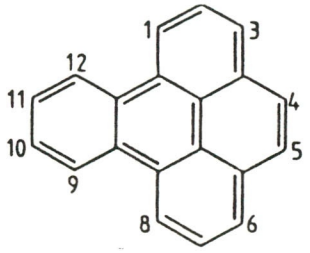


(k)

benzofluoranthenes

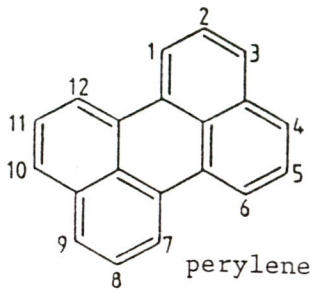


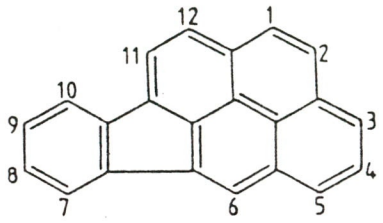
benzo(a)pyrene

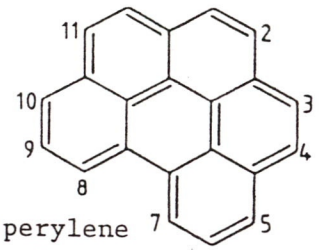


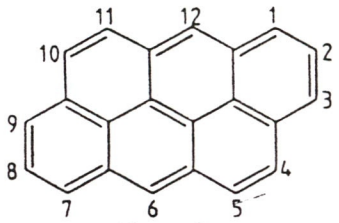
benzo(e)pyrene

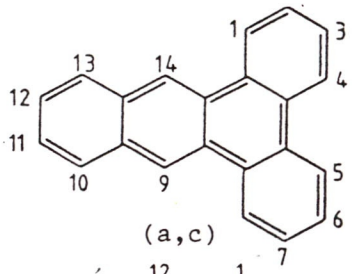
Table 2.2 PAHs selected for the MASH study (continuation)

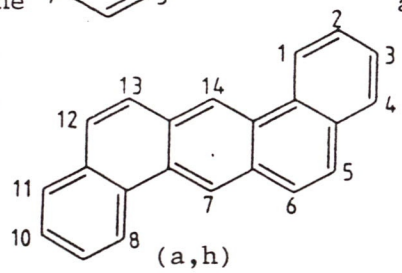


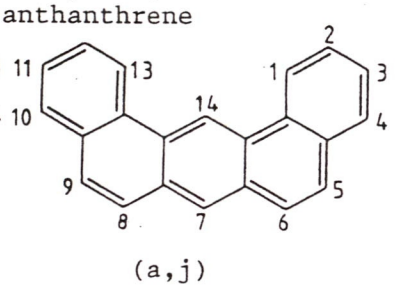




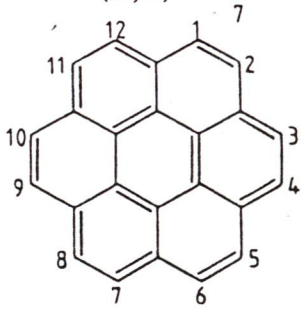








dibenzoanthracenes



2.3 Emission factors

Emission factors are used as statistical tools for the approximate estimation of emissions. They are defined as average values, relating emission rates to process parameters. The latter should be as specific as possible. For PAHs emitted from processes the emission factors are usually related to quantities produced (industry) or destroyed (incineration). The latter relation can also be used for combustion pro-

cesses, although there is an alternative in relating the emission to produced energy (electric or mechanical). According to practice the emission factor for combustion is defined as the ratio between the emission rate and the quantity of fuel burned per unit of time, so it is conveniently expressed in $ng.MJ^{-1}$ or in $\mu g.kg^{-1}$. For PAH in road vehicles exhaust gases emission factors may be related to fuel consumption or to vehicle kilometers. The choice depends on the availability of statistical data. In this study fuel consumption data will be used, these being available for all countries.

2.4 Emission profiles

In the vicinity of a source the emitted PAHs appear to be present partly in the gaseous state and partly as particulates. Low molecular PAHs (consisting of 3 or 4 carbon rings) have a relativily low vapour pressure and are mainly present as a gas.
The ratios in which the several PAHs are emitted vary between processes and may even vary in one process as a function of process conditions. This has been found by sampling of air in the vicinity of PAH sources. These ratios, the so-called PAH profiles, together with the biological activity of the compounds, determine the potential harm of sources, apart - of course - of the emission rates representative for that source type, its representativiness increasing the more detailedly the source is described (e.g. temperature and air supply for combustion processes). Then the emission of a certain compound can be found by multiplying the emission of a selected reference PAH compound with a so-called profile factor for that source type. This factor is defined as the ratio between the emission of that PAH and the emission of the reference PAH. Alternativily profile factors may be related to the total PAH emission or to part of the components.
Daisey et al. (1986) selected benzo(e)pyrene as a reference PAH compound because of its stability and because (as they stated) this compound is found almost exclusivily in the particulate phase. This may be true for emissions from e.g. aluminium reduction and coke plants as is found by Björseth et al. (1978) but is not generally valid for combustion emis-

sions. Den Boeft et al. (1984) showed that the PAHs emitted from combustion of wood may be mainly found in the vapour phase under certain experimental conditions. Daisey et al. analysed literature data for different sources which they believed to be significant contributors of PAH emission. As an illustration of the variation of profile factors of PAHs originating from different source types Table 2.3 shows these factors for some areas in the Federal Republic of Germany which are more or less representative for a certain source type. Still larger differences may exist near the sources.

The emission factors given in the older PAH literature refer, almost exclusivily, to total PAH or to benzo(a)pyrene. Emission factors for benzo(e)pyrene can be easily calculated from that of benzo(a)pyrene by dividing them by the profile factor of benzo(a)pyrene provided this factor is known. For many processes this factor appears to be about 1.

In this study profile factors for most sources have been taken from literature. They will be assumed to be representative for specific sources. It will be seen that sometimes there are large differences, especially for low molecular PAHs. For older data this may be due to the fact that sampling techniques were inappropriate to capture gaseous PAH completely.

The disadvantage of relating an emission to that of one PAH (benzo(e)-pyrene) however is that, if the emission of that reference PAH from a source shows a deviating behaviour, the profile factors of all other PAHs have seemingly abnormal values. Therefore profile factors are preferently presented as a percentage of total PAH, in spite of the fact that some PAHs may have not been completely sampled or detected.

It is tempting to present also emission data for total PAH. However, one has to realize that identical concentrations of total PAH may have very different toxic effects depending on the fractions of PAHs with biological activity. Apart from that, measurements of several authors not always include all low molecular PAHs; sometimes anthracene and phenanthrene are not recorded. Therefore presenting an emission factor for total PAH has a limited value. A possibly better approach would be to present the emission of PAHs in two categories, one consisting of low molecular PAHs which, because of their relativily high vapour pressure,

are predominantly in the gaseous state (e.g. up to and including the C18 PAHs: cyclopenta(cd)pyrene, benzo(c)phenanthrene, chrysene and benzo(a)-anthracene) and the other with high molecular PAHs which are at least partially bound to aerosols. It appears that the transport ranges of these categories are different, which can be attributed to differences in deposition rates and, possibly more important, differences in degradation rate: it is believed that PAHs in the gaseous state are more subject to degradation by radicals in the atmosphere than PAHs bound to aerosols.

Table 2.3 Ratios of concentrations of some PAHs and benzo(e)pyrene in Essen, FRG (Grimmer et al, 1980, quoted by Daisey et al., 1986)

PAH	Residential coal-burning area	Residential oil-burning area	Coke ovens	Tunnel (road transport)
Anthracene	0.4	0.4	0.3	2.2
Benzo(c)phenanthrene	0.4	0.6	0.3	2.2
Benzo(a)anthracene	1.4	1.0	1.2	1.2
Cyclopenta(cd)pyrene	0.02	0.4	0.4	5.3
Chrysene	2.5	2.6	1.8	1.8
Benzo(b)fluoranthene	1.4	1.7	1.3	1.2
Benzo(j+k)fluoranthenes	1.2	1.5	1.0	1.0
Benzo(a)pyrene	0.6	0.9	1.0	1.2
Perylene	0.08	0.25	0.3	0.2
Indeno(1,2,3-cd)pyrene	0.6	1.0	0.6	0.8
Benzo(ghi)perylene	0.7	1.0	0.6	1.8
Anthanthrene	0.07	0.3	0.07	0.5
Coronene	0.2	0.3	0.08	0.9
Low mol. PAH (total)	4.7	5.0	4.0	12.7
High mol. PAH (total)	4.9	6.95	4.95	7.6

In calculating PAH concentrations at large distances from a source it must be realized that some PAHs may desintegrate or are oxidized. As a consequence profiles may change during transportation.

In view of the arguments given before it must be concluded that the most appropriate way to present PAH emission data is to give data for each PAH seperately. In other words, PAHs have to be regarded as separate compounds. For comparing PAH data, however, it may sometimes be advan-

tageous to use an emission factor for total PAH. Then its lower boundary has to be standardized. The reason for this is that emission profiles show less variation than emission factors. The emission factor for a certain PAH then can be assessed by multiplying an average emission factor derived from different data with an average profile factor which has been estimated with a higher accuracy. Moreover, sometimes only concentration profiles are reported; in these cases where no emission factors can be derived directly, profiles can still be used in combination with an emission factor for total PAH resulting from other information.

2.5 Source identification

Many chemical and physical processes have been identified as sources of PAHs. Several authors reviewed these and estimated their contributions to environmental burdening: Hangebrauck et al.(1967), National Research Council, Committee on Pyrene and Selected Analogues (1972), Suess (1976), Blackwood and Archer (1979), Grimmer (1979, 1981), Verhoeve en Compaan (1980), Ramdahl et al.(1983), Smith (1984), Nikolaou et al. (1984), Björseth and Ramdahl (1986). Referring to the nature of the PAHs forming processes the sources of PAHs can be distinghuised in the following categories:

1. Residential combustion (coal, wood, oil, gas).
2. Heat and power generation.
3. Industrial productions (coke, aluminium, iron, etc.).
4. Incineration and open burning (municipal waste, coal waste, automobile refuse, agricultural waste and forest fires).
5. Mobile sources (gasoline and diesel automobiles, rubber tire wear).

It is worthwile to estimate roughly the relative importance of these source categories, since the contribution of some categories may be negligible with respect to the accuracy with which the contribution of others can be estimated.
Table 2.4 presents reported contributions of different sources and fuels to national annual PAH emissions. The estimations appear to be partly based on earlier studies of others.

Table 2.4 Estimation of PAH emissions from various sources (relative contribution, in %)

Author(s):	Hangebrauck et al.	Nat.Res. Council	Grimmer	Peters	Björseth and Ramdahl		
	(1967)	(1972)	(1979)	(1982)	(1986)		
Country:	U.S.A.	U.S.A.	U.S.A.	U.S.A.	U.S.A.	Norway	Sweden
Source:	1)	1)	1)				
Residential combustion:							
- coal	85.1	33.6	33.3	0.9	11.5*	16.0*	38.4*
- wood		3.1	3.2	34.8			
- oil	0.3	0.2	0.2	<0.1	0.2**	4.8**	14.4**
- gas	0.3	0.2	0.2	<0.1			
Electricity and heat generation:							
- coal/oil fired power plants	1.0	0.1	0.1	0.1	<0.1		<0.1
- industrial boilers		1.2	0.8	6.3	6.6	0.4	2.6
- peat, wood, straw						<0.1	2.6
Industry							
- coke manufacturing	low	15.0	15.1	5.7	10.4	1.7	7.2
- charcoal manufactur.				<0.1			
- aluminium production	low				16.5	53.3	14.0
- iron/steel sintering	low					11.3	
- ferroalloy industry						1.2	
- petroleum cracking	3.9	0.5	0.5				<0.1
- carbon black product.				<0.1	<0.1		<0.1
- asphalt production	<0.1	<0.1	<0.1	<0.3	<0.1	<0.1	<0.1
Incineration and open burning							
Enclosed:							
- municipal waste	<0.1	<0.1	2.6	<0.1	0.8	0.1	0.9
- industrial waste	1.0	1.8		0.5			
Open:							
- prescribed burning				9.7			
- municipal waste						0.1	
- coal waste		26.5	27.0	0.3			
- automobile refuse	1.2		4.0				
- agricultural waste	2.0	10.9	11.1	10.8		2.0	
- forest fires				13.4	1.6	2.3	0.5
- land clearing waste				1.6			
- structural fires				0.8			
Mobile sources							
- gasoline automobiles	3.9	0.8	1.7	19.6	34.6	4.3	13.2
- diesel automobiles	0.4	0.9	<0.1	0.9	1.2	2.3	5.6
- aircraft and ships					<0.1	<0.1	<0.1

1) benzo(a)pyrene * incl. wood ** incl. gas

The figures for the U.S.A. and Sweden presented by Björseth and Ramdahl differ from those given by the same authors before (Ramdahl, Alfheim and Björseth, 1983). For the U.S.A. the estimated relative contribution of some sources was considerably lower: residential combustion of coal (5.2%), coke manufacturing (2.9%), gasoline automobiles (24.4%), that of other sources was much higher: residential combustion of oil (10,8%), aluminium production (24.2%) and especially iron sintering (36.3%). In the more recent assessment of the authors the large contribution of the last source was omitted; as a consequence the other contributions were doubled for Sweden where it amounted to half of the total emission.

From literature data on emissions in the U.S.A., Verhoeve and Compaan (1980) estimated the benzo(a)pyrene emissions in the Netherlands. They found the following contributions:

Electricity and heat generation	16 %
Coke manufacturing	61 %
Municipal incineration (closed)	0.3%
Industrial incineration (closed)	10.7%
Petroleum cracking	1.8%
Traffic	4.6%
Forest fires etc.	5.4%

Recently PAH emissions in the Netherlands have been estimated again (Slooff et al, 1988). The inventory included 10 PAHs, one of which was naphtalene. According to this estimation the following sources predominate:

Space heating (wood)	29%
Aluminium production	10%
Coke manufacturing	3%
Wood preservation	39%
Road traffic	14%

Of these source types, wood preservation is not mentioned elsewhere in the literature as an important source. Because it is known that preservative agents contain PAHs (mainly naphtalene, phenanthrene and fluoranthene), however, this type of source may be of importance although estimation of its PAH emission is difficult because of the

scarcity of information about the evaporation rate of these substances after the preservation process.

PAH emissions in the Federal Republic of Germany (1981) have been given by Grimmer (1985). Residential combustion of coal appeared the major source (56.3%) divided in combustion of brown coal (36.9%), hard coal briquettes (14.3%) and bituminous coal (5.0%). Other important sources were coke manufacturing (30.8%) and gasoline automobiles (12.1%).

The large discrepancies in estimates from different authors primarily are the result of differences in economic activities between countries but also illustrate the lack of well-based information on emission factors.

2.6 Source selection

Table 2.4 shows that in the oldest estimation the majority of PAHs emissions into the atmosphere has been attributed to the combustion of coal. More recent estimations add some other primary emitters. Source types which contribute at least 5% to total national emissions, are given in Table 2.5.

Table 2.5 Important sources of PAHs

Source type	Relative maximal contribution to national emissions (%)
Residential combustion of coal	33*
Residential combustion of wood	35
Residential combustion of oil	15
Coke manufacturing	15
Aluminium production	53
Iron sintering	36
Open burning of coal waste	27
Open burning of agricultural waste	11
Mobile sources	35
Wood preservation	39

* The very high figure of Hangebrauck et al. has been discarded.

Other sources types are of minor importance, although they may dominate local concentrations near a source.
In this study the source types given in Table 2.5 will be considered.

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2.8 Residential combustion

2.8.1 Residential combustion of coal

Coal is the most important fuel in the Western world. In several countries, however, coal for residential combustion has been replaced largely by oil and gas. Since oil and, especially, gas produce less PAHs than coal, emissions of PAHs in those countries have been reduced.
Profiles and emission factors for residential combustion not only depend on the type of coal (anthracite, bituminous, etc.) but also on the combustion unit and operation characteristics (e.g. burn rate).
Emission factors for a limited number of PAHs (anthracene, phenanthrene, fluoranthene, pyrene, benzo(a)pyrene, benzo(e)pyrene and benzo(ghi)-perylene) for a non-specified coal were determined already in 1967 by Hangebrauck et al. Their results show a large spread but in all cases except one the low PAH dominate (see Table 2.6).

Table 2.6 Emission factors for residential combustion of a non-specified coal (Hangebrauck et al., 1967)

Combustion unit	Emission factor ($mg.kg^{-1}$) low PAH	high PAH	% high PAH
Underfeed stoker, iron sectional boiler	2	0.3	12
	18.5	4.4	19
	31	5.1	17
Id., hot air furnace	4.1	0.5	11
	15.8	4.5	22
Hand stoked hot air furnace	70	110	60
	260	115	30
	725	190	21

Later investigations (of other authors) result in considerably lower emission factors. Emission factors for total PAH from hard coal burning have been presented by Ramdahl (1983) and Den Tonkelaar (1984), the latter from a literature review. Their results are summarized in Table 2.7.

Table 2.7 Emission factors of total PAH for residential combustion of coal

Coal type	Author(s)	Combustion unit and operation characteristics	Emission factor ($mg.kg^{-1}$)
Not specified	Ramdahl et al.	coal furnace, nominal burn rate	ca. 60 *)
,,	,, (1983)	wood stove	40
,,	,,	fire place	29
Not specified	Den Tonkelaar (1984)	universal burner	350
Bituminous c.	Sanborn et al.	coal stove, high burn rate	69
,,	,, (1983)	,, ,, low ,, ,,	31

*) Typical value, range between 1 and 1200 $\mu g.kg^{-1}$.

The influence of the coal type on the profile is illustrated by the results of Brockhaus and Tomingas (1976). Profile factors calculated from the concentrations of PAHs in flue gases are given in Table 2.8. They are related to benzo(e)pyrene as a reference PAH. Concerning low molecular PAHs, the information is limited to only four substances.

Table 2.8 Profile factors of PAH emissions for residential combustion of some coal types; benzo(e)pyrene =1 (Brockhaus and Tomingas, 1976)

Coal type: / PAH:	Anthra-cite	Anthra-cite briquette	Brown coal briquette	Smokeless fuels: ancite	extracite	Coal coke
Fluorene						
Anthracene						
Phenanthrene						
Fluoranthene	0.5	1.9	2.0	5.8	0.9	-
Pyrene	0.13	0.4	0.4	0.19	0.14	<0.01
Cyclopentapyrene						
Benzo(a)anthracene	0.4	0.8	0.6	2.7	0.14	0.01
Chrysene	0.6	0.8	0.5	5.2	0.55	0.02
Benzo(c)phenanthrene						
Benzo(b)fluoranthene	0.9	1.0	0.4	2.8	0.5	0.06
Benzo(k)fluoranthene	0.14	0.3	0.1	0.03	0.02	0.01
Benzo(a)pyrene	0.06	0.3	0.15	<0.01	0.02	0.01
Benzo(e)pyrene	1.0	1.0	1.0	1.0	1.0	1.0
Perylene	0.2	0.7	0.4	0.2	-	0.02
Benzo(ghi)perylene	0.10	0.5	0.6	0.1	0.16	0.10
Dibenzo(a,h)anthracene	0.08	0.11	0.3	0.08	-	-
Anthanthene						
Coronene	0.02	0.2	0.2	0.02	0.05	0.01
High mol. PAH	2.5	4.1	3.15	4.2	1.75	1.2

It should be noted that the authors found large differences between emissions during different phases of the combustion (start, stationary state, end).

Profile factors of bituminous coal can be derived from results of other authors. These are given in Table 2.9. It can be seen from this table that PAHs from the combustion of bitumious coal mostly are low molecular. This applies also to other types of coal with the exception of brown coal which produces predominantly high molecular PAH. Other results of Den Boeft et al. however show that this applies only to nominal burn rate, for throttled burn rate the majority of the PAHs is low molecular.

Table 2.9 Profile factors of PAH emissions for residential combustion of bituminous coal (% of total PAH)

Authors:	Hangebrauck et al. *) (1967)		Truesdale et al. (1982)	Sanborn et al. (1983)		
PAH:	Under-feed stoker	Hand stoked furnace	Wood stove	Wood stove moderate burn rate	Coal stove high burn rate	Coal stove low burn rate
Fluorene			13	9	8	10
Anthracene	5	8	9	7	8	12
Phenanthrene	35	19	34	>15	30	21
Fluoranthene	25	27	12	12	14	9
Pyrene	19	22	9	8	8	8
Cyclopentapyrene						
Benzo(a)anthracene			4	8	5	5
Chrysene			9	6	6	4
Benzo(c)phenanthrene						
Benzo(k)fluoranthene			< 0.1	12	7	11
Benzo(a)pyrene	6	10	1.1	5	4	6
Benzo(e)pyrene	3	4	1.7	4	4	4
Perylene	0.6	1.1	4	0.7	0.5	0.6
Indeno(1,2,3-cd)pyrene				7	0.5	4
Benzo(ghi)perylene	5	7	< 0.1	1.8	1.9	3
Anthanthrene	0.5	1.5		0.5	0.2	0.8
Dibenzoanthracenes						
Coronene	0.4	0.3	< 0.1	0.7	2	1.0
Total high mol. PAH	16	24	11	34	20	30

*) Coal type not specified; it is supposed to have been bituminous

For the most important coal types emission factors can be derived from literature data. These factors depend on the combustion units used. Tables 2.10 to 2.13 give emission factors for anthracite, bituminous coal, brown coal briquettes and other briquettes.
The emission factors for bituminous coal can be compared with those for total PAH from hard coal burning presented by Ramdahl et al. (1983) and Den Tonkelaar (1984) (Table 2.7).

In some countries brown coal briquettes are an important fuel. As can be seen from Table 2.12 the emission factors and the emission profile

as found by Den Boeft et al. depend on the burn rate. Therefore, the emission factors of different PAHs may depend on the burn rate in a different way. It can be seen from these data that, while for anthracite (Table 2.10) the emission of all PAHs is reduced by a factor of 2-10 in case of baffled emission, for brown coal this applies only to the higher PAHs; the emission of the lower PAHs increases strongly by this way of combustion.

Table 2.10 PAH emission factors for residential combustion of anthracite ($\mu g.kg^{-1}$)

Authors:	Sanborn et al. (1983)			Den Boeft et al. (1984)	
PAH:	Coal stove High rate	Coal stove Low rate	Wood stove Low rate	Wood/coal stove Nominal	Wood/coal stove Baffled
Fluorene	14	3.5	23		
Anthracene	18	3.6	28	21	6
Phenanthrene	168	36	170	266	72
Fluoranthene	133	38	89	133	28
Pyrene	96	21	70	133	20
Cyclopentapyrene					
Benzo(a)anthracene	82	5	21	43	4
Chrysene	90	9	28	48	4
Benzo(c)phenanthrene					
Total low mol. PAH	601	116	429	644	134
Benzofluoranthenes	10	5	25	120	48
Benzo(a)pyrene *)	1.5	3.5	3	26	4
Benzo(e)pyrene *)	2.4	1.8	6	37	8
Perylene	0.3	0.9	0.8	5	1
Indeno(1,2,3-cd)pyrene	6	1.8	3.2	< 3	12
Benzo(ghi)perylene	5	1.8	1.7	50	24
Anthanthrene	0.1	0.4	0.4	< 3	< 4
Dibenzoanthracenes					
Coronene	3.2	0.4	2.5		
Total high mol. PAH	28	16	43	241	99

*) These values are significantly lower than the values used by Grimmer (1985) for assessing emissions in the F.R.G. from slow residential combustion:
benzo(a)pyrene: 14 $\mu g.kg^{-1}$ ("Durchbrandofen and "Unterbrandofen");
40 $\mu g.kg^{-1}$ ("Universaldauerbrenner").
benzo(e)pyrene: 90 $\mu g.kg^{-1}$ ("Durchbrandofen and "Unterbrandofen");
110 $\mu g.kg^{-1}$ ("Universaldauerbrenner").
It appears, however, that even these high values lead to a small contribution to PAH emissions from anthracite when compared with those from other coal types.

