

# Organic compounds from coal utilisation

**Lesley Sloss**

CCC/51

September 2001

Copyright © IEA Coal Research 2001

ISBN 92-9029-364-0

## **Abstract**

Coal combustion can lead to emissions of organic compounds to the atmosphere, if the combustion system is inefficient. International protocols on emissions of some organic species have been established due to concern with respect to their role in ground level ozone formation and potential human health effects. These protocols acknowledge that efficient coal combustion in large coal-fired power plants is a negligible source of organic emissions. However, coal use in less efficient sectors such as residential stoves and some industrial practices can be a significant source of local emissions.

Evaluating emissions of organic compounds from sources such as coal combustion can be difficult due to the low concentrations and the large number of different compounds released. Emission inventories are commonly based on emission factors. This report reviews data on emissions from coal combustion from large-scale pulverised units down to small residential stoves. Emissions from industrial coal use such as for coke manufacture, metal production and cement kilns are also included. The effects of parameters such as fuel type, combustion conditions and pollution control systems are summarised. Best practices, many of which concentrate on increasing efficiency, are reviewed for all coal-related sources.

## Acronyms and abbreviations

AFBC	atmospheric fluidised bed combustion	PAS	photoelectric aerosol sensor
ANEPCC	Australian National Environmental Protection Council	PASH	polycyclic aromatic sulphur heterocycles
ar	as received	PCB	polychlorinated bi-phenyls
B[a]P	benzo(a)pyrene	PCDD	polychlorinated dibenzodioxin(s)
BAT	best available technology	PCDF	polychlorinated dibenzofuran(s)
BATEA	best available technology economically feasible	PCP	pentachlorophenol
BCURA	British Coal Utilisation Research Association	PDMS	polydimethylsiloxane
BFBC	bubbling fluidised bed combustion	PIC	products of incomplete combustion
BTX	total of benzene, toluene and xylenes	PID	photoionisation detection
CARB	Californian Air Resources Board, USA	POCP	photochemical ozone creation potential
CEC	Commission of the European Communities	POP	persistent organic pollutant
CEM	continuous emissions monitor	POPP	pyrolysis of organic polymer from particulate
CEN	Comité Européen de Normalisation (European Standards Committee)	PUF	polyurethane foam
CFBC	circulating fluidised bed combustion	RAINS	regional air pollution information and simulation model
daf	dry, ash free	RDF	refuse derived fuel
DDT	dichlorodiphenyltrichloroethane	SCR	selective catalytic reduction
DETR	Department of Energy, Transport and the Regions, UK	SNCR	selective non-catalytic reduction
DOAS	differential optical absorption spectroscopy	SPME	solid phase microextraction
DTI	Department of Trade and Industry, UK	SVOC	semi-volatile organic compound(s)
ECD	electron capture detection	TCDD	2,3,7,8-tetrachlorodibenzodioxin
ECE	Economic Commission for Europe	TEQ	toxic equivalency quotient
EMEP	Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe	THC	total hydrocarbons
EU	European Union	TNMOC	total non-methane organic compounds
FBC	fluidised bed combustion	TOC	total organic carbon
FGD	flue gas desulphurisation	TOFMS	time-of-flight mass spectrometry
FID	flame ionisation detection	TOF-SIMS	time-of-flight secondary ion mass spectrometry
FMW	focused microwave extraction	TRI	Toxics Release Inventory, USA
FTIR	Fourier transform infrared spectroscopy	TSMP	Toxic Substance Management Policy, Canada
GC	gas chromatography	WHO	World Health Organisation
HCB	hexachlorobenzene	UKEA	United Kingdom Environment Agency
HPLC	high performance liquid chromatography	UNECE	United Nations Economic Commission for Europe
IR	infrared	US EPA	United States Environmental Protection Agency
IRDIAL	infrared differential absorption lidar	VDI	Verein Deutscher Ingenieure, Germany
LIF	laser induced fluorescence	VOC	volatile organic compound(s)
LMPI	laser multiphoton ionisation	VOST	volatile organic sampling train
LOAEL	lowest observed adverse effect level		
MCR	maximum combustion rate		
MMT	metal-coated multi-layer Tedlar		
MSSV	micro-sealed vessel pyrolysis		
MSW	municipal solid waste		
MWe	megawatt (electric)		
MWI	municipal solid waste incinerator		
MWth	megawatt (thermal)		
NDIR	non-dispersive infrared spectroscopy		
NMHC	non-methane hydrocarbon(s)		
NOAEL	no observed adverse effect level		
NPRI	National Pollutant Release Inventory, Canada		
PAH	polycyclic aromatic hydrocarbon(s)		

# Contents

1	Introduction	5
2	Global and regional emissions	6
2.1	Definitions	6
2.2	Emission factors	10
2.3	Global emissions	14
2.4	Regional emissions	14
2.4.1	Europe	14
2.4.2	Germany	15
2.4.3	UK	15
2.4.4	Canada	16
2.4.5	USA	17
2.5	Comments	17
3	Legislation	18
3.1	International	18
3.2	National	19
3.2.1	Australia	19
3.2.2	Belgium	19
3.2.3	Canada	19
3.2.4	Germany	20
3.2.5	People's Republic of China	20
3.2.6	USA	21
3.3	Comments	21
4	Sampling and analysis	22
4.1	Sampling criteria	23
4.2	Sample collection	24
4.2.1	Grab sampling	25
4.2.2	Solid sampling media	25
4.2.3	Sampling trains	26
4.2.4	Cryogenic sampling	28
4.3	Sample preparation	29
4.4	Analysis	30
4.4.1	Chromatography	30
4.4.2	Flame ionisation detection	32
4.4.3	Infrared	32
4.4.4	Ultraviolet	32
4.4.5	Mass spectrometry	32
4.4.6	Other methods	33
4.5	Example of problems at a coal-fired plant	33
4.6	Comments	33
5	Emissions from coal-fired power plant	34
5.1	Reactions during combustion	34
5.2	Pulverised coal fired plants	35
5.2.1	Effect of fuel type	35
5.2.2	Effect of combustion conditions	37
5.2.3	Effect of pollution control systems	38
5.3	Comments	39
6	Emissions from industrial and residential coal use	40
6.1	Industrial coal combustion	40
6.2	Fluidised bed combustion	41
6.2.1	Effect of fuel type	41
6.2.2	Effect of combustion conditions	42
6.3	Residential coal combustion	45

---

6.4	Industrial coal use	47
6.4.1	Coke production	47
6.4.2	Aluminium, iron and steel production	48
6.4.3	Cement kilns	49
6.5	Comments	49
7	Practices to reduce emissions	50
7.1	Coal-fired power plants	50
7.1.1	Combustion conditions	50
7.1.2	Pollution control systems	50
7.2	Industrial and residential coal combustion	51
7.3	Industrial coal use	52
7.3.1	Coke production	52
7.3.2	Aluminium, iron and steel making	53
7.3.3	Cement kilns	53
7.4	Coal as a control option for waste incineration	53
7.5	Comments	54
8	Conclusions	55
9	References	56

# 1 Introduction

Thousands of different organic compounds may arise from coal utilisation. Although advances are being made in the measurement and study of organic emissions, the subject is still vast and complex. According to Lewis (2000) our present description of hydrocarbons in the atmosphere is a gross over simplification. Only a fraction of detectable organic compounds in urban air have been studied comprehensively and there are no current models which deal effectively with all the compounds present.

Interest in organic compounds has increased considerably in recent years with growing concern over health risks. These include ground level ozone formation and possible links between organic emissions and increased incidences of cancer in humans. It has been consistently shown that organic compounds from the clean and efficient use of coal are negligible and therefore not of environmental concern. However, less efficient uses of coal, such as inefficient residential combustion in less developed countries and coke-making in old coke ovens, have been associated with possible increased incidences of cancer.

In order to understand the behaviour of different organic compounds, several subgroups have been defined. These subgroups include (Ridge and Seif, 2000):

- VOC, volatile organic compounds;
- SVOC, semivolatile organic compounds;
- TOC, total organic compounds – VOC + SVOC;
- THC, total hydrocarbons, the subset of total organic compounds containing only carbon and hydrogen;
- TNMOC, total non-methane organic compounds, TOC – methane;
- PAH, polycyclic aromatic hydrocarbons, or POC, polycyclic organic matter, organic compounds with more than one benzene ring;
- BTX, benzene, toluene and xylenes;
- PCDD/F, polychlorinated dibenzodioxins and polychlorinated dibenzofurans.

This report concentrates largely on VOC, PAH and PCDD/F as these are the groups of organic compounds most commonly studied from coal utilisation.

VOC are of concern because of their role in the formation of tropospheric ozone. VOC vary greatly from each other in their reactivity and their potential to form ozone and other photochemical oxidants. Individual VOC have been given their own photochemical ozone creation potentials (POCP) in order to rank their importance relative to ozone production. This will help in the determination of appropriate strategies to reduce VOC effects (Altenstedt and Pleijel, 2000).

The concentration of PAH in ambient air is of concern with respect to possible health effects, especially cancer. Evaluating the potential for harmful exposure to PAH is difficult as these chemicals are always encountered as

complex mixtures containing many different compounds in varying concentrations (DETR, 1999).

PCDD/F are organic compounds which all have a very typical structure of two six-membered rings joined by a ring containing oxygen. PCDD/F have become of concern following chemical release incidences where increased incidences of human cancer were reported following exposure to high concentrations of these compounds.

This report evaluates recent data on what is known and what is speculated about organic compounds emitted from coal utilisation. It updates a previous reports by the Clean Coal Centre on organic emissions (Sloss and Smith, 1993; Smith, 1984). Global and regional emissions are reviewed in order to put emissions from coal combustion into context with emissions from other sources in different areas of the world. International and national legislation is then summarised, concentrating on how action plans to reduce emissions of organic compounds may impact on coal utilisation in the different sectors. A chapter is included on the basics of sampling and analysis of organic emissions. This is an area of great importance as emission estimates, emission factors and the successful application of any legislation and emission control all rely upon accurate measurement data. Emissions from sources such as coal-fired power stations and industrial and residential uses of coal are reviewed individually, concentrating on the importance of parameters such as fuel type and combustion conditions. Finally, strategies and practices to reduce emissions of organic compounds from the different areas of coal utilisation are discussed.

## 2 Global and regional emissions

Organic compounds can be released from natural sources such as plants, geological activity (including volcanoes) and fires. Any human activity involving the incomplete combustion of carbon-based fuels (for example, coal, oil, wood and gas) will also release organic compounds. Because so many different compounds can be produced, emission estimates are accompanied by considerable uncertainty factors (DETR, 1999). Lohmann and others (2000) agree that reliable, quantitative estimates of emissions are notoriously difficult to obtain. Inventory estimates give only crude figures with large uncertainties attached. It is perhaps because of the large number of pollutants and the considerable uncertainty that few data are available on organic emissions on either a global or regional scale. According to Lefevre and others (2000) Asian developing countries do not record emission inventories for atmospheric pollutants such as organic compounds. They also do not have any database on economic parameters of emission control equipment. This situation has hindered the precise estimation of atmospheric pollutants in the region.

Another reason for the lack of emission data is the lack of emission factors from which inventories can be calculated. Section 2.2 reviews the emission factors published in the available literature. The sections following Section 2.2 then review the few data there are on global and regional emissions of organic compounds. However, before comparing emissions it is important to understand the definitions of the groups of organic compounds being compared. These groups are not necessarily mutually exclusive and therefore some confusion may arise in the classification of certain compounds.

### 2.1 Definitions

A hydrocarbon is an organic compound comprising of only carbon and hydrogen. The general term non-methane hydrocarbons, **NMHC**, therefore covers all compounds, other than methane, which are hydrocarbons. This includes compounds such as alkanes and alkenes, as well as more complex compounds such as PAH. Individual studies of NMHC tend to define their own list of compounds which varies with the source being studied.

Volatile organic compounds, **VOC**, include methane, some carbon chain molecules and single (and some double) ring systems. Sometimes the term **NMVOC** (non-methane VOC) is used to emphasise that methane is rarely included as a VOC. VOC may include elements other than carbon and hydrogen. The UNECE has defined VOC within its 1999 protocol on the control of emissions or their transboundary fluxes as '*all organic compounds of anthropogenic nature, other than methane, that are capable of producing photochemical oxidants by reactions with nitrogen oxides in the presence of sunlight*' (UNECE, 1999b). A similar definition is given by the US Environmental Protection Agency (US EPA): '*an organic compound that participates*

*in atmospheric photochemical reactions; that is, an organic compound other than those that the Administrator of the EPA designates as having negligible photochemical reactivity*'. However, this US EPA definition, for legislative purposes, is slightly different from the US EPA definition used for analytical purposes, which is '*compounds which have a vapour pressure greater than or equal to 0.13 kPa (1 mm Hg) at 20°C*'. Semi-volatile compounds (**SVOC**) are '*the subset of all volatile organic compounds with boiling points of 300-600°F or vapour pressures  $\geq 10^{-1}$  mm Hg as collected by . . . EPA equivalent methods*' (Ridge and Seif, 2000).

The UNECE has defined the POCP, the photochemical ozone creation potential, of a VOC within its 1999 protocol as '*the potential of an individual VOC, relative to that of other VOCs, to form ozone reaction with oxides of nitrogen in the presence of sunlight*' (UNECE, 1999b).

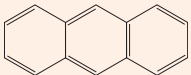
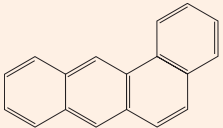
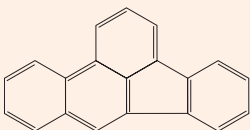
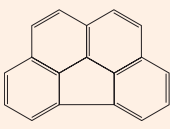
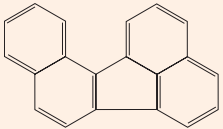
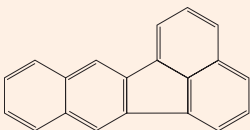
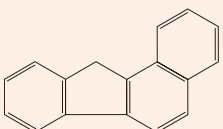
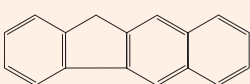
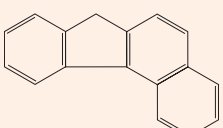
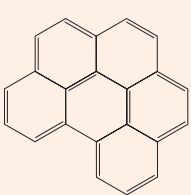
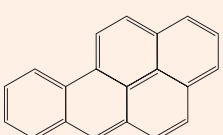
By definition, polycyclic aromatic hydrocarbons, **PAH**, are hydrocarbons made up of several carbon rings, normally six-membered benzene rings. Table 1 shows the formulae and characteristics of selected PAH compounds and Table 2 shows the different categories of PAH most commonly used in the literature at the moment (EMEP, 1996). The US EPA has included 16 PAH as priority pollutants in their Clean Air Act. However, only five of these compounds are considered carcinogenic and only 4-6 are regularly recorded in emission inventories.

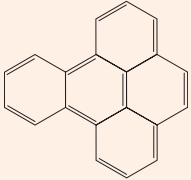
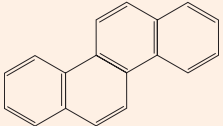
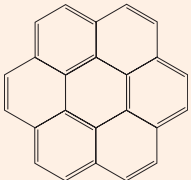
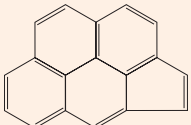
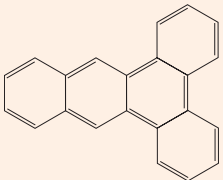
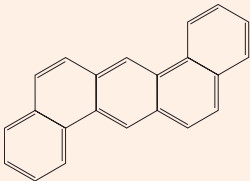
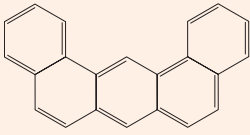
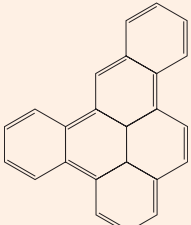
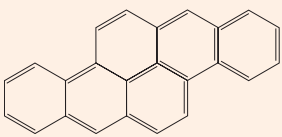
Lighter PAH compounds, such as phenanthrene, are found almost exclusively in the gas phase at ambient temperatures whereas heavier PAH, such as benzo[a]pyrene, B[a]P are almost totally adsorbed onto particles. PAH associated with fine particles will remain airborne longer, by several days, than PAH which are in the gas phase. PAH are generally insoluble in water, but dissolve in fats and oils (DETR, 1999).

In order to simplify PAH studies, B[a]P is often used as a marker for PAH exposure and air quality standards are sometimes set on this basis (DETR, 1999). BTX, the total of benzene, toluene and xylenes, is also used occasionally as an indicator of total PAH.

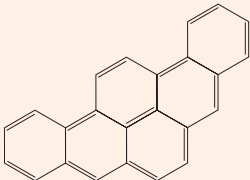
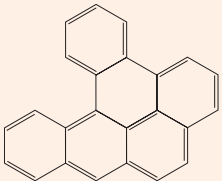
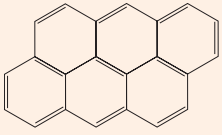
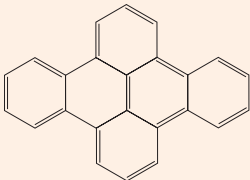
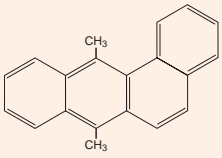
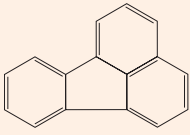
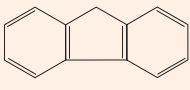
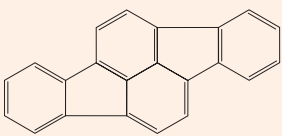
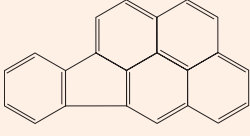
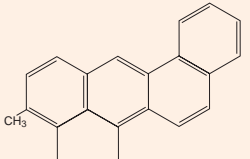
Polychlorinated dibenzo-dioxins and polychlorinated dibenzo-furans, commonly known as dioxins and furans or **PCDD/F**, are compounds with two six-membered carbon rings joined by a ring containing oxygen, as shown in Figure 1. There are many sites where the chlorine atoms can be substituted in these molecules and thus a large number of PCDD (75) and PCDF (135) is possible. The most notorious PCDD is 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD) which is reported to be extremely toxic to animals and man. PCDD/F are solids with high melting points and low solubility in water and therefore are relatively stable in the environment.

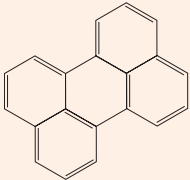
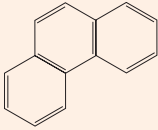
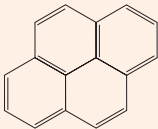
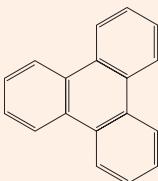
**Table 1 Characteristics of selected PAH compounds (Smith, 1984)**

Carcin-Compound ogen- icity*	Structure	Formula	Acronym	Mol weight	Melting point, °C	Boiling point, °C	Vapour pressure, mPa
	Anthanthrene (see Dibenzo[ <i>cd,jk</i> ]pyrene)						
-	Anthracene 	C <sub>14</sub> H <sub>10</sub>	A	178	216	342	25.0
+	Benz[ <i>a</i> ]anthracene = (tetraphene) = (1,2-benzanthracene) 	C <sub>18</sub> H <sub>12</sub>	BaA	228	158-159	400	14.7x10 <sup>-3</sup>
++/ +++	Benzo[ <i>b</i> ]fluoranthene = (2,3-benzfluoranthene) 	C <sub>20</sub> H <sub>12</sub>	BbF	252	168	481	
-	Benzo[ <i>ghi</i> ]fluoranthene 	C <sub>18</sub> H <sub>10</sub>	B <i>ghi</i> F	226	149	432	
++/ +++	Benzo[ <i>j</i> ]fluoranthene = (7,8-benzfluoranthene) 	C <sub>18</sub> H <sub>12</sub>	B <i>j</i> F	252	165	480	
+	Benzo[ <i>k</i> ]fluoranthene = (8,9-benzfluoranthene) 	C <sub>20</sub> H <sub>12</sub>	B <i>k</i> F	252	216	481	2.8x10 <sup>-9</sup>
-	Benzo[ <i>a</i> ]fluorene = (1,2-benzofluorene) 	C <sub>17</sub> H <sub>12</sub>		216	189-190	413	
-	Benzo[ <i>b</i> ]fluorene = (2,3-benzofluorene) 	C <sub>17</sub> H <sub>12</sub>		216	209-210	401-402	
-	Benzo[ <i>c</i> ]fluorene = (3,4-benzofluorene) 	C <sub>17</sub> H <sub>12</sub>		216		406	
±	Benzo[ <i>ghi</i> ]perylene = (1,2benzoperylene) 	C <sub>22</sub> H <sub>12</sub>	B <i>ghi</i> P	276	278	542	13.5x10 <sup>-9</sup>
++++	Benzo[ <i>a</i> ]pyrene = (1,2-benzpyrene) = (3,4-benzpyrene) 	C <sub>20</sub> H <sub>12</sub>	BaP	252	178	495	372x10 <sup>-9</sup>

-	Benzo[e]pyrene = (1,2-benzpyrene) = (3,4-benzpyrene)		C <sub>20</sub> H <sub>12</sub>	BeP	252	179	493	739x10 <sup>-9</sup>
±	Chrysene		C <sub>18</sub> H <sub>12</sub>	CH,CHR 228		255-256	448	
-	Coronene		C <sub>24</sub> H <sub>12</sub>	Cor	300	438-440	525	196x10 <sup>-12</sup>
+ / ++	Cyclopenta[cd]pyrene = (cyclopentadieno[cd]-pyrene)		C <sub>18</sub> H <sub>10</sub>	CP	226	170	439	
±	Dibenz[a,c]anthracene = (benzo[b]triphenylene) = (1,2-3,4-dibenzanthracene)		C <sub>22</sub> H <sub>14</sub>		278	206	535	
+++ / ++++	Dibenz[a,h]anthracene = (1,2-5,6-dibenzanthracene)		C <sub>22</sub> H <sub>14</sub>	DBahA	278	266-267	524	
++	Dibenz[a,j]anthracene = (1,2-7,8-dibenzanthracene)		C <sub>22</sub> H <sub>14</sub>		278	197	531	
++ / +++	Dibenzo[a,e]pyrene = (naphtho[1,2,3,4-def] -chrysene = (1,2,4,5-dibenzpyrene)		C <sub>24</sub> H <sub>14</sub>		302	233	592	
++++	Dibenzo[a,h]pyrene = (1,2-6,7-dibenzpyrene) = (dibenzo[b,def]chrysene) = (3,4-8,9-dibenzpyrene)		C <sub>24</sub> H <sub>14</sub>	DBahP	302	317	596	



+++	Dibenzo[ <i>a,l</i> ]pyrene = (2,3-6,7-dibenzpyrene) = (4,5-8,9-dibenzpyrene) = (benzo[ <i>rs</i> ]pentaphene) = (3,4-9,10-dibenzpyrene)		C <sub>24</sub> H <sub>14</sub>	DBaP	302	282	594
+++	Dibenzo[ <i>a,l</i> ]pyrene = (2,3-4,5-dibenzpyrene) = (dibenzo[ <i>def,p</i> ]chrysene) = (1,2-3,4-dibenzpyrene)		C <sub>24</sub> H <sub>14</sub>		302	162	595
+ / ++	Dibenzo[ <i>cd,jk</i> ]pyrene = (anthracene) = (dibenzo[ <i>def,mno</i> ]chrysene)		C <sub>22</sub> H <sub>12</sub>	ANT	276	264	
	Dibenzo[ <i>e,l</i> ]pyrene = (dibenzo[ <i>fg,op</i> ]tetracene) = (1,2,6,7-dibenzpyrene -dibenzpyrene)		C <sub>24</sub> H <sub>14</sub>		302		592
++++	7,12-Dimethylbenz[ <i>a</i> ]anthracene = (9,10-dimethyl-1,2-benz- anthracene) (not an air pollutant)		C <sub>20</sub> H <sub>16</sub>	DMDA	256	121-123	
-	Fluoranthene		C <sub>16</sub> H <sub>10</sub>	FLU	202	111	375
-	Fluorene		C <sub>13</sub> H <sub>10</sub>	F	166	116-117	295
	Indeno[1,2,3- <i>cd</i> ]fluoranthene = (peri-phenylene-fluoranthene)		C <sub>22</sub> H <sub>12</sub>	IF	276		531
++	Indeno[1,2,3- <i>cd</i> ]pyrene = (o-phenylenepyrene) = (2,3-o-phenylene-pyrene)		C <sub>22</sub> H <sub>12</sub>	IP	276	164	534
+++	3-Methylcholanthrene = (3-methyl-1,2-dihydrobenz- [ <i>j</i> ]aceanthrylene) (not an air pollutant)		C <sub>21</sub> H <sub>16</sub>	MCA	268	178-180	506

–	Perylene		C <sub>20</sub> H <sub>12</sub>	Per,PER 252	273-274	497	
–	Phenanthrene		C <sub>14</sub> H <sub>10</sub>	PA	178	101	340 90.7
–	Pyrene		C <sub>16</sub> H <sub>10</sub>	P,PYR	202	150	393 91.3x10 <sup>-6</sup>
	Triphenylene = (9,10-benzphenanthrene)		C <sub>18</sub> H <sub>12</sub>	TRI	228	199	425
* number of + corresponds to carcinogenic potential: +++++ is highly carcinogenic; – is not carcinogenic							

**Table 2 Categories of PAH (EMEP, 1996)**

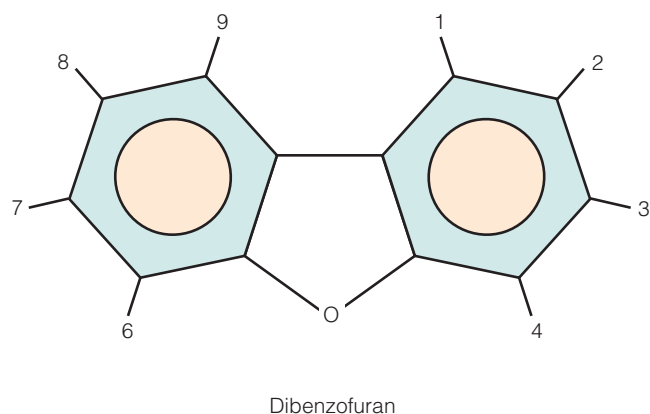
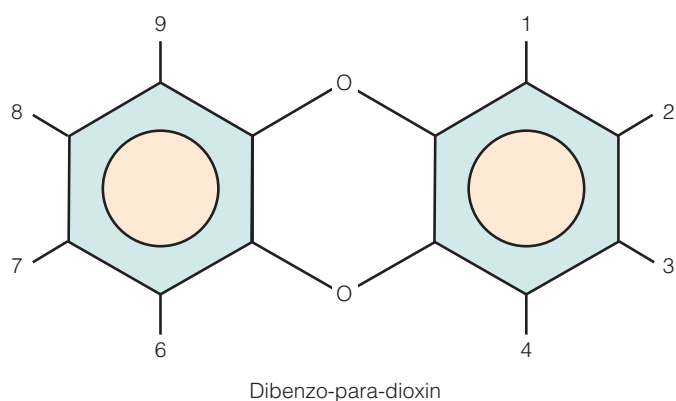
PAH	US EPA priority pollutant	IARC* carcinogen	Borneff†	UNECE POP‡
naphthalene	yes			
acenaphthalene	yes			
acenaphthene	yes			
fluorene	yes			
anthracene	yes			
phenanthrene	yes			
fluoranthene	yes		yes	
pyrene	yes			
benz[a]anthracene	yes	yes		
chrysene	yes			
benzo[b]fluoranthene	yes	yes	yes	yes
benzo[k]fluoranthene	yes	yes	yes	yes
benzo[a]pyrene	yes	yes	yes	yes
dibenz[a,h]anthracene	yes			
indeno[1,2,3-cd]pyrene	yes	yes	yes	yes
benzo[g,h,i]perylene	yes		yes	

\* International Agency for Research on Cancer defined carcinogen to humans  
† Borneff selected PAH for use in some emission inventory calculations  
‡ United Nations Economic Commission for Europe defined persistent organic pollutants, used as indicators for emission inventories

Co-planar polychlorinated biphenyls (PCBs), those having four or more chlorine atoms with only a few substitutions at the ortho positions (2, 2', 6 and 6'), have been shown to behave similarly to PCDD/F and have been designated as the 'WHO PCBs' as the World Health Organisation (WHO) has derived toxic equivalency quotients (TEQ) for these congeners relative to 2,3,7,8-TCDD. The US EPA is currently developing standards for measurement of these species from waste incinerators (Riley, 2001).

## 2.2 Emission factors

As mentioned earlier, emission factors for organic compounds are known to have high uncertainty factors. This is due to the large number of different compounds which may be released and the variability of these releases with source conditions. It is perhaps because of this uncertainty that few emission factors are published. Some of the emission factors



**Figure 1 Basic structure of dioxins and furans**

quoted in this section are quite dated but still applicable. Of the organic compounds reviewed in this report, the majority of data are on VOC emission factors. This is because there are national and international agreements and legislation on VOC and emissions must be reported. This has not been the case for PAH or PCDD/F, although countries such as Canada and the USA are now introducing reporting requirements for PCDD/F (*see* Chapter 3). This should lead to increased amounts of data in the coming years.

This section deals with general emission factors for different

fuel types and combustion systems. These are the type of emission factors which would be used for emission inventories, such as those covered in Section 2.3. Chapters 5 and 6 deal with more specific factors which relate to changes in combustion systems.

Emission factors for **VOC** emissions from different fuels in the energy sector calculated for use in emission estimates by the UK Department of Trade and Industry in 1998 were as follows (DTI, 2000):

coal	18 g/GJ
oil	2 g/GJ
natural gas	5 g/GJ

Values calculated by Stewart and Walker (1997), also for the UK, are slightly lower, as shown in Table 3. The emission factors are also lower for plants with low NO<sub>x</sub> burners (*see* Chapter 5). The emission factors produced by Stewart and Walker (1997) are lower than those published by the US EPA but higher than those used in the UK in the National Atmospheric Emissions Inventory (NAEI). The average emission factors, on g/GJ basis, are also lower than those used in the European emission inventory calculations, Corinair. Emission factors for VOC from oil and gas are lower, on an energy basis, than those from coal combustion.

Environment Australia has also produced emission factors for both black and brown coal combustion. The emission factor for VOC is 1.7 t/PJ (10<sup>15</sup> joules; equivalent to 1.7 g/GJ). This is an order of magnitude lower than the value used by the DTI in the UK and has an unknown certainty rating. It is not clear whether the difference in emission factors between the UK and Australia is a reflection of differences in coal or simply a result of the great uncertainty and variability of such emission factors.

The Australian emission factor can be used to estimate the total VOC emissions from a typical power plant in Australia burning black coal, such as Bayswater in New South Wales. Assuming the plant runs for 5000 hours/year at a fuel consumption rate of 50 t/h, the total VOC emissions would amount to around 10 t/year. The emission factor for VOC from natural gas boilers was 0.6–2.3 g/GJ. VOC emission

**Table 3 VOC emission factors for full-scale power stations in the UK (Stewart and Walker, 1997)**

Fuel	Aggregate range g/kg (daf)	Average emission factors		Published emission factors		Average emission factor, g/GJ	Published emission factor, Corinair g/GJ
		g/kg (daf)	g/kg (ar)	NAEI (ar) g/kg	US EPA (ar) g/kg		
coal							
unmodified	0.034-0.097	0.056	0.041	0.0228	0.055	1.7	30
low NO <sub>x</sub>	0.014-0.083	0.044	0.032	0.0228	0.055	1.3	30
all coal units	0.014-0.097	0.050	0.037	0.0228	0.055	1.5	30
oil	0.019-0.021	na	0.020	0.036	0.125	0.49	10
orimulsion	na	na	<0.06	–	–	<2.3	–
gas	na	na	0.04 g/m <sup>3</sup>	0.050 g/m <sup>3</sup>	0.028 g/m <sup>3</sup>	1.2	5
daf	dry, ash free						
ar	as received						
na	not applicable						
Corinair	as used in Europe						
NAEI	UK National Atmospheric Emissions Inventory						

factors for gas turbines were 2.1–10.3 g/GJ with the lower values being for distillate rather than natural gas (EA, 2001b).

Environment Australia has also produced emission factors for several toxic emissions from black and brown coal combustion in different boiler configurations (wall-fired versus tangentially fired). However, the results are identical for the different boiler configurations for each of the groups of organic compounds (EA, 2001b):

VOC	40 g/t coal
PAH	0.01g/t coal
PCDD/F	8.8 x 10 <sup>-7</sup> g/t coal

The emission factor for VOC is considered of above average certainty whereas those for PAH and PCDD/F are considered to be of average to below average certainty.

Emission factors for coal and other fuel vary with the source. Larger, more efficient sources have lower emission factors than small, less efficient ones. Table 4 summarises VOC emission factors for different coals and other fuels in both power plants and industrial units. The emission factors for the industrial units are around an order of magnitude higher due to the lower combustion efficiency (CEC, 1998a).

VOC emission factors for different fuels in residential combustion appliances are shown in Table 5 (CEC, 1998a). The emission factors, collated from several, unnamed sources, range quite dramatically with the greatest emissions arising from coal, lignite, wood and peat.

As mentioned earlier, there is no legal requirement to report PAH emissions from coal combustion and therefore data are hard to find in the literature. PAH emission factors are likely to include variation caused by different measurement techniques and their inherent inaccuracies. Comparisons between studies will confound these analytical differences and also include any differences in study conditions. Therefore values obtained from different studies should not be compared too closely.

Fuel type	Power plant emission factor	Industrial plant emission factor
hard coal	3.4	20–30
brown coal	–	30
lignite	3.4	–
brown coal briquettes	–	30
coke	–	1–30
wood	–	60–100
fuel oil	6.8	–
gas oil	–	5
residual fuel oil	–	8
natural gas	0.45	5
coke-oven gas	–	5
blast furnace gas	–	5
manufactured gas	–	5
refinery gas	–	5
LPG	–	5

Default emission factors for B[a]P used in European emission inventory calculations are shown in Table 6 (EMEP, 1996). It is clear that smaller industrial plants are less efficient and therefore have higher emission factors. Emission factors for the anode baking industry and aluminium production (fuel not specified) are far higher than those for combustion on a g/t basis.

PAH emission factors for various combustion sources, as a ratio to B[a]P emissions, are shown in Table 7 (EMEP, 1996). There is a difference in the amount of each individual PAH compound released from each combustion source. This ratio may well also change with combustion conditions and fuel characteristics. Data reviewed previously (Sloss and Smith, 1993) also suggested that the emission factors for individual PAH compounds varied with ash content and combustion conditions. Average emission factors were around 20 g/t fuel for coal in full-scale plants. The variation in PAH emission factors for different coals in different coal-fired power stations indicated that no real trends or conclusions could be drawn. PAH emission factors for industrial coal combustion are also highly variable. Davies and others (1992) quoted values from 3–13 g/t for a 5.5 MW travelling grate to 260 g/t for a 0.15 MW under-feed system.

Emission factors for PAH from domestic coal combustion are several orders of magnitude higher than those from full-scale power plants and industrial units. Davies and others (1992) gave an emission factor of 1800 g/t for a closed domestic fire and 3000 g/t for an open fire. The study of the effect of coal type on PAH emissions from domestic combustion systems is often masked by variations in the measurements. For example, measurements for emissions from the same fuel in two separate open grates differed by a factor of three. Emission factors varied from 30 g/t for the combustion of anthracite in an open grate, up to 2300–2700 g/t for smokeless fuel on an open grate with a back boiler, and between 100 and 6100 g/t for bituminous coal on an open grate (Davies and others, 1992).

Emission factors for PCDD/F from full-scale coal-fired power units are commonly very low. Table 8 shows emission factors for PCDD/F from different coal fired systems from

Fuel	Emission factor		
	1	1	3*
hard coal	350	200	500
lignite briquettes	500	150	450
coke	20	15	5
peat	500	–	450
wood	90	100	800
kerosine	–	15	–
residual oil	20	10	5
natural gas	40	30	5
LPG	0	0	–
manufactured gas	–	30	–

\* factors from different but unspecified information sources

**Table 6 Default emission factors for B[a]P used in European emission inventory calculations (EMEP, 1996)**

Source	Process/fuel type	Emission factor	Comment†
industrial combustion	large plant, coal	0.14 mg/t	effective end-of-pipe control, D rating
	small, plant, coal	1500 mg/t	no control, E rating
	total coal sector	775 mg/t*	E rating
	large plant, wood	2 mg/t	effective end-of-pipe control, D rating
	small plant, wood	1300 mg/t	no control, E rating
	total wood sector	650 mg/t	E rating
residential combustion	bituminous coal	500-2600 mg/t (1550 mg/t)*	no control technologies, D rating
	smokeless fuel	330 mg/t	no control, E rating
	wood	600-2000 mg/t (1300 mg/t)*	no control, E rating
anode baking aluminium production	Al industry	6.5-135 g/t	various, D rating
	pre-baked process	30-8600 mg/t (100 mg/t)*	various, E rating
	HSS process	na	
	VSS process	172 g/t	wet scrubber and ESP, D rating
natural fires/open burning		0.2-14.3 g/t	no control, D rating

\* best estimate to be used when no information is available on plant type  
† rating of emission factor on a scale of A-E where A is based on a large number of measurements and E is based on assumptions only  
na not available

**Table 7 PAH mission factors for various combustion sources, as a ratio to B[a]P emissions (EMEP, 1996)**

PAH	Coal industrial and residential	Wood industrial and residential	Natural fires/ biomass burning	Anode baking
benzo[a]pyrene	1.0	1.0	1.0	1.0
benzo[b]fluoranthene	0.05	1.2	0.6	2.2
benzo[k]fluoranthene	0.01	0.4	0.3	2.2
indeno[1,2,3,c,d]pyrene	0.8	0.1	0.4	0.5

**Table 8 PCDD/F emissions from coal combustion (Brain and others, 1995)**

Source	Fuel	MCR, %	Emission, ng/m <sup>3</sup> TEQ	Emission factor, g/t TEQ
500 MWe	coal	80	0.006	0.09
36 MW CFBC	coal	28	0.016	0.016
4.6 MW top feed	coal	75	0.004	0.07
2.7 MW	oil	100	0.002	-
13kW gravity feed	anthracite	n/a	0.008	0.15
domestic open fire	bituminous coal	n/a	0.93	14.0
	smokeless fuel	n/a	0.07	1.40

MCR maximum combustion rate  
n/a not applicable

full-scale coal-fired utilities down to domestic open fires. As would be expected, emission factors for the larger, more efficient systems are lower than those for the less efficient residential systems (Brain and others, 1995).