Table 2.11 PAH emission factors for residential combustion of bituminous coal ($\mu g.kg^{-1}$).

Authors:	Sanborn et al. (1983)			Truesdale and Cleland (1982)
PAH:	Coal stove high rate	Coal stove low rate	Wood stove low rate	Wood stove
Fluorene	5600	3200	4500	6200
Anthracene	5600	3600	3500	4100
Phenanthrene	20800	6500	> 7100	16100
Fluoranthene	9600	2700	5800	5700
Pyrene	5600	2500	4100	4400
Cyclopentapyrene				
Benzo(a)anthracene	3500	1700	3700	2000
Chrysene	4000	1300	3000	4300
Benzo(c)phenanthrene				
Total low mol. PAH	54700	21500	>31700	42800
Benzofluoranthenes	5100	3300	6000	
Benzo(a)pyrene *)	2900	1900	2600	500
Benzo(e)pyrene *)	2700	1400	1800	800
Perylene	350	200	350	1700
Indeno(1,2,3-cd)pyrene	370	1300	3200	
Benzo(ghi)perylene	1300	900	1550	< 30
Anthanthrene	110	250	580	< 30
Dibenzoanthracenes				
Coronene	1600	300	910	< 30
Total high mol. PAH	14400	9500	17100	3000

*) These values are significantly lower than the values used by Grimmer (1985) for assessing emissions in the F.R.G. from slow residential combustion:
benzo(a)pyrene: 1140 $\mu g.kg^{-1}$ ("Durchbrandofen and "Unterbrandofen"); 4500 $\mu.kg^{-1}$ ("Universaldauerbrenner").
benzo(e)pyrene: 3200 $\mu g.kg^{-1}$ ("Durchbrandofen and "Unterbrandofen"); 8900 $\mu g.kg^{-1}$ ("Universaldauerbrenner").

Table 2.12 PAH emission factors for residential combustion of brown coal briquettes ($\mu g.kg^{-1}$)

Authors:	Brockhaus and Tomingas *) (1976)	Den Boeft et al. (1984)	
PAH:	Universal stove (Universal-Dauerbrenner)	Wood/coal stove Nominal	Baffled
Fluorene			
Anthracene		53	1670
Phenanthrene		393	9460
Fluoranthene	2250	481	2880
Pyrene	500	802	1300
Cyclopentapyrene			
Benzo(a)anthracene	675	583	718
Chrysene	500	583	737
Benzo(c)phenanthrene			
Total low mol. PAH		2950	16900
Benzofluoranthenes	570	ca.1800	ca.200
Benzo(a)pyrene **)	160	1600	160
Benzo(e)pyrene **)	1100	1220	< 70
Perylene	400	207	79
Indeno(1,2,3-cd)pyrene		752	< 27
Benzo(ghi)perylene	650	945	< 51
Anthanthrene		65	< 7
Dibenzoanthracenes	330	< 84	<168
Coronene	200		
Total high mol. PAH	ca.3400	ca.6600	ca.700

*) Values calculated from concentrations in flue gas by assuming a total high PAH emission from combustion of anthracite under comparable conditions of 15 $\mu g.kg^{-1}$.

**) These values are significantly lower than the values used by Grimmer (1985) for assessing emissions in the F.R.G. from slow residential combustion:
benzo(a)pyrene: 1140 $\mu g.kg^{-1}$ ("Durchbrandofen and "Unterbrandofen"); 4500 $\mu g.kg^{-1}$ ("Universaldauerbrenner").
benzo(e)pyrene: 3200 $\mu g.kg^{-1}$ ("Durchbrandofen and "Unterbrandofen"); 8900 $\mu g.kg^{-1}$ ("Universaldauerbrenner").

Apart from brown coal briquettes, hard coal briquettes are used as a residential fuel. They consist of coal particles bound together by compression with the aid of cohesives from pitch or bitumen. These are considerable sources of PAH emissions. Nowadays brown coal briquettes are manufactured merely by compressing, while anthracite briquettes as Ancite and Extracit contain special cohesives which do not produce smoke. Emission factors for these briquettes, burned in a universal burner, have been investigated by Brockhaus and Tomingas (1976); their results are shown in Table 2.13. The authors only presented concentrations of PAHs in the flue gas; for a conversion to emission factors it is assumed that the emission factor of high PAHs for combustion of anthracite (which has also been determined by the authors) is 15 $\mu g.kg^{-1}$, which is about equal to the low burn rate emission factor found by Sanborn et al. (Table 2.10). The results of Brockhaus and Tomingas obtained for different fuels are comparable as the same combustion unit (a "Universal-Dauerbrandofen", UDB) was used and the fuel/air ratios were in the same range (between 1 : 2 and 1 : 4). Table 2.13 shows that the total emission of high PAHs from combustion of Ancit has the same order of magnitude as that from combustion of anthracite which is low compared with that of bituminous coal. Table 2.13 contains also emission factors for combustion of two types (CS and RA) of anthracite briquettes obtained by Ratajczak et al. (1983). The type CS was burned in a UDB, the type RA was burned in a "Durchbrandofen" (DB).

The comparibility of these data is low. The general conclusion can be drawn that conventional coal briquettes have an emission factor comparable to that of bituminous coal, whereas smokeless briquettes are comparable to anthracite. Nothing can be concluded, however, about the profiles.

Table 2.13 Emission factors of PAHs ($\mu g.kg^{-1}$) for residential combustion of coal briquettes (Brockhaus and Tomingas, 1976; Ratajczak et al., 1983)

Authors :	Brockhaus and Tomingas				Ratajczal et al.	
PAH:	Anthra-cite briquette	Brown coal briquette	Smokeless fuels: ancite	extracite	Anthracite type CS (UDB)	Briquette type RA (DB)
Fluorene						
Anthracene						
Phenanthrene						
Fluoranthene	12200	2250	126	0.9	530	27000
Pyrene	2800	500	4.2	0.14	670	20500
Cyclopentapyrene						
Benzo(a)anthracene	5100	675	59	0.15	380	)
Chrysene	5300	500	113	0.6	590	)12700
Benzo(c)phenanthrene						
Benzo(b)fluoranthene	6600	100	30	0.5	140	)
Benzo(k)fluoranthene	2200	470	0.8	0.02	130(j+k)	) 9900
Benzo(a)pyrene	2100	160	0.07	0.02	9	4100
Benzo(e)pyrene	6400	1100	22	1.0	69	2800
Perylene	4500	400	4.5	-	4	900
Indeno(1,2,3-cd)pyrene						3100
Benzo(ghi)perylene	3100	650		-	9	2700
Anthanthene						
Dibenzo(a,h)anthracene	700	330				
Coronene	1300	200	0.4	0.05		800
High mol. PAH	26900	3400	92	1.8	292	24300

Other products as coke and charcoal, which are not intensivily used in residential burning, appear to emit also small quantities of PAHs. The total high PAHs emission factor for coke is estimated to be about 45 $\mu g.kg^{-1}$ (based on the concentration in the flue gas, determined by Brockhaus and Tomingas). Total low PAHs emission factors cannot be derived from their data as only four low PAHs are measured. For charcoal Ramdahl et al. (1982) present emission factors from which can be seen that the emission factor for total PAH amounts to 95 $\mu g.kg^{-1}$ of which only 1 $\mu g.kg^{-1}$ are high mol PAHs.

Emission factors for total PAH, used to estimate overall factors for this study, are presented in Table 2.14. Apart from the reported data that have been discussed in this paragraph, some are added from a recent EPA study (EPA, 1987). Profile data were compared and averaged. Profiles, chosen for this study, are presented in table 2.31.
No means were available to differentiate between burn rates. On the other hand, a time-pattern would be needed to profit from such a differentiation, i.e. temporal fractions per country (or, better, per climatic zone) of nominal and low burn rates should be known. The proposed factors will have to be used for annual average emissions, taking into account the months in which there is no space heating.

Table 2.14 Emission factors for total PAH for residential combustion of coal ($\mu g.kg^{-1}$)

	Anthracite	Bituminous coal	Brown coal briquette
Sanborn et al. (1983)	0.63 0.13 0.47	69 31 50-60	
Den Boeft et al. (1984)	0.89 0.23		9.6 17.6
Truesdale and Cleland (1982)		53	
Brockhaus and Tomingas (1976)			8-18
Giammar et al. (1976) 1)	0.28 2.0	71(11-167)	19±7 4.7
DeAngelis and Reznik (1974) 1)		225 25	
Factor chosen for this study	0.5(0.2-0.8)	50(30-70)	12(7-18)

1) quoted in EPA (1987)

2.8.2 Residential combustion of wood

Emissions of PAHs from the combustion of wood have been measured by several authors. Profile factors of PAHs calculated from them are given in Table 2.15. Some of them are averages of values obtained under different combustion conditions. Because of the spread the averages have been rounded off to 0.5%. According to Daisey, Cheney and Lioy (1986) the variation in PAH profile factors of wood combustion and the dependency of them on combustion conditions is larger than for other fuels.

Table 2.15 Profile factors of PAHs for residential combustion of wood in stoves (% of total PAH)

Authors:	Truesdale et al. (1982)	Cooke et al. (1982)	Ramdahl et al. (1982)		Truesdale et al. (1982)	Cooke et al. (1982)	Den Boeft et al. (1984)	
Wood type: / PAH:	Seasoned oak		Birch 1)	Spruce 1)	pine	pine	pine 1)	pine 2)
Fluorene	15	5			2	9		
Anthracene	20	5	5	6	22	6	3	5
Phenanthrene	32	33	35	44	36	34	40	61
Fluoranthene	12	16	17	16	14	5	8	10
Pyrene	8.5	10	16	12	11	3	6	7
Cyclopentapyrene								
Benzo(a)anthracene	0	5	3	3	4	1	5	2
Chrysene	5	4	4	*	2	1	6	3
Benzo(c)phenanthrene								
Benzofluoranthenes	0	6.5	6	6	0	7	8	4
Benzo(a)pyrene	2	4	3.5	2.5	2.5	4.5	5	2
Benzo(e)pyrene	2	1.5	2	2	3	5	6	3
Perylene	2.5	0.5	1.5	1	0.5	0.5	8	0.5
Indeno(1,2,3-cd)pyrene		3.5	2.5	2	3.5	12.5	0	0
Benzo(ghi)perylene	0	4	3.5	2	0.5	10	4	2.5
Anthanthrene							0.5	0
Dibenzo(a,h)anthracene	0							
Coronene	0	2			0.5	5		

* Covered by unknown compound
1) Normal burn rate
2) Baffled

Emission factors for wood combustion are shown in Table 2.16. Den Boeft et al. found that emission factors strongly depend on log size and shape and also on combustion conditions (this was also found by other authors).

Table 2.16 Emission factors for residential combustion of wood ($\mu g.kg^{-1}$)

a. Seasoned oak								
Authors:	Peters (1982)			Truesdale Cleland (1982)	Cooke et al. (1982)			
PAH:	Fire place	Stove nom. rate	Stove baffled	Stove nom. rate	Stove side draft	Stove up draft	Stove down draft	Stove high turb.
Fluorene				4700	1800	870	470	160
Anthracene	) 8200	) 61800	) 74500	6000	1710	490	1500	150
Phenanthrene	)	)	)	9790	5870	2140	13000	2300
Fluoranthene	<1400	20800	18000	3700	1940	990	9210	880
Pyrene	<1400	16900	15600	2600	1080	770	5140	570
Cyclopentapyrene	<1400	5100	4800					
Benzo(a)anthracene	)	)	)	60	650	1410	850	160
Chrysene	)<1400	) 7600	)12500	1600	630	900	1160	150
Benzo(c)phenanthrene	400	1600	1600					
Total low mol. PAH	<14200	113800	127000	28450	13680	7570	31330	4370
Benzofluoranthenes	<1400	11200	12800		1410	1930	510	100
Benzo(a)pyrene	)	)	)	600	500	1350	36	51
Benzo(e)pyrene	)<1400	)8400	)8300	500	350	440	74	52
Perylene	)	)	)	800	60	90	24	54
Indeno(1,2,3-cd)pyrene					1440	550	43	110
Benzo(ghi)perylene		4300	4500	40	2090	440	30	75
Anthanthrene								
Dibenzoanthracenes								
Coronene					950	110	23	84
Total high mol. PAH	<2800	24900	25600	1940	6800	4910	740	526

Table 2.16 Emission factors for residential combustion of wood ($\mu g.kg^{-1}$) (continuation)

b Pine						
Authors:	Peters (1982)			Truesdale Cleland (1982)	Cooke et al. (1982)	Den Boeft et al. (1984)
PAH:	Fire place	Stove nominal rate	Stove baffled	stove nominal rate	stove side draft	stove nominal rate	stove baffled
Fluorene				1900	2190		
Anthracene	)	)	)	20200	1630	122	195
Phenanthrene	) 6900	) 103400	) 146300	33500	8590	1930	2580
Fluoranthene	1600	18800	31600	12600	1170	405	432
Pyrene	1600	18800	24000	10000	770	291	279
Cyclopentapyrene							
Benzo(a)anthracene	)	)	)	3400	270	245	81
Chrysene	) 2700	) 37100	) 13800	1500	290	306	112
Benzo(c)phenanthrene	1300	4600	2300				
Total low mol. PAH	14100	182700	218000	83100	14910	3299	3679
Benzofluoranthenes	1600	14100	15900		1780	390	170
Benzo(a)pyrene	)	)	)	2400	1100	222	93
Benzo(e)pyrene	)1400	)9400	)11600	2700	600	291	139
Perylene	)	)	)	300	160	382	16
Indeno(1,2,3-cd)pyrene				3190	3190		< 9
Benzo(ghi)perylene	1500	4700	9900	300	2520	200	111
Anthanthrene						18	5
Dibenzoanthracenes *)	<50	<50	<1400				
Coronene					1340		
Total high mol. PAH	4500	28200	ca38000	8890	10690	1503	540

*) incl. dibenzophenanthrenes

Table 2.16 Emission factors for residential combustion of wood ($\mu g.kg^{-1}$) (continuation)

c Other wood types:	Spruce		Birch	
Authors:	Ramdahl et al. (1982)		Ramdahl et al. (1982)	
PAH:	stove nominal rate	stove baffled	stove nominal rate	stove baffled
fluorene				
anthracene	119	1859	822	1654
phenanthrene	834	8390	5821	5060
fluoranthene	296	3245	2843	1334
pyrene	232	3822	2690	1488
cyclopentapyrene				
benzo(a)anthracene	60	781	476	326
chrysene	*	829	615	481
benzo(c)phenanthrene				
total low mol. PAH	ca 1600	18926	13267	10343
benzofluoranthenes (b)	108	1016	1002	179
benzo(a)pyrene	46	617	560	237
benzo(e)pyrene	35	347	350	166
perylene	23	38	274	25
indeno(1,2,3-cd)pyrene	33	291	415	170
benzo(ghi)perylene	34	285	544	188
anthanthrene				
dibenzoanthracenes				
coronene				
total high mol. PAH	279	2594	3145	965

* Covered by unknown compound

As can be seen from this table the values found by den Boeft et al. are relatively small which might indicate that their experiments have been carried out under relatively favourable combustion conditions.

Emissions of total PAH are given in Table 2.17. Notwithstanding the apparent fact that recently much attention has been given to wood

combustion, results show not much consistency. Emission rates clearly depend on many parameters, but although knowledge is increasing, detailed emission factors are of little value if needed for a large-area inventory. Lack of statistical data is the reason for this.
For this study overall factors have been chosen therefore. It remains to be seen whether the distinction between emissions from stoves and fireplaces can be made in the MASH inventory.
The profile for wood combustion is shown in Table 2.31. Only one profile is proposed since no significant differences appeared to be found.

Table 2.17 Emission factors of total PAH for residential combustion of wood ($mg.kg^{-1}$)

	Stoves
DeAngelis (1980) 1)	270
Rudling and Ahling (1982)	5-6; 140
Cooke et al. (1982)	19(5-33); 27
Peters (1982)	189; 212; 319; 372
Ramdahl et al. (1982)	2.5; 33; 20; 40
Truesdale and Cleland (1982)	48; 113
TVA (1982) 1)	53(3-200); 140(5-240); 260(250-290); 140(20-270)
Knight et al. (1983)	75(25-125)
Lao et al. (1983) 1)	0.1-3.4
Den Boeft et al. (1984)	5.0;4.3
Truesdale (1984) 1)	130(7-300)
EPA (1985)	190-370
Factor chosen for this study	100(10-200)
	Fireplaces
DeAngelis (1980) 1)	29
Rudling and Ahling (1982)	6-10
Peters (1982)	<24;36
EPA (1985)	17-44
Factor chosen for this study	25(10-40)

1) quoted in EPA (1987)

2.8.3 Residential combustion of oil

Profiles referring to distillate oil have been measured by Brockhaus and Tomingas (1976). Table 2.18 shows their results obtained with an oil vaporizing burner. The authors found that the production of some PAHs, among which benzo(e)pyrene, was strongly influenced by the combustion conditions. In comparison to combustion of vaporized oil, combustion of atomized oil appeared to produce only small quantities of PAHs. Note that no data have been given for the usually large emissions of some lower PAHs.

Table 2.18 Profile factors of PAHs for residential combustion of distillate oil (Brockhaus and Tomingas, 1976)

Combustion conditions: PAH:	Normal	Opened air valve	Puffing
Fluorene			
Anthracene			
Phenanthrene			
Fluoranthene	0.10	0.53	0.14
Pyrene	0.07	0.25	0.13
Cyclopentapyrene			
Benzo(a)anthracene	0.07	0.50	0.09
Chrysene	0.07	0.25	0.07
Benzo(c)phenanthrene			
Benzo(b)fluoranthene	0.17	0.78	0.10
Benzo(k)fluoranthene	0.04	0.40	0.05
Benzo(a)pyrene	0.08	0.48	0.10
Benzo(e)pyrene	1.0	1.0	1.0
Perylene	0.18	0.78	0.12
Benzo(ghi)perylene	0.37	1.03	0.49
Anthanthene			
Dibenzo(a,h)anthracene	-	-	-
Coronene	0.05	0.38	0.07

Emission factors for combustion of oil for residential heating depend strongly on the nominal power of the combustion unit; besides that they show large variations (Ramdahl et al, 1973). For a nominal power of 30 kW the emission factor for total PAH was in the range of 6-750 $\mu g.kg^{-1}$ with a typical value of 150 $\mu g.kg^{-1}$; the emission factor

for benzo(a)pyrene (which is of the same or-der of magnitude as that of benzo(e)pyrene) was in the range of 2-4.4 $\mu g.kg^{-1}$ with a typical value of 2.2 $\mu g.kg^{-1}$. This value is of the same order of magnitude as those given by Grimmer (1985): 4 $\mu g.kg^{-1}$ and by Ratajczak et al. (1982): 2 $\mu g.kg^{-1}$. For a nominal power of 7.5 MW the emission factor for total PAH appeared to be about three times as large; no factor for benzo(a)-pyrene has been given but even if this factor is also three times as large as that for the 30 kW unit this factor is several orders of magnitude smaller than those for coal and wood combustion. It is suggested by these data that distillate oil in residential combustion emits PAHs in the same rate as anthracite (or maybe less). Since no reliable emission factor can be derived, this comparison should be maintained.

2.8.4 Literature

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2.9. Industrial production

2.9.1 Coke production

Coke ovens are major sources of PAH emission, for a large part caused by leaks from the oven doors. Emissions appear to vary within a large range. Referring to Trenholm and Beck (1978), Björseth and Ramdahl (1985) present a "typical" emission factor of 15 g PAH (total) per ton of coal used which corresponds with 22 g PAH per ton of coke produced.
For benzo(a)pyrene an emission factor of 1.8 g per ton coke is frequently mentioned (Grimmer (1979), Verhoeve and Compaan (1980), Eisenhut et al. (1982)) which probably originates from M.W. Smith (1970). This value corresponds with a profile factor of 8% of total PAH. Eisenhut et al. state that the leakage of coke oven doors can be considerably reduced by using doors with spring loaded seals instead of the conventional doors with rigid sealing. From their measurements it appears that the emission factor of benzo(a)pyrene was reduced from maximally 82 mg to 13 mg per ton coke. They estimated that maximally 0.2 g benzo(a)pyrene is emitted per ton coke. For total PAH this emission factor would then be 2.5 g per ton coke (if the fraction benzo(a)pyrene is 8%).
In the measurements of Eisenhut et al. only 12 PAHs were involved and the usual large emissions of several low molecular PAHs were not measured. It is tried to estimate the total PAH emission as follows: Concentration profiles of PAHs emitted from the battery top of a coke plant were determined by Björseth et al. (1978). The emission of 12 PAHs, in the experiments of Eisenhut et al. together 87.6 mg per ton coke, amounted to 43% of the total PAH emission. If this percentage applies to the oven doors as well, the total PAH emission in the experiments of Eisenhut et al. would be 187 mg per ton coke, so the emission of benzo(a)pyrene (13.2 mg per ton coke) would then be 7% of the total PAH emission, which corresponds reasonably well with the 8% mentioned before. Reported profiles are presented in Table 2.19. The values given by Eisenhut et al. have been corrected for the large contributions to total PAH of some low molecular PAHs which were not measured by these authors (only 12 PAHs were measured).

Table 2.19 Profile factors of PAHs for coke production (% of total PAH)

Authors: / Site of measuring:	Björseth et al. (1978) Battery top (average)	Björseth et al. (1978) Personal sampling (average)	Eisenhut et al. (1982) Oven doors	Den Tonkelaar et al. (1983)
Total PAH emission factor ($mg.kg^{-1}$)	15		2.5	8
Fluorene	4.4	0.6		
Phenanthrene	19.8	2.6		45.9
Anthracene	6.2	1.1		7.6
Fluoranthene	12.8	11.9	1.5	14.3
3,6-dimethylphenanthrene				0.8
Benzo(b)fluorene	1.3	4.1		2.1
Pyrene	9.5	8.4	0.9	6.9
Benzo(c)phenanthrene	0.8	2.8		
Benzo(a)anthracene	3.4	8.5	4.7	3.1
Chrysene+trifenylene	4.4	11.0	5.9	3.4
Total low mol. PAH	88	62		84
Benzo(b)fluoranthene	)		)	2.5
Benzo(j)fluoranthene	) 1.9	4.7	) 5.7	-
Benzo(k)fluoranthene	)		2.1	1.1
Benzo(a)pyrene	2.2	7.7	7.1	2.5
Benzo(e)pyrene	1.8	4.3	6.2	1.6
Perylene	0.6	1.8	2.4	0.5
Indeno(1,2,3-cd)pyrene	1.5	3.6	6.2	1.8
Benzo(ghi)perylene	1.3	2.9	6.2	4.4
Anthanthrene	0.9	1.7		0.7
Coronene	0.7	4.5		
Dibenzo(a,h)anthracene			4.4	
Dibenzo(a,j)anthracene				0.3
Dibenzo(a,i)pyrene				0.3
3-methylcholanthene				0.3
Total high mol. PAH	12	38		16

From this source type, too, insufficient data are available for a reliable estimation of a profile. Based on these data, a profile is suggested that is given in Table 2.31.