The new Toxics Release Inventory (TRI) requirements in the USA (*see* Chapter 3) may mean that PCDD/F emissions from coal-fired power plants have to be reported. Most of these reported values will be estimates based on emission factors.

However, it has been suggested that, since so few actual emissions of PCDD/F are measured from full-scale coal-fired power plants, current emission factors may be unreliable (ES&T, 2000).

INERSIS, the French Ministry of the Environment, has commissioned a study into the estimation of PCDD/F from different sources. This study is concentrating on emissions from sources such as biogas combustion, copper salvage,

municipal waste incinerators and treated wood combustion and does not include any coal related sources (Perret, 2001). This can be seen as an indication that PCDD/F emissions from coal combustion are not considered to be of great concern, compared to emissions from other sources.

Emission factors for PCDD/F from waste incinerators may be significantly higher than those from efficient coal combustion at between 54–2,600 µg/t (Sloss and Smith, 1993).

More specific emission factors, relating to variations in combustion conditions and so on, are discussed in the appropriate sections in Chapters 5 and 6.

## 2.3 Global emissions

There are indications of a general trend in emissions of organic compounds in the developed world. According to Lohmann and others (2000), the reduction in organic emissions from large sources in industrialised countries has increased the relative importance of diffuse and numerous small-scale sources (such as residential combustion) in national and regional patterns of emissions in recent years.

The most recent data on global VOC emissions appears to be a review by Piccot and other from 1992. Emissions from coal combustion were not significant enough to be included as a source category. Major sources were:

	%
fuel wood utilisation	20
savanna burning	16
petrol (gasoline) preparation, transport and use	16
refuse disposal	8
organic chemical manufacture	7
solvent use	7
deforestation and agriculture	3
surface coating operations	2
other miscellaneous sources	21

Although the total amount of emissions and the relative contribution from the major sectors may have changed since this estimate was prepared, it is unlikely that coal has increased its relative contribution significantly.

Within the EMEP calculations for NMVOC emissions in Europe, emissions from power plants are described as of 'minor relevance' (EMEP, 1996).

Data on global PAH emissions appear to be even more sparse than those for VOC. Estimates from the 1980s suggest that emissions from power generation, in both power plants and industrial boilers, were less than 1% of total PAH emissions in most countries. Industrial processes including coke manufacture, and residential combustion would have been responsible for a greater proportion of the emissions (Sloss and Smith, 1993). More information is necessary in this area.

Global emission values for PCDD/F have been estimated by one study at around 3000 kg/y, based on emission factors. The estimated deposition was estimated at 13,000 kg/y, a factor of four or more higher. Another study suggested that

deposition may actually be greater than emissions by 6 or even 20 times. Baker and Hites (2000) believe that the disagreement is due to some form of de novo synthesis of PCDD/F in the atmosphere, probably from photochemical conversion of PCP (pentachlorophenol, a wood preservative and fungicide) in the aqueous phase in the atmosphere. If this is correct, then direct emissions of PCDD/F from combustion on a global scale are a very small fraction of the total contribution of PCDD/F to the atmosphere from human activities.

## 2.4 Regional emissions

The following sections review the available information on emissions of organic compounds from Europe as a whole and from individual countries around the world. The majority of the data available relate to emissions of VOC and NMVOC, as these compounds are included in national and international legislation (*see* Chapter 3) and therefore have to be reported. However, since it is clear that coal utilisation is not a major source of VOC or NMVOC, the data on these emissions have only been reviewed briefly for a few countries as examples.

### 2.4.1 Europe

GENEMIS is a joint European project aimed at harmonising emission inventories for Europe. NMVOC are included in the project along with the more major pollutants of concern (SO<sub>x</sub> and NO<sub>x</sub>). Friedrich (1997) cites data for NMVOC emissions in Europe in 1990. Of the total 21.8 t/y, less than 0.1 t/y (<1%) was from power plants and only 0.2 t/y (<1%) from industrial combustion. Commercial and residential combustion contributed around 4%. The greatest sources of emissions of NMVOC were road transport (31%), solvent use (23%) and nature (20%). It is predicted that total emissions of NMVOC in Europe will have decreased by 20–30% between 1990 and 2000.

Data from the European RAINS (regional air pollution information and simulation) model, suggest that, by 2010, emission reductions for VOC could be up to between 60 and 70% for countries such as Belgium, Germany, Luxembourg, The Netherlands and the UK (based on 1990 levels and predicted control measures). Emissions from Finland, France, Ireland and Sweden could be reduced by 50–60%, Denmark, Italy and Portugal by 40–50% and Austria, Greece and Spain by 30–40%. Emissions from countries outside the EU, such as the Czech Republic, Hungary, Norway and the Ukraine, are also expected to decrease by as much as 48% whereas emissions from countries such as Albania and Romania may actually increase by a few percent (Options, 1998).

Table 9 shows the estimated PCDD/F emissions for selected individual countries. It was found that the PCDD/F emission rate correlated well with both the gross domestic product of each country and also with the CO<sub>2</sub> emission rate. This would suggest that fuel combustion is the major source of PCDD/F emissions. Separate studies in Sweden, Germany and the UK have shown that the estimated deposition of PCDD/F is at least an order of magnitude greater than the estimated emissions in each country (Baker and Hites, 2000).



**Table 9 Annual PCDD/F and CO<sub>2</sub> emissions and gross domestic product for various countries (Baker and Hites, 2000)**

Country	PCDD/F, kg/y*	GDP, B\$US	CO <sub>2</sub> emissions, Mt/y
Austria	7.3	164	164
Belgium	29	197	279
Denmark	3.0	130	170
Finland	4.1	125	142
France	67	1200	1020
Germany	50	1690	2650
Greece	7.3	71	199
Ireland	2.0	44	88
Italy	63	1150	1100
Luxembourg	3.0	ND	28
The Netherlands	7.0	291	379
Norway	2.5	106	160
Portugal	7.6	69	114
Spain	20	527	600
Sweden	5.3	237	146
Switzerland	11	230	114
United Kingdom	56	978	1580
USA	180	5610	13460

\* emission estimates in kg TEQ/y – converted to kg/y by multiplying by 60  
ND no data

It is interesting to note that a European study co-ordinated by dk-Teknik Energy and Environment in Denmark aims to evaluate PAH, PCDD/F and PCB emissions from sources in Europe. This study will not include emissions from coal-fired power stations as they are not considered a significant source (Schleicher, 2001).

## 2.4.2 Germany

According to Friedrich (1997) and Wickert and others (1998) emissions of NMVOC in East Germany have been reduced by around 50% between 1989 and 1994 from around 800 kt/y to 400 kt/y. Emissions from the energy sector were minimal. These reductions were not caused by emission reduction measures but rather were as a result of economic decline (Friedrich, 1997).

## 2.4.3 UK

Total fossil fuel use was responsible for around 30% of VOC emissions in the UK in 1998, as shown in Table 10. Less than 1% of this was from fossil fuel use in power plants. The largest sources of VOC emissions were solvent use and road transport at 27% each. The extraction and distribution of fossil fuels was responsible for 15% of total VOC emissions in the UK. Total emissions of VOC in 1998 were 25% lower than in 1990 but only 14% lower than in 1970. In the 1970s and 1980s declining emissions from the residential sector were more than offset by increases from road transport and offshore gas and oil activity. However, emissions from road transport have been falling since 1989 resulting in an overall drop in emissions of VOC every year since (DTI, 2000).

The most recently published values for total PAH and B[a]P emissions in the UK are for 1996 and are shown in Table 11. Emissions from coal-fired power stations are included within 'other sources' along with waste incineration and iron and steel production. Industrial coal combustion was responsible for around 18% of emissions in 1995 and, although emissions from this sector decreased by 140 t/y between 1995 and 1996, the relative contribution to total emissions stayed constant. Residential coal combustion contributed around 9% of the total PAH emissions in 1995. Despite an actual reduction in emissions from this sector of 30 t/y by 1996, the relative contribution had risen slightly to 11% due to greater reductions in other sectors such as anode baking (comprising the Söderberg process and pre-baked anode process; unspecified fuel) (DETR, 1999).

Measurements made by the UK National Toxic Organic Micro-pollutants Network between 1991 and 1997 indicate a general downward trend in atmospheric concentrations of measured PAH species. For example, background concentrations of B[a]P have decreased from 1.1 ng/m<sup>3</sup> in 1991 to 0.6 ng/m<sup>3</sup> in 1997. Older data suggested that the current concentrations of B[a]P in London are more than ten times lower than during the era of peak urban coal combustion (DETR, 1999).

**Table 10 Emissions of volatile organic compounds in the UK in 1998 (DTI, 2000)**

By fuel	kt	%
coal	28	1
solid smokeless fuel	3	–
petroleum:		
motor spirit	361	18
DERV*	62	3
gas oil	15	1
fuel oil	1	–
burning oil	–	–
other petroleum	4	–
natural gas	18	1
other emissions†	1466	69
<i>Total</i>	1958	100
Under UNECE definitions		
power stations	6	–
domestic	27	2
commercial and public service	4	–
industrial combustion	8	1
non-combustion processes	289	15
extraction and distribution of		
fossil fuels	298	15
solvent use	532	27
road transport	527	27
other transport	48	2
waste treatment and disposal	29	1
forests	178	9
<i>Total</i>	1958	100

\* DERV – diesel engine road vehicles  
† includes industrial processes and solvents, petrol evaporation, offshore oil and gas activities, gas leakage, waste disposal and forests

**Table 11 Estimated emissions of PAH and B[a]P in the UK, t/y (DETR, 1999)**

Source	1995*		1996	
	Total PAH	B[a]P	Total PAH	B[a]P
Industrial power				
coal	600	5	460	4
wood	20	0.1	24	0.1
Domestic power				
coal and smokeless fuel	300	2	270	2
domestic wood	200	1	210	1
Specific industrial processes				
coke ovens	90	1	90	1
aluminium production	200	1.3	190	1.3
anode baking	1500	9	860	4
Road transport				
petrol	200	6	150	5
diesel	30	1	30	1
Wood treatment	100	<0.1	100	<0.1
Natural fires and open burning	100	3	100	3
Other sources†	30	0.4	27	0.4
<b>Total emissions</b>	<b>3370</b>	<b>30</b>	<b>2511</b>	<b>23</b>

\* total (particulate and gas phase) of naphthalene, acenaphthylene, acenaphthene, fluorene, anthracene, phenanthrene, pyrene, benz[a]anthracene, chrysene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[ah]anthracene, indeno[123cd]pyrene and benzo[ghi]perylene  
† includes power generation, waste incineration and iron and steel works

Dyke and others (1997) reviewed data on PCDD/F emissions in the UK and concluded that the inventory was based on old and limited data sets. Estimates of releases from sources such as municipal solid waste incinerators (MSW) and chemical waste incineration varied by over three orders of magnitude. The estimates for coal combustion were as follows:

	g TEQ/y
power stations	1.6–81
all industrial	0.015–4.3
domestic: ash	0.090–0.31
domestic: soot	0.16–30
total UK emissions	1500–12,000

Although the numbers may be known to be inaccurate, it is clear that coal combustion is not a major source of PCDD/F emissions in the UK. The largest sources were municipal solid waste combustion (MSW; up to 2400 g TEQ/y), open use of chemicals (up to 3000 g TEQ/y), accidental fires (up to 2400 g TEQ/y), pesticides production (up to 2000 g TEQ/y), per- and tri-chloroethylene production (up to 630 g TEQ/y), secondary aluminium production (up to 230 g TEQ/y) and secondary lead production (up to 220 g TEQ/y).

Lohmann and others (2000) suggest that around 10% of the total PCDD/F TEQ emissions come from residential coal and wood combustion.

The EC Municipal Waste Directive limits emissions from waste incinerators to 1 ng TEQ/m<sup>3</sup>. This has been applied to all plants in the UK effectively reducing emissions from

waste incinerators by over 99% between 1996 and 1997 (UKEA, 2000).

#### 2.4.4 Canada

A total of 2.5 Mt of VOC were released from all sources in Canada, according to Placet and others (2000; year for data was unspecified). Industrial sources contributed 1.0 Mt of these emissions and only 0.3 Mt/y arose from fuel combustion (all fuels, all sources). Other sources included incineration (0.7 Mt), forest fires and prescribed burning (0.3 Mt) and miscellaneous sources (0.7 Mt).

Separate estimates from Environment Canada for 1995 put total VOC emissions at over 3.5 Mt. The greatest contribution, 0.94 Mt, was from industrial sources including the iron and steel industries (0.028 Mt). Within industry, the greatest single source was the upstream oil and gas industry (0.69 Mt). Electrical utilities were responsible for only 0.003 Mt of the total emissions. Around the same value came from residential fuel combustion (0.002 Mt) but residential fuel wood combustion was a much greater source (0.4 Mt) (EC, 2001a).

Since 2000, PCDD/F emissions have had to be reported within the National Pollution Release Inventory (*see* Chapter 3). Total emissions of PCDD/F are around 150 g TEQ/y. The largest single source of contributions is waste incineration, contributing 27% of emissions. However, the total emission



from waste incinerators has been reduced from 282 g TEQ/y in 1990 to 41 g TEQ/y by 1999. Emissions from electric power generation amounted to only 5 g TEQ/y in 1999, 3% of the total, but this was an actual increase in emissions from 3 g TEQ/y in 1990. Emissions from iron manufacture in sintering plants amounted to 6 g TEQ/y in 1999, 4% of the total and showed a considerable drop from 25 g TEQ/y in 1990. Steel manufacturing in electrical arc furnaces was responsible for 11 g TEQ/y in 1999, up slightly from 9 g TEQ/y in 1990. Emissions from base metal smelting and cement kilns each contributed around 1–2% of emissions in 1999 (EC, 2001b).

been reduced as, in general, emissions from this sector are usually too insignificant to appear on national emission inventories.

Data for emissions of other organic compounds, PAH and PCDD/F, are scarce as, in the past, there have been no requirements for monitoring of these species. The few data available suggest that the clean and efficient use of coal is not a significant source of these emissions. However, less efficient uses of coal, such as some industrial combustion systems, coke manufacture and domestic combustion, can be significant contributors to regional inventories of emissions.

## 2.4.5 USA

There has been a general downward trend in VOC emissions in the USA since the mid 1960s (Goklany, 1998). Placet and others (2000) reviewed estimates for VOC emissions from the USA in 1975 and 1995. A total of 14.8 Mt of VOC were released in 1975 and only 0.73 Mt of this arose from fuel combustion in general (all fuel in all sources). By 1995 the total had only increased to 15.0 Mt of which only 0.78 Mt arose from fuel combustion. By far the greatest source of VOC emissions was solvent storage and transport, contributing 8.6 Mt in 1975 and 9.0 Mt in 1995. Data on point source emissions suggest that VOC emissions from fuel combustion (all fuels) in electrical utilities amounted to 38.4 kt in 1995 (less than 1% of the total). Emissions from industrial combustion were greater at 129.4 kt/y (3.2%). Other fuel combustion amounted to 10.8 t/y of the total 4032 kt/y emissions from all point sources.

Data for 1997 from the US EPA put VOC emissions from coal combustion in electric utilities at 32 kt/y, less than 1% of the total. Emissions from coal combustion in the industrial sector (7 kt/y) were even lower (US EPA, 1998).

Khalili and others (1995) cite data for PAH emissions in the USA during the 1980s, pointing out that such information is rarely published. The major source of PAH emissions was motor vehicles, contributing 35% of the total. Aluminium production and forest fires each contributed 17% followed by residential wood combustion (12%), coke manufacturing (11%), power generation (all fuels: 6%) and incineration (3%). No value for the total emission was given.

## 2.5 Comments

Estimating emissions of organic compounds from sources such as coal combustion is hindered by the lack of emission factors. Although emission factors are available, they are generally accepted as being highly variable and are often given as ranges rather than single values or have known associated errors. It is probably because of this known inaccuracy that few emission inventories are published.

Despite the lack of data it is clear that there has been a downward trend in total VOC emissions from most developed countries over the last decade or so. It is difficult to determine whether emissions from coal combustion have

## 3 Legislation

Much of the legislation which relates to emissions of organic compounds is concerned with ozone formation and therefore concentrates on VOC and NMVOC. Since, as shown in Chapter 2, coal utilisation makes only a minor contribution to VOC emissions, this legislation will only be reviewed briefly.

There is also legislation relating to organic emissions which have been shown to be linked to cancer in humans. This legislation relates to human exposure and therefore takes the form of maximum concentrations in ambient air or in work locations. Human exposure limits may be defined in terms of the lowest observed adverse effect level (LOAEL) or no observed adverse effect level (NOAEL) (DETR, 1999). It is widely held that PAH cannot be characterised by a threshold and that no absolutely safe exposure level can be defined. Exposure to PAH is invariably to a mixture of compounds with different potencies and effects. It is therefore common for PAH exposure limits to be defined in terms of B[a]P concentrations (DETR, 1999). This form of legislation is beyond the scope of this report.

Legislation on coke oven emissions has been covered in more detail in a separate report by the Clean Coal Centre (Reeve, 2000). Much of this legislation applies to dust, visible emissions (opacity) and odour, all of which may include organic emissions to some extent. The following sections only include details of legislation which applies specifically to emissions of organic compounds to the air from coal utilisation, including coke manufacture, not to waste water or to ambient standards.

### 3.1 International

There are a number of relevant international agreements relating to emissions of organic compounds. The United Nations Economic Commission for Europe (UNECE) has recently recognised the importance of VOC emissions in relation to photochemical oxidants and introduced a protocol for their reduction (UNECE, 1999b). The protocol, published in 1999, aims to control and reduce both national annual emissions of VOC and transboundary fluxes. The protocol specifies that signatory countries shall, as soon as possible, reduce their national annual emissions of VOC by at least 30% by the year 1999, using 1988 levels as a basis or any other annual level between 1984 and 1990. In countries where the annual emissions of VOC in 1988 were lower than 500 kt/y and 20 kg/inhabitant and 5 t/km<sup>2</sup>, the required emission reduction is lowered to meeting the 1988 levels by the year 1999. The protocol also requires the application of 'appropriate national or international emission standards to new stationary sources based on the best available techniques which are economically feasible.'

Within the protocol, the UNECE recognises the lack of accurate data on VOC emissions and behaviour and calls for

further studies involving monitoring and modelling and for the improvement of emission inventories. It is important to note that, within the protocol, coal-fired power plants are not identified as target sources. Indeed, the protocol emphasises that, *'for most countries, the VOC reduction potential for power plants is negligible'*. Eight stationary sources are named as primary targets for emissions control. These are:

- the use of solvents;
- the petroleum industry;
- organic chemical production;
- food industry;
- handling and treatment of wastes;
- agriculture;
- the iron and steel industry;
- small-scale combustion sources (residential heating and small industrial boilers).

Of these, only the latter two have any relevance to emissions from coal utilisation.