Den Tonkelaar and van Giezen (1983) report emissions derived from con-

centration measurements near a coke plant in the Netherlands. The emission factor of total PAH (calculated from the yearly emission and the yearly production, 400000 ton) appears to be 8 $g.ton^{-1}$.
Other emission rates have been reported. Table 2.20 gives an overview which makes clear that no straightforward derivation of an emission factor is allowed. The differences apparently are attributable to differences in operation and maintenance of the process and these should be a guide in the development of factors for different locations. Actually, however, only a roughly estimated value can be given. For this study 10(2-20) $g.t^{-1}$ of coke is taken for uncontrolled emissions. It is assumed that door leaks dominate total emissions. For controlled emissions 0.2 $g.t^{-1}$ of coke may be taken (Eisenhut, 1982).

Table 2.20 PAH emission factors for coke production

	Total PAH (g.t-1)		Benzo(a)pyrene (mg.t-1)		wt %
	coal	coke	coal	coke	
Trendholm and Beck (1978)	15	(22)			2.2
Smith (1970)				1800	8
Eisenhut (1982), conventional doors				82 3)	
spring loaded door seals	(0.19)		13 3)	(7)	
maximum emission		(4) 5)		200 3)	
De Tonkelaar and van Giezen (1983)		8			2.5
Siebert (1978) 1)	4.3 2)	(6.3)	1.8-1400	(2.6-2000)	0.03-32
Barrett (1978) 1)					2.6;0.14
Nat.Res.Council(1983) 1); Lao(1975) 1)					7
Björseth et al. (1978) 4)					7.7±1.6

Notes:
1) quoted in EPA (1987).
2) including naphtalene.
3) particulate PAH only.
4) concentrations measured at six locations at oven; average of six averages.
5) 5% benzo(a)pyrene assumed.

2.9.2 Primary aluminium production

Pasteing, baking and consumption of anodes in the reduction of aluminium oxide are sources of PAH emission in primary aluminium production. With regard to this emission a distinction has to be made between processes

in which the anodes, containing tar and pitch as binders, are baked from paste during the reduction process in the cell (the Söderberg process) and technology in which prebaked anodes are used (prebaked in the same plant or elsewhere).

Emission factors and profiles for the Söderberg process are given by Alfheim and Wickström (1984). They collected samples at a anode paste (AP) plant and at two aluminium reduction plants using Söderberg electrodes with horizontal studs (HS) and vertical studs (VS) and yearly productions of 13000 and 70000 tons, respectivily. Total PAH emission factors were estimated to be:
for the anode paste plant: 91 $g.ton^{-1}$;
for the (older) HS aluminium reduction plant: 4400 $g.ton^{-1}$;
for the (newer) VS aluminium reduction plant: 680 $g.ton^{-1}$.
Emission factors for benzo(a)pyrene were also given:
AP: 0.17 $g.ton^{-1}$, 0.2% of the total PAH emission;
HS: 112 $g.ton^{-1}$, 2.5% of the total PAH emission;
VS: 10 $g.ton^{-1}$, 0.7% of the total PAH emission factor.
The emission factors for the individual PAHs were calculated from total PAH emission factors and profile factors derived from a figure given by the authors. These factors are given in Table 2.21.
Referring to unpublished results of Björseth and Wickström, Ramdahl et al. (1983) give the following typical values for the emission factors of the Söderberg process plant:
Anode baking: 50 $g.ton^{-1}$ (total PAH); 0.066 $g.ton^{-1}$ (benzo(a)pyrene).
Aluminium reduction: 235 $g.ton^{-1}$ (total PAH); 15 $g.ton^{-1}$ (benzo(a) pyrene).
As the figures for the aluminium reduction do not correspond with the data given by Alfheim and Wickström relating to the same plant there is doubt about their correctness (for unknown reasons they used a much lower emission rate than the original investigators did).

For aluminium production with prebaked anodes separate emission factors for prebaking and reduction have been derived from the data of Verhoeve and Compaan (1980). The authors report an annual emission of 275 kg benzo(a)pyrene from a Dutch industry producing 80000 tons carbon elec-

trodes using annually 18000 tons tar and pitch. This corresponds with an emission factor of 3.4 $g.ton^{-1}$ baked electrode or, since 0.5 ton electrode is used to produce 1 ton of aluminium, with 1.7 $g.ton^{-1}$ of aluminium. Assuming that the emission factors of the individual PAHs are proportional to the contents of them in pitch, the emission factor of other PAHs can be calculated from the composition of the pitch. As pitch contains about 1% benzo(a)pyrene and about 25% PAH (Table 2.22) the emission factor for total PAH will be about 40 $g.ton^{-1}$ aluminium. Because of the large variations in composition found by different authors the total PAH contents in pitch and thus the emission factors may vary strongly.

Table 2.21 Profile factors of some PAHs for aluminium production (% of total PAH) (Alfheim and Wickström, 1984)

Site of measuring:	Anode paste plant	Electrodes with horizontal studs	Electrodes with vertical studs
Fluorene	11	2	5.5
Anthracene	6	2.4	4
Phenanthrene	37	15	25
Fluoranthene	18	22	14
Pyrene	10	17	10
Cyclopentapyrene			
Benzo(a)anthracene	0.9	5	2.0
Chrysene(+triphenylene)	1.1	8	3.5
Benzo(c)phenanthrene	1	1	0.1
Total low mol. PAH	85	72.4	64.1
Benzo(b)fluoranthene	0.5	6.1	1.7
Benzo(j)fluoranthene	) 0.4	) 4.1	) 1.1
Benzo(k)fluoranthene	)	)	)
Benzo(a)pyrene	0.3	2.7	0.8
Benzo(e)pyrene	0.3	4 0	1.2
Perylene	0.2	0.7	0.3
Indeno(1,2,3-cd)pyrene		0.5	0.5
Benzo(ghi)perylene		1.5	0.5
Anthanthrene			
Dibenzo(a,h)anthracene		0.5	0.2
Coronene			
Total high mol. PAH	1.7	20.1	6.3

With regard to emissions from aluminium production the authors refer to a private communication of one of the aluminium producers in the Netherlands stating that the yearly benzo(a)pyrene emission from his plant (production 95000 tons, prebaked anodes) amounts to 20 kg; this emission corresponds with an emission factor of 0.21 $g.ton^{-1}$ which is two or three orders of magnitude lower than the emission factor of benzo(a)pyrene estimated for the Söderberg process plants investigated by Alfheim and Wickström (112 and 10 $g.ton^{-1}$, respectivily).

From this scarce data only order of magnitude values for emission factors can be derived. Suggested values are (mg/kg):

Electrode production: 70(40-120).

Primary Al production (prebaked anodes): 30(10-50).

Primary Al production (Söderberg process): 1000(500-5000).
The only available information for estimating a profile is from Alfheim and Wickström. Data are given in Table 2.31.

Table 2.22 Composition of coal tar pitch (weight %) (Visschers and Verschueren, 1988)

Reference:	a	b	c	d
Fluorene			0.08-0.4	
Anthracene				
Phenanthrene			0.75-4.0	
Fluoranthene	4.0-4.3	2.0-3.3	0.52-3.9	2.8
Pyrene	2.0-2.9	1.8-2.4	0.45-3.5	2.0
Cyclopentapyrene				
Benzo(a)anthracene	0.9-1.3	16.9-32.4		
Chrysene	0.74-1.0	4.3-8.8	0.26-1.7	
Benzo(c)phenanthrene				
Benzo(k)fluoranthene	0.7-0.9	0.17-0.45		1.2
Benzo(a)pyrene	0.8-1.3	0.43-1.1	0.45-4.3	
Benzo(e)pyrene	0.5-0.7	0.54-0.7		
Perylene	0.2-0.3	0.21-0.6		
Indeno(1,2,3-cd)pyrene	0.7-0.9			
Benzo(ghi)perylene	0.3	0.08-0.04		
Anthanthrene				
Dibenzo(a,h)anthracene		0.03-0.17		
Coronene				
Total PAH	11-14	27-50	3-18	6

2.9.3 Iron ore sintering, ferrous fondries, ferroalloy industry

According to Ramdahl et al (1983) iron ore sintering is a source of PAH emissions. The authors refer to work of others resulting in a typical emission factor of 17 $mg.ton^{-1}$ for benzo(a)pyrene. Assuming this to be 3% of the total PAH emission factor, this factor would be 0.5 $g.ton^{-1}$. As there is no information on emission factors of other PAHs these factors can only be guessed from assumed profile factors.
The only other figure available from literature is 0.6-1100 $mg.ton^{-1}$ of sinter feed (Siebert et al., 1978, p 78-79). It will be clear, then,

that no basis is present for an emission factor for sinter plants.
Referring to a private communication and a report, Ramdahl et al give the following total PAH emission factors for metallurgical industries:
Ferrous fondries : 7.7 $g.ton^{-1}$
Ferroalloy industry: 10 $g.ton^{-1}$
Iron works : 60 $g.ton^{-1}$
From these few figures it is assumed that primary iron- and steel industries in industrialized countries do not significantly contribute to total PAH emissions.

2.9.4 Wood preservation

Wood preservation is not widely recognized as an important source of PAHs. It should, however, not be neglected as preserving agents will evaporate (at least partly) during and after the preservation process. Two types of agents are in use: carbolineum and creosote oil, which are tar distillates (both part of the so-called heavy tar fraction, boiling range 240-280 °C).
Another reasoning to illustrate the possible contribution from wood preservation is that steel production implies coke production, which yields coal tar. From an economic point of view, coal tar is made profitable, hence e.g. the production of carbolineum and creosote. The slow evaporation of these products from wooden constructions, preserved with them, is a source of PAH. From these products carbolineum contains most of the higher PAHs. Slooff et al. (1988) assessed emissions of some PAHs from it from the distillation curve. For other PAHs the fractions have been assessed here by relating them to the amounts of PAH in the tar and in the distillate. It was assumed that half of the PAHs present in carbolineum vaporize (Sloof et al., 1988). Table 2.23 shows PAH emission factors related to the amount of carbolineum used.

Table 2.23 PAH emission factors for carbolineum use (Slooff et al., (1988)

	$g.kg^{-1}$	wt.%
Fluorene	25*	11.4
Anthracene	-	
Phenanthrene	67	31
Fluoranthene	53	24
Pyrene	35*	16
Cyclopentapyrene		
Benzo(a)anthracene	5	2.3
Chrysene	17	7.8
Benzo(c)phenanthrene		
Benzo(k)fluoranthene	3	1.4
Benzo(a)pyrene	4	1.8
Benzo(e)pyrene	3*	1.4
Perylene	1*	0.5
Indeno(1,2,3-cd)pyrene	3	1.4
Benzo(ghi)perylene	1	0.5
Anthanthrene		
Dibenzo(a,h)anthracene	1*	0.5
Coronene		
Total	218	100

* Assessed from the PAH contents of tar (Visschers and Verschueren, 1988).

Creosote oil is used in large amounts (in the Netherlands about 11000 ton). Its PAH composition may vary. Analyses by some authors have been reviewed by Visschers and Verschueren (1988). According to Slooff et al. it is uncertain whether detectable quantities of high PAHs are present in the creosote oil which is used nowadays. The authors estimated the emission of some low PAHs for the Netherlands, caused by evaporation during storage of treated wood products. The emission factors used are given in Table 2.24.

Table 2.24 PAH emission factors for creosote oil evaporating from treated wood products during storage ($mg.kg^{-1}$) (Slooff et al., 1988)

Phenanthrene	5.1
Anthracene	0.3
Fluoranthene	0.3

2.9.5 Literature

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2.10 Open burning

Estimation of benzo(a)pyrene emissions from incineration and open burning of refuse in the world and, specifically, in the United States has been reviewed by Suess (1976). From this work it can be concluded that more than 90% of these emissions have to be attributed to open burning. More than half of open burning emissions originate from burning of coal refuse tips in mining areas. Such burning can be spontaneously ignited and may go on for long periods. The estimation of the emission, presented by the committee on biological effects of atmospheric pollution of the National Research Council (1972), is merely based on a personal communication and no emission factors are given. Moreover, this type of burning will occur only accidentally, so it is not well suited to be subject of a systematic study which has to lead to an source inventory. Of other uncontrolled burning, forest and agricultural fires (about 30%) and vehicle disposal (about 10%) appear to be the most important sources. Part of the emissions from these sources, given by the National Research Council have been estimated using emission factors taken from Hangebrauck et al. (1967). These factors are presented here in the form of a total PAH emission factor and profile factors (Table 2.25) for separate PAHs. Note that only 10 PAHs have been measured, so it is still possible that open burning produces some other important PAHs as bezo(a)anthracene and indeno(1,2,3-cd)pyrene, and that the total PAH emissions factor may therefore be somewhat higher than given in this table.

Particulate PAHs from burning pine needles were measured by McMahon and Tsoukalas (1977). The influence of headfire (fires, the direction of which is determined by the direction of the wind) vs. backfire (fires forced to burn against the wind direction) and of flaming vs. smoldering fire was investigated. From this work emission factors for forest wildfires or prescribed fires can be derived. They are presented in $mg.kg^{-1}$ biomass and therefore have to be converted into mass units per area unit because statistics are given in area units. At the time of writing this report leaf biomass factors for vegetations just have begun to attract attention for the estimation of natural VOC emissions. Therefore no

reliable data sets are available. A rough estimation can be made, however, by taking a high value for a biomass factor so as to account for burning twigs. If 1000 $g.m^{-2}$ is taken, values of 5-25 $mg.kg^{-1}$ (McMahon and Tsoukalas) give 5-25 $kg.km^{-2}$. No statistical treatment of the frequency of occurence of head- vs. backfires or of flaming vs. smoldering fires is expected to be feasible. Also the degree of destruction of vegetation is not easy to account for. A best guess, assuming that flaming fires prevail in terms of time and that the biomass factor used is still too low, might be 10 $kg.km^{-2}$. The profile data for headfires (9 sets) could be averaged. Backfires appeared to have a different profile. Headfires are to be preferred for wildfires because of the absence of control.

Table 2.25 Total PAH emission factors and profile factors of some PAHs (% of total PAH) for open burning (Hangebrauck et al.,1967)

Type of refuse :	Municipal	Grass clippings, leaves, branches	Automobile components
Total PAH emission factor ($mg.kg^{-1}$) :	4.1	35.5	223
Phenanthrene			9.5
Anthracene			1.4
Fluoranthene	39.3	31.3	24.0
Pyrene	43.1	48.3	33.8
Benzo(a)pyrene	8.2	9.7	12.3
Benzo(e)pyrene	5.7	4.3	6.5
Perylene		1.1	1.2
Benzo(ghi)perylene	3.8	4.5	8.8
Anthanthrene		0.7	1.0
Coronene			1.1
Total low mol. PAH	82	80	69
Total high mol. PAH	18	20	31

2.10.1 Literature

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2.11 Mobile Sources

Expectedly, PAHs have been detected in the exhaust gases of internal combustion engines. They originate from three sources:

- PAHs present in the fuel.
- Synthesis from fuel hydrocarbons.
- Pyrolysis of lubricating oil.

Emission rates depend, apart from the fuel type, on ignition timing, engine speed, engine temperature (cold start) and other parameters. For a reliable comparison of measured emissions similarity between engines and driving conditions therefore is required.

When published data are studied it appears however that contradictory results of effects have to be compared. As a first approximation therefore, an attempt was made to develop emission factors and profiles from all available data, differentiating only with respect to fuel type.

Since recently engine performance has been improved both for the sake of fuel saving and pollution abatement, it was attempted to restrict the literature survey to not too old research. In the tables 2.26-2.29 the available data are given.

Kraft and Lies (1981) and Kraft et al (1982) studied the methods to analyse PAHs in automobile exhaust. Automobiles were tested over three operation modes: the driving cycle of the 1975 Federal Test Procedure (FTP), the Highway Fuel Economy Test (FET) and the European Cycle (ECE). In the second investigation only diesel automobiles were tested, but with and without dilution of the exhaust. The difference between the two analytical methods is small.

Westerholm et al (1986) studied the effect of different particulate traps on emissions of a heavy duty diesel engine. From this study results without a trap and with regular fuel were taken. They refer to urban driving (bus cycle, developed in the FRG). Westerholm et al (1988) investigated PAH emissions from a gasoline powered automobile according to FTP-73 with different fuels. Results with a regular fuel are given in table 2.26.

Rijkeboer (1987) measured PAH emissions of gasoline powered automobiles without and with controlled exhaust (lean-burn and/or catalyst) in three

driving modes. The results from the uncontrolled vehicle are presented. Rijkeboer and Steenlage (1985) investigated the effect of different fuels on PAH emissions.

Lopez et al (1987) measured PAHs, emitted by a diesel automobile. Results were reported as concentrations and could only be used for the estimation of a PAH profile.

On inspection of these data a serious inconsistency exists in that one respectively two of the substances phenanthrene, anthracene and pyrene, together making up more than half of total PAH, are missing in some of these studies. Analysis of the profiles (Tables 2.28 and 2.29) showed that no significant difference exists between the two fuels with the exception of anthracene and benzo(a)anthracene. Therefore the same profile has been estimated from the available data (Table 2.31). It is in general good agreement with older reported data (Grimmer, 1977).

This composition was used to adapt emission rates to that of the 14 PAHs in the profile. Adapted figures are presented in Tables 2.26 and 2.27 in parenthesis and from these, emission factors were developed. Real emission rates will be 10-20% higher (ignoring naphtalene and its derivatives).

Emission factors are given in $\mu g.km^{-1}$. This unit is unsuitable for estimating emissions in most of the countries covered by the project.

Since fuel consumption data are far more completely available and spatial distribution of emissions can be estimated with population density data (which is sufficiently accurate for large-area modeling) emission factors were expressed per mass unit of fuel. For this purpose generalized driving mode distributions and fuel consumptions were used as given in Table 2.30. The resulting overall factors are given in the same table.

Thijsse and Den Tonkelaar derived a value of 1300 $\mu g.km^{-1}$ from measurements of tunnel air, representative for heavy-duty traffic. Conversion to a fuel based factor results in a ca. 25% higher diesel emission factor.

The much lower results of Westerholm et al (1986) however, prohibit such a correction.

Table 2.26 PAH emission rates from gasoline-powered automobiles $\mu g.km^{-1}$)

	Nr. of vehicles	ECE Cold start	ECE Hot start	FTP	FET	90 $km.h^{-1}$	120 $km.h^{-1}$
Kraft and Lies (1981)	3	475(880)[1)] 544(1007) 196(363)		185(343) 168(311) 163(302)	181(335) 136(252)		
Rijkeboer (1987)	1	47(57) 130(157) 73(88) 111(139)	79(95) 122(147)				25(30)
Steenlage and Rijkeboer (1985)	1		113(136)			97(117)	589(710)
Westerholm et al (1988)	1			317(196)			

1) Values in parenthesis: adapted to PAHs as given in Tables 2.28 and 2.29.

Table 2.27 PAH emission rates from diesel-powered automobiles $\mu g.km^{-1}$)

	Nr. of vehicles	ECE Cold start	ECE Hot start	FTP	FET	90 km.h^{-1}	120 km.h^{-1}
Kraft and Lies (1981)	4	163(302)[4]		224(415)	129(239)		
		198(367)		190(352)	134(248)		
		331(613)		241(446)	155(287)		
		288(533)		231(428)	176(326)		
Kraft et al (1982)	3 d[5]	168(311)		153(283)	148(274)		
	u	155(287)		174(322)	130(241)		
	d	327(609)		259(480)	203(376)		
	u	329(609)		239(443)	154(285)		
	d	276(511)		230(426)	161(298)		
	u	285(528)		234(433)	173(320)		
Steenlage and Rijkeboer (1985)	2[1]		437(527)			207(249)	145(175)
	2[2]		1117(1346)			425(512)	419(505)
				bus cycle			
Westerholm et al (1986)	1[3]			237			
				231			
				241			

1) < 50.000 km.
2) > 100.000 km.
3) Engine of heavy duty vehicle.
4) Values in parenthesis: adapted to PAHs as given in tables 2.28 and 2.29.
5) d = diluted exhaust gas; u = undiluted exhaust gas.

Table 2.28 Profiles of PAH emissions from gasoline-powered engines (weight %)

	Kraft and Lies (1981)			Westerholm et al (1988)	Steenlage and Rijkeboer (1985)		
	ECE	FTP	FET		ECE	90 $km.h^{-1}$	120 $km.h^{-1}$
Fluorene				16.2			
Phenanthrene				35.0	67.2	61	35.5
Anthracene				10.9	15.5	13	6.6
Fluoranthene	33.1	41.1	31.9	7.9	<1	17	27.0
Pyrene	33.1	35.7	31.4	8.4			
Benzo(a)anthracene				1.7	0.9	1	2.4
Chrysene	13.7	7.8	22.2	1.6	<1	<1	6.5
Benzofluoranthenes	6.7	6.0	6.2	3.2	<2	<2	5.4
Perylene	0.7	0.1	0.2		<1	<1	0.5
Benzo(a)pyrene	1.8	2.1	2.5	2.6	1.7	<1	1.0
Benzo(e)pyrene	4.0	2.9	2.9	1.0	<1	<1	3.1
Indeno(1,2,3-cd)pyrene	1.6	1.1	0.8	0.6	<1	1	3.4
Benzo(ghi)perylene	3.8	2.6	1.7	2.4	1.7	1	3.6
Anthanthrene					7.8	<1	<0.2
Coronene	1.5	0.6	0.2	0.9			
Other PAH (without naphtalenes)				7.6	2		4.8

Table 2.29 Profiles of PAH emissions from diesel fueled engines (weight %)

	Kraft and Lies (1981)			Kraft et al (1982)	Lopez et al (1987)	Steenlage and Rijkeboer (1985)			Thysse and Den Tonkelaar (1987)	Westerholm et al (1986) 1)
	ECE	FTP	FET			ECE	90 km.h^{-1}	120 km.h^{-1}		
Fluorene					20.1					
Phenanthrene					17.2	67.0	54.8	40.7	47.8	10.5
Anthracene					1.8	3.9	3.3	10.0	3.5	1.3
Fluoranthene	23.0	42.3	34.0	36.1±3.4	14.7	13.2	23.3	12.7	5.8	16.0
Pyrene	33.8	33.7	36.2	37.3±3.1	16.2				14.4	43.9
Benzo(a)anthracene					1.8	1.8	2.9	4.7	0.5	3.0
Chrysene	21.5	8.1	12.4	7.9±2.9	2.1	3.2	4.8	12.0	2.8	10.6
Benzofluoranthenes	3.4	5.9	5.5	6.2±1.0	5.9	0.5	<1	5.3	1.2	7.7
Perylene	0.3	0.1	0.2	0.25±0.14		<0.2	<0.5	<0.7	0.2	
Benzo(a)pyrene	1.5	2.9	3.4	2.2±0.87	0.5	<0.2	<0.5	<0.7	0.3	0.9
Benzo(e)pyrene	2.1	4.0	3.7	3.2±0.6	1.5	0.7	1.0	2.7	5.5	1.7
Indeno(1,2,3-cd)pyrene	2.1	0.7	1.0	2.8±1.1	0.7	<0.2	<0.5	<0.7	<0.1	0.9
Benzo(ghi)perylene	7.8	1.8	2.7	4.0±1.2	0.9	<0.2	<0.5	1.3	0.3	1.4
Anthanthrene						<0.2	<0.5	<0.7	0.0	
Coronene	4.5	0.5	0.9		0.2				0.5	0.3
Other PAH (without naphtalenes)					16.4	9.1	8.6	7.3	17.5	6.8

1) Heavy duty vehicle; particulates only.

Table 2.30 Development of fuel-based PAH emission factors for mobile sources

1. Assumed distribution of driving modes (% of mileage):

	Urban	Highways	Other
Light duty vehicles	40	20	40
Heavy duty vehicles	20	30	50

2. Assumed fuel consumption ($g.km^{-1}$):

	Urban	Highways	Other
Light duty vehicles	80	70	50
Heavy duty vehicles	250	220	160

3. PAH emission factors from Tables 2.26 and 2.27

	($\mu g.km^{-1}$)			
	Urban	Highways	Other	($mg.kg^{-1}$)
Gasoline fueled	250	250	250	4(2-6)
Diesel fueled	400	300	300	5.3(3.5-7)

2.11.1 Literature

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2.12 Summary

In this paragraph the proposed emission factors for selected sources of PAHs are presented together with their profiles (Table 2.31). Since a selection has been made from known PAHs, based on data availability, these factors do not apply to total PAH. Moreover, the scarce available data do not allow the development of complete profiles.
Nevertheless, taking into account the objective of the inventory, the proposed emission factors still can be used for a representation of reality as long as compounds are considered. This is, because the fraction of PAHs not taken into account can be estimated to be only 15-25%.
Surprisingly, the profiles show a certain degree of similarity. Average values of the low molecular PAHs have coefficients of variation between 20 and 30% (with the exception of fluorene). Those of the high molecular PAHs show less consistency, having coefficients of variation between 50 and 70%. In view of the uncertainties of the profiles it seems not to be unrealistic to use a uniform profile for model input or, alternatively, to use average values as a default profile for those sources for which no profile data are available.
They are given in Table 2.32.
No explanation is offered for this similarity in profiles for very different processes (which have in common, on the other hand, the phenomenon of combustion). It would be interesting to make it an object of further study.

Table 2.31 PAH emissions factors and profiles for selected sources and substances

	Residential combustion				Coke prod.	Prim. Al production		Mobile sources	Burning of biomass
	Anthra-cite	Bit. coal	Brown coal briq.	Wood		Anode prod.	Söderberg[5] process		
Emission factor ($mg.kg^{-1}$):	0.5(0.2-0.8)	50(30-70)	12(7-18)	100(10-200)	10(2-20)	70(40-120)	1000(500-5000)	see Table 2.30	
Profile (weight %):									
Fluorene	3	10	-	6	2	13	5	6	
Phenanthrene	30	25	20	37	30	43	26	40	} 44
Anthracene	3	9	7	9	8	7	4	6	
Fluoranthene	19	12	19	12	14	21	22	14	2)
Pyrene	14	9	7	10	9	11	16	17	13
Chrysene	6	6	5	4	4	1[4]	7[4]	5	} 7
Benzo(a)anthracene	4	6	5	3	5	1	4	2	
Benzo(c)phenanthrene	-	-	-	1	2	1	1		3
Low mol. PAHs	79	77	64	82	74	98	85	90	
Benzofluoranthenes	13	6	6	5	5	0.5	8	3.5	2
Perylene	0.5	1	3	1	1	0.5	0.5	0	1
Benzo(a)pyrene	2	4	2	3	5	0.5	2	1	1
Benzo(e)pyrene	3	4	12	2	4	0.5	3	2.5	1
Indeno(1,2,3-cd)pyrene	1	4	3	3	3	-	0.5	1	3)
Benzo(ghi)perylene	1	2	7	3	3	-	1	1.5	3)
Anthanthrene	0	1	0	0	1	-	-	0	
Dibenzoanthracenes	-	-	2	0	2	-	0	-	
Coronene	0.5	1	1	1	2	-	-	0.15	
High mol. PAHs	21	23	36	18	26	2	15	10	

1) Fireplaces: 25(10-35).
2) Fluoranthene: 10%; fluoranthene + methylpyrene: 16%.
3) Only in backfires (indeno(1,2,3-cd)pyrene: 2.2%; benzo(ghi)perylene: 3.9%).
4) + triphenylene.
5) Prebaked anodes: 30(10-50) mg/kg.

Table 2.32 Average PAH profile for all selected sources (weight %)

Fluorene	5(2-8)
Phenanthrene	32(24-38)
Anthracene	7(5-9)
Fluoranthene	17(12-20)
Pyrene	11(8-15)
Chrysene	5(4-6)
Benzo(a)anthracene	4(3-5)
Benzo(c)phenanthrene	0.5(0-1)
Benzofluoranthenes	5(3-7)
Perylene	1(0.5-2)
Benzo(a)pyrene	2.5(1-4)
Benzo(e)pyrene	3(2-4)
Indeno(1,2,3-cd)pyrene	2.5(1-4)
Benzo(ghi)perylene	2(1-3)
Anthanthrene	0.5(0-1)
Dibenzoanthracenes	1(0-2)
Coronene	1(0.5-1.5)
	100

3. SOURCES OF POLYCHLORINATED BIPHENYLS AND THEIR EMISSION FACTORS

3.1 Introduction

Polychlorinated biphenyls (PCBs) are derivatives of biphenyl in which one or more hydrogen atoms have been substituted by chlorine; 209 isomers may occur. Of these, more than 60 different substances with different chemical and biological properties can now be identified. Commercial products are mixtures of them in which the chlorine content is between 21 and 68%. Such mixtures show subacute and chronical toxic effects. Since PCBs appear also to be persistent in the environment and tend to accumulate in food chains their worldwide dispersion gives rise to concern.

PCBs may enter the environment during their production, use, and disposal by release into the air, water or soil. An estimate of possible routes of PCBs into the environment of North America has been made by Nisbet and Sarofim (1972). Their scheme is given in Figure 1.

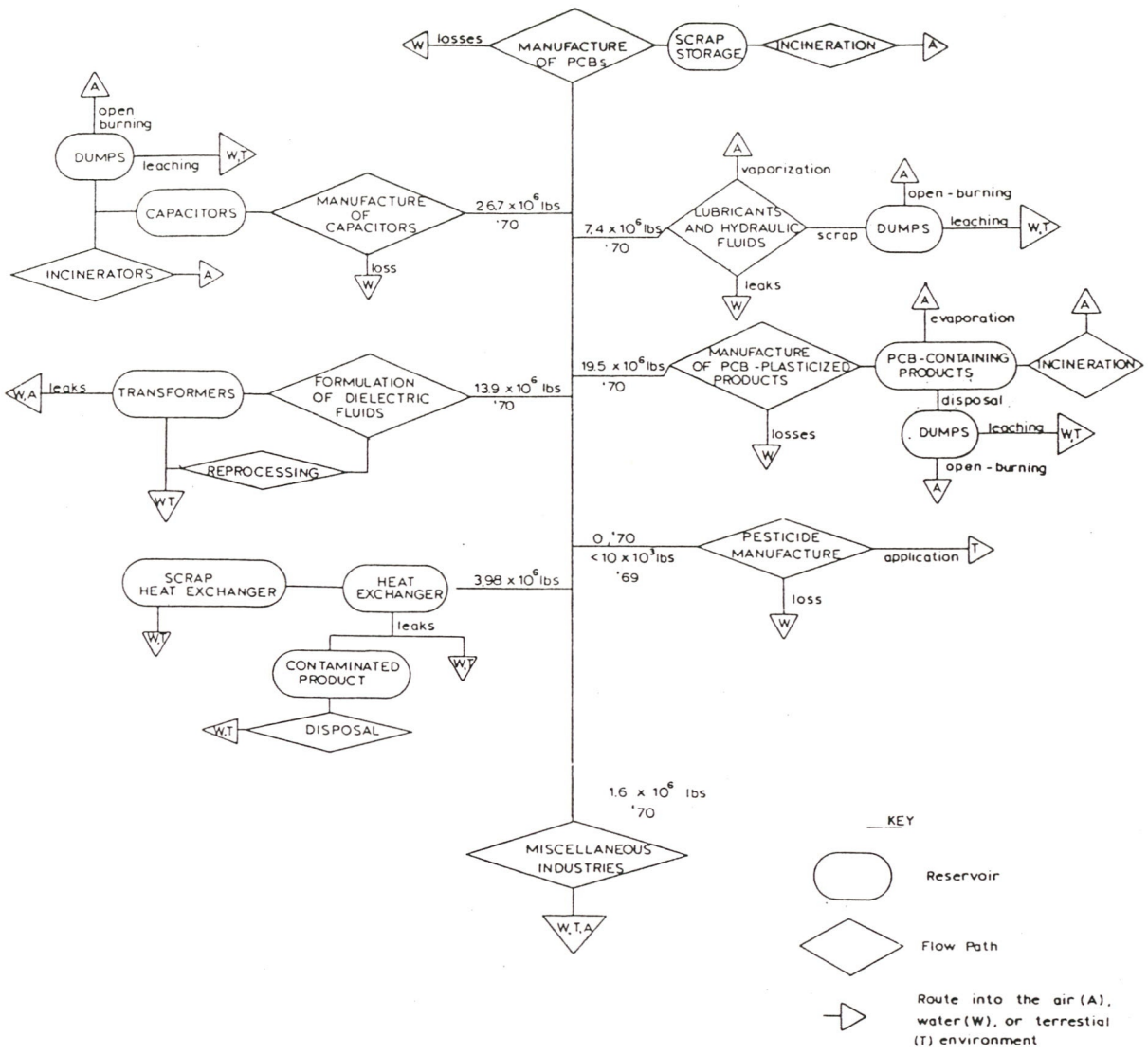

Figure 1 Possible routes of PCBs into the environment (Nisbet and Sarofim, 1972)

According to the objective of the study an assessment shall be restricted to emissions into the air by an inventory of source types and an estimation of their strengths by using emission factors. An ideal situation would include a detailed inventory together with toxicological properties of all isomers separately. However, most of the information refers only to commercial products which are mixtures of PCBs which have been produced in the past or are still produced. Therefore the study has to be reduced to emission factors for PCBs as a total.

3.2 Source identification

Although PCBs were already introduced into commerce in 1929 they were regarded as an environmental contaminant only in the late sixties after some accidents (Panel on hazardous substances, 1972). Since then the number of studies on dispersion and effects has increased strongly. The hazardous properties of PCBs are widely recognized now. The total world production of PCBs from 1930 to 1974 is estimated to be 5.94 x 105 ton (National Academy of Sciences, 1979). Nowadays environmental policy has resulted in a strong reduction. For example, in the OECD countries the quantities produced in 1983 are only 20% of that in 1973. In 1980 PCBs were only produced in France, West Germany, Italy and Spain. Since 1985 France is still the only country in Western Europe where PCBs are produced (Van der Laag, 1987). Therefore present emissions of PCBs originate to a large extent from their production in the past and are mainly related to use and/or disposal of products containing PCBs. Consequenty an inventory of sources has to be based for a large part on production data of former years and the lifetime of such products.

In some studies on sources of PCBs a distinction has been made between emissions from the use in open and in closed systems. The following sources are mentioned in the literature (Masuda et al. (1972), Sahied et al. (1973), Copius Peereboom et al. (1980), Lorenz and Neumeier (1983):
Closed systems, in which PCBs were or still are used are:
- transformers (PCBs as dielectric fluids),
- capacitors (id., e.g. in fluorescent light ballasts),
- hydraulic systems (e.g. in mining),
- heat exchangers.
- lubricants (for gas turbines and vacuum pumps),

Open PCB systems are:
- manufacturing sites,
- open burning or incinerators (of oils containing PCBs, or of contents of closed systems containing PCBs), especially if poorly operated,
- disposal sites,

- PCB containing fluids and solids:
  laminating agents,
  drilling and cutting oils,
  sealing liquids (in measuring instruments),
  heavy oil in ring scales,
  printing inks, paints (fire-retardants),
  plastics and rubber (plasticizers, fire retardants),
  synthetic resins, waxes, polishes,
  adhesive tape,
  wood and textile (preservation),
  carbon-free copy paper,
  packing paper and cardboard,
  recycling paper,
  cement.

Closed systems may become open systems by accidents. For example, a hydraulic fluid for mining that has been set free underground can reach the environment through ventilation systems, mine output and pit water.

In 1973 the OECD Council decided for the continued use of PCBs in closed systems, from which escape is unlikely but gave priority to their elimination in open uses. It is believed that nowadays PCBs are no longer used in such systems (Anonymus, 1985); in the European Community evaporation from them will hardly occur (Copius Peereboom and Reijnders, 1980). However, there may be still about 500 000 tonnes present in small capacitors and open uses in the OECD or exported to non-member countries and a large part of that amount could be set free in the environment (Bletchly, 1983b).

Several authors who discuss the possible routes of PCBs into the environment refer to the scheme of Nisbet and Sarofim (1972). In this, the release of PCBs has been differentiated to the compartments air, water and soil (Figure 1). The amounts refer to emissions in North America in 1970.

The authors assume that the PCBs which are emitted into air by vaporization originate either from disposed plasticized products or during open burning.

MacLeod (1979) regards as most likely sources of PCBs incinerators, dumps and landfills (also to air), leaking transformers and capacitors, manufacturing sites and deliberate spills but concludes from comparing different sources in indoor and outdoor air that a landfill and a transformer manufacturing site tested by her were not major sources of PCB. Elevated levels of PCBs were found in the immediate area of the sites but did not contribute substantially to the levels found at some distance. Defective light ballasts however appear to emit large quantities of PCB and so are important indoor sources of PCBs. Capacitors in small electric equipment may also be important sources.
Landfills appeared to be sources of PCBs from elevated concentrations in their neighbourhood. Sgontz and Howes (1985) measured concentrations up to 100 $\mu g.m^{-3}$ on landfills and 0.3 to 0.8 $\mu g.m^{-3}$ at distances 0.3-0.4 km downwind (upwind < 0.1 $\mu g.m^{-3}$).

Murphy et al. (1985) mention as possible sources of PCBs into the air:
- the evaporation of PCBs used in the past from open systems (paints, wood preservatives, plasticizers, etc.);
- the evaporation of spilled or leaked PCBs from transformers, large capacitors, hydraulic systems, and equipment containing large volumes of PCBs and still in service or in storage;
- the evaporation from landfills or incinerators of PCBs from materials disposed of in municipal refuse;
- the evaporation of PCBs improperly disposed of to open areas such as the use of waste PCB fluids to oil roads;
- emissions of PCBs from engines and furnaces burning liquid or gaseous fuels containing PCBs or contaminated with them;
- the reevaporation of PCBs from land areas where they have been deposited by wet and dry deposition from the atmosphere.

Note that, unlike Nisbet and Sarofim (1972), Murphy et al. did not exclude evaporation from closed systems (transformers, etc.) as a possible source of PCBs to air.

3.3 Emission rates and emission factors

Emission rates of PCBs depend strongly on the source type. Closed systems release only in case of leakage and after disposal. Nisbet and Sarofim (1972) estimated the emissions in North America for the year 1970, in which the production of PCBs (by Monsanto) reached its maximum value. Sources with rates of input in the environmental compartments are given in Table 3.1; they were estimated by the authors from an annual sales of 22.10^3 tons of PCBs as dielectric fluid and in heat exchangers and 13.10^3 tons of PCBs for other applications (lubricants, plasticizers). It was assumed that about 20% of total sales, some 7.10^3 ton.year^{-1}, represented a net increase in the amount of PCBs in service, in transformers, capacitors and heat exchangers.

Table 3.1 Gross estimates of emissions into environmental compartments of PCBs (Aroclors, trade name of Monsanto) in North America (1970) (Nisbet and Sarofim, 1972)

Source	Environmental compartment	Emission (103 ton.y^{-1})	PCB grade Types	Boiling range (°C)
Dumps and landfills	soil	18	1242-1260	325-420
Leaks and disposal of industrial fluids	water	4-5	1242-1260	325-420
Vaporization from plasticed products	air	1-2	1248-1260 (mainly)	340-420
Vaporization during open burning of disposited scrap and	air	0.4	1242	325-366

Note: The two last figures of the type number indicate the degree of substitution by chlorine (%). Solubilities, vapour pressures and vaporization rates of the Aroclors are given by Kalmaz and Kalmaz (1979), Lorenz (1983) and MacLeod (1984).

According to Nisbet and Sarofim the emission into the atmosphere by vaporization amounted to 10-20% of the sales for plasticizing products (9.10^3 ton. y^{-1}, which is about a quarter of total sales). This may be an overestimation because from the evaporation experiment cited by the authors it appears that 14% of Aroclor 1254 in plasticized resins maintained at 87 °C had been evaporated in 24 hours which corresponds to two years at 15 °C. The evaporation during one year should therefore be taken as 7%, so a value of 600 ton.y^{-1} is suggested instead of 1000-2000 ton.y^{-1} for the emission caused by vaporization of plasticized products. The emission during open burning amounted to 2% of the total disposed quantity in open incinerators, dumps and sanitary landfills (22.10^3 ton.y^{-1}) of which 10-20% is supposed to be destroyed. This will give an emission of 400 ton.y^{-1}. It is expected that most of these PCBs will be adsorbed on particles, but only for a small part on fine particles that will reside in the atmosphere for extended periods and can be transported to remote, areas while the larger part will be deposited within 2-3 days. To the authors opinion incineration is of minor importance, as only 0.25% of the PCBs are supposed to evaporate in incineration.
Therefore, regarding emissions into the air two important sources may exist: vaporization from PCB containing products in which PCBs are used as lubricants, plasticizers etc. and open burning of a relativily small part (2%) of PCB-containing products from dumps. The emission into the atmosphere of the USA in 1970 is estimated to be about 1000 ton.y-1. Relating this quantity to the number of inhabitants of the USA an emission of about 4 g.$inh^{-1}.y^{-1}$ results. However, since the production and the consumption of PCBs have been largely reduced it is expected that nowadays the emission will be no more than half this figure.

From the concentrations in the atmosphere of the U.S.A. which averagely are 0.05 ng.m^{-3} in rural and oceanic areas (90% of the total area) and 5 ng.m^{-3} in urban and suburban areas (10% of the total area), and a mixing height of 2 km, it has been calculated (National Academy of Sciences, 1979) that the air over the U.S.A. (16.25 x 106 km^2, which is

about twice the land area) contains about 18000 kg of PCBs. Murphy et al. (1985) used this figure together with an assumed average residence time of 1 week (corresponding to a deposition velocity of 0.33 $cm.s^{-1}$) to estimate the annual input of PCBs into the atmosphere over the U.S.A. The annual emission will be about 900 $ton.y^{-1}$ which results in an average input into, or deposition from, the atmosphere of about 60 $g.km^{-2}.y^{-1}$ while the average deposition from the atmosphere in rural/ oceanic areas and urban/suburban areas will be about 5.2 g.km-2.y^{-1} and 520 $g.km^{-2}.y^{-1}$, respectivily. If related to the average population densities for which 5 and 100 $inh.km^{-2}$ are assumed these emission densities correspond with 1 and 5 $g.inh^{-1}$ (average value for the USA as a whole: 2.4 $g.inh^{-1}$). Note that the annual emission as estimated by Murphy et al. is about equal to the emission rate estimated on the basis of the (corrected) data of Nisbet and Sarofim (1000 $ton.y^{-1}$).

Murphy et al. (1985) experimentally studied the emission from landfills and incinerators. With regard to landfills the authors state that sanitary land-fills are expected to be continous sources of PCBs because of the fact that PCBs will be carried out together with gases generated by anaerobic decomposition. They estimated a release of 10-100 $kg.y^{-1}$ for the U.S.A. from these source types together which is small compared with the total emission. The same applies to refuse and sewage sludge incinerators. According to the authors the major sources of PCBs to the atmosphere are yet to be identified.

An important source of PCBs may be the combustion of refuse oils to which PCBs have been admixed deliberately after which these oils are sold as fuels at attractive prices. In some samples of such oils considerable amounts of PCBs were found, up to 122 $mg.kg^{-1}$. It is supposed that the average concentration of PCBs in these oils is 5 $mg.kg^{-1}$ (CCRX, 1986). Part of the PCBs may remain undestroyed during combustion. For the rest there is a lack of data about PCBs contents of refuse oils.
Bletchly (1984a) assessed capacities and emissions of incinerators which are in operation for fluids containing PCBs in West-European countries. From some of these data emission factors have been derived or claimed; these are given in Table 3.2.

Table 3.2 Capacities, emissions and emission factors of incinerators for fluids containing PCBs (Bletchly, 1984a)

Company (country)	Capacity ($kg.h^{-1}$)	Emission ($g.h^{-1}$)	Emission factor ($mg.kg^{-1}$)
Sté Tradis (St Tradi, France)	400	2	5
Sté Prodelec (Pont de Claix, France)	700	1	1.5
PCUK (Jarrie, France)			25
Hessische Industriemull GmbH (W. Germ.)			1
Teknisk STAB (Brevik, Norway)	50		1
Ceanaway Ltd. (Ellesmere Port, U.K)			100
Rechem Intern. Ltd. (3 plants in U.K.)	400		1

These data show that the reported or claimed emission factors vary between 1 and 100 $mg.kg^{-1}$ which corresponds with destruction efficiencies of 99.99 to 99.9999%. The destruction efficiency depends on the combustion temperature which should be about 1200 °C.
In the future PCBs which are nowadays present in oils, transformers and capacitors have to be replaced and so have to be disposed of mainly by incineration. Bletchly also assessed the total capacity needed for disposal of PCB contaminated liquids from transformers and large capacitors. According to his estimation the average annual supply in Europe is now about 20.000 tonnes and will reach its maximum in the year 2000 when it will be about 42.000 tonnes. From these figures it can be estimated, assuming an emission factor of 10 $mg.kg^{-1}$ (destruction efficiency 99.999%), that incineration of liquids containing PCBs, which are now in use in Europe, will cause a annual emission of 0.4 to 0.8 ton. These quantities are small in comparison with the quantities evaporating from products containing PCBs which are still applied in open systems, which was assessed to be 900 or 1000 $t.y^{-1}$ in the USA.

In the estimations given above the contribution of leakage and subsequent evaporation of closed systems has been left out of consideration. The same applies to illegal dumping, for which no assessments can be made.

MacLeod (1979) refers to work of others in which was found that a municipal refuse incinerator released 2-34 $\mu g.m^{-3}$ into the air whereas an industrial incinerator burning fluids containing 10-17% PCBs at the time of sampling released only 0.3-0.7 $\mu g.m^{-3}$.

The small emission from incinerators has been confirmed by Scheffer (1986) who measured emissions of PCBs from 3 refuse incinerators in the Netherlands. These emissions (in 1981) were 250, 250 and 38 mg PCBs.ton^{-1} refuse. Using the average (144 mg.ton^{-1}) as an emission factor for incineration of domestic refuse the total emission of PCBs from all installations was estimated to be 0.34 ton.y^{-1}. Relating the emission to the number of inhabitants involved (5.36×10^6) an emission factor of 64 mg.inh-1.y-1 is found. For the Netherlands (14×10^6 inhabitants) the emission, calculated with this factor, would be 0.9 ton.y-1, which agrees reasonably with the 0.6 ton PCBs emission in the Netherlands mentioned in another report (Dutch Tweede Kamer der Staten-Generaal, 1985).

Incineration of PCBs containing refuse, if properly operated, hence produces considerably less PCBs than vaporization. Its emission factor is much lower than the emission factor for vaporization from PCBs containing products during their use and residence in disposal sites.

It is interesting to compare the estimations of deposition fluxes mentioned before with results obtained from experimental data on areal burdening. Recently Swackhamer et al. (1988) used a mass balance approach for the study of transport of PCBs from water surfaces to the air and reverse. The authors estimated the evaporation rate from lakes in the U.S.A., which may be regarded as rural areas, to be 8.5 g.$km^{-2}.y^{-1}$. The deposition fluxes of PCBs in rain, snow and aerosol appeared together to be 14.1 g.$km^{-2}.y^{-1}$ which is larger by a factor 2.7 than the value derived by Murphy.
Another way of determining the atmospheric input of PCBs has been followed by Rapaport and Eisenreich (1988). These authors measured the accumulation of PCBs in peat cores taken in the midlatitudes of Eastern North America together with applying dating methods on the peat samples.