With respect to control of VOC from stationary sources, the protocol recognises that optimal VOC emissions from stationary combustion depend on the efficient use of fuel at the national level as well as 'good' operational procedures, efficient combustion appliances and advanced combustion management systems. The protocol specifically recommends the replacement of old stoves/boilers and/or fuel switching to gas. The replacement of single room stoves with central heating was also suggested, again emphasising that fuel switching to gas is a 'very effective' control measure, providing the system is leakproof (UNECE, 1999b).

The UNECE has published a 1998 protocol to the LRTAP convention which deals with persistent organic pollutants (POPs) (UNECE, 1999a). These POPs are defined within the protocol as organic substances which:

- possess toxic characteristics;
- are persistent;
- are bioaccumulative;
- are prone to long-range transboundary atmospheric transport and deposition;
- are likely to cause significant adverse human health or environmental effects near to and distant from their sources.

This protocol applies largely to the industrial production and use of compounds such as DDT and PCB, although PCDD/F, PAH and hexachlorobenzene (HCB) are also covered.

Major sources of PCDD/F are listed in the protocol and include several categories relevant to coal use:

- combustion plants providing energy;
- residential combustion;
- thermal metallurgical processes (such as aluminium, iron and steel production);
- waste incineration (including co-incineration).

The major sources of PAH are:

- residential wood and coal heating;
- open fires;
- coke and anode production;
- aluminium production (the Soedeborg process);
- wood preservation installations.

The major sources of HCB are:

- waste incineration (including co-incineration);
- thermal sources of metallurgical industries;
- use of chlorinated fuels in furnace installations.

The protocol calls for increased monitoring of these substance. It also calls for the application of best available technologies (BAT) to reduce the production of these compounds as well as the use of any process modifications or flue gas treatments available to control emissions. More details of the suggested control strategies are given in Chapter 7.

Within the protocol the following limits for PCDD/F have been set:

municipal solid waste (>3 t/h)	0.1 ng TEQ/m <sup>3</sup>
medical solid waste (>1 t/h)	0.5 ng TEQ/m <sup>3</sup>
hazardous waste (>1 t/h)	0.2 ng TEQ/m <sup>3</sup>

(where TEQ is the toxic equivalent quotient of all the congeners present relative to that of 2,3,7,8-TCDD).

This standard does not apply to coal-fired power plants but may become relevant in the future with the increase in the co-combustion of waste with coal in some coal-fired power plants in Europe.

There are no EU directives focusing on coke-oven operations specifically. However, directives on other issues, such as air and water quality and industrial pollution control, include coke ovens in the list of categories covered. Many of these directives are quite general in that they specify BAT or best practices (Reeve, 2000).

## 3.2 National

Many countries have chosen to set emission standards over and above those required by international agreements. The following sections give information on legislation within selected individual countries.

### 3.2.1 Australia

The Australian National Environmental Protection Council (ANEPCC) has developed a National Pollutant Inventory (NPI) in order to provide information on releases of specific substances to air land and water. The NPI reporting list specifies threshold values for individual elements or compounds. Emissions of each substance need only be reported if the threshold is exceeded.

The reporting lists specify a limit of 10 t/y of any element or compound and this applies to a large number of individual organic compounds such as benzene (Category 1). These

limits would not be reached by any coal-fired power plant. PAH emissions are included in Category 2a with a threshold value of 400 t/y or 1 t/h. Again these values are way above what would normally be released from a coal-fired power plant. These limits are to be tightened by the end of 2001, to be reported by September 2002. The limits for benzene and PAH remain the same and a new limit for PCDD/F is being introduced of 2,000 t/y or 2,000 t/60,000 MWh. Again, both these threshold values would not be reached by a coal-fired power plant and, since emissions do not have to be measured if they are expected or known to be below the threshold value, no action for monitoring or control is required (EA, 2001a). Emissions from sources such as coal combustion can be estimated using standardised emissions factors (EA 2001b). These emission factors were discussed in Chapter 2.

There are no state regulations applying specifically to coke making. However, all plants need a 'licence to operate' which requires ongoing environmental performance reports. Steel manufacturers have agreed to pollution reduction programmes which put a priority on environmental improvements across the steel works. New technologies must be 'best available technology economically achievable' (BATEA). Under the 1997 Protection of the Environment Operations Act a load-based licensing scheme has been introduced on the 'polluter pays' principle. The annual fee, based on an administration fee plus an operation cost, is based on the amount of a pollutant emitted, the location of the industry and the degree of harm the pollutant might cause. Batteries such as the Port Kembla battery no 3 have had to be shut down because of visible smoke emissions. No information was available on specific limits for organic emissions from coke plants (Reeve, 2000).

### 3.2.2 Belgium

In Belgium it has been shown that short term emission monitoring for PCDD/F from waste incinerators may be underestimating actual total emissions. In response to the growing concern over these emissions, the governments of the Flemish and Walloon regions of Belgium required that all waste incinerators be fitted with continuous emission monitors (CEM) for PCDD/F. This target was achieved in 1999 for all Flemish incinerators and in 2000 for all those in the Walloon region. Belgium therefore is now the country with the most extensive monitoring system for PCDD/F (Reinmann, 2001).

### 3.2.3 Canada

In 1993 the Toxic Substances Management Policy (TSMP) was developed under the original Canadian Environmental Protection Act of 1988. Within this act 16 toxic substances are identified as being released by the steel industry and coke production, including two organic species – benzene and PAH. Since then, recommendations on enhanced voluntary programmes and non-regulatory environmental performance standards have been made and directions are being established for this sector to the year 2015. There has been a call for a reduction of benzene emissions from 1993 levels by

55% by 2000, 80% by 2005 and 90% by 2015. This would be achieved by best environmental practices and enhanced monitoring. The recommendation for PAH emissions relates to coke-oven batteries. Emissions should be reduced from 1993 values by 45% by 2000, 65% by 2005 and 70% by 2015. The implementation schedule for PAH reduction targets is based on a value of emissions per unit of production, as shown in Table 12. Any new facilities would be required to meet 2015 limits. Specific targets for Ontario steel mills are shown in Table 13. New monitoring regimes have been introduced with daily inspections by plant staff and regular spot audits by provincial ministry officials (Reeve, 2000).

Environment Canada records and publishes all emissions of specified substances from all stationary sources in the National Pollutant Release Inventory (NPRI) and lists these on an impressively detailed website – [www.ec.gc.ca/pdb/npri\\_home\\_e.cfm](http://www.ec.gc.ca/pdb/npri_home_e.cfm). Since 2000, the NPRI has been required to include details of PCDD/F emissions. The NPRI gives actual emissions from individual sources such as coal-fired units and waste incinerators in different regions of Canada. This is a form of 'name and shame' approach where sources can demonstrate how well they are controlling emissions (EC, 2001b).

Canada has an Annex with the US relating to ground level

ozone pollution. The Annex was signed in December 2000 and commits both countries to reducing NO<sub>x</sub> and VOC. The Annex specifically requires a reduction of 43% of both pollutants by 2010 during the summer ozone season in Ontario, Quebec, Atlantic Canada and 18 US states. The Canadian government is spending \$77 million on reaching this target. There is concern that the target will not be met in Ontario. Ontario's coal-fired power plants are omitted from the Annex (ES&T, 2001).

### 3.2.4 Germany

In 1999 Germany specified an emission standard of 20 mg/m<sup>3</sup> for total hydrocarbons from power plants. This is the only legislation which relates directly to organic emissions from coal-fired power plants (Zevenhoven, 2001).

The German TA-Luft emission standards are more stringent than those specified by the European Union and specify minimum operating and performance requirements for sources such as charge-hole lids and coke oven doors. Although there are no emission standards for organic emissions from coking plants, there are stringent waste water standards. Emission controls and treatments such as dust control and dry and wet emission quenching mean that most of the toxic emissions are trapped in waste effluents rather than released to the air (Reeve, 2000).

### 3.2.5 People's Republic of China

The People's Republic of China is now the largest supplier of coke in the world with over 10.6 Mt produced in 1997. Beehive coke production rose almost six times as fast as conventional coke production between 1980 and 1997. It is argued that this is only possible because of China's lenient approach to environmental protection. However, the government of Shanxi Province has set more strict standards

**Table 12 Target and schedule for PAH emission reductions from Canadian coke- oven batteries** (Shaw, 1999)

Phase	Target date	PAH emission standard, g/t dry coke
1	2000	13.2
2	2005 (Level playing field date)	9.8
3	2015	8.2

**Table 13 Targets and schedules for PAH emission reductions from Ontario steel mills** (Environment Canada, 1997)

Steel mill	Emission, t 1993	Emission reduction,		
		2000*	2005*	2015*
<b>Benzene</b>				
Algoma Steel Inc	314	73	92	94
Dofasco Inc	454	48	71	83
Stelco Hilton Works	328	51	89	91
Stelco Lake Erie Works	141	66	86	89
<i>Totals</i>	1237	57	83	89
<b>PAH</b>				
Algoma Steel Inc	80.3	51	79	83
Dofasco Inc	45.4	27	44	54
Stelco Hilton Works	45.7 (estimated)	56	66	72
Stelco Lake Eries Works	15.0 (estimated)	21	39	50
<i>Totals</i>	186.4	44	64	70

\* % relative to values for 1993

**Table 14 Emission standards for existing and new mechanised coke ovens in the People's Republic of China (Tian-Rui Li, 1999)**

Pollutant	Standard level 1	Standard level 2	Standard level 3
<b>Existing mechanised coke ovens</b>			
particulates, mg/m <sup>3</sup>	1	3.5	5
benzene soluble organics, mg/m <sup>3</sup>	0.25	0.8	1.2
B[a]P, mg/m <sup>3</sup>	0.001	0.004	0.0055
<b>New mechanised coke ovens</b>			
particulates, mg/m <sup>3</sup>	–	3.5	5
benzene soluble organics, mg/m <sup>3</sup>	–	0.8	1.2
B[a]P, mg/m <sup>3</sup>	–	0.004	0.0055

**Table 15 Emission standards for existing and new unmechanised coke ovens in the People's Republic of China (Tian-Rui Li, 1999)**

Pollutant	Standard level 1	Standard level 2	Standard level 3
<b>Existing unmechanised coke ovens</b>			
particulates, mg/m <sup>3</sup>	100	300	350
sulphur dioxide, mg/m <sup>3</sup>	240	500	600
B[a]P, mg/m <sup>3</sup>	1	2	3
<b>New unmechanised coke ovens</b>			
particulates, mg/m <sup>3</sup>	250	300	–
sulphur dioxide, mg/m <sup>3</sup>	400	450	–
B[a]P, mg/m <sup>3</sup>	1.5	2	–

for new coke plants. Tables 14 and 15 show the emission standards for existing and new mechanised and non-mechanised coke ovens in China respectively. The standards include details of monitoring requirements – every 4 hours for mechanised ovens (Tian-Rui Li, 1999; Reeve, 2000).

### 3.2.6 USA

The USA does not have any definitive legislation concerning PAH abatement. However, the US EPA has specified 16 PAH as priority pollutants. These are (Mastral and Callen, 2000): naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-c,d]pyrene, benzo[g,h,i]perylene, dibenzo[a,h]anthracene

Should emissions of any of these compounds exceed 10 t/y from any source, monitoring and MACT (maximum achievable control technologies) would be invoked. This would be very unlikely with the low concentrations of PAH emitted from coal-fired power plants.

Under new Toxic Release Inventory (TRI) requirements, coal and oil fired power plants will be required to calculate PCDD/F releases for the year 2000. The US EPA expects most of these values to be emission estimates rather than actual measured emission values. Later this year (2000) the

US EPA will publish guidelines on how to calculate releases of PCDD/F and other persistent bio-accumulative toxic (PBT) chemicals. However, there is concern that the use of standard emission factors for all coal-fired plants will not be representative of actual emissions from individual plants (ES&T, 2000).

### 3.3 Comments

International legislation and action plans have concentrated on VOC as the organic emissions of most concern due to their importance in ground level ozone formation. These plans recognise the insignificance of emissions from coal utilisation. As a result, no requirements for the reduction of VOC emissions from coal utilisation are made other than recommending increased efficiency or fuel switching in the most inefficient of systems (such as domestic combustion sources).

Some PAH compounds and PCDD/F are included in national legislation in several countries because of the potential cancer risk. However, emissions from efficient coal combustion are so low that they are unlikely to trigger any requirements for monitoring or control.



## 4 Sampling and analysis

It is well recognised that the measurement of organic emissions from any source is often difficult and confusing for a number of reasons (Ridge and Seif, 2000):

- the terms TOC, NMHC, VOC and others are often confused and interchanged;
- there is no straightforward way to measure all organic compounds since they differ so greatly in properties and behaviour;
- all of the test methods have inherent limitations that restrict their applicability.

In the legislation covered in Chapter 3, a VOC was defined as *'an organic compound that participates in atmospheric photochemical reactions; that is, an organic compound other than those the administrator of the EPA designates as having negligible photochemical reactivity'*. For sampling and analysis purposes, the definition of VOC is more fundamental: *'compounds which have a vapour pressure greater than or equal to 0.13 kPa (1 mm Hg) at 20°C'* (Ridge and Seif, 2000). This means that some VOC species are not covered by legislation since, although volatile, they do not participate in ozone formation. Therefore, although it is true that most coal combustion systems do not produce large amounts of the VOC of concern (ozone forming), they may still produce measurable quantities of VOC. In order to demonstrate that the VOC produced from any source are not of concern, samples must be taken and the individual VOC must be characterised to determine whether they have any ozone formation potential. This may not be necessary for most coal-fired utility plants where the fuel and combustion conditions are relatively stable and the emissions have been characterised previously. However, smaller and more variable systems, such as industrial boilers and residential systems, may require evaluation more often to characterise and evaluate VOC emissions.

Some PAH compounds are also, by definition, VOC, since they are volatile at the specified temperature and pressure. Sampling systems for VOC will therefore capture both these groups of compounds and further analysis will be required to identify the compounds more accurately. Many of the sampling systems discussed in this Chapter have the potential to capture all three of these groups simultaneously. Because of this confusion, this Chapter includes sampling and analysis methods for all organic emissions – VOC, PAH and PCDD/F.

Deciding which method to use to monitor emissions from a specific source can require previous knowledge of the emissions. Before commencing measurement several factors must be considered (Ridge and Seif, 2000):

- the chemical composition of the organic compounds being studied;
- the expected concentration range;
- the chemical properties of the compounds (boiling point, reactivity, solubility and so on);
- the characteristics of the flue gas or effluent (such as temperature, moisture, %CO<sub>2</sub>);

- the advantages and disadvantages of the available test methods;
- the national or state testing requirements.

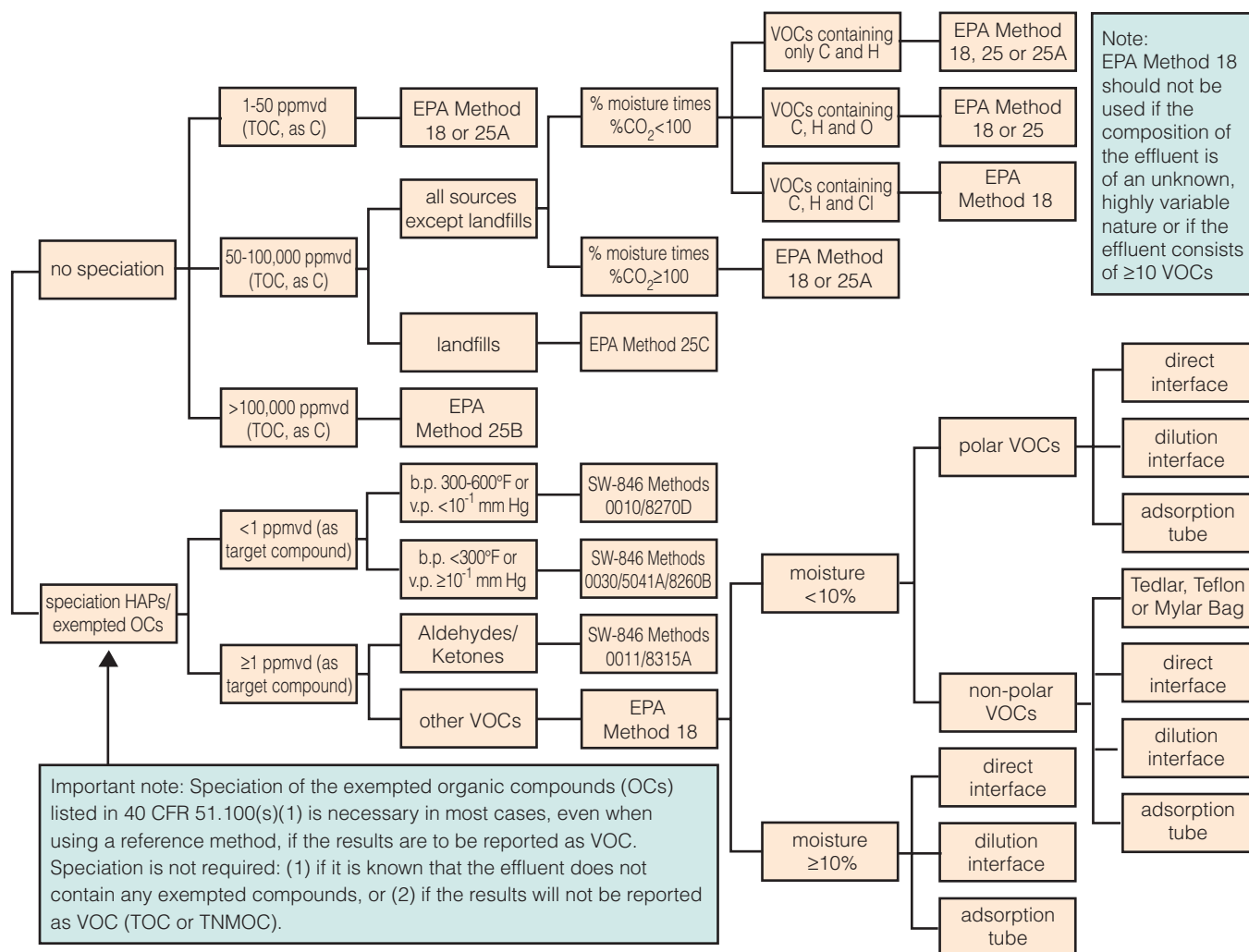
Numerous methods do cover a range of compounds. However, it is more cost-effective to focus on a small number of compounds. Figure 2 shows a general scheme for selecting a suitable method for VOC analysis (Ridge and Seif, 2000). Table 16 lists the common methods used for each of the different organic groupings in the USA. The most relevant of the individual test methods mentioned in the figure and table are discussed in more detail in the rest of this chapter.

In most situations, a pre-test is necessary in order to determine which compounds are likely to be present at a source and in what concentrations. After the pre-test, an appropriate combination of sampling and analysis techniques can be selected. Due to the large number of different compounds included within organic emissions, sampling and analysis methods tend to be relatively complex, time consuming and expensive. Results are commonly presented as total VOC or TOC as propane, as units of the most common compound present, or in units of an approved surrogate. Determination and quantification of individual compounds may be done for research purposes. However, the measurement of total organic emissions without speciation is more common. Ultimately, in many cases, the national regulations on emissions dictate what compounds must be measured.