They found that the areal burdening rate with PCBs closely follows their historical production and use rate. Between 1960 and 1970 the highest values were reached after which the deposition flux decreased; the average value on 9 locations in 1980 was only half of that in 1970, which amounted to 2.6 $g.km^{-2}.y^{-1}$ which is half of the value for rural areas estimated by Murphy from the average concentration given by the National Academy of Sciences (1979). Recent fluxes (post 1980) are between 0.1 and 4 $g.km^{-2}.y^{-1}$ with an average value of 1.3 $g.km^{-2}.y^{-1}$ which is half of that in 1970. The authors refer to studies by others on sedimentation in lakes which showed burdens of equal order of magnitude (with one exception: Lake Ontario, the burden of which is an order of magnitude larger).

Regarding emissions in urban and suburban areas Lorenz and Claus (1983) refer to Wrabetz (1980) who estimated the emission flux in the Leverkusen area to be 180 $g.km^{-2}.y^{-1}$ which is a third of the value estimated by Murphy from the concentrations in similar areas given by the National Academy of Sciences (1979).

Emission of PCBs in European countries may be estimated from sales in an analogous way by using emission factors, relating the quantities dumped or incinerated to emitted quantities. Such relations, however, are unsufficiently supported by experimental evidence. Nevertheless it has been tried to estimate these emissions by using the following assumptions:

1. The emissions into air only originate from vaporization from open systems containing small amounts of PCBs which are still manufactured. The quantities of PCBs which are used for these applications are equal to the annual sales of PCBs which are not used for transformers and large capacitors (emission to air because of leakage or disposal of these objects are supposed to be negligible).
2. The quantities emitted from the products mentioned before are 7% of their PCBs contents (half the value used by Nisbet and Sarofim). In other words, it is assumed that the remaining 93% is either destroyed by incineration or open burning, or is released to soil or water.

3. According to the assumption made by Nisbeth and Sarofim 2% of this quantity is emitted by open burning (it is assumed that nowadays no capacitor or transformer fluids are subject to open burning). Together with the 7% this will give an emission of 9% of the PCB contents of the products mentioned before.
4. The emission of PCBs in an certain area is proportional to its number of inhabitants.
5. Emissions from incineration of domestic refuse can be estimated with an emission factor derived from literature data. The same applies to emissions from incineration of refuse liquids containing PCBs which have to be disposed of. These emissions will be relativily small.

Annual production, domestic sales and exports in some OECD member countries of PCBs for usage in transformers, large capacitors, and other applications have been presented by Bletchly (1984b). It is assumed that productions, after subtraction of domestic sales and exports to OECD member countries, represent the quantities subject to vaporisation (15%). Possibly this is an overestimation as part of the quantities are exported to non-member countries for usage in transformers and capacitors as well. The calculated quantities are shown in Table 3.3.

Table 3 Annual domestic sales in and exports from some OECD member countries other than for usage in transformers or capacitors, in ton.year-1. (Bletchly, 1984b).

Country	1970-1974 (average)	1975-1979 (average)	1980
France	1119	2469	4199
Germany (F.R.G.)	2926	2896	3106
Italy	159	112	291
United Kingdom	2818	1290	0
United States	11236	2461	0

Remark: The figures for the F.R.G. were calculated with the assumption that 58% of the production is used for transformers and large capacitors (domestic sales and exports to OECD member countries).

From this table it can be seen that in the European OECD member countries maximally 7500 tonnes of PCBs may still be produced for use in open systems and small capacitors. We assume that this quantity serves to replace the present quantity. If 9% of this quantity is released into the air, the emission from open systems will be about 700 tonnes. With 315 x 10^6 inhabitants the emission factor for vaporisation from open systems is ca. 2 g.inh^{-1}.y^{-1}. This emission factor is half as large as that, calculated for the U.S.A. in the year 1970 on the basis of the (corrected) data of Nisbet and Sarofim (4 g.$year^{-1}$.inh^{-1}) which will now be certainly lower. It also agrees well with the average value for the USA (2.4 g.inh^{-1}.y^{-1}) derived from the emission estimated by Murphy et al (1985) whereas the values in rural areas may be lower and that in urban areas may be higher by half a decade.
In an attempt to reconcile measurements and estimates, transformed to some emission factor, it is proposed to relate PCB emissions to population density with a factor of 2(1-5) g.$inh.^{-1}y^{-1}$. This value may represent the order of magnitude of present emissions, except those caused by incidental leakages and illegal activities.

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4. SOURCES OF LINDANE AND THEIR EMISSION FACTORS

4.1 Introduction

Lindane is the common name of a substance containing 99.0% or more of the gamma isomer of hexachlorocyclohexane (gamma-HCH). A substance of lower purity is called technical HCH.
Since many years Lindane is widely used as a pesticide. The use of technical HCH, however, has been banned in several European countries because of its disagreeable persistent smell. Lindane, however, is accepted although some restrictions have been made in many countries.
Lindane shows sub-acute toxicity with possible effects on the liver. It is persistent in air, water and soil, and as it is relativily volatile, it may be transported over large distances. The transport distance is restricted by depostion. The restriction by dry deposition can be estimated as follows: Assunming a dry deposition rate of about 2 $mm.s^{-1}$ and a mixing height of 2 km the half life time of Lindane in the atmosphere is estimated to be about 200 hours which corresponds with a transport distance of about 3000 km if the wind speed is 4 $m.s^{-1}$.
Reevaporation of deposited Lindane is not to be regarded as a large source because it has been calculated from McKay's fugacity model (RIVM, 1988) that in the state of equilibrium more than 99% of it will be present in soil and water.
Lindane is found in plants and animals far away from anthropogenic sources. Therefore it may influence ecosystems over the world (RIVM, 1988).

4.2 Source identification

For Lindane emissions a distinction between point sources and area sources can be made. The following source types have been mentioned (De Bruin, 1979):

1. Point sources:
   - Manufacturing plants
   - Formulating plants
   - Wood treatment installations

2. Diffuse sources:
   - Agricultural uses
   - Veterinary use
   - Use in wood preservation

Apart from these source types some are mentioned which are of minor importance:
- Public health use (control of the breeding of mosquitos in stagnant waters);
- Household use (insecticidal products for indoor plants).

4.3 Source selection

The relative importance of these source types is demonstrated from the pollution pattern in the EEC estimated by De Bruin (1979):

Point sources:
- Manufacturing : 3 200 $kg.y^{-1}$
- Formulating : 3 800 ,,
- Other : 200 ,,

Diffuse sources:
- Agriculture : 2 000 000 ,,
- Veterinary use: 100 000 ,,
- Other : 200 000 ,,

According to this estimation the emission by diffuse sources is overwhelming. Moreover, manufacturing and formulating plants of Lindane are supposed to emit mainly in the effluent water (De Bruin, 1979). It has to be examined, however, whether the dominating role of diffuse sources also applies to emissions into the atmosphere. For the Netherlands RIVM (1987) estimates the following partition of emissions of hexachlorocyclohexane (HCH) over the environmental compartiments (Table 4.1):

Table 4.1 Partition of HCH emissions in the Netherlands 1983 over the environmental compartments, in tonnes (RIVM, 1987) [1]

Activity Emission in:	Air	Water	Soil	Refuse [3]
Formulating	+	+	-	+
Soil treatment (excl. greenhouses)	+	+	19.7	-
Seed treatment	+	+	2.0	-
Crop treatment	0.3	+	0.2	+
Use in greenhouses	+	-	0.3	-
Veterinary use [2]	0.5	+	1.5	+
Abatement of creeping insects in buildings	0.4	-	-	-
Abatement of wood insects in buildings	1.9	0.1	-	-
Wood preservation	+	-	1.8	+
Domestic use	0.1	0.1	-	+
Other uses	0.1	-	-	-
Total	3.3	0.2	25.5	+

1) +: Source of limited extent -: No emission.
2) Control of ecoparasites on domestic animals (e.g. sheep).
3) To be destroyed by incineration.

From these figures it follows that in the Netherlands as the most important sources of Lindane to air are considered:

- crop treatment
- veterinary use
- abatement of creeping insects in buildings
- abatement of wood insects in buildings.

Emissions into the atmosphere might be 10-20% of total losses. If these figures also apply to losses in the EEC, total non-diffuse sources still would be a few percent of total losses.

Lindane or technical HCH manufacturing plants can be added to these four source types, of course only in countries where they are present. In 1979 there were plants in several European countries: France, F.R.G., G.D.R., Poland, Rumania, Spain, U.S.S.R. and Yugoslavia (De Bruin, 1979). There is no detailed information about production data. For some of these countries the capacity for the production of Lindane (from

technical HCH, which contains about 12.5% of the gamma-isomer) has been estimated; in France it amounted in 1979 to 3000 $t.y^{-1}$, in the F.R.G. to 1700 $t.y^{-1}$ (De Bruin, 1979). These amounts may have changed in the meantime; in 1983 a production of 1500 $t.y^{-1}$ was reported for the Boeringer factory in the F.R.G. (Schulze and Weiser, 1983). Discharges however are expected to take place predominantly to surface water.
The same applies to formulating plants of which a loss of 0.1% to process water is reported (De Bruin, 1979).
Since in other European countries somewhat different regulations exist as in the Netherlands, the relative importance of sources may there differ quantitativily from that in the Netherlands. Nevertheless the above mentioned sources will be assumed to be the most important ones in other European countries as well.

4.4 Emission factors

It is assumed that the emission of Lindane to the atmosphere will be approximately equal to the sum of the emissions of the most important source types mentioned before, that is, crop treatment, veterinary use, and abatement of creeping and wood insects in buildings. Each of these emissions should be estimated from some parameter characterizing the extent of the activity and an emission factor typical for the source type.
Such factors should have been derived from experiments in which the emission (for example, the amount of Lindane evaporated as a function of time) and the extent of the activity (for example, the amount of Lindane that has been sprayed on a crop) had been determined. Unfortunately there are no data of this kind. In practice, the fraction of the used Lindane that evaporates in the course of time is roughly estimated for different applications. Such estimations have been done by the RIVM in the Netherlands (Table 4.2).

Table 4.2 Emission factors of HCH to air calculated from the emission data presented for the Netherlands (RIVM, 1987), in $g.kg^{-1}$.

Activity	Related to	Average emission factor
Soil, seed and crop treatment, use in greenhouses	area of arable land and permanent crops	14
Veterinary use	area of pasture	250
Abatement of insects in buildings, household, wood preservation	number of inhabitants	500
Total of activities		110

Apart from this uncertainty there is insufficient information about the quantities of Lindane used for the different activities. For example, there is only qualitative information about the crop types to which Lindane is applied. Nor it is known which part of the quantity which is sold in a certain country is used for a certain application, e.g. spraying of potatoes. In addition to that, such quantities may be subject of continuous changes since it is attempted to replace Lindane by other pesticides. Nowadays alternatives are available for several but not for all applications (Van Haasteren, 1988). It is not known, however, to what extent they are used. Appendix 1 presents agricultural applications of Lindane together with availabilities of alternatives.
The only data available for emission factor development are those on consumption and emission in the Netherlands (Tables 4.1 and 4.2). Taking differences between countries in the proportions of Lindane used in agriculture and cattle breeding into consideration, an emission factor of 5 (3-10)% of agricultural consumption (or of total consumption) according to Table 4.9, column 4 (or column 6) is proposed.
In a similar way emissions from other applications are assumed to be 50% of consumption.

4.5 Consumption data

Consumption data of Lindane for different applications in some European countries are given in Table 4.3. These data are the result of a literature search. Attempts to collect additional information from authorities and experts failed.

In the Netherlands, public authorities list agricultural applications in a qualitative way (no quantities or percentages). This information has been given in Appendix 1.

Institutes, offices or agencies specifically dealing with legalisation of pesticides and the abatement of plant diseases in the Netherlands could only provide information of a general nature and referred to manufacturers for consumption data.

Individual formulating industries appeared to have an incomplete view on the fate of their products. The Dutch Foundation for Phytopharmacy, of which manufacturers are members, was reluctant in giving more information than the total consumption but is possibly not able to give more.

Inquiries in other countries were also not very successful. The international group of national associations of manufacturers of agrochemical products (GIFAP) made reference to the Centre International d'Études du Lindane (CIÉL) in Brussels. On request, a copy of the contract was sent to this institute (with permission of the contractor) to explain the background of the inquiry, but an answer was never obtained.

The British Pest Control Association appeared not to be in the position to give the required information and made reference to the Department of Environment. Again, no answer was obtained.

The Danish Environment Protection Agency wrote not to be able to supply data about the use of pesticides.

Finally, Mr. Walsh of the Commission of the European Communities tried to find the required information but did not succeed. He informed about the Commission's Scientic Committee for Pesticides evaluation of Lindane. It is not clear whether any results from this evaluation still can be used for the MASH-project.

Table 4.3 Consumption of Lindane for different applications in European countries (ton.year^{-1}).

Country	Year	Agri-culture	Veteri-nary use	Abat. of creeping insects	Wood preser-vation	Other	Total	Ref.
Austria	1983						37.6	2
Belgium	1977	12	8		1	1	22	1
Czechoslowakia	1974-6						98.7	2
Denmark	1977	5	10				15	1
,,	1981						8.7	5
,,	1983						7.3	2
Finland	1974-6						5.8	2
,,	1981	5.0					5.0	6
France	1977	1125	-		10	1	1137	1
Germany,F.R.	1977	175	4		110	3	292	1
Hungary	1982						195.3[a]	2
Iceland	1982						0.1	2
Ireland	1977	2	3				5	1
Italy	1977	425	18		22		465[b]	1
,,	1982						267[b]	2
Netherlands	1977	24	12		1		37	1
,,	1983	22.5	2	0.4	3.8[c]	0.3	29	4
Norway	1982						6.6	3
Poland	1983						200.4	2
Portugal	1982						4.3	2
Sweden	1982						6.0	2
U.K.	1977	240	45		60		345	1

a) Contrary to the most other countries the consumption of Lindane in Hungary decreased strongly since 1974-76, when it was 2207 ton/year.
b) 20% of the original data as these data probably refer to the formulated product which contains 20% Lindane (De Bruin, 1979).
c) Including abatement of wood insects in buildings.
1) De Bruin (1979).
2) FAO Production Yearbook (1985).
3) Paulsen, J. (1984), letter to Dr. J. Pacyna.
4) RIVM, Basis document Lindane (in preparation).
5) Kemikalienkontrollen (1982).
6) Tiittanen and Blomqvist (1982); consumption mainly in forestry.

It follows from Table 4.3 that, on the average, 95% of the Lindane is used in agriculture and for veterinary use (with the exception of the F.R.G.). For assessing emissions in countries in which only total consumptions are known it will be assumed that in those countries also 95%

of the total Lindane consumption is for these applications.
Another conclusion is that consumption rates for agricultural and veterinary use differ largely. In some countries they are of the same order whilst in other countries the veterinary use is of minor importance. This is caused by differences in legislation.
Also, the data suggest a decreasing consumption in time, 1982 data being about two thirds of 1977 ones in some countries.

An attempt to relate the veterinary use of Lindane to the number of sheep in countries (Lindane is most frequently applied to sheep in the Netherlands) failed for the countries of which veterinary use data are known (see Table 4.3). These data were compared with numbers of sheep (The Europa Year Book 1987). The consuption per sheep appeared to vary in a very wide range (between 0.001 and 0.1 kg/sheep.year).
Another estimation could be based upon the assumption that agricultural use is related to the area of arable land and permanent crops, whilst veterinary use, depending on the number of cattle, is related to the area of grassland. Specific consumption rates for these uses are shown in Tables 4.4 and 4.5. The consumption data refer to the countries from Table 4.3 for which separate uses are known. Data (1983) about areas have been obtained from FAO (1985).

Table 4.4 Consumption rates of Lindane for agricultural use (annual consumption per unit of area) ($kg.km^{-2}.y^{-1}$).

Country	Arable land + perm.crops (km^{-2})	Consumption rate ($ton.y^{-1}$)	Consumption rate ($kg.km^{-2}.y^{-1}$)
Belgium/Luxemburg	8270	12	1.45
Denmark	26390	5	0.2
France	187200	1125	6.0
Germany, F.R.	74490	175	2.35
Ireland	9720	2	0.2
Italy	122220	425	3.5
Netherlands	8650	23	2.6
U.K.	69860	240	3.4
Average (stand. dev.)			2.5 (1.9)
Median value			2.5

The uncertainties of the average values raise doubt about the reliability of estimates of consumption rates in countries for which no data are available. This is illustrated in Table 4.6, where the median values are used to calculate total consumptions. On comparison with the real data, Austria, Czechoslovakia, Hungary and, to a somewhat lesser extent, Norway and Poland show a good to acceptable agreement. Portugal and Sweden, however, have much lower consumptions.

Table 4.5 Consumption rate of Lindane for veterinary use (annual consumption per unit area) ($kg.km^{-2}.y^{-1}$).

Country	Permanent pasture (km^{-2})	Consumption rate ($ton.y^{-1}$)	($kg.km-2.y_{-1}$)
Belgium/Luxemburg	6720	8	1.2
Denmark	2420	10	4.1
Germany,F.R.	46300	4	0.1
Ireland	48600	3	0.1
Italy	50510	18	0.4
Netherlands	11430	2	0.2
U.K.	117050	45	0.4
Average (stand. dev.)			0.9 (1.4)
,, (except Denmark)			0.4
Median value			0.4

Table 4.6 Calculated consumption of Lindane for agricultural and veterinary use (consumption per unit area) ($kg.km^{-2}.y^{-1}$)

Country	Arable land + perm.crops area (km^{-2})	cons.rate ($kg.km^{-2}.y^{-1}$)	Permanent pasture area (km^{-2})	cons.rate ($kg.km^{-2}.y^{-1}$)	Consumption rate [a] calc.	Table 2 ($ton.y^{-1}$)
Austria	15170	38	20200	8	44	36
Czechoslowakia	51700	129	16650	7	134	94
Hungary	52920	132	12790	5	136	186
Iceland	80	0.2	22740	9	7	0.1
Norway	8530	21	960	0.4	21	6
Poland	148290	371	40800	16	383	190
Portugal	35500	89	5300	2	91	4
Sweden	30030	75	7000	3	77	6

a) Consumption rates for agricultural and veterinary use are assumed to be 95% of the total consumption rate.

As the consumption of Lindane is mainly in agriculture, an alternative may be to relate the combined consumption for agricultural and veterinary use to the area of arable land and permanent crops. In addition the downward trend in consumption is taken into account by taking 60% of

the 1977 values based on the data from Table 4.3. Table 4.7 shows the results.

Table 4.7 Consumption rate of Lindane for agricultural and veterinary use (estimated consumption in 1982 per unit area) ($kg.km^{-2}.y^{-1}$)

Country	Agric.+ veter. consumption ($t.y^{-1}$)	Arable land + perm.crops (km^{-2})	Consumption rate ($kg.km^{-2}.y^{-1}$)
Belgium/Luxemburg	12	8270	1.4
Denmark	9	26390	0.3
France	680	187200	3.6
Germany, F.R.	110	74490	1.5
Ireland	3	9720	0.3
Italy	270	122220	2.2
Netherlands	25	8650	2.8
U.K.	170	69860	2.4
Average (stand. dev.)			1.8 (1.2)
Median value			1.9

Since the accuracy of these results is not inferior to that of those relating the agricultural and veterinary consumptions separately to respectivily the areas of arable land and pasture, it is proposed to use these results as a default value for estimating consumptions; 2 $kg.km^{-2}.y^{-1}$ will be taken.

Consumption rates of Lindane as an agent for the abatement of insects (incl. wood preservation) in buildings of a certain region are supposed to be proportional with the number of inhabitants. It is assumed that this is also the case with the non-specified other applications. Specific consumption rate values, derived from the data in Table 4.3 are listed in Table 4.8.

Table 4.8 Consumption rate of Lindane for abatement of insects, wood preservation and other applications ($g.inh^{-1}.y^{-1}$)

Country	Population (10^6 inh)	Consumption rate ($ton.y^{-1}$)	($g.inh^{-1}.y^{-1}$)
Belgium/Luxemburg	9.9	2	0.2
France	54.7	11	0.2
Germany, F.R.	61.4	113	1.8
Italy	56.8	22	0.4
Netherlands	14.4	4.5	0.3
U.K.	56.4	60	1.1
Average (stand. dev.)			0.76 (0.68)
Median value			0.3-0.4

1) Figures refer to 1977 except those for the Netherlands: 1983.

Just as for agricultural and veterinary use there is not much consistency. It is suggested to use the median value (0.3-0.4 $g.inh^{-1}.y^{-1}$) as a default value. After correction for the assumed downward trend 0.2 $g.inh^{-1}$ results for consumption other than for agricultural and veterinary use.

Although it is realized that the consumption data of Table 4.3 may be neither sufficiently reliable nor necessarily complete (see e.g. data on wood preservation), it is the only data set with at least some status. Applying the discussed assumptions and default values to it, a consumption pattern of rather high uncertainty results (Table 4.9). This pattern out of necessity has to be used in combination with the estimated emission factors from Table 4.2 to find spatially distributed emissions.

The uncertainty of these figures can hardly be estimated. In Table 4.9 reported and converted data are entered for a comparison. Legislative and economic differences between countries frustrate attempts to analyse data in a comparative way, however. One could, then, put a question mark to the distinction between agricultural and other use. The reason for this is the difference in the estimated values of the emission factors and the expected effect of the very large population concentrations in the - relative - neighbourhood of the receptor areas.

For 9 out of the 25 countries no data at all were available. Uncertainty South and East of the Baltic is very high since only for Finland some data are available, but without any indication about location. A certain consumption pattern can be seen but it is, of course, rather artificial. Several countries are outside this pattern, of which France and Hungary are high for agricultural and veterinary use, and the F.R.G., Hungary and the U.K. are high for other applications.

4.6 Emissions

Emission factors proposed in par. 4.4, together with the consumption data from Table 4.9, give area- resp. inhabitant-related annual emissions. The large difference between estimated losses from agricultural and veterinary use (1.4 resp. 25%) presents a problem. Only for some countries both consumption data are available. Weighed average losses vary from 2.4% in Italy to 17% in Denmark. There is no relation between sheep breeding intensity and Lindane application. Losses from consumption in agricultural areas therefore cannot be estimated even on an order of magnitude level. For the MASH project they are assumed to be 5%, but a variation between 1% and 20% is possible.
For other applications the estimated loss is 50% (Table 4.2).
National emissions, estimated - or, rather assumed - in this way are presented in Table 4.9. Due to the larger loss in non-agricultural applications the contribution of these is ca. 30% of total emissions in Europe, which are believed to be about 400 tons in 1982.

Table 4.9 Lindane consumption and emissions in Europe (1982)

Country	Arable land + perm. crops (10^3 km²)	Population (10^6)	From reported consumption data: Agricultural and veterinary use (ton) 1977	1982, 1983	(kg.km^{-2}) 1977	1982, 1983	Other use (ton) 1977	1982, 1983	(g.inh.$^{-1}$) 1977	1982, 1983	Total use (ton) 1977	1982 1983	Estimated consumption in 1982 6): Agr. and vet. use (kg.km²)	Other use (g.inh.$^{-1}$)	Total use (ton)	Estimated emissions in 1982 (ton): Agr. and vet. use	Other use
Albania	7.1	2.8											2	0.2	15	0.7*	0.3
Austria	15.1	7.5										37.6	2.4	0.25	37.6	2 *	0.9
Belgium 1)	8.3	10.2	20		2.4		20		2		22		1.4	0.12	13	1.3	0.6
Bulgaria	41	8.9											2	0.2	80	4 *	0.9
Czechoslovakia	52	15.4									~95		1.1	0.19	60	3 *	1.5
Denmark	26	5.1	15	~8	0.6	~0.3					8		0.3	0.08	8	1.3	0.15
Finland	195 4)	4.9									5		0.02 4)	0.04	5	0.1	0.1
France	187	54.0	1125		6.0		11		0.2		1137		3.6	0.13	680	9.5	3.5
Germany, DR	50	16.7											2	0.2	100	5 *	1.7
Germany, FR	74	61.4	179		2.4		113		1.8		292		1.5	0.1	175	21	34
Greece	40	9.8											2	0.2	80	4 *	1
Hungary	53	10.7										195	3.5	0.9	195	9 *	5
Ireland	9.7	3.5	5		0.5								0.3	0.06	3	0.5	0.1
Italy	122	56.8	443	~270	3.6	~2.0	22		0.4		465	267	2.2	0.23	267	6.4	6.5
Netherlands	8.7	14.3	36	24.5	4.1	2.8		4.5		0.3		29	2.8	0.3	29	0.8	2.1
Norway	8.5	4.1										6.6	0.8	0.07	6.6	0.3*	0.15
Poland	148	36.6										200	1.3	0.3	200	10 *	5
Portugal	36	10.0										4.3	0.1	0.02	4.3	0.2*	0.1
Romania	106	22.6											2	0.2	220	11 *	2
Spain	205	38.2											2	0.2	400	20 *	4
Sweden	30	8.3										6	0.2	0.04	6	0.3*	0.15
Switzerland	4.1	6.3											2	0.2	10	0.4*	0.6
United Kingdom	70	55.7	285		4.1		60		1.1		345		2.4	0.65	200	8.7	18
U.S.S.R.	1500 2)	215 3)											2 5)	0.2	3000	150 *	20
Yugoslavia	78	22.8											2	0.2	160	8 *	2
	ca. 29.00	702														278	110

1) + Luxemburg
2) 65% in EMEP area, estimated
3) 80%, in EMEP area, estimated
4) Forest area
5) Reportedly high; no data available (Komarov, 1980).
6) Reported values, 95% of total use for agr. + vet. use, 1982 consumption = 60% of 1977 consumption, and default values.
* 5% loss.

4.7 Literature

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APPENDIX: APPLICATIONS OF LINDANE IN AGRICULTURE AND CATTLE-BREEDING

Lindane is applied in agriculture for soil, seed and crop protection as an insecticide for the following plants:

Plant	Soil/seed/crop	Alternative?
Open air		
Arboriculture	soil	no
,,	crop	yes
Beetroot	seed	yes
Cabbage	seed	yes
Cereals	seed	no
Flax	seed	no
Flower bulbs	soil (limited)	?
Fruit trees	crop	yes (some exceptions)
Maize	soil	partly
,,	seed	no
Pasture	crop	yes
Potato	crop	yes
Rape-seed	seed	no
Sugar beet	soil, seed	partly
,,	crop	yes
Under glass		
Flowers	soil	no
,,	crop (limited)	no
Vegetables	soil (one insect)	no

Further, Lindane has a veterinary application as it is used for washing sheeps. No alternative is known.

5. SOURCES OF HEXACHLOROBENZENE AND THEIR EMISSION FACTORS

5.1. Introduction

Hexachlorobenzene is a selective fungicide which was used as a protectant against seed and soil disease. Nowadays this application is practically abandoned. Already ten years ago its use in agriculture was completely banned in Belgium, the F.R.G, France and the Netherlands, in Italy a total ban was under preparation, and in some other countries (Denmark, Ireland and U.K.) it was no longer used (De Bruin, 1979).
In spite of this, HCB may still be in circulation in agriculture as some pesticides contain small amounts of it as impurities. They will be discussed below.

Non-agricultural applications of HCB are its use as a fire retardant and in pyrotechnics and ordnance materials (e.g. smoke signals). For these applic-ations alternative compounds are available, but it is not known to what extent HCB has been replaced by them.

Finally, HCB is formed as a by-product in the manufacturing of highly chlorinated C_1 and C_2 hydrocarbons. It can easily be removed by distillation because of its relativily high boiling point.

5.2 Source identification

Manufacturing plants of some chlorinated hydrocarbons may be regarded as point sources (Table 5.1). HCB wastes and HCB containing wastes in the pesticide industry may also be sources. Quinlivan et al (1977) estimated for the U.S.A. that these annually amount to 1655 and 2633 ton, respectivily.
The materials, however, predominantly are emitted with waste water (De Bruin, 1979), leaving the minor part, which is incinerated, as relevant for this study. According to Carpenter et al. (1986) the destruction efficiency is over 99.9%, so a fraction smaller than 10^{-3} will be emitted from industrial incinerators as point sources of HCB.

The importance of chlorine manufacturing as a source of HCB (De Bruin, 1979) has decreased since nowadays more and more chlorine factories use anodes made from titanium instead of graphite.

Table 5.1 Chlorinated hydrocarbons with HCB as a by-product in manufacturing (De Bruin, 1979; Carpenter et al., 1986)

Substance	Kg HCB in waste per ton of product	
	De Bruin [1]	Carpenter et al. [2]
Tetrachloroethylene	2.5 - 5	8 - 10
Trichloroethylene	0.5 - 1	2 - 8
Carbon tetrachloride	0.2 - 0.4	4 - 26
Vinyl chloride	0 - 0.006	

1) Figures quoted from Mumma and Lawless (1976) and Fishbein (1979).
2) Calculated from concentration ranges of HCB in by-products given by Environ Corp. (1985) and OSW (1985), and assuming that 40 kg by-product is formed per ton of substance.

Municipal incinerators also appear to be point sources of HCB as has been reported by several authors (Müller, 1982; Carpenter et al., 1986; Scheffer, 1987). During combustion of chlorinated substances HCB may be formed. From averaging the results of combustion experiments by Ahling et al. (1978) it can be concluded that polyvinyl chloride may form 0.7 mg HCB per kg PVC.

Diffuse sources originate from the use of some pesticides which are contaminated with HCB. These pesticides and their HCB content are given in Table 5.2.

Table 5.2 Pesticides containing small amounts of HCB (Carpenter, 1986)

Name of pesticide	Application	HCB content (kg/ton pest.)
Quintozene (pentachloronitrobenzene,PCNB)	fungicide (soil/seed/crop)	5
Chlorthal-dimethyl (dimethyltetrachloroterephthalate,DCPA)	herbicide	3
Chlorothalonil	fungicide (crop)	0.5
Picloram	herbicide	0.2
Pentachlorophenol	wood preservation	0.1

Regarding the use of HCB as a pesticide in agriculture the FAO reported a consumption of 2550 ton in Italy and 2 ton in Portugal in 1974-76 but no consumptions in later years (FAO, 1985).
Finally some HCB may still be emitted into air by slow volatilization from landfills. No quantitative release data are available.

5.3 Source selection

An impression about the relative importance of emissions of HCB sources mentioned above can be obtained from the data of Carpenter et al. These authors assessed the annual emission in the U.S.A. originating from these sources. Their results are given in Table 5.3.

Table 5.3 Estimated emissions of HCB in the U.S.A. (Carpenter et al., 1986).

Source	Quantity ($ton.y^{-1}$)	HCB concentration ($kg.kg^{-1}$)	HCB emission into air ($kg.y^{-1}$)
Production of [1]			
- tetrachloroethylene	10400	0.20-0.25	2100-2600
- trichloroetylene	2600	0.05-0.20	130- 520
- carbon tetrachloride	12900	0.10-0.65	1300-8400
Municipal waste incineration	5.55x106		
- as a gas [2]		$10 - 77 \times 10^{-9}$	54- 428
- in particulates [3]		$0.6- 4.7 \times 10^{-9}$	3- 26
Use of pesticides [4]			
- quintozene (PCNB)	1140	0.005	5675
- chlorthal-dimethyl (DCPA)	2180	0.003	6540
- chlorothalonil	3410	0.0005	1700
- picloram	455	0.0002	91
- pentachlorophenol	33640	0.0001	3360

1) Quantities refer to waste (heavy ends and still bottoms: 40 g/ton of substance). It is assumed by Carpenter et al. that 0.1% of the HCB in it is emitted into the atmosphere after incineration.
2) Concentration values taken from different authors (see Carpenter et al.).
3) Estimated fraction of particulates in the flue gas: <0.5 μm: 5.4%; >0.5 μm: 0.8% (Janssens et al., 1982).
4) It is assumed that HCB is completely emitted into the atmosphere. This may not quite be true for quintozene which is also used in soil and on seeds. Again, it may not be true for pentachlorophenol.

The data in Table 5.3 indicate that in the U.S.A. emissions from the production of chlorinated hydrocarbons and from the use of four of the five regarded pesticides dominate.

Municipal waste incineration appears to be relativily unimportant, thanks to the low emission factor. The factor used by Carpenter et al. ($1.0-7.7 \times 10^{-8}$ $kg.kg^{-1}$, related to the amount of municipal waste) corresponds reasonably with that resulting from a recent Dutch investigation (1.1×10^{-8} $kg.kg^{-1}$) (Scheffer, 1987).

Roughly estimating the production of tetrachloroethylene and of carbon tetrachloride to be 2x the production in the USA and the production of trichloroethylene to be 5x the USA production, and taking into account possible lower HCB contents in wastes according to De Bruin (Table 5.1) emissions from the production of chlorinated hydrocarbons may be ca. 10 $t.y^{-1}$ in Europe.
Because Europe has ca. 50% more arable land than the USA, emissions might be proportionally larger and amount to 25-30 $ton.y^{-1}$.
It will be assumed, therefore, that in the MASH area this part of the chemical industry and the application of some pesticides in agriculture are the relevant sources of HCB.

5.4 Emission factors

1. Production of chlorinated hydrocarbons:

According to Carpenter et al. (1986) using data of Bomberger et al. (1985) incineration of industrial waste of these processes has efficiencies between 99.9 and 99.99%. The authors used the conservative assumption of 99.9%. Emission factors can be derived from the data of Table 5.1. For this study the following values are chosen ($g.t^{-1}$):

tetrachloroethylene	6(3-10)
trichloroethylene	3(1-6)
carbon tetrachloride	8(1-20).

2. Application of pesticides:

Emission factors are given in Table 5.3 in wt/wt units. For spatial allocation they have to be expressed in activity units, similar to Lindane. However, with regard to the application of pesticides hardly any application data are available (this applies to all pesticides).
In 1966 66 ton quintozene (together with the related compound tecnazene, which contains also some HCB) has been used in the U.K. (De Bruin, 1979). If it is assumed that the use of these pesticides is proportional to the total area of arable land and permanent crop, this figure corresponds with an consumption of 0.95 kg $quintozene.km^{-2}.y^{-1}$ or

5 $g.km^{-2}.y^{-1}$.

From the annual consumption in the U.S.A. (Carpenter et al., 1986) and the area of arable land and permanent crops an application rate of quintozene of 0.60 $kg.km^{-2}.y^{-1}$ and an emission of 3 $g.km^{-2}.y^{-1}$ can be calculated.

For chlorthal-dimethyl De Bruin roughly estimated a consumption which is twice as large as his value for quintozene, corresponding with an application rate of 1.9 $kg.km^{-2}.y^{-1}$ or an emission of 5.7 $g.km^{-2}.y^{-1}$. From the USA consumption an application rate of 1.15 $kg.km^{-2}.y^{-1}$ and a HCB emission rate of 3.4 $g.km^{-2}.y^{-1}$ can be derived.

As for the other three pesticides no other than the U.S.A. data are available. They will be used here, regardless of their applicability. A similar calculation gives the following results: chlorothalonil: application rate 1.8 $kg.km^{-2}.y^{-1}$, HCB emission 0.9 $kg.km^{-2}.y^{-1}$; pentachlorophenol: application rate 17.7 $kg.km^{-2}.y^{-1}$, HCB emission 1.8 $kg.km^{-2}.y^{-1}$; picloram: application rate 0.24 $kg.km^{-2}.y^{-1}$, HCB emission 0.05 $g.km^{-2}.y^{-1}$.

For pentachlorophenol, the use of which may be more related to the number of inhabitants than to the area of arable land and permanent crops, the emission rate resulting from the U.S.A. data is 14.3 $mg.inh^{-1}.y^{-1}$.

Combining the data for agricultural pesticide application and taking into account the comparability of European and USA data for the two mainly contributing pesticides an emission factor of 10(5-15) $g.km^{-2}.y^{-1}$ is proposed. Emissions from the use of pentachlorophenol will be related to population and estimated with 15 $mg.inh^{-1}.y.^{-1}$.

A comparison can be made with results of recent investigations on the burdening of peat core in the USA (Rapaport and Eisenreich, 1988). The authors derived from HCB concentrations in peat that the deposition rate (post 1980) is 0.03-0.4 $g.km^{-2}.y^{-1}$ which is much lower than the total emission caused by the use of pesticides (10 $g.km^{-2}.y^{-1}$).

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Ref. no. : 89-037
File no. : 8725-16098
Date : January 1989
P

Title
A BASIC ANALYSIS OF COGENERATION ECONOMICS

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INTRODUCTION

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A BASIC ANALYSIS OF COGENERATION ECONOMICS

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ABSTRACT

The economics of small scale gas turbine based cogeneration systems are analyzed on the basis of avoided costs for an electric utility exploiting such systems. This concerns a theoretical study in which the cogeneration system as a means for electricity generation is assumed to supplant the building of new central electricity generating plant.

The results show that with increasing oil and gas price levels, the economics of cogeneration will become more favourable when the supplanted capacity is for peak load rather than for base load electricity generation. This implies a preference for applications with cogeneration operation taking place mainly during on-peak hours of the electricity demand

INTRODUCTION

Cogeneration economics can be looked at from two basically different points of view. One as a consumer of heat and electricity, employing cogeneration as an alternative to on-site heat production and buying electricity from an outside utility. The other as a utility company exploiting cogeneration as a means of supplying both heat and electricity to its customers.

An important difference lies in the value attributed to the produced electricity.

In the case of a consumer exploited cogeneration system this value will correspond to the utility tariff, with some deduction being made for any services that are still desired from the utility company (availability of standby capacity, possibility of supplemental or return delivery of electricity).

In the utility exploited case the value may be expected to conform more directly to the cost of meeting the same electricity demand by conventional generating means.

Because the purchase price of electricity is generally higher than the avoided costs, the economics will generally look better in the case of consumer exploited cogeneration systems. On the other hand, the economics of the utility exploited systems probably give a truer picture of the national cost benefits of cogeneration.

The general aim of the following paper is to explore the economics of small scale gas turbine based cogeneration systems (say 3 to 5 MW_e) on the latter basis. This concerns a theoretical cost analysis based on the assumption that the cogeneration installation as a means of electricity generation is to supplant the building of new central electricity generating capacity.

In both cases electricity is delivered to the national grid. In the case of cogeneration heat is delivered to (a) specific customer(s) at a price that is competitive with heat generation by means of an on-site boiler.

HEAT RATE FOR ELECTRICITY GENERATION

As a preliminary to performing the proposed cost analysis it is proposed to first determine and compare the heat rate of electricity generation with and without net heat recovery. The heat rate is in this context defined in terms of kWh of fuel energy per kWh of electricity production.

η = efficiency [−]

I = specific investment $ / kW

suffixes
cen : central electricity generation
e : electricity section cogeneration
h : heat section cogeneration
t : total cogeneration
b : reference boiler

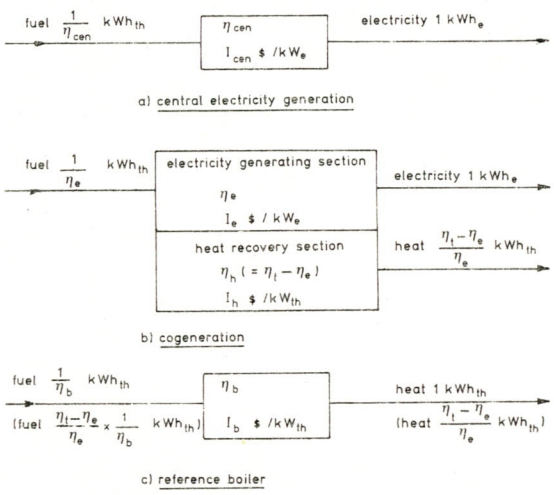


Figure 1: Block diagrams as a basis for deriving energy and cost equations.

In the case of central electricity generation without (net) heat recovery, the heat rate hr can be simply calculated with the equation:

$$hr_{cen} = \frac{1}{\eta_{cen}} \quad [\frac{kWh_{th}}{kWh_e}] \qquad (1)$$

in which η_{cen} is a thermal or power generating efficiency (figure 1a) that is assumed to include the losses of transport and distribution of electricity.

In the case of a cogeneration process the heat rate for electricity generation includes a credit for the produced heat. As illustrated in figure 1b and 1c, this is done by subtracting the fuel consumption of a reference boiler from the fuel consumption of the cogeneration installation. This implies that the whole of the energy savings is attributed to the electricity-generating function of the cogeneration process.

The equation for calculating the heat rate for electricity generation by means of cogeneration $hr_{e.cog}$ then becomes:

$$hr_{e.cog} = \frac{1}{\eta_e} - \frac{\eta_t - \eta_e}{\eta_e} \times \frac{1}{\eta_b} \quad [\frac{kWh_{th}}{kWh_e}] \qquad (2)$$

in which:

η_e = the power generating efficiency of the cogeneration system [−]
η_t = the total efficiency of the cogeneration system [−]
η_b = the efficiency of the reference boiler [−]

In figure 2 the resulting heat rate values are presented as a function of the various energy conversion efficiencies (with all efficiency values assumed to be related to the lower heating value of fuel).

Characteristic for the cogeneration process is that the heat rate is very much less influenced by a change in the power generating efficiency η_e. In fact, when the total efficiency η_t is equal to the reference boiler efficiency η_b, the heat rate is completely independant of the value of η_e. As the value of η_t drops below the value of η_b, the heat rate increases, the rate of increase being higher at the lower levels of η_e and η_t. There remains however, a distinct advantage in comparison with electricity generation without heat recovery.

Indicated in figure 2 are also lines of constant heat to power ratio for the cogeneration proces H/E. As may be expected, this ratio increases with decreasing value of η_e.

SPECIFIC FUEL CONSUMPTION COSTS

A similar looking but significantly different picture emerges when considering the fuel costs per kWh of electricity production.

For central electricity generation the value of these specific fuel consumption costs (sfcc) is very simply calculated as the quotient of fuel price and electricity generating efficiency:

$$sfcc_{cen} = \frac{fp_{cen}}{\eta_{cen}} \quad c/kWh_e \qquad (3)$$

The fuel price fp is expressed in c/kWh of net calorific heating value of the fuel, which is equal to 100/293 of the fuel price in $/MMBtu.

For electricity generation by cogeneration means the equation for determining the specific fuel consumption costs is again rather more complicated. These costs will be equal to the fuel costs of the cogeneration installation per kWh of electricity production, from which must be subtracted a certain cost benefit for the produced heat. This cost benefit should take into account the possibility of the fuel price for the cogeneration installation being different from that for the reference boiler(s)(which may consist of a large number of decentralized boilers). Also there may be a need for offering a discount on the price of the heat delivered to the consumers as an incentive for buying this heat rather than choosing for on-site heat production by means of a proprietary boiler.

The equation for calculating the specific fuel consumption cost then becomes:

$$sfcc_{e.cog} = \frac{fp_{cog}}{\eta_e} - \frac{H}{E} \times \frac{fp_b}{\eta_b} \times (1 - \frac{d}{100}) \quad c/kWh_e \qquad (4)$$

in which:

fp_{cog} = fuel price for cogeneration c/kWh_{th}
fp_b = fuel price for the reference boiler(s) c/kWh_{th}
d = a discount percentage on the price of delivered heat

$\frac{H}{E} = \frac{\eta_t - \eta_e}{\eta_e}$ = heat/power ratio of the cogeneration process.

The results can be expressed in a non-dimensionalized form by dividing the values of the sfcc by some value of a fuel price, for instance the fuel price for cogeneration fp_{cog}.

The results are presented in figure 3. Lines A and B represent electricity generation by cogeneration means. The total efficiency is assumed to be 0.85 (for a reference boiler efficiency of 0.90) and the fuel price for cogeneration installation and reference boiler are assumed to be the same. Line A represents a discount of 0% and line B a discount of 10% on the price of heat delivered to the consumers. For further evaluation purposes the cross-hatched area will be considered representative of what may be achieved with present-day gasturbines based cogeneration installations with a capacity of say 3 MW_e or higher.

Lines C and D represent (central) electricity generation without net heat recovery.

For line C the fuel price for (central) electricity generation is assumed to be 10% lower than the fuel price for the cogeneration and reference boiler installations. This would be representative of a situation in which natural gas is consumed in all cases, but in which a 10% discount is given for quantity delivery.

On this line point 1 may be regarded as representative for a combined cycle (steam and gasturbine) plant for base load electricity generation (η_{cen} = 0.48) and point 2 for a simple cycle gasturbine for peak load duty (η_{cen} = 0.35).

Line D is based on the fuel price ratio for central electricity generation relative to cogeneration being 0.75. This is meant to represent a situation in which the oil and gas price level is sufficiently high to make coal gasification economically attractive.

According to EPRI, 1988 this situation may be expected to occur when the price of natural gas rises to a level of around 6 $/MMBtu (circa 2 c/kWh).

That coal gasification will result in a change in various fuel price ratios is based on the following rather simplified line of reasoning.

In the case of base load central electricity generation, the coal gasification plant may be located near or even be integrated with the electricity generating installation. The quality of the gas (e.g. the heating value) can also be less than what would be required if the gas is to be transported to decentralized cogeneration installations. In the latter case the gas produced from coal would very probably have to be in the form of a synthetic natural gas. The higher cost of producing such a gas, together with the cost of distribution, implies a reduction of the fuel price ratio which for evaluation purposes is assumed to be equal to 0.75. Point 1' would then be representative for the relative specific fuel consumption costs for base load central electricity generation.