There are legal requirements for monitoring organic compounds from many industrial processes. For example, Italian law requires that 54 organic compounds be determined in flue gas emissions from industrial combustion plants (Maspero and others, 2001). Emissions from such sources have to be monitored because they are known to be of relatively high concentrations. Emissions of organic compounds from coal combustion are generally much lower. At the moment, values for total organic emissions from coal combustion are all that may be required.

As discussed previously in this report, there are a great number of different organic compounds and isomers and only a fraction of these are well understood. According to Lewis (2000), over the next few years new technology is likely to have a significant impact on our understanding of organic compounds in the atmosphere. New techniques for on-line measurement and speciation of organic emissions are being developed.

Organic compounds may be present in both the gas and solid phase and so the sampling system must be designed to capture both solid and gas phases efficiently. There are a number of problems associated with the capture and detection of trace organic compounds. This is mainly due to their reactivity, decomposition, temperature sensitivity and volatility. For example, in the review by Mastral and Callen



**Figure 2** General scheme for the selection of a VOC reference method (Ridge and Seif, 2000)

Table 16 Methods for stack sampling organic species (Bursey, 2001)		
Compound	Sampling method	Analysis method
total organic mass	US EPA 0040 (Tedlar bag)	GC/FID
	US EPA 0010 (Semi-VOST)	GC/FID
VOC	US EPA 0040	GC/FID; GC/ECD, GC/MS
	US EPA 0030/31 (VOST)	GC/MS
SVOC	US EPA 0010 (Semi-VOST)	GC/MS
PAH	US EPA 0010	High resolution GC/MS
PCDD/F	US EPA 23 (Resin)	GC/MS

(2000), data are cited which indicate that measurements of PAH in ambient air differ by as much as 40% depending on the sampling system and analytical technique used.

An in-depth study of the many different methods for

measuring organic compounds is beyond the scope of this report. The following sections briefly review the different methods used for sampling and analysis of organic compounds from coal utilisation. Methods for measurement of ambient concentrations are also included. This information should give the reader enough background information to understand the complexity of organic compounds and the limitations in research into their behaviour.

## 4.1 Sampling criteria

One of the main problems with sampling any pollutant is proving that the sample collected is representative. Unless the measurement is being performed by a continuous emission monitoring system, the sample collected is arguably just a 'snap-shot' and may not be truly representative of the total source emissions. Although emissions from large coal-fired power plants tend to be relatively stable over time (except at start-up and shut-down), this is not the case for other sources. Smaller industrial units, waste incineration systems and residential stoves burn fuel in more distinct batches with different fuel characteristics and combustion temperatures over time. For example, Heger and others (2001) describe the sampling in real-time of PCDD/F emissions at a hazardous

waste incinerator using on-line analysis (TOFMS, *see later*). The study demonstrated clear differences in emissions between stationary combustion conditions and transient emission 'puffs'. Choosing the time of analysis can be just as important as the selection of position and of the type of equipment to be used if representative results are to be obtained. It is important to remember the transient nature of many coal combustion and utilisation source emissions when reviewing emission data.

There are a number of different locations where organic samples may be collected. The methods used for sampling and analysis in each case are based on the same principles and therefore are often quite similar. Flue gas sampling is relatively straightforward compared to ambient sampling and fugitive sampling (sampling from an open source such as a coke oven door or a domestic fire). Each stack is required by law to have an access port for sample collection. A probe is inserted through this port and the flue gas is either analysed in situ or a sample is withdrawn for analysis elsewhere. The sample may be withdrawn isokinetically (at the same velocity as the stack to provide a representative sample) or non-isokinetically (where the sample nozzle inlet velocity is different from that in the stack). In most cases sampling is performed at several points across the cross-section of the stack to reduce effects of potential stratification and uneven distribution of particulates. A minimum distance is required between the sampling location and any disruption to the flue gas flow, such as cyclones, jets, bends or turns in the pipes. This helps avoid situations such as cyclonic flow or stagnant areas of gas close to stack walls where the concentrations of pollutant species may be much higher or lower than elsewhere.

Ambient organic compounds are commonly sampled by passive diffusion into tubes containing a sorbent such as charcoal, Tenax or silica gel. Since the concentration of organic compounds in ambient air is generally very low, passive sampling allows the collection of sample over extended periods of time – days or even weeks. The trapped sample can then be released directly to the analysis system following thermal desorption. For example, US EPA Method TO-15 collects whole air samples in passive canisters for such analysis. An excellent review of ambient sampling for organic compounds is given by Aragon and others (2000). The capture of organic compounds associated with ambient PM<sub>10</sub> and PM<sub>2.5</sub> particulate matter is discussed in more detail in a separate report from the Clean Coal Centre (Sloss, 1998).

US EPA Method 21 is a procedure for identifying VOC leaks from process equipment such as valves, flanges, pumps, compressors and other vents and seals commonly found at chemical and petroleum process facilities. The method allows the use of portable ambient VOC detection devices based on FID or IR absorption (*see below*) (Westlin, 2001).

Fugitive sampling may be performed occasionally to evaluate sources such as leaks in coke oven doors where organic compounds are released by an uncontrolled means. These sources are not standardised either in size, shape or flow rate. Direct stack emission methods are not suitable as it would be difficult to select a sample point which would be shown to be

truly representative. On the other hand, ambient measurement close to the emission point would arguably not be representative either as the spread of emissions from the point or points of release would not be uniform. Fugitive emissions are often sampled by creating some form of control area or hood into which leaks are released. A combination of ambient or stack methods is then used to try and obtain a representative sample from the controlled area which will then be analysed and the results calculated such that a figure is obtained for total release into a defined area over time. Oanh and others (1999) used a hood to capture emissions from residential stoves burning various fuels including charcoal. Sampling was performed through a sampling port in the hood pipe. A sample of the gas was drawn isokinetically into a standard VOC sampling train (*see below*). The sampling period covered the whole burning cycle from the moment of stable firing to the end of the burning process when all visible combustion had stopped. Values for fugitive emissions are clearly prone to great amounts of error and should be used only as an indicator to the order of magnitude of potential emissions.

As mentioned above, the selection of an appropriate measurement method for organic compounds requires planning and care as samples vary in concentration, reactivity and so on. Knowledge of the chemical composition of the organic compounds present in advance is often necessary. For example, the use of US EPA Method 18, based on sampling and then analysis by gas chromatography, for quantifying emissions of specific target compounds is problematic until one has a good knowledge of the stack gas constituents and the range of expected concentrations. US EPA Method 25 may not be adequate when the effluent contains chlorinated organic compounds and/or oxygenated compounds (Ridge and Seif, 2000).

It is clear that a large amount of information on the source and its emissions is required before sampling should commence. For new or unique sources this means a pre-test with various methods to make an initial determination of what kind of organic compounds and approximate concentrations may be present. For well established sources such as coal-fired power plants, emissions are generally very similar from source to source and so more standardised procedures may be adopted. The following section reviews the most common methods for sampling organic compounds.

## 4.2 Sample collection

Emission monitoring for organic compounds may be performed in two ways:

- in situ, with a system which detects these compounds in the flue gas as they travel through the stack or ambient air; or
- extractive, where the sample is trapped by one of the following means:
  - a in an inert bag (a grab sample);
  - b in a liquid impinger solution; or
  - c in solid media (activated carbon or resin).

Many in situ systems can offer continuous and almost



immediate results whereas extractive methods normally involve the sample being stored or sent to a laboratory elsewhere for analysis. Extractive systems may not produce results immediately but do produce samples which are suitable for more detailed analysis. In situ systems are generally analysis systems which are directly interfaced to the emission source, avoiding the sampling step. Analysis systems are discussed in Section 4.4.

There are a number of problems which arise when samples of organic species are withdrawn from the stack for analysis. High sampling temperatures can cause thermal desorption and burning of resins and therefore the flue gas is commonly cooled to around 20°C before entering any sampling system. Flue gases from coal combustion system are generally acidic due to the presence of species such as SO<sub>2</sub> and HCl. Accumulation of acidic material in the apparatus can interfere with analysis of the sample and neutralisation may be necessary. Professional sampling teams are trained to minimise such problems.

Sources such as coal-fired power plants are generally regarded as 'wet'. The water present in the flue gas can interfere with analysis by diluting the collection media or causing problems with the analytical system. Cooling and drying treatments are therefore common in the sampling systems chosen.

In some tall stacks it is common for the sampling crew to use a long umbilical tube between the sample port and the capture and analysis system. This saves the carrying of heavy and delicate equipment up the side of the stack. However, the extended surface area of the umbilical probe can be a site for significant loss of organic species.

### 4.2.1 Grab sampling

US EPA Method 18 allows an option for grab sampling based on the capture of flue gas in a Tedlar bag which is kept chilled during transport and storage. For organic compounds with boiling points below 30°C the Tedlar bag system is used and the sample can be applied directly to the analysis system. US EPA Method 0040 also specifies sampling with Tedlar bags.

In general, samples collected in Tedlar bags must be analysed within 48 hours of collection. A spike of known quantity is added to the sample bag at the time of collection of the sample in order to calculate the recovery of the sample. Aluminised Mylar bags are recommended for low concentration studies because of the lower permeation rate. VOC samples must be protected from sunlight at all times by covering or wrapping the sample. Teflon tubing must be used throughout; Tygon tubing is not acceptable (Ridge and Seif, 2000).

An alternative to the Tedlar bag is the canister method, described under US EPA Method TO-14. This is primarily an ambient monitoring method and is still under development for use on flue gases and some argue that it should not be considered for this purpose at all. The canister is made of

stainless steel with an internal coating of chrome-nickel oxide. The canister is evacuated prior to use and a sample is taken isokinetically at an appropriate point in the flue. The collected condensate is removed and discarded. Commercial canisters such as Silco steel are commonly used for ambient studies. Canisters are required to be clean to below the detection limit (0.2 ppbv C) for organic studies (Daughtrey and others, 2001).

It is unclear to what extent flue gas components within a grab sampling bag or canister may undergo reactions or decomposition (Sloss and Gardner, 1995). Fan and others (2001) describe the design and evaluation of a metal-coated multi-layer Tedlar (MMT) bag for the capture and detection of ambient gases including total hydrocarbons. Initial results showed that the compounds were more stable in the MMT bag than in a standard Tedlar bag and that no 'significant' changes in concentration were noted for any species after three months storage at room temperature. Other advantages include the lower cost, lighter weight and recycling potential of the system.

### 4.2.2 Solid sampling media

Some of the more volatile organic species cannot be captured easily by condensation or in solution and require the use of specific sorbents. Commonly used sorbents include carbon and commercial media such as XAD resin (for semivolatiles, boiling points >100°C) and Tenax. US EPA Method 18 for stack sampling allows the sampling of VOC with any adsorption material that meets performance criteria. Charcoal adsorption tubes cannot be used if the moisture content exceeds 3% (Ridge and Seif, 2000). Several commercial ambient monitors for VOC are based on passive diffusion into solid sample media.

Different studies have been performed to evaluate different media. For example, Tolnai and others (2000) compared different adsorbents for the diffusive sampling of VOC in ambient air in Hungary. Although the different media produced good agreement, Carbopack B was found to be more sensitive than Tenax TA or Tenax GR for volatile compounds. However, its accuracy was limited for the less volatile compounds. Even at low background concentrations (unspecified), ten days of sampling was found to be sufficient for the analysis of all the ten VOC compounds studied.

Bertoni and others (2000) describe the development of a new 'Analyst' ambient sampler which allows both collection and solvent extraction of VOC in the same vial. The adsorbent used is activated charcoal. Once the sample has been collected and the vial sealed for transport and storage, solvent and an internal standard can be injected by means of a syringe. An aliquot of the resulting sample solution can then be withdrawn for injection directly into a gas chromatography (GC; *see* Section 4.4) column. By keeping the system sealed during this process, the possibility of contamination is greatly reduced. The system also reduces the operator's contact with toxic solvent solutions.

Carbon-based sorbents cannot be reused but Tenax is

routinely cleaned and re-used after being subjected to extensive pre-cleaning procedures to ensure artifact-free analysis (Aragon and others, 2000). Most analyses on samples from stationary sources are based on thermal desorption methods rather than solvent desorption. The use of solvents is effectively a dilution stage which is avoided when dealing with the trace concentrations encountered in flue gas studies. Thermal desorption followed by cryogenic condensation allows the whole sample to be analysed.

### 4.2.3 Sampling trains

Sampling trains, involving a combination of filters, solid media and liquid impingers are the most common method used for stack sampling. The US EPA have produced a modified version of a universal sampling train (Method 5) for the capture of organic compounds. This system is commercially available as the Andersen Universal sampler, as shown in Figure 3. This method, US EPA Method 25, captures VOC in impingers. If the flue gas contains high

moisture and high CO<sub>2</sub> then a high bias is likely. The method also has a relatively high detection limit, around 50 ppm as C. US EPA Method 25 is based on FID detection which responds to hydrocarbons and is therefore not recommended for the measurement of chlorinated organic compounds (Ridge and Seif, 2000).

US EPA Method 0010 uses this system for the capture of semivolatile organic compounds and is known as the SVOC train. It is also the method adopted by Environment Canada and is the most widely accepted method for the measurement of organic compounds with boiling points above 100°C. The sample stream is collected isokinetically and passes through an optional cyclone and filter (to remove larger particles) and then through a glass fibre filter. It then passes through a water-cooled condenser into a tube containing XAD-2 resin. This resin is kept below 20°C by water cooling. The condensate is collected in a condensate trap. The impingers in the train which follow the condenser and resin contain deionised water and ethylene glycol as a back up to the resin. Silica gel also be included to protect the pump from

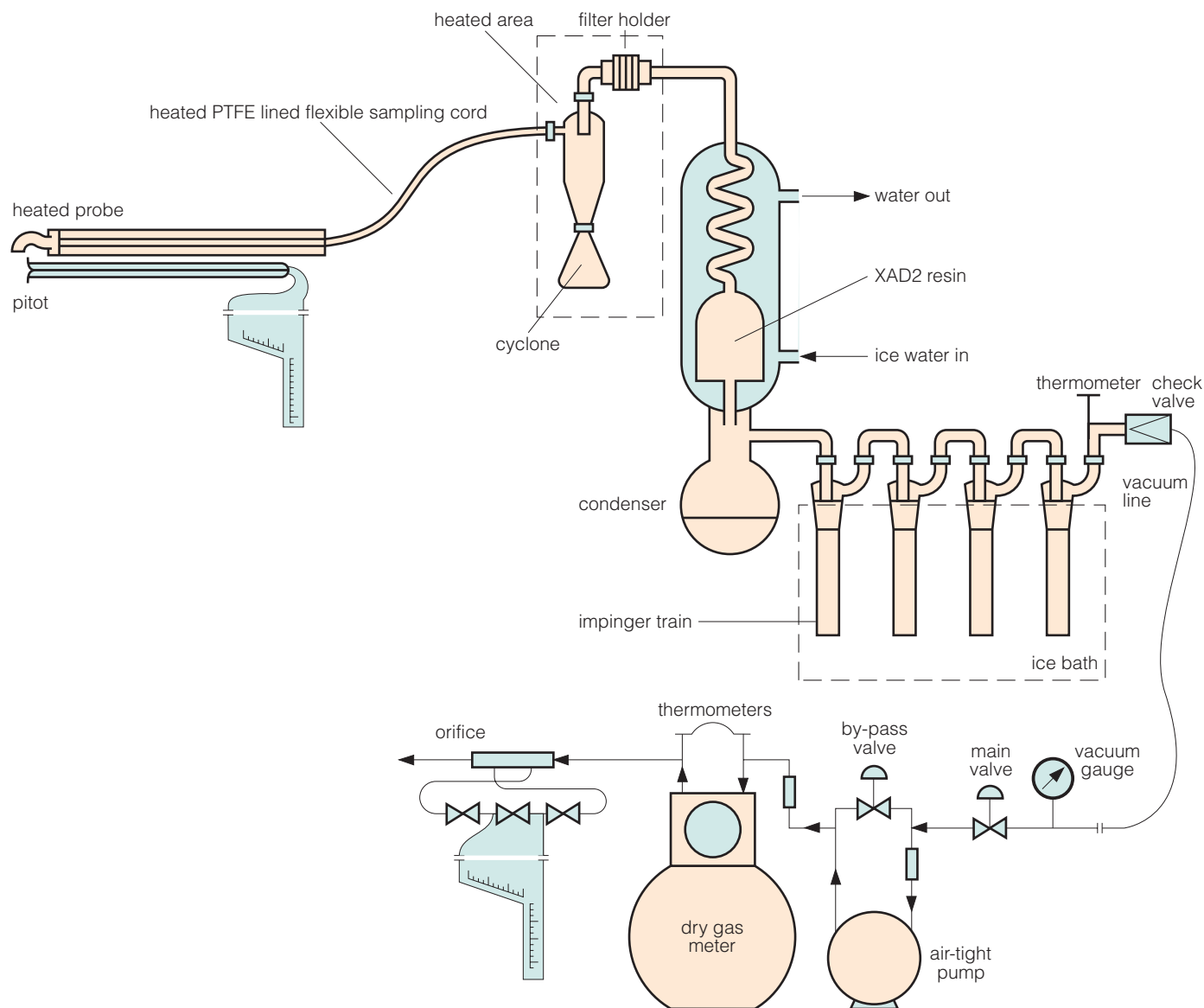


Figure 3 Modified US EPA Method 5 sampling train (Jackson and King, 1993)

contamination. Moisture is removed in the condenser and receiver to prevent the build up of water which may introduce channels through the resin or block pores, lowering the organic affinity. Sampling times are normally quite long – between 2 and 8 hours – to allow a large enough sample to be collected for analysis (a minimum of 3.4 m<sup>3</sup> of gas).

The SVOC system also captures halogenated compounds including PCDD/F. Although the SVOC method can be used to measure over a hundred different substances, more accurate results are obtained when the sample is split into several extracts for multiple analysis, concentrating on the individual species or species types.

US EPA Method 0030 (or Method 0031) is known more often as the volatile organic sampling train (VOST). This train uses solid sorbents (Tenax and charcoal) to trap VOC. The system is non-isokinetic and is suitable for compounds with boiling points within the range 30–100°C. The VOST train uses some of the same components as the SVOC train and is shown in Figure 4. Particles are captured in a glass wool filter which is discarded since the low-boiling compounds are not associated with this fraction. The Tenax and charcoal cartridges catch the organic compounds. Multiple sampling is often required to provide enough sample for analysis. Because the detection limits for these species are low and the volatility high, the samples are generally heat desorbed directly onto the analytical system. The VOST also captures halogenated compounds. Problems have been reported for the VOST system including claims that it produces extremely variable and often non-reproducible results for benzene and toluene (Sloss and Gardner, 1995).