The situation will be somewhat different for peak load central electricity generation. The relatively low number of operating hours would seem to preclude an integration of gasification and electricity generating installations. Also some kind of storage capacity would

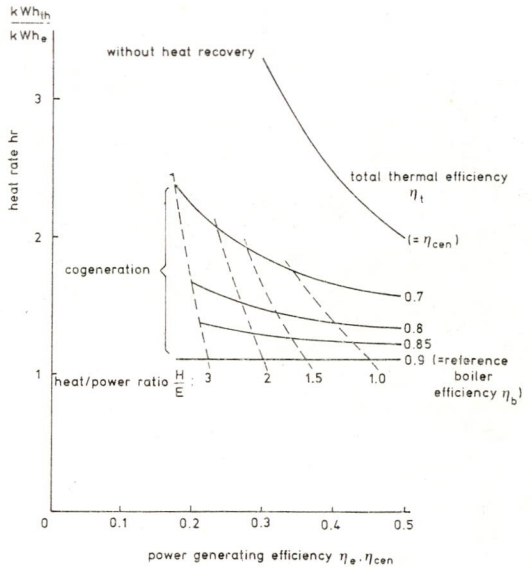
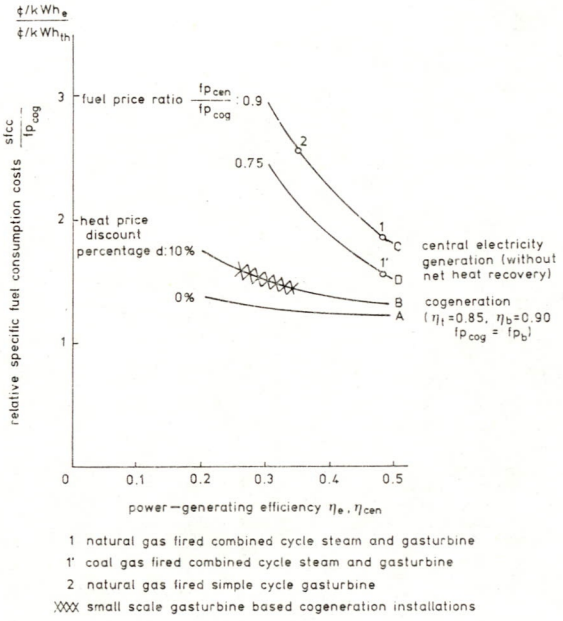


Figure 2. Heat rate as a function of energy conversion efficiencies



1 natural gas fired combined cycle steam and gasturbine
1' coal gas fired combined cycle steam and gasturbine
2 natural gas fired simple cycle gasturbine
XXX small scale gasturbine based cogeneration installations

Figure 3. Relative specific fuel consumption costs.

be required in order to ensure a sufficiently high utilization in the case of a separate coal gasification plant.

As a result the price of coal gas would still be relatively high, notwithstanding the acceptability of producing a lower quality gas. For evaluation purposes the fuel price ratio is therefore assumed to remain 0.9, with point 2 still being representative of the sfcc for peak load central electricity generation.

figure 3. It is clear the economics of a given district system may be greatly influenced by the type of thermal electric generation plant it is supposed to supplement.

It is true to a large and valid use of the cogeneration plant during light and weekend, then the possible fuel and capital savings in comparison to the difference between the electricity sold to the public and the steam-heating load may be very much smaller than in the case of industrial cogeneration being restricted to mainly peak hours of the electric demand. The study mentioned above [3] has shown that the economic feasibility of a district heating cogeneration plant is quite considerably influenced by the highest number of operating hours per year obtainable with the number of hours in the base load area.

On the other hand, the economics of cogeneration will also be determined by the investment and maintenance costs of the thermal generating equipment supplanted. In the case of a remotely situated hydroelectric station, the specific investment will be considerably higher than for a large thermal unit near load centres. The higher investment and maintenance costs for cogeneration plant may even annihilate the economic advantage of cogeneration in comparison to the cheaper thermal generation.

It is obviously necessary to quantify and differentiate in order to reach any decision on the type of cogenerator applicable to the district heating project. This is done by distinguishing between three generic types of cogeneration and applying to each specific type of thermal electricity generating plant the appropriate combination of heat and power.

A 1000 megawatt operating nuclear station (Beznau I and II, Mühleberg, Leibstadt, Kaiseraugst)

This would be represented in Fig. 4 with the operation mainly taking place during the daytime period of working days. This would be the district heating demand mainly occurring during the winter, by the application of heat storage facilities it could be possible to operate the cogeneration unit all year round to cover hours of the electricity demand.

The type of normal electric generating capacity being supplanted is assumed to be a simple gas turbine for peak load duty.

The specific investment costs are assumed to be 300 $/kW$ (gas turbine) and the electric efficiency as assumed to be 0.3.

b. 4500 hours/year operation of an oil-fired steam

4500 hours/year

This may be considered representative for a heating demand or a process heat demand (district heating) with a relatively large thermal storage. The type of heating capacity being supplanted might be a combined cycle gas turbine plant with a capacity of 600 $/kW$ (gas turbine and steam turbine) at 0.42.

IMPLICATIONS FOR COGENERATION ECONOMICS

An important implication of what is shown in figure 3, is that the economics of a cogeneration system may be heavily influenced by the type of central electricity generating plant it is supposed to be supplanting.

If this is a base load unit, due to the cogeneration plant also operating during nights and on weekends, then the specific fuel cost savings will correspond to the difference between the sfcc according to the points 1 or 1' and the sfcc corresponding to some point in the cross-hatched area. This difference can be very much smaller than in the case of cogeneration being restricted to mainly peak-hours of the electricity demand. In this case the difference in sfcc will be between point 2 and the cross-hatched area. It is quite conceivable that the latter case will yield the highest fuel cost savings per year, notwithstanding the number of operating hours being very much lower than in the base load case.

On the other hand, the economics of cogeneration will also be determined by the investment and maintenance costs of the central generating capacity being supplanted. In the case of a combined cycle base load station, the specific investment will be considerably higher than for a simple cycle peak load station. This implies a higher investment allowance for a cogeneration installation supplanting base load capacity than for a cogeneration installation supplanting peak load capacity.

It is obviously necessary to quantify such differences in order to reach any conclusions as to what type of cogeneration application has the best economic potential. This is done by differentiating between three generic types of cogeneration application and making cost comparisons with the appropriate type of central electricity generating capacity. The distinction mainly concerns the number of (equivalent) full load operating hours per year.

a. 2000 hrs/yr of operation during on-peak hours of the electricity demand (2000 hrs/peak load)

This would be representative of cogeneration operation mainly taking place during the daytime hours of working days. This would be due to either the heat demand mainly occurring during these periods, or due to the application of heat storage facilities in order to shift cogeneration operation from off-peak to on-peak hours of the electricity demand.
The type of central electricity generating capacity being supplanted is assumed to be a simple cycle gasturbine for peak load duty.
The specific investment of such a unit has been set at 300 $\$/kW_e$ (EPRI, 1988) and the thermal efficiency is assumed to be 0.35.

b. 4500 hrs/yr during on- and off-peak hours (4500 hrs/base load)

This may be considered representative of cogeneration being applied for meeting a space-heating demand on a more or less continuous basis (without thermal storage). The type of central electricity generating capacity being supplanted might typically be a combined cycle base load plant with a specific investment of 600 $\$/kW_e$ (EPRI, 1988) and a thermal efficiency of 0.48.

c. 6000 hrs/yr during on- and off-peak hours (6000 hrs/base load)

This case may be regarded as typical for many industrial applications with basically a year-round heat demand. The type of central electricity generating capacity might again be a combined cycle base load plant (η_{cen} = 0.48, specific investment 600 $\$/kW_e$), but in this case the economic feasibility of an integration with coal gasification would occur at a lower level of the natural gas price.

TABLE 1 ASSUMED VALUES FOR COST CALCULATIONS

η_b	=	0.9
η_t	=	0.85
d	=	10%
sfp_{cog}	=	sfpb
i	=	0.06
rf	=	0.04
rm	=	0.02
m	=	0.05
L	=	15 yrs.

METHOD OF ASSESSING COGENERATION ECONOMICS

For an electric utility contemplating the choice between electricity generation by cogeneration means or by central generating means, it would seem suitable to make a cost comparison on the basis of a difference in life cycle costs. As indicated in appendix I, these life cycle costs may be calculated as the sum of the present worth of fuel costs, investment costs and maintenance and miscellaneous other costs.

However, rather than making a direct comparison between the calculated differences in life cycle costs, it is considered preferable to express the results in terms that relate more directly to the costs of the gasturbine and electrical equipment forming part of the total cogeneration system.
According to this approach (and as indicated in figure 1) the cogeneration system is distinguished in an electricity generating section and a heat recovery section. The life cycle costs for electricity generation by cogeneration means is then determined by subtracting a certain credit for heat production from the total life cycle costs of the cogeneration system. For a certain value of the specific investment of the electricity generating section I_e, these costs will be equal to the life cycle costs of the central electricity generating capacity with which a cost comparison is to be made. The value of this specific investment is then referred to as the (maximum) allowable value $I_{e.all}$.

For each of the generic types of cogeneration application being compared with the appropriate type of central electricity generating plant, the value of $I_{e.all}$ is calculated as a function of fuel price levels and power generating efficiency of the cogeneration process. The assumed values for all other cost and performance parameters are as indicated in table 1.

The method used for calculating $I_{e.all}$ is explained in appendix II. As indicated in eq. (14) this value is determined as the sum of a number of investment terms that can be distinguished in two categories. One concerns actual investments and the other differences in fuel costs that are expressed as equivalent investment allowances.

Investment allowances corresponding to differences in fuel cost

The difference in fuel costs mainly concerns the fuel cost savings according to the specific fuel consumption costs indicated in figure 3. The equivalent (specific) investment allowance ΔI_{fcs} is calculated as indicated in eq. (12a).

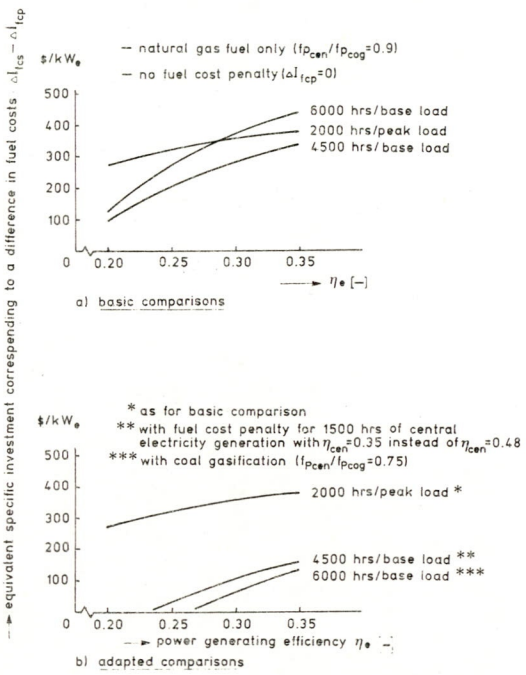


Figure 4 Equivalent specific investment corresponding to net fuel cost savings of cogeneration proces (for cogeneration fuel price fp_{cog}=2 ¢/kWh or 5.86 $/MMBt)

The values of ΔI_{fcs} are presented in fig. 4a as a function of the electricity generating efficiency η_e and fuel prices of 2 ¢/kWh and 1.8 ¢/kWh for cogeneration and central electricity generation respectively. This represents the situation of natural gas being used in both cases (fuel price ratio of 0.9).

The results confirm the expectation that due to higher differences in specific fuel consumption costs the yearly fuel cost savings in the 2000 hrs/peak load case are comparable with those for the 4500 hrs/base load and 6000 hrs/base load cases. This notwithstanding the very much lower number of operating hours per year.

This already favourable situation for the 2000 hrs/peak load case is further enhanced when considering two disadvantages that may be expected to especially apply to the base load cases. This concerns the effect of coal gasification reducing the fuel price for central electricity generation and the effect of electricity generation by cogeneration means being limited to periods with a substantial heat demand.

The disadvantageous effect of coal gasification causing the fuel price ratio fp_{cen}/fp_{cog} to decrease from 0.9 to 0.75 is shown in figure 4b for the 6000 hrs/base load case.

The disadvantageous effect of electricity generation by cogeneration means being limited to periods with a substantial heat demand is expected to apply especially to the 4500 hrs/base load case.

The cogeneration installation supplanting base load central electricity generating capacity will in this case result in a reduced availability of high efficiency capacity during the non-heating season. This implies the necessity for an increase in the operating time of central generating capacity with a lower efficiency. The corresponding increase in fuel costs should consequently be debited to the cogeneration system.

The resulting reduction in the equivalent specific investment for the 4500 hrs/base load case is shown in figure 4b for an assumed 1500 hrs of central electricty generation with a thermal efficiency of 0.35 instead of 0.48 (calculated with the use of eq. (13) in appendix II). Obviously the disadvantageous effect would be even greater if it were coupled with the effect of a fuel price decrease due to coal gasification.

Total allowable specific investment $I_{e.all}$

The value of the total allowable specific investment $I_{e.all}$ is determined by adding various (differential) investment terms to the previously determined investment allowances for net savings in fuel costs (eq. (14)).

The main item is an investment allowance conforming to the specific investment I_{cen} of the central electricity generating capacity which is supposed to be supplanted by the cogeneration system. For a combined cycle base load installation (600 $/kW$_e$) this allowance is assumed to be considerably higher than for a simple cycle peak load unit (300 $/kW$_e$).

A next item is indicated by the term H/E x ΔI_h which represents an increased investment for the heat recovery section of the cogeneration system as compared to an investment credit which is given for supplanting the reference boiler(s). The heat/power ratio acting as a multiplicator indicates that the negative effect on the value of $I_{e.all}$ increases with decreasing value of the electricity generating η_e (figure 2).

In the context of this cost analysis the value of ΔI_h is assumed to be only 25 $/kW$_{th}$, suggesting cogeneration applications that do not require significant investment increases for additional heat transport or heat storage facilities.

Finally there is the possibility of certain credits being allowed as a result of the relatively small scale cogeneration systems providing decentralized electric generating capacity. This concerns credits for a reduction in investments for the electricity grid (ΔI_{tr}) and/or for acting as reserve capacity for providing emergency power in the case of a grid failure (ΔI_{res}). However, because such credits will not basically affect the comparison between the generic cogeneration applications, they are mentioned here for reference purposes only.

The results presented in figure 5a are correspondingly calculated according to eq. (14) for ΔI_{tr} and ΔI_{res} being equal to zero. The values of the investment allowance for differences in fuel costs ($\Delta I_{fcs} - \Delta I_{fcp}$) are taken according to what is presented in figure 4b.

Figure 5 Allowable specific [illegible]

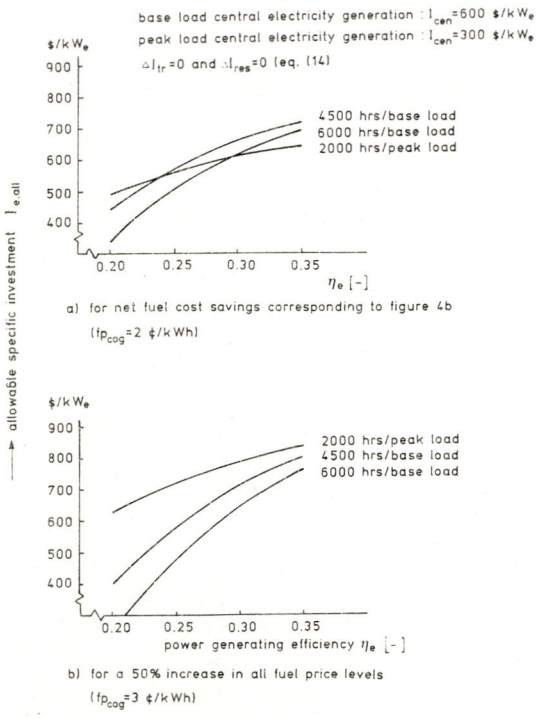


Figure 5 Allowable specific investment for electricity generating section of cogeneration system.

Comparing figure 5a with figure 4b then makes it clear that the marked advantage in fuel cost savings for the 2000 hrs/peak load case would be practically wiped out by the allowance for the specific investment for the supplanted central generating capacity I_{cen} being 300 $/kW$_e$ lower.

However, figure 5b shows that if all fuel prices are assumed to be 50% higher, the 2000 hrs/peak load case will again show a clear advantage over the two base load cases.

These results suggest that with increasing levels of oil- and gas prices the economics of cogeneration will require electricity to be generated mainly during the peak periods of the electricity demand. This trend will be accentuated if a further decrease in fuel price ratio fp_{cen}/fp_{cog} is accompanied by an increase in the thermal efficiency of central electricity generation. This may be the result of further advances in gas turbine technology or to the introduction of new energy conversion technologies, for example fuel cells with basically a higher ceiling for the attainable thermal efficiency.

It also worth noting that the economics of cogeneration in the peak load case are less susceptible to a decrease in the value of the power generating efficiency of the cogeneration process. This suggests that a greater emphasis should be placed on achieving low investment and maintenance costs rather than on achieving the highest level of the power generating efficiency. However, because a lower value of η_e also results in an increasingly negative influence of any additional heat recovery investment (proportional to the heat/power ratio H/E), this compromise should not be allowed to go too far.

CONCLUSIONS

The results of a simplified theoretical cost analysis indicate that future increases in oil- and gas prices will very likely cause the economics of cogeneration to become increasingly more favourable for systems being operated mainly during peak periods of the electricity demand. This applies to the case of an electric utility exploiting relatively small scale gas turbine based cogeneration systems as an alternative to installing new central electricity generating capacity.

REFERENCE

[1] Utility Turbopower for the 1990s, EPRI Journal, April/May 1988.

APPENDIX I

CALCULATION OF LIFE CYCLE COSTS LCC

$$LCC = PWF + PWI + PWM$$
$$= PWF + (1 + f_m) \times I \qquad \$/kW_e \qquad (5)$$

in which:

PWF = present worth of life cycle fuel costs

$$= sfcc \times T \times \left\{1 - \frac{\left(1 - \frac{i-rf}{1+rf}\right)^{-L}}{\frac{i-rf}{1+rf}}\right\} \qquad (6)$$

PWI = present worth of investment costs
= initial investment I (for no other investments during life cycle period and residual worth = 0)

PWM = present worth of life cycle maintenance costs

$$= m \times I \times \left\{1 - \frac{\left(1 - \frac{i-rm}{1+rm}\right)^{-L}}{\frac{i-rm}{1+rm}}\right\}$$

$$= f_m \times I \qquad (7)$$

and with:

T = number of equivalent full load operating hours, hrs/yr
L = life cycle duration, yrs
i = interest rate
rf = yearly rate of increase in fuel price level
rm = yearly rate of increase in maintenance costs
m = yearly maintenance costs as a proportion of investment I
f_m = life cycle maintenance costs as a proportion of investment I

$$\cos\varphi = \frac{P}{\sqrt{3}\,U\,I} \qquad (8)$$

In which:

$\cos\varphi$ = electric displacement of real power in a ...

P = specific resistance of the conductor, ...

U = ...ing section of a conducting system ...

I = specific resistance of the conductor ...

A/E = ...temperature system ...

$$\eta = \frac{\dots}{\dots}$$

... (maximum) allowable ...

... the rule ... for ...

... electrical ... on ... resistance ...

... equal to the ... total ...

Generation of ...

$$\dots$$

The left side of ... reference between ... in ... cosine ... can be ... percentage.

... penalties, and ... assumptions, the ... following:

$$\dots$$

In which E_b = specific ... in $\dots$.

Combining eq. (8) and ...

$$\dots$$

$$= \dots$$

$$\dots$$

$$\dots$$

In which the ... final ...

APPENDIX II

CALCULATION OF (MAXIMUM) ALLOWABLE SPECIFIC INVESTMENT FOR ELECTRICITY GENERATING SECTION OF COGENERATION INSTALLATION ($I_{e.all}$)

From figure 1:

$$I_{cog} = I_e + H/E \times I_h \qquad \$/kW_e \qquad (8)$$

in which:

I_{cog} = specific investment of total cogeneration system $\$/kW_e$

I_e = specific investment of the electricity generating section of a cogeneration system $\$/kW_e$

I_h = specific investment of heat recovery section of cogeneration system $\$/kW_{th}$

H/E = heat/power ratio of the cogeneration proces $\left(= \frac{\eta_t - \eta_e}{\eta_e}\right)$

The (maximum) allowable specific investment $I_{e.all}$ is the value of I_e for which the life cycle costs of electricity generation by cogeneration means is equal to life cycle costs for central electricity generation, or:

$$\{PWF + I \times (1 + f_m)\}_{e.cog} = \{PWF + I \times (1 + f_m)\}_{cen} \qquad (9)$$

The left side of this equation represents a difference between the life cycle costs for the whole cogeneration system and (1 - d/100) x the life cycle costs for a reference boiler system (d = a discount percentage).

Disregarding certain cost credits and cost penalties, and introducing a number of simplifying assumptions, the value of $I_{e.all}$ can be calculated as follows.

$$I_{e.cog} = I_{cog} - H/E \times (1 - d/100) \times I_b \quad \$/kW_e \qquad (10)$$

In which I_b = specific investment of reference boiler in $\$/kW_{th}$.

Combining eq. (8) and (10) and with $I_e = I_{e.all}$:

$$I_{e.cog} = I_{e.all} + \frac{H}{E} \times \{I_h - (1 - \frac{d}{100}) \times I_b\}$$

$$= I_{e.all} + \frac{H}{E} \times \Delta I_h \qquad \$/kW_e \qquad (11)$$

Assuming m, r_m, r_f and L to be the same for all installations, and combining (9) and (11):

$$I_{e.all} = \frac{PWF_{cen} - PWF_{e.cog}}{1 + f_m} + I_{cen} - H/E \times \Delta I_h \qquad (12)$$

in which the equivalent specific investment differential corresponding to the fuel cost savings is:

$$\Delta I_{fcs} = \frac{PWF_{cen} - PWF_{e.cog}}{1 + f_m} \qquad (12a)$$

$PWF_{e.cog}$: calculate with the use of equations (4) and (6)

PWF_{cen} : calculate with the use of equations (3) and (6)

The disregarded cost credits and penalties concern the following:

- A fuel cost penalty due to cogeneration operation being limited to periods with a substantial heat demand. When supplanting base load central electricity generating capacity with a high thermal efficiency η_1, this may lead to the need for T'hrs/yr of central electricity generation with a lower thermal efficiency η_2. The equivalent specific investment differential corresponding to this fuel cost penalty is calculated with the equation:

$$\Delta I_{fcp} = \frac{PWF_2 - PWF_1}{1 + f_m} \qquad (13)$$

- (Possible) credits for the cogeneration system due to the decentralization of electric generating capacity. This concerns reduced investments for electricity transport (ΔI_{tr}) and availability of reserve capacity for providing emergency power in the case of a failure of the main electricity grid (ΔI_{res}).