The VOST can be run at different flow rates:

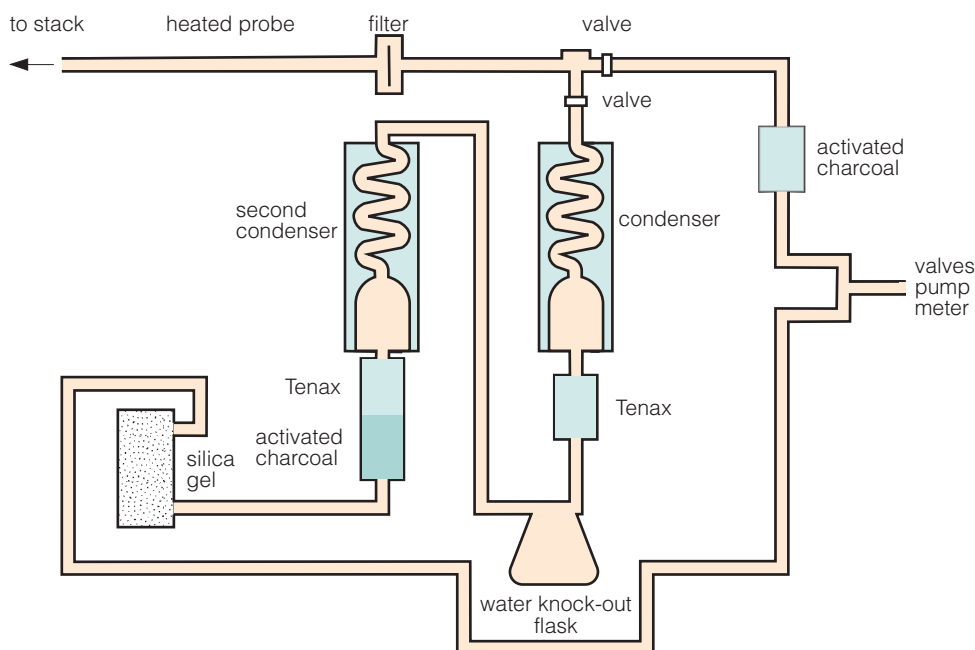
- FAST-VOST, 1 l/min for 20 minutes;
- SLO-VOST, 0.25 l/min for 1 hour.

The SLO-VOST is the preferred method for the capture of VOC with boiling points below 35°C.

German VDI method 3873 involves isokinetic sampling and dilution 10:1 with dried filtered air. The temperature of the sample is lowered from stack temperature (over 170°C) down to 50°C. A paraffin impregnated filter is used to trap particles and condensed organic matter whilst those remaining in the vapour phase and captured in the back-up absorbent trap containing a solid sorbent such as Porapak or Florisil. This is a high volume method where a large volume of sample is taken over an extended period of time (hours) to ensure that a representative sample is obtained (Sloss and Gardner, 1995).

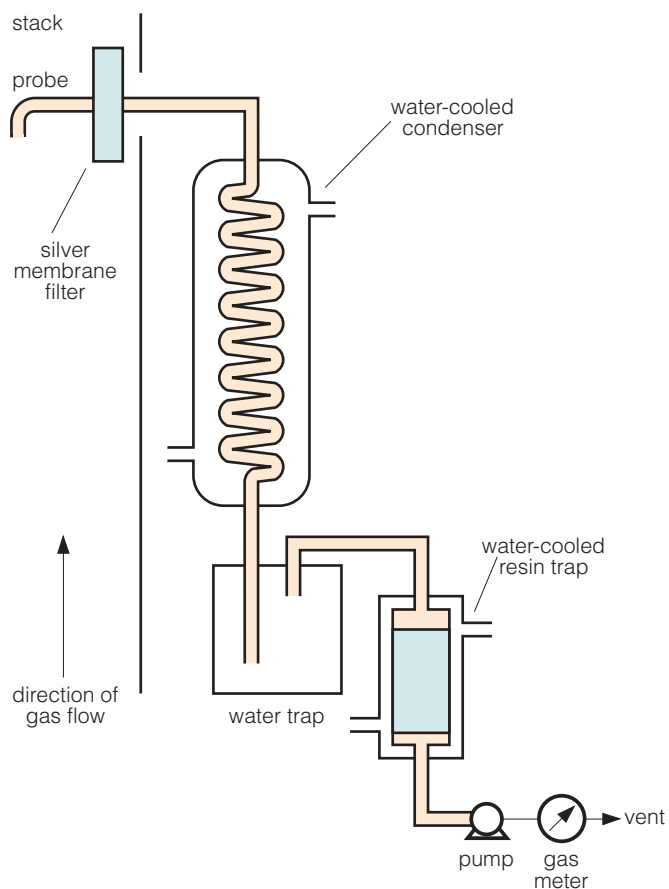
US EPA Method 23 has been defined for the capture of PCDD/F and is shown in Figure 5. Similar, if not identical, methods have been adopted in Europe by the Nordic Council of Ministers. It has been adopted as the French National Standard and also as the German standard VDI 3499. The sampling train includes a receiver between the condenser and the XAD-2 resin module and also includes a low temperature third impinger. Stainless steel nozzles must be nickel plated or made of glass or quartz and the inner liners of the probes and particle collection systems must also be made of glass or quartz, depending on the stack temperature. This prevents possible reaction on metallic surfaces. The European standard for PCDD/F, EN 1948 parts 1-3, was approved and ratified in 1996 and is similar to US EPA Method 23. A continuous sampling system called the AMESA has been commercialised by Becker Messtechnik in Germany. The system captures PCDD/F in a series of XAD-2 cartridges in an automated Method 23 train. The capture of the PCDD/F can be continuous and average results given for the whole of the sampling period. All waste incinerators in Belgium are now fitted with this technology (Reinmann, 2001).

The Californian Air Resources Board (CARB) has developed



**Figure 4** Volatile organics sampling train (Sloss and Gardner, 1995)

a combined train for sampling both PAH and PCDD/F simultaneously. The method is, like the others, a modified Method 5 impinger train using the sorbents methanol, toluene and methylene chloride. It is virtually identical to a method recommended by Environment Canada.



**Figure 5 US EPA Method 23 train for dioxins and furans (Coleman, 1993)**

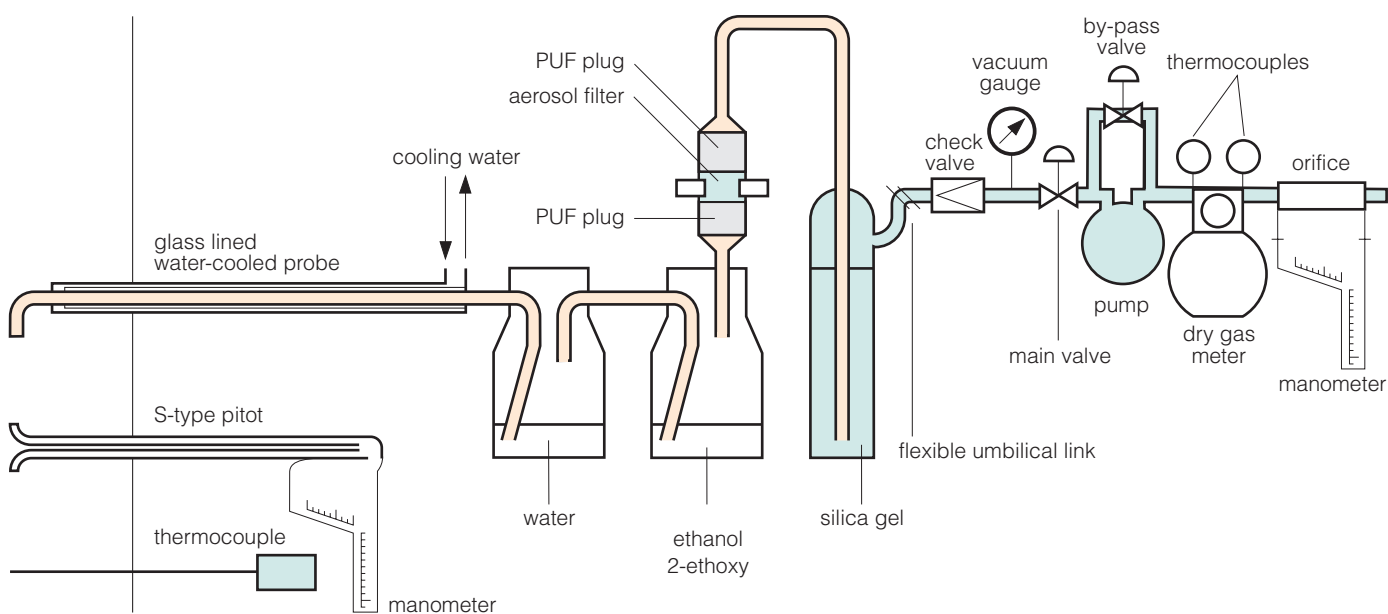
A simpler and smaller version of the hydrocarbon sampling trains has been designed for use on narrow ducts of elevated platforms. The Compact Trace Hydrocarbon Sampler incorporates a filter holder which can be placed inside or outside of the stack, depending on the available space. The isokinetic system passes the filtered flue gas through a water-cooled condenser with a water trap to a water-cooled resin trap.

Several different sources in countries such as Sweden, Norway and Finland have all, independently, developed very similar water-cooled probes for PCDD/F sampling. Figure 6 shows the basic system. There is no filter or early particle capture system. Instead rapid condensation is induced so that the particles are collected as condensation nuclei with the liquid condensate. There is a 2-ethoxyethanol impinger, a polyurethane foam (PUF) plug and an aerosol filter followed by a second PUF plug to catch gas-phase PCDD/F.

A High Volume Sampler has been designed for the capture of greater quantities of PCDD/F. The system incorporates a BCURA (British Coal Utilisation Research Association) cyclone system behind the initial filter and prior to the condensation and resin traps. The system is operated pseudo-isokinetically and samples at five to ten times the flow rate of the other modified Method 5 systems discussed above (Sloss and Gardner, 1995).

#### 4.2.4 Cryogenic sampling

Cryogenic sampling has been used for the pre-concentration of ambient VOC prior to analysis by GC-FID. Cryogenic trapping can be used, more commonly on dilute ambient samples, to pre-concentrate VOCs trapped in canisters or grab bags (Aragon and others, 2000).



**Figure 6 Water-cooled probe (Coleman, 1993)**

### 4.3 Sample preparation

The sampling techniques discussed in this chapter collect a complex mixture of many different types of organic compounds. Once sampled, organic compounds must be stored and transported to a suitably qualified laboratory for analysis. Many samples are in liquid form, either as condensate or in liquid impingers. Cleaning and pre-separation of these species is therefore necessary prior to analysis.

Sample collection requirements are commonly defined within the sampling standard, for example sample clean-up methods are defined in the US EPA standard methods. The method of removing samples from various parts of the sampling train depends on the type of sampling system and the physical state of the sample (particulate, liquid or gas) and the type of analysis which is to be performed.

Filtered particles may contain a significant proportion of the target organic species, especially if the target species are PCDD/F. Solid samples in cyclones or on filters are removed by shaking and brushing. Removal of organic species from particulates is commonly achieved with Soxhlet extraction, the transfer of the species of interest into an organic solvent such as toluene. Subsequent treatment to remove this solvent can concentrate the sample into a small volume (around 2 ml) which is ideal for analysis.

Holland and others (1996) argue that bulk extraction of organic compounds from substrates such as fly ash particles can end up with results being non-quantitative. Irreversible adsorption of some species to substrates may limit the accuracy of extraction-based techniques. Extractions give average results for a large number of particles and recover organic material from particle pores as well as the surface of the particles. This loses any information on organic surface components and their distribution and may give false information on the availability of some species for release or reaction in the environment. Once the total organic components have been extracted it is impossible to correlate the information with surface elemental composition. Holland and others (1996) therefore suggest that surface analysis of particles with methods such as scanning electron microscopy and secondary ion mass spectrometry would give more representative results (*see below*).

Samples trapped in solutions in impinger bottles are generally capped, wrapped in foil (for light sensitive species) and kept cool. Contents of separate impingers may be pooled to provide a larger sample for analysis. Solutions are often removed from the impingers by rinsing with fresh impinger solution, again noting the dilution ratio. Material collected from rinses and impingers can be evaporated to a small volume which is filtered and extracted several times with methylene chloride. The organic phase is then dried with anhydrous sodium sulphate and the volume reduced to a small concentrated sample for analysis.

Portions of the sample may be attached to solid resin material. Resin tubes are covered with foil during storage to

prevent photo-degradation of the trapped organic matter. Samples adsorbed to Tenax are desorbed thermally at temperatures of around 250°C. The desorbed gases can be carried directly into the analytical system (such as FTIR) by a carrier gas such as nitrogen. Samples collected by the VOST system (*see* Section 4.2.3) have to be thermally desorbed and concentrated onto a cooled, analytical sorbent trap such as Tenax before analysis can take place. A purge gas and thermal desorption is then used to transfer the analytes directly to the analysis system (Sloss and Gardner, 1995). Organic compounds of high molecular weight (larger than naphthalene) may not be removed easily by heat desorption from resins and may require study by a different means such as Soxhlet extraction. Microwave digestion can also be used to desorb samples from solid collection media (Aragon and others, 2000).

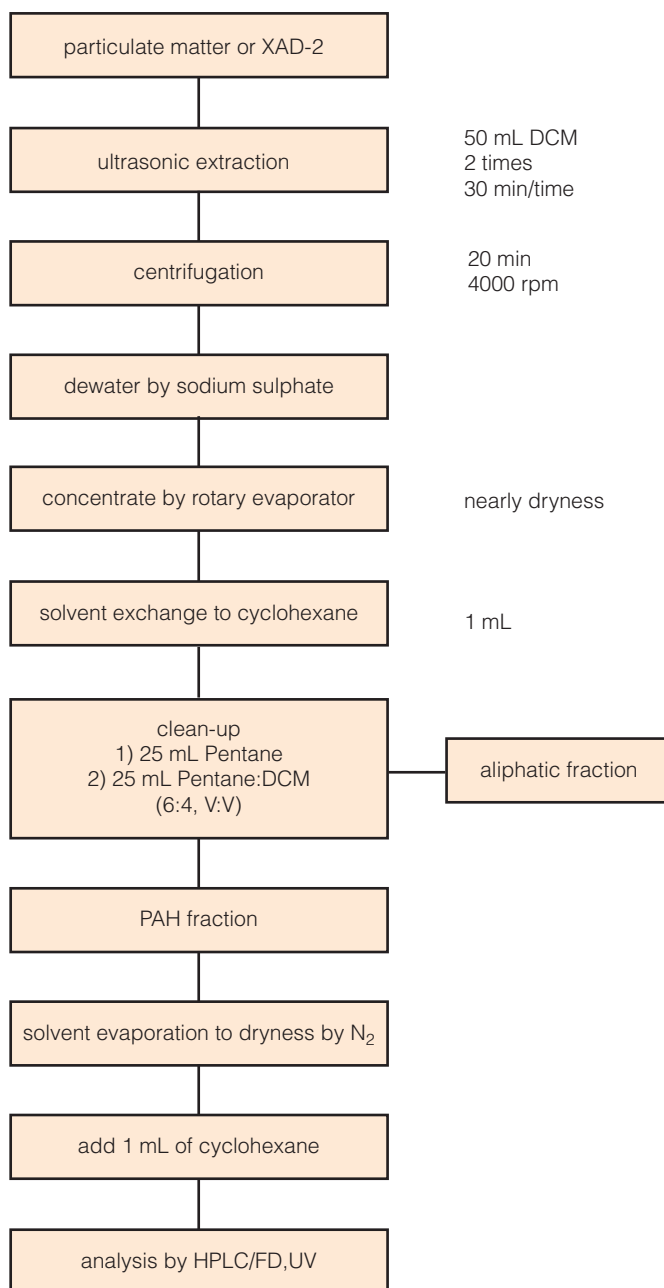
Ultrasonic extraction is based on the principle of high frequency disruption caused by sound waves. Supercritical fluid extraction is a popular method for the extraction of organic compounds from solid environmental samples. Focused microwave extraction (FMW) is a quicker method (10 minutes) and requires a lower solvent volume (Aragon and others, 2000).

Figure 7 shows an example of an extraction procedure. This system is very typical and was used by Oanh and others (1999) to measure PAH in particulate matter from residential fuel combustion.

Koziel and Pawliszyn (2001) describe the use of solid phase microextraction (SPME) for the study of VOC in ambient air. SPME offers the advantage over other sampling methods in that the steps for sample collection, pre-concentration and transfer of analytes for GC analysis are all combined. SPME can also be interfaced with conventional autosamplers to provide continuous VOC analysis. SPME is used most commonly for indoor sampling but is being tested for use in other ambient and source measurements. The principle of SPME is the use of an appropriate fibre coating to adsorb the organic compounds. Examples of suitable fibres include several based on polydimethylsiloxane (PDMS).

Although the majority of the sample is collected in the target filter, resin, impinger or in all three, some of the sample may actually be deposited within the workings of the sampling system – on the nozzle, along the inside of the probe and other connecting systems. The probe leading up to the filter is brushed to remove any particles which have adhered to the probe wall. If any organic compounds are expected to be present in this particulate phase then the brushed particles are added to the filter catch prior to analysis. The solvents used to rinse down the inside of probes varies from method to method. Hexane, acetone, methylene chloride or toluene may be used separately or combined. If extended flexible links (umbilicals) are used then these must be cleaned thoroughly as they are a major site for sample loss and cross-contamination between studies. This rinsing step is effectively a dilution step and so great care must be taken to accurately record the amount of liquid used in each step. Studies have shown the loss of as much as 50% of captured organic species may be associated with glassware, including





**Figure 7 Sample preparation procedures** (Oanh and others, 1999)

the probe and the impingers (Sloss and Gardner, 1995). Unless care is taken to recover this fraction, results will clearly be inaccurate.

Once collected, the sample must be transported quickly for analysis before any form of degradation can occur. Sample spikes of known quantities of selected species, commonly isotopically labelled compounds, are added to determine losses during sampling and storage. Blanks from a complete but unused sampling system provide data on background contamination from the system itself.

## 4.4 Analysis

Since the legislation on organic emissions from sources such

as coal combustion has been relatively sparse to date, most analysis has been for total hydrocarbons or total VOC. However, if necessary, analytical techniques are available to determine individual organic compounds quantitatively from a varied mixture. The complex chemistry of organic compounds results in many isomers of the same chemical formula. For example,  $C_{16}H_{10}$  could be one of four PAH with 28 possible monomethyl isomers. Even more complexity occurs with larger compounds which have multiple substitutions or saturated ring substitutions. Since there are 75 polychlorinated dibenzo-dioxins and 146 polychlorinated dibenzofurans it is not practical to analyse each of these compounds routinely. According to Lewis (2000) of the huge number of instruments and methods reported, historically most describe, at best, the determination of 30 or 40 individual compounds, irrespective of chemical functionality, column or detector type. For the moment, the majority of studies on organic emissions from sources such as coal-fired power plants will concentrated simply on measuring total organic emissions as TOC or VOC. Similarly, until there is any legislation which applies to specific congeners, PCDD/F analysis will continue to be performed on groups according to the amount of chlorine substitution (tetra, penta and so on). However, currently available analysis methods are providing necessary information on organic compounds and their behaviour in coal utilisation systems for research purposes.

### 4.4.1 Chromatography

**Liquid column chromatography** is a common technique used between sample cleaning and preparation, and analysis as it allows separation of the compounds into individual fractions which can be analysed successively. The choice of chromatographic column depends on the type of compounds being studied and various commercial columns are available. For example, many systems are based on multi-column liquid chromatography purification with silica gel slurred in hexane followed by a fluorisil column (84% silica, 15% magnesia, 1% sodium sulphate). The final elution is with dichloromethane/hexane and the resulting solution is solvent exchanged to nonane.