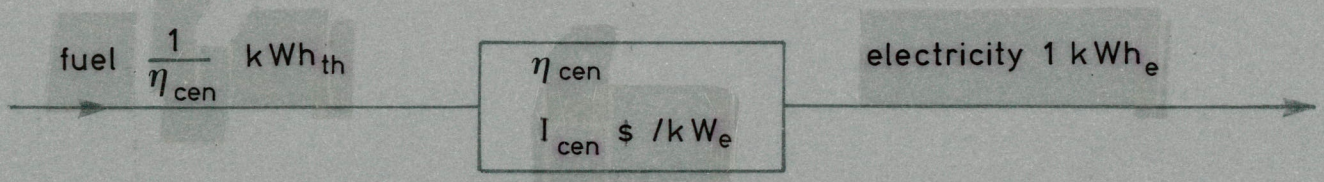
Taking into account these additional terms changes (12) to:

$$I_{e.all} = \Delta I_{fcs} - \Delta I_{fcp} + I_{cen} + \Delta I_{tr} + \Delta I_{res} - H/E \times \Delta I_h \ \$/kW_e \qquad (14)$$

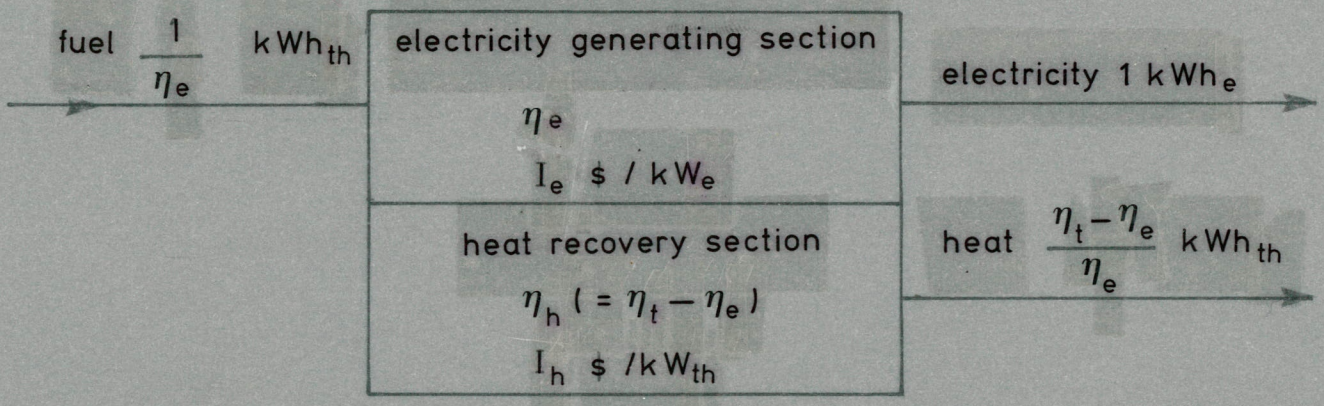
η = efficiency [–]

I = specific investment
$ / kW

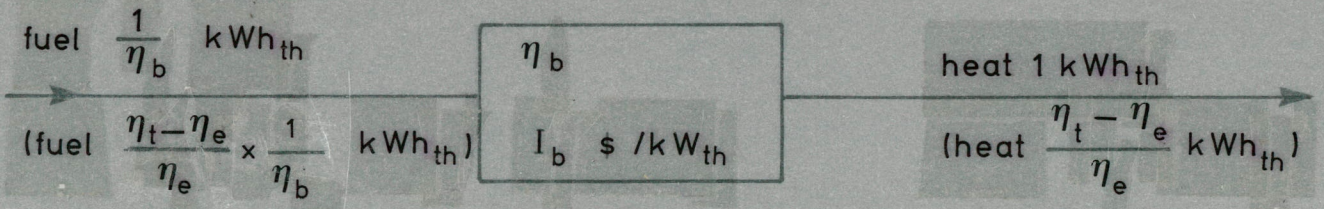
suffixes
cen : central electricity generation
e : electricity section cogeneration
h : heat section cogeneration
t : total cogeneration
b : reference boiler



a) central electricity generation



b) cogeneration



c) reference boiler

Figure 1. Block diagrams as a basis for deriving energy and cost equations.

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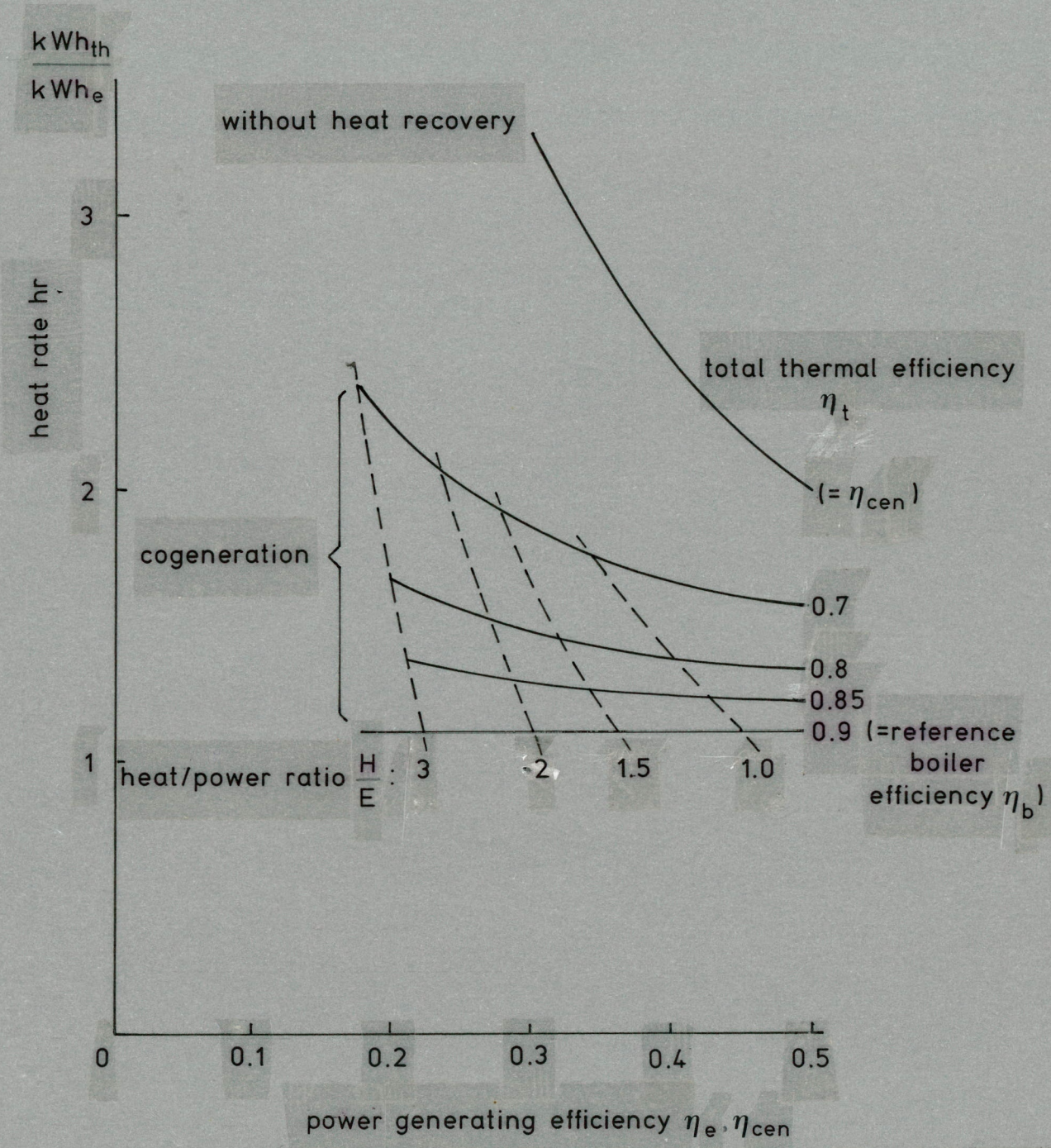


Figure 2. Heat rate as a function of energy conversion efficiencies

Figure 2. Heat rate as a function of energy conversion efficiencies

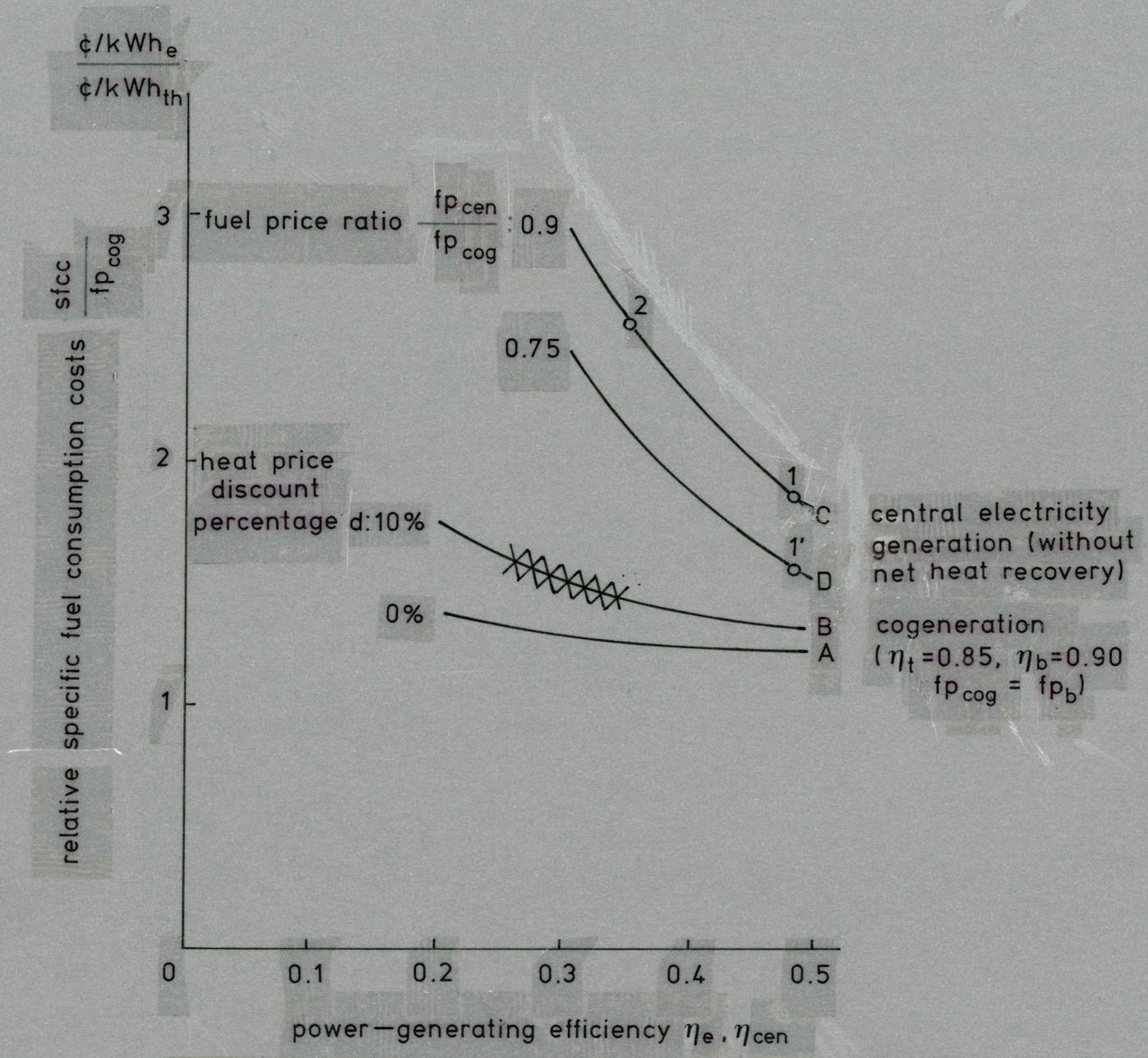
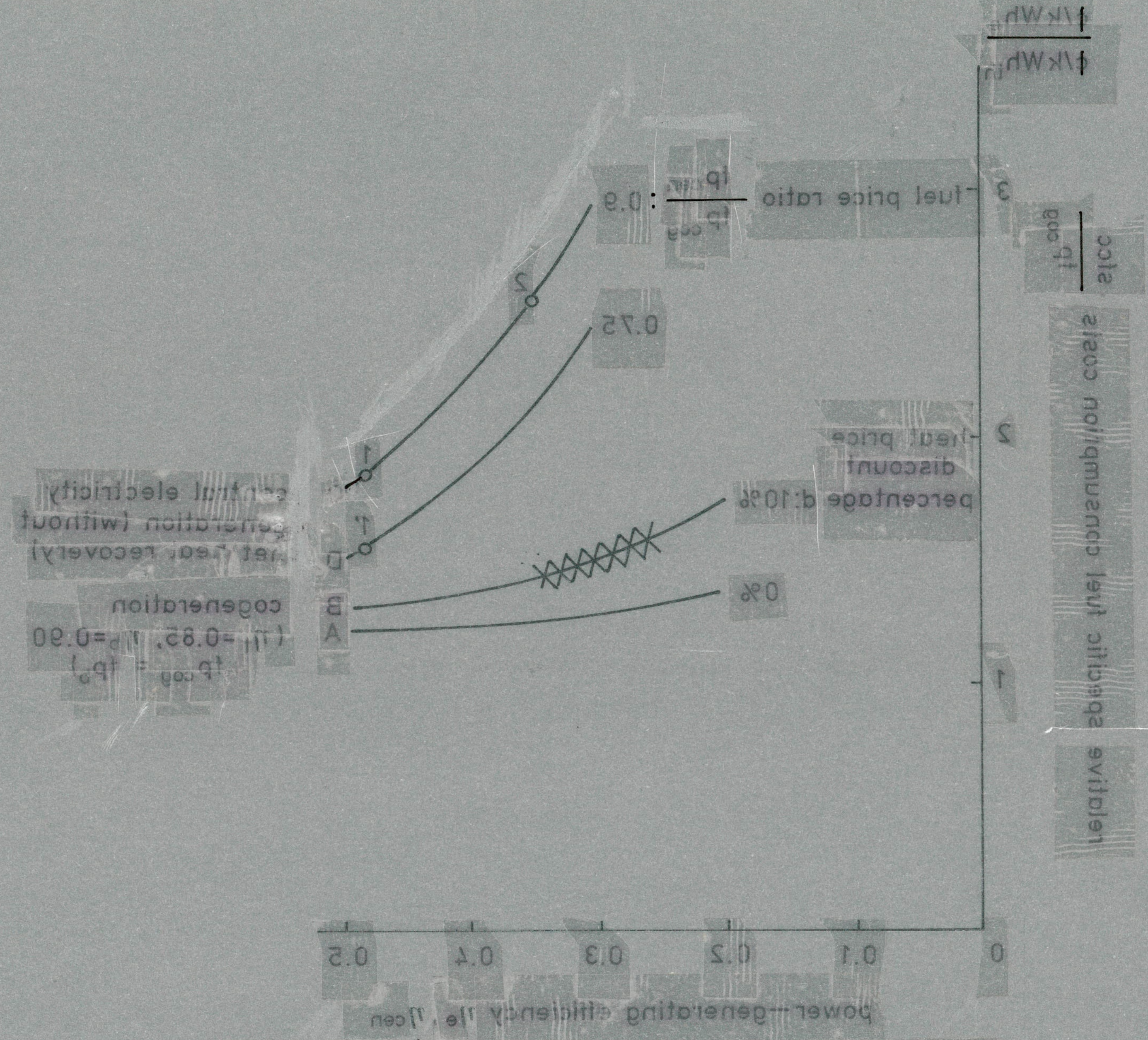


Figure 3. Relative specific fuel consumption costs.



1 natural gas fired combined cycle steam and gasturbine

1' coal gas fired combined cycle steam and gasturbine

2 natural gas fired simple cycle gasturbine

XXX small scale gasturbine based cogeneration installations

Figure 3. Relative specific fuel consumption costs.

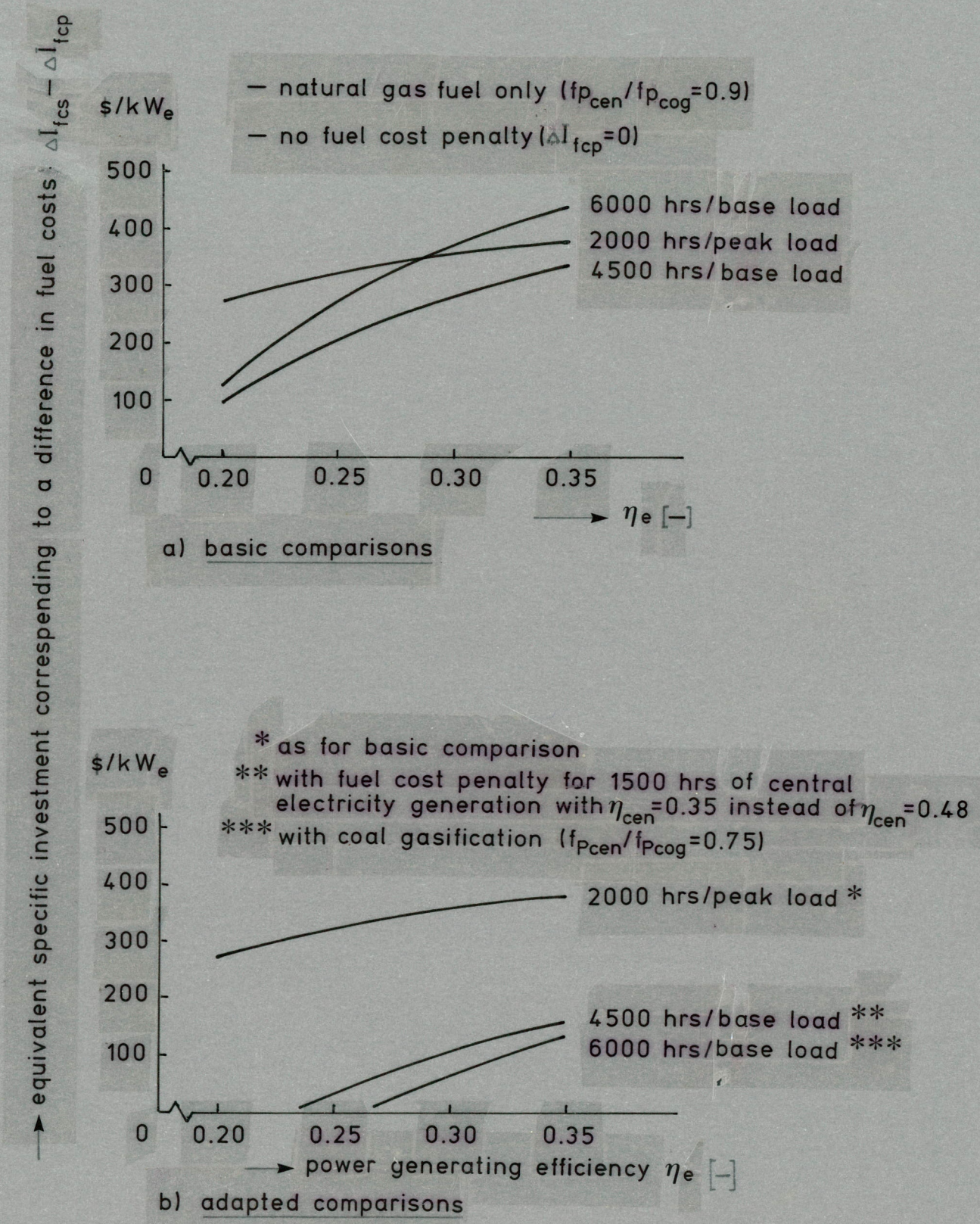
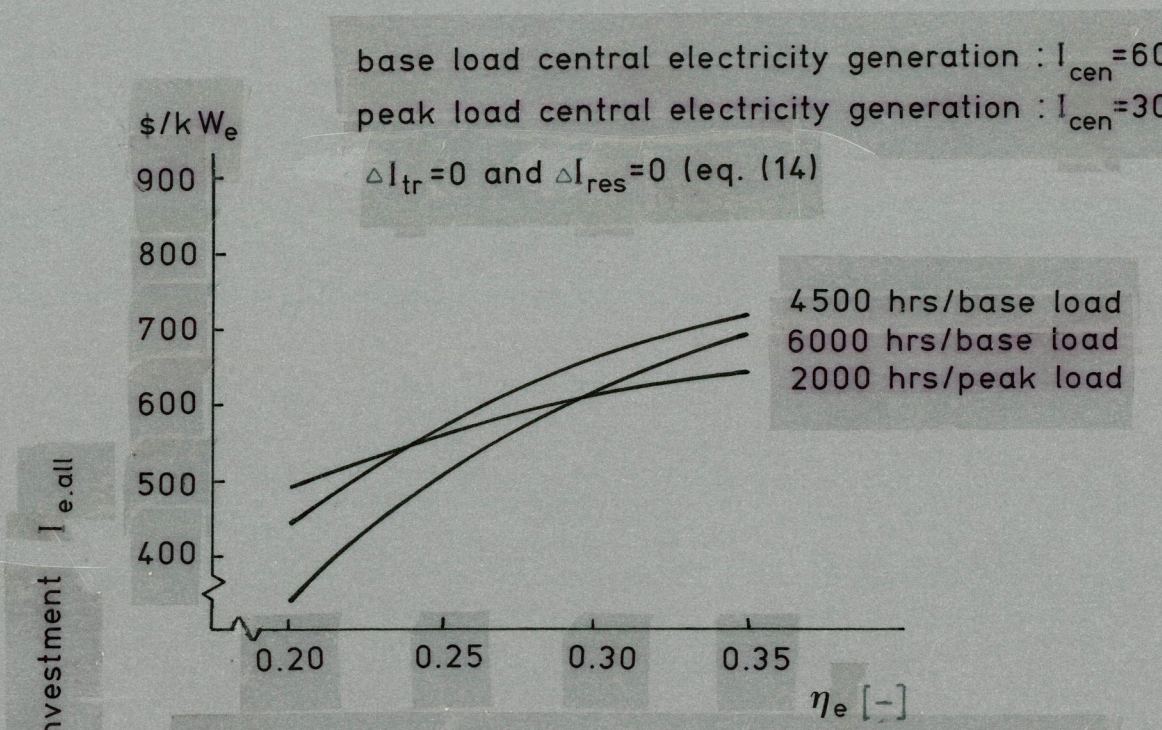


Figure 4 Equivalent specific investment corresponding to net fuel cost savings of cogeneration proces

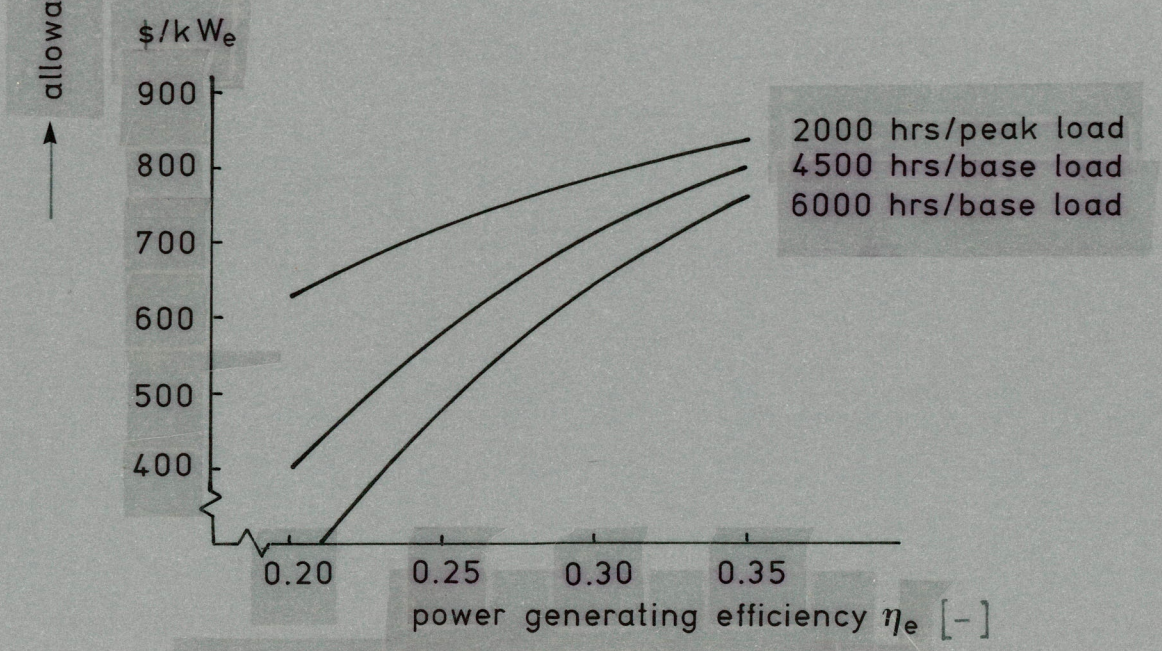
(for cogeneration fuel price fp_{cog}=2 ¢/kWh or 5.86 $/MMBt)

Figure 4 Equivalent specific investment corresponding to net fuel cost savings of cogeneration cases

(for cogeneration fuel price i_{cog}=2 $/kWh or 5.86 $/MMBt)



a) for net fuel cost savings corresponding to figure 4b (fp_{cog}=2 ¢/kWh)



b) for a 50% increase in all fuel price levels (fp_{cog}=3 ¢/kWh)

Figure 5 Allowable specific investment for electricity generating section of cogeneration system.

Figure 5 Allowable specific investment for electricity generating section of cogeneration system.