For VOC with fewer than 24 carbon atoms, wall coated open-tubular capillary columns made from fused silica may be used. A wide range of liquid phases can be used to solve a number of analytical problems using these columns as a base. Elution is commonly performed with hexane and the final sample can be further concentrated by freeze drying. Despite the availability of numerous commercial columns, the large number of similar organic compounds means that co-elution is a common problem.

**Gas chromatography (GC)** is a more advanced version of gel or solid column chromatography which allows compounds present in the now cleaned sample to enter the detection device separately. This final separation stage is probably the most critical part of the analysis as the compounds are often identified by elution times. The principle of gas chromatography is the separation of compounds by their different speeds of transport through a

stationary phase coated on the inside of a fused silica capillary column. The organic compounds are retained by the strength of their interaction with the stationary phase. The selection of the stationary phase depends upon the target species. The temperature range is selected to ensure that the species being studied remain volatile. GC is commonly used for the detection of compounds containing up to 24 carbon atoms.

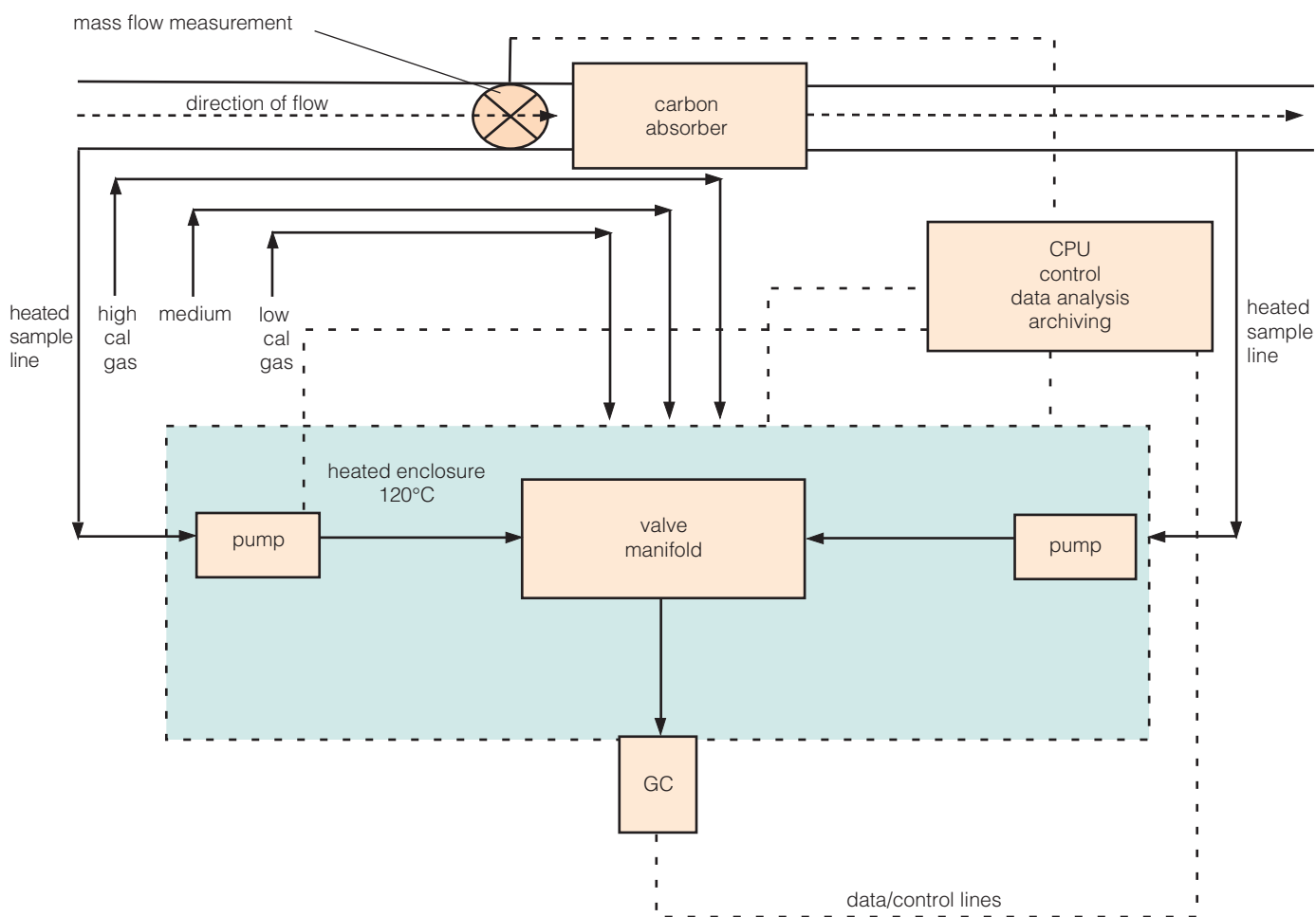
US EPA Method 18 for VOC allows the capture of samples by either grab sampling or any suitable adsorption material (*see* Section 4.2.3). The sample is then analysed by GC analysis. The method requires five injections of sample per run and triplicate calibration (Westlin, 2001).

In most labs, GC is interfaced directly with a detector, commonly a mass spectrometer (GCMS). The sample is injected into the capillary column and then the column is heated at a continuous rate to allow the individual compounds to elute separately into the detector. PAH commonly elute at between 80 and 300°C whereas the range for PCDD/F may be smaller at around 140–275°C. Elution times vary from minutes to hours depending on the compounds and the amount of resolution required. Identification of individual compounds is made by correlating results with the elution of known calibration standards.

Skilled interpretation of mass spectra is required for unknown compounds (Sloss and Gardner, 1995).

Coleman and others (1996) describe the development of a continuous emission monitor based on GC analysis for VOCs. A diagram of the system is shown in Figure 8. Coleman and others argue that currently available CEM systems for VOC cannot speciate individual compounds and are accurate only if they measure one compound or if the relative proportion of compounds in the mixture do not change. The system is based on a dual-column gas chromatograph equipped with thermal conductivity detectors in which separation is optimised for fast chromatography. Nine different VOCs plus methane and CO<sub>2</sub> can be separated and quantified every two minutes with a reproducibility of better than 5% for most VOCs. More VOCs can be analysed by using a selection of chromatography columns. The system is reported to be rugged and reliable and does not need to be operated by highly trained personnel as is the case with other organic analysis systems.

**High Performance Liquid Chromatography (HPLC)** is more useful than GC for high molecular weight organic compounds (non-volatiles) and has an upper size limit of around 38 carbon atoms (13 rings). It is considered more isomer specific than GC and is more suitable for polar,



**Figure 8** Functional system diagram of a GC CEM (Coleman and others, 1996)

fragile or thermally labile compounds. In HPLC the sample must be soluble in the mobile phase. Analysis can be performed with UV detection and, as with GC, the identification of individual compounds is made by correlation to calibration standards. HPLC is faster and cheaper than GCMS but often not as sensitive.

#### 4.4.2 Flame ionisation detection

Flame ionisation detection (FID) is the most common method used for detection of VOC. A current is produced which is proportional to the mass flow rate of the organically bound carbon atoms. The sum of the total hydrocarbons is therefore detected. By heating the sample gases to 950°C in a platinum furnace all hydrocarbons other than methane are oxidised. The oxidation may not be complete and methane can still influence the results but this is not a problem in coal-fired plants where methane concentrations should be very low. FID is a simple method for on-line detection of total hydrocarbon contents of flue gas and is the designated method for measuring total organic compounds in countries such as the USA (US EPA Method 25A). The European standard for TOC is method PrEN12619 which includes an option for the use of FID.

FID systems are commonly calibrated with methane or propane and the results are therefore expressed as ppmv of methane or propane equivalents. Not all substances give a molar response and therefore a response factor may be calculated for a reference substance. FID is less sensitive to carbon compounds containing sulphur, oxygen and halogens and therefore other techniques are recommended for such compounds. Detection limits for FID are around the ppm level. At low concentrations there can be erroneous results caused by sample manipulation (oxidation, reduction, backflushing and so on) (Ridge and Seif, 2000).

FID can be used in conjunction with GC to provide quantitative information on individual components but this method is considered relatively non-selective compared to other techniques. Daughtrey and others (2001) compared GCMS and GCFID for the study of VOC in ambient air and found that, if the concentrations were sufficiently above detection limits, the agreement between the methods, even with independent calibration, was excellent.

**Photoionisation detection (PID)** is variation on FID which may be more appropriate for some compounds, especially chlorinated forms. PID can be used in conjunction with electron capture detection (ECD) for the analysis of chlorinated aromatic compounds (Sloss and Gardner, 1995).

#### 4.4.3 Infrared

Organic compounds can be detected in the infrared range. The Fourier Transform version (**FTIR**) can detect up to 100 compounds simultaneously and almost continuously. Although FTIR can be performed on-line on filtered flue gases, problems can arise with contamination and the high

temperatures encountered. It is also possible for the sample to be collected on a resin such as Tenax and introduced to the FTIR system following thermal desorption. FTIR can be operated remotely for the detection of ambient VOC over large areas (Aragon and others, 2000).

Non-dispersive IR (**NDIR**) differs from other IR systems in that the radiation is not split prior to passing through the system but instead the absorption of radiation passing through the sample cell is compared with radiation passing through a reference cell. NDIR systems tend to be cheaper than other IR based systems but less sensitive due to the interferences from other gases. Scrubbing systems may be used prior to analysis to remove gases such as SO<sub>2</sub>, NO<sub>2</sub> and CO<sub>2</sub>. NDIR is specified within US EPA Method 25B.

Infrared differential absorption lidar (**IRDIAL**) can detect ambient VOC at long distances (up to several km). Differential optical absorption spectroscopy (**DOAS**) is reported to have high sensitivity and good time resolution (a few minutes) (Aragon and others, 2000).

#### 4.4.4 Ultraviolet

Not all the common analysis methods described above will detect all the species of interest at the accuracy or resolution required. UV detectors can be used in parallel with fluorescence detectors to detect less sensitive compounds. For example, acenaphthylene does not fluoresce and must be detected with a UV detector.

#### 4.4.5 Mass spectrometry

In mass spectrometry (MS) the sample is ionised by a high energy electron beam and fragmented into charged pieces. The fragments are separated by a magnetic field and the charge to mass ratio is measured. This ratio is used to identify the components and quantify them. MS therefore provides molecular weight values and some structural information. In some, but not all, cases it can distinguish between isomers. Selective ionisation can be used to detect specific classes of PAH such as nitro-PAH. Identification of individual compounds is by comparison with standards along with complex criteria relating to isotope ratios, peak maxima, signal to noise ratio and so on. The precision of MS is therefore very dependent upon operator skill and objectivity but detection limits can be down as low as around the ppt level. MS is the method specified in US EPA Method 23 for the analysis of PCDD/F in stationary sources.

Gas chromatography (*see* Section 4.4.1) in conjunction with MS (GCMS) is a popular method. Allen and others (1997) used GCMS for the measurement of PAH associated with PM<sub>10</sub> particles from urban air and reported a detection limit of around 5 pg/m<sup>3</sup>.

Since standard MS frequently cannot be used for monitoring polar VOCs, new systems have been developed. These include membrane introduction quadrupole MS, ion trap MS and electron impact MS (Aragon and others, 2000). Holland



and others (1996) report on the use of time-of-flight secondary ion mass spectrometry (TOF-SIMS) for the in situ investigation of PAH on individual environmental particles. TOF-SIMS uses a microprobe to provide surface elemental and chemical information at high resolution (<1  $\mu\text{m}$ ). According to Holland and others (1996) ambient PAH levels on fly ash are estimated to be in the range of  $10^{-4}$  monolayers which means that they cannot be detected on particles by TOF-SIMS imaging. To make the layers thicker and thus easier to study, Holland and others used particle loaded filters in a method 0010 sampling train (*see above*) to increase the PAH loading.

#### 4.4.6 Other methods

There are an increasingly large number of new techniques being developed for the study of organic compounds. The majority of these would be used mainly for research purposes and not for general monitoring routines. This report is not intended to be a complete review of all the methods available. Instead a few examples are given to indicate the wide range of technologies available.

In laser-induced fluorescence (LIF) a photon flux is used to excite target molecules. The system is coupled to a suitable analysis system, such as MS, chromatography, plasma ionisation and laser breakdown spectroscopy, to detect the species of interest (Gridin and others, 2000). These fluorescence techniques are likely to be prone to problems with interference from the complex matrix of species present in flue gases. Like LIF, laser multiphoton ionisation (LMPI) is a method of exciting species such as PAH for detection by a suitable analysis system. Gridin and others (2000) have used LIF and LMPI simultaneously for PAH analysis of ambient air. The LIF provides a 'finger-print' type, PAH specific, fluorescence spectrum while LMPI would be initiated when LIF fails. The combination of the two provides unique analytical information. The system has proven successful for quantification and speciation of PAH in solution and has now been adapted for sub-micron airborne PAH.

Hahn and others (1999) describe the use of a photoelectric aerosol sensor (PAS) for the detection of particle-bound PAH from combustion sources (gas and oil). The system is based on KrCl lamp radiation at 222 nm to ionise particle bound PAH and then measurement of the current produced by the resulting charged particle. PAH in the vapour phase are not detected. The response factors for the instrument are reported to be around 0.3 to 1  $\mu\text{g}/\text{m}^3$  of PAH which gives a detection limit of around 3–10  $\text{ng}/\text{m}^3$ .

Gould (1998) reported on the development of a system called POPP – pyrolysis of organic polymer from particulate. The system is based on micro-sealed vessel pyrolysis (MSSV), a method used by geochemists to breakdown unbound organic components in rocks. The method is reported to be 'gentle' and does not create artefacts. Because the system is sealed, all compounds are available for analysis. A further advantage is that the sample size required for analysis is 5% of the amount required for solvent extraction techniques.

## 4.5 Example of problems at a coal-fired plant

Ridge and Seif (2000) give an excellent example of the problems associated with selecting suitable sampling and analysis methods at different emission sources. They list several factors to be considered when measuring VOC emissions from a coal-fired boiler fitted with a cyclone.

These are:

- the chemical composition of the VOC being emitted are unknown;
- the expected concentration of VOC is low (<50 ppm as C);
- the chemical properties of the VOC are unknown;
- the duct temperature is around 300°F, the effluent moisture is around 3% and the  $\text{CO}_2$  concentration is around 6%.

Because the chemical composition of the VOC is unknown, US EPA Method 18 (grab sampling or solid collection media followed by GC analysis) is not an option. US EPA Method 25 is also excluded because the VOC concentration is so low. US EPA Method 25A (FID) should be suitable and provides real-time data.

In this instance, Ridge and Seif (2000) recommend the use of Method 25A and Method 18 (Tedlar bag sample, GC/FID analysis) for determination of compounds such as methane and ethane at the coal-fired plant. The sample must be analysed within 48 hours and propane should be used to calibrate the analyser. Method 25A can then also be used to measure TOC rather than VOC. This is less expensive but may not be acceptable for compliance purposes.

## 4.6 Comments

One of the main problems with the sampling and analysis of organic compounds is that the selection of technique depends on the type and concentrations of compounds present. This is a circular problem as the compounds must be sampled and analysed to provide the information necessary to determine which method to use. In the case of emissions from coal-fired power stations, it is well established that emissions are likely to be very dilute. Obtaining a large enough sample to provide quantitative data on the different species present requires a specialist operator and expensive analytical equipment. Long sampling times may also be necessary to overcome problems with the low concentrations of organic species. Although advanced techniques such as GCMS are available for the individual measurement of organic species, for the most part, only values for total emissions of VOC, expressed as methane or propane equivalents, are required in practice.

Emissions from other coal use such as in coking plants or residential combustion is even more problematic as the emissions tend to be fugitive, diffuse and more variable. Obtaining a sample which will be accepted as truly representative of the total emissions is difficult.

## 5 Emissions from coal-fired power plants

Emissions of organic compounds from coal combustion are sometimes referred to as PIC, products of incomplete combustion, emphasising the importance of combustion conditions on organic emissions (Chagger and others, 1999). Arguably, if the combustion of coal or related fuels was efficient and complete, there would be no emissions of organic compounds at all. In reality, achieving totally complete and efficient combustion is difficult. As discussed in Chapters 2 and 3, large coal-fired power plants do not give rise to significant amounts of organic emissions. This is less true for more inefficient forms of coal use such as in smaller scale combustion systems and in industrial uses such as coking plants (*see* Chapter 6).

The sections below review the mechanisms leading to the release of organic compounds from coal in large-scale coal-fired systems. Emission factors are included, where available, along with the effects of variable factors such as fuel type and combustion conditions. Emissions from industrial boilers (including FBC systems) and residential uses of coal are discussed separately in Chapter 6. To begin with, the reactions which occur during combustion are reviewed briefly to give an idea of how organic compounds are released from combustion systems.

### 5.1 Reactions during combustion

When coal is heated, its structure undergoes chemical and physical changes and organic fractions are released which can undergo various reactions. Organic compounds can be released from the fuel intact as a result of incomplete combustion. However, during combustion, PAH and their precursors are involved in two main reaction pathways (Mastral and Callen, 2000):

- pyrolysis** on heating, organic compounds are partially cracked to smaller and more unstable fragments. These fragments are mainly highly reactive free radicals with short lifetimes which form more stable PAH by the second of the two pathways;
- pyrosynthesis** recombination reactions of free radicals into larger and more stable PAH.

Under flaming conditions (>300°C) the weaker carbon bridges in the coal structure such as those in carbon chains or ether links ( $-\text{CH}_2-\text{O}-\text{CH}_2-$ ) are broken first, but not links between ring structures. This is immediately followed by a loss of functional groups. The primary chemical reactions which occur under flaming conditions are pyrolysis, bond cleavage and fission. Under smouldering conditions (<300°C), organic compounds and their products are released by volatilisation and steam stripping effects. This is dependent on the coal moisture content (Oros and Simoneit, 2000).

PAH formation during combustion has been described as a

‘waterfall’ process in which compounds are formed as radicals add together in sequence until compounds of higher molecular weight are formed. Long linear hydrocarbon compounds may also play a role in PAH formation by taking part in the alkylation of aromatic units found in fossil fuels. Hydrogen transfer between phenyl radicals play an intermediary role in high temperature reactions that lead to the formation of polycyclic compounds (Mastral and Callan, 2000). It has been shown that it is possible to synthesise benzo[a]pyrene from ethane under pyrolysis conditions (Liu and others, 2000b).

If other variables are kept constant, the tendency for hydrocarbons to form PAH varies, theoretically, as follows: aromatics > cycloalkenes (cycloolefins) > alkenes (olefins) > paraffins

The formation of PAH in different fuels can therefore be ranked as follows:

coal > lignite > wood > waste oil > residual oil > distillate oil

However, this ranking may not hold in practice as other variables, such as temperature, will affect the efficiency of combustion reactions.

Coal and other fuels contain many other chemical species which may react with organic compounds to produce substituted compounds. Fuels can be ranked according to average chlorine content:

bituminous coal > wood > lignite > residual oil > distillate oil

This is a very crude assumption since coal chlorine content is highly variable increasing with conditions such as exposure to a marine environment.

It has been proposed that PCDD/F and other chlorinated organic compounds can be formed during combustion by the Deacon reaction:



This reaction is reported to be favoured at temperatures over 600°C (Li and others, 1997). However, the complete formation of PCDD/F, not just the ring addition reactions, have been shown to occur in the 250–350°C range (UNECE, 1999a). This de novo synthesis may take place at low combustion temperature or in cooler areas of the plant. Flue gases containing fly ash, HCl, O<sub>2</sub> and water at 300–400°C may provide ideal conditions for PCDD/F formation. Studies have shown concentrations of PCDD/F to be 100 times greater in the ESP downstream of an incinerator than at the furnace exit (Sloss and Smith, 1993). Gerasimov (2000) studied PCDD/F emissions from chlorine-containing coals in Russia, proposing various reaction mechanisms both for formation of these compounds on fly ash and for their degradation in the plume downwind of a coal-fired plant.

It has been reported that sulphur (SO<sub>2</sub>) may hinder the formation of PCDD/F by interacting with chlorine and water to produce sulphate and hydrochloric acid. This may be important in situations where coal is being burned with waste materials (Li and others, 1997; *see* Section 5.2.1).

Bromination of organic compounds is possible in combustion systems but less likely due to the lower concentration of bromine in most fuels. Nitrogenated compounds can also be detected but are commonly formed by secondary reactions downwind of combustion sources rather than in the combustion zone itself. Similarly, thio-organic compounds (containing sulphur) are more likely to be formed in downstream plume reactions.

More detailed analysis of reaction mechanisms for the formation of organic compounds during combustion is given by Vovelle and Delfau (2000), to which the interested reader is referred.

## 5.2 Pulverised coal fired plants

Generalised emission factors for coal combustion in full-scale coal-fired power plants were discussed in Chapter 2. This section concentrates more on the variability of emissions with factors such as fuel type, combustion conditions and so on.

### 5.2.1 Effect of fuel type

According to Oros and Simoneit (2000), VOC emission rates generally decrease with an increase in coal rank. This is due to higher levels of reactive oxygen bearing functional groups in lower rank coals. No other recent data were found on variations in VOC emissions with coal type.

Zhao and others (1999b) compared PAH concentrations in

different coals prior to combustion by organic extraction followed by GC/MS (*see* Chapter 4). The total PAH content varied from 1.2 mg/kg to 28.3 mg/kg and it was found that the total amount of PAH decreased as the carbon content of the coal increase in the range 81–85%. However, above a carbon content of 85%, the total amount of PAH decreased significantly. Smaller (less than three rings) were found in the lowest carbon content coals and also the highest carbon coals. However, in general, there was no relationship between the number of fused aromatic rings and coal rank. This disagrees with numerous previous studies which suggested that the hydrocarbons in coal become increasingly aromatic through the coalification process and therefore higher rank coals have PAH with more fused aromatic rings (Sloss and Smith 1993).

Examples of measured PAH emissions from (unspecified) power stations firing different coals are shown in Table 17 (Chagger and others, 1999). It is clear that emissions of some PAH can vary greatly between coals. For example, the individual PAH emissions from the two Australian coals, both burned in 600 MWe plants, varied by almost an order of magnitude. This is probably due to differences in combustion conditions.

In a separate report by the Clean Coal Centre, Davidson (1999) reviewed the effect of co-combustion of waste materials with coal on organic emissions. The co-combustion of 12 wt% binder-enhanced densified refuse derived fuel, RDF, pellets with coal in a 440 MWe cyclone combustor resulted in no detectable emissions of PCBs or benzene/toluene/xylenes (BTX). Only small traces of naphthalene (1.4 µg/m<sup>3</sup>) and phenanthrene (0.15 µg/m<sup>3</sup>) were found when combusting coal alone in the system and the concentrations were even lower during co-combustion (0.12 µg/m<sup>3</sup> naphthalene and 0.078 µg/m<sup>3</sup> phenanthrene). Fourteen other PAH compounds that were tested for were below the detectable limits in all the tests (Ohlsson, 1993; 1994).

**Table 17 Emissions of PAH from coal-fired power stations firing different coals, ng/m<sup>3</sup>** (Chagger and others, 1999)

Plant	Polish coal	French coal	South African coal	Australian coal	Australian coal
Rated power	250	250	600	600	600
Excess O <sub>2</sub> (%)	6	9	–	7	5
PAH					
1-methylnaphthalene	nm	nm	nm	600	2730
2-methylnaphthalene	nm	nm	nm	60	450
fluorene	nm	nm	500	50	390
phenanthrene	nm	nm	60	830	4430
fluoranthene	130	375	160	380	2470
pyrene	20	85	350	570	6370
benzo(a)anthracene	20	25	20	140	390
chrysene	15	70	80	200	500
benzo(b)fluoranthene	t	15	130	0	t
benzo(e)fluoranthene	t	8	180	0	t
benzo(e)pyrene	t	35	t	5	20
benzo(a)pyrene	0	25	t	0	t
t trace nm not measured					

**Table 18 PAH in the combustion products from coal and RDF combustion, ng/m<sup>3</sup>** (Bonfanti and others, 1994)

Fuel Sampling point Sample type	Coal:RDF boiler			60:40* stack			Coal boiler			stack		
	F	V	F+V	F	V	F+V	F	V	F+V	F	V	F+V
2 rings	26	2737	2763	1818	8785	10603	496	6505	7000	568	2859	3427
3 rings	34	550	584	2375	1310	3685	147	440	587	64	117	181
4 rings	21	129	150	823	1310	3685	57	236	294	13	83	95
5 rings	13	31	44	57	141	198	41	95	136	6	11	17
6 rings	6	2	8	10	14	23	54	73	127	–	–	–
7 rings	–	–	–	1	3	4	9	18	27	–	–	–
total PAH	99	3449	3548	5085	10651	15736	804	7368	8171	650	3070	3720

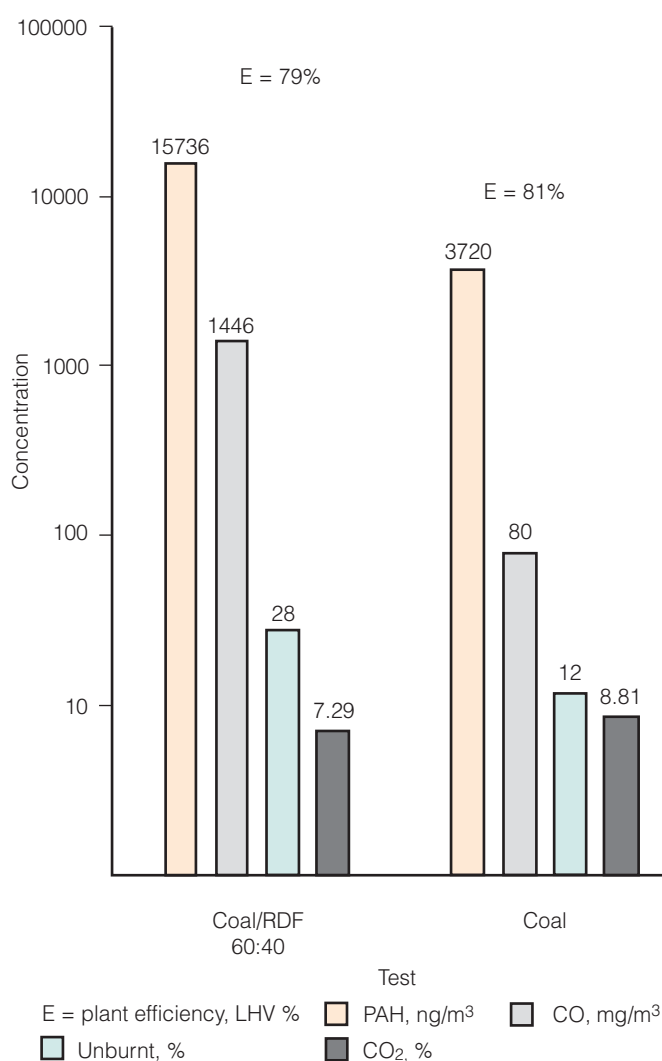
\* mass flow ratio  
F fly ash  
V organic vapour

Bonfanti and others (1994) compared PAH emissions from coal combustion to those from coal and RDF combustion in a 7 MW slag forming cyclone combustor test boiler in Williamsport, PA, USA. The coal was a USA bituminous coal and the RDF was obtained from Italian municipal solid waste via mechanical processing. PAH and PCDD/F emissions were measured using Modified US EPA Method 5 (see Chapter 4). Results are shown in Table 18 and Figure 9. Total emissions of PAH from cofiring were concluded to be 'very low' although higher than those from the combustion of coal alone. Cofiring also resulted in a higher proportion of the more volatile PAH and PAH with 3–4 rings (24% increase).

PCDD/F emissions from coal-fired power plants in Canada have been reported at around 0.01–0.81 g TEQ/y (EC, 2001b). Data cited in a Danish study suggest average concentrations of 0.02–0.2 ng/m<sup>3</sup> TEQ (Schleicher, 2001). Bonfanti and others (1994) compared PCDD/F emissions from co-combustion of coal and RDF in their 7 MW slag forming combustor (as mentioned above). The results are shown in Figure 10. The results varied for different PCDD/F congeners implying different formation mechanisms. PCDD concentrations were actually significantly reduced on passing through the plant (74–98% reduction), regardless of the fuel. PCDF showed different behaviour with the different fuels – the concentrations decreased with coal combustion (54–88% reduction) but increased with cofiring (2–4 times).

Emissions of PCDD/F from the cofiring of 12 wt% binder-enhanced densified RDF pellets with coal in a 440 MWe cyclone combustor were low at 0.246 ng/m<sup>3</sup>. This is well below current US standards but above the 0.1 ng/m<sup>3</sup> limit for waste incinerators in Europe. No PCDD/F were measured in the same system when combusting coal alone (Ohlsson, 1993; 1994).

Studies on the combustion of **waste** in municipal waste incinerators (MWI) have shown that the ash can provide additional reactants and/or catalytic sites for PCDD/F formation. However, this has been shown to occur only in conditions of 'poor combustion' and high temperature ash collection, conditions which would not be encountered in most coal fired power plants. It has been suggested that the



**Figure 9 PAH emissions from a 7 MW slagging combustor firing coal and coal with RDF** (Bonfanti and others, 1994)

sulphur present in coal can reduce the formation of PCDD/F in MWI but initial results were ambiguous, depending more on combustion conditions and ash collection temperature. It may be that the effect is simply due to the improvement of



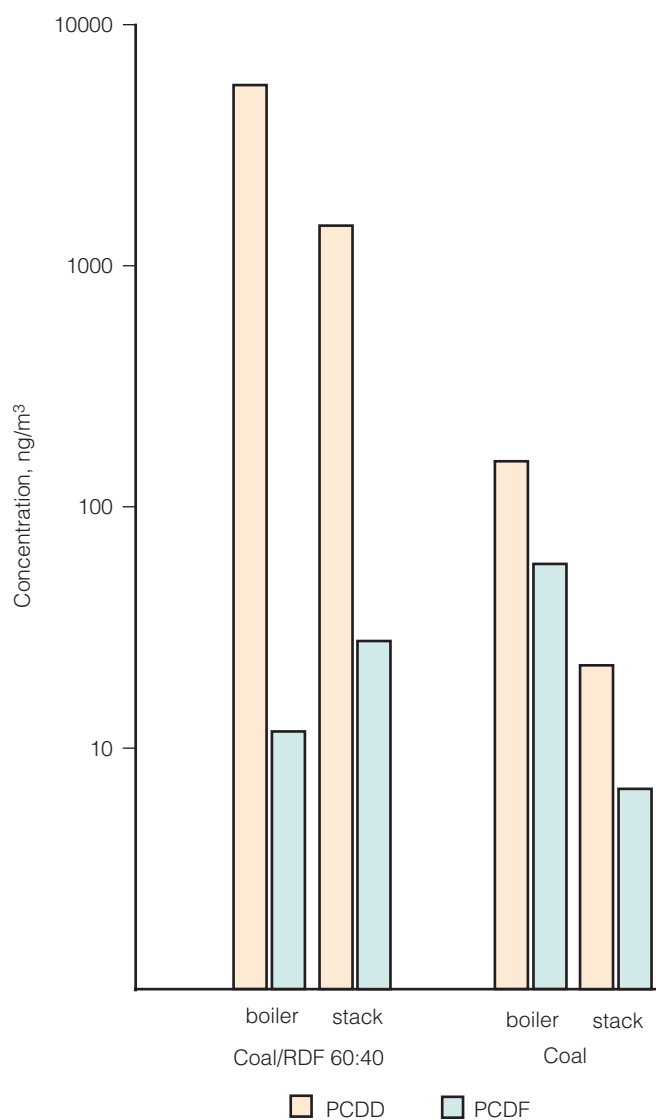
combustion conditions in the presence of coal. Similar reductions in PCDD production were demonstrated when coal was co-combusted with plastic wastes. The addition of a high chlorine Illinois coal to the combustion of plastic wrap material in a 30:1 weight ratio reduced the production of the chlorinated benzenes by 77% even at the low combustion temperature of 500°C.

Liu and others (2000a) cite several cases where the addition of coal was used to reduce PCDD/F emissions from the combustion of wastes such as municipal solid waste and paper recycling residues. The addition of coal, especially high sulphur coal, is proposed to reduce PCDD/F formation by the following reaction:



The removal of the active  $\text{Cl}_2$  reduces the rate of PCDD/F formation.

Davidson (1999) suggested that adding waste to coal



**Figure 10** PCDD and PCDF emissions from a 7 MW slagging combustor firing coal and coal with RDF (Bonfanti and others, 1994)

combustion systems would make better sense, with respect to controlling PCDD/F formation, than adding coal to waste. This use of coal for the reduction of emissions from another sector is discussed in more detail in Chapter 7.

According to Dyke and others (1997), **straw** contains significant amounts of chlorine and, burned alone, can release PCDD/F. Co-combustion of 23 th% straw with coal at the 125 MW unit 1 of the Vestkraft PF plant was shown to release less PCDD/F than coal combustion alone. However, the degree of accuracy of the results was low (1.2–2.7 ng/s) and the emissions were of the same order of magnitude so the difference was assumed to be unclear (Davidson, 1999).

Davidson (1999) cites data on the co-combustion of **sewage sludge** with pulverised coal. For 20 th% sewage sludge blended with Götterborn coal, the PCDD/F levels were 0.04 ng/m<sup>3</sup> when coal was injected through the annulus of the burner and sewage sludge through the centre. When the configuration was reversed, and coal was injected centrally, the PCDD/F concentration rose to 0.3 ng/m<sup>3</sup>.

Although **tyres** emit higher concentrations and greater numbers of PAH than coal in drop-tube furnace tests, blends of coal and tyre crumb can produce PAH at the same concentrations as coal alone, in fuel-lean or stoichiometric conditions. The co-combustion with coal may facilitate the oxidative destruction of the PAH emitted from the tyres with the coal acting as an ‘after-burner’ for the tyre emissions (Levendis and others, 1998a,b).

Although fuel type clearly has an effect on organic emissions, coal type is reported to have less effect of emissions from coal-fired power plants than furnace type or load size (Mastral and Callan, 2000). Ruuskanen and others (1994) suggest that maintaining the combustion temperature above 816°C and maintaining adequate fuel/air mixing during co-combustion of coal with other materials should ensure that all organic compounds are destroyed, over-riding any effect from fuel changes.

## 5.2.2 Effect of combustion conditions

The formation and release of organic compounds from coal combustion depends on the efficiency of combustion. Therefore those factors which increase combustion efficiency are most likely to result in lower concentrations of organic emissions. Concentrations of organic species decrease rapidly with increasing temperature, efficient fuel mixing and sufficient residence times. Above **temperatures** of 1500°C even single ring aromatic compounds rupture. Most coal-fired boilers operate at 800–1500°C which would cause the destruction of all organic compounds.

Total hydrocarbon emissions from different coal-fired units have been measured by Owen and others (1997) and are shown in Table 19. Because of the limited amount of data and the known inaccuracy of such studies, firm conclusions cannot be drawn. However, the data suggest that larger, more efficient plants have lower THC emissions and that emissions may be lower in steady state operating conditions than during

**transient periods** of increasing or decreasing load. Table 20 shows the changes in THC emissions during off line periods. As the load decreases and the power station cools down, the THC emissions clearly increase.

Chagger and others (1999) compared VOC emissions from unspecified power stations at different **loads**. There was a trend towards increasing VOC, in some but not all cases, with increased load.

**Fuel size** affects the combustion rate. Combustion of solid particles occurs in a series of repeated steps – combustion of volatile components near the surface of the particles followed by burning of the residual solid structure. This results in the exposure of fresh unreacted material and the cycle repeats. The larger the particle the more cycles are necessary for complete combustion and therefore the residence time becomes more important. Boilers burning non-pulverised coal therefore have higher organic emissions.

Turbulence, air mixing and the **air:fuel** ratio affect the combustion process. Efficient fuel and air mixing is the most important factor with respect to efficient combustion and therefore the most important factor with respect to organic emissions. Systems involving frequent start-up and shut-down will suffer from poor air:fuel ratios. Poor fuel

distribution is a common symptom of hand or stoker fired solid fuel systems but is less common in large-scale pulverised coal fired plants. Fluidised bed systems have good air and fuel mixing by design. FBC systems are discussed in more detail in Chapter 6.

Abnormal situations, such as **soot blowing**, can also lead to increased organic emissions. A report by the Coal Research Establishment in the UK noted that VOC emissions from a 500 MWe plant firing bituminous coal increased from 2.7 mg/m<sup>3</sup> to 21 mg/m<sup>3</sup> during soot blowing (CEC, 1998a).

### 5.2.3 Effect of pollution control systems

Table 3 in Chapter 2 showed lower VOC emission factors for full-scale coal-fired units in the UK which had **low NOx burners** fitted. Table 19 also included data for THC emissions from a 500 MWe coal-fired plant with NOx burners. The steady state emissions from this plant were the same as emissions from a similar plant without low NOx burners. Table 20 contained further data from these two plants and showed similar concentrations from each, although the range of emissions from the plant with the low NOx burners (190–241 g/min) appeared to be slightly higher than that for the plant without low NOx burners (150–202 g/min). There is clearly a lack of information on the effect of low NOx burners on organic emissions and more research is necessary.

**ESP** systems and **baghouses** are designed to catch particulate matter and therefore will remove any organic compounds associated with fly ash. At 150°C and above, the temperatures encountered in ESP and baghouses, most organic compounds are expected to be present in the gaseous form. Gaseous organic compounds will pass through particulate devices uncaptured. Some organic species may adsorb preferentially to smaller (submicron) fly ash particles because of the larger surface area to mass ratios.

Tagashira and others (1999) studied PCDD/F removal by a baghouse in a test-scale CFBC unit. They found that the

**Table 19 Total hydrocarbon emission factors for large pulverised coal units, kg/TJ (Owen and others, 1997)**

Unit size, MWe	Low NOx burners	Combustion burners	THC emissions, kg/TJ net
666	no	low air	<1
666	no	normal air	<1
666	no	high air	<1
500	no	transient	5
500	no	steady state	3
500	yes	transient	5
500	yes	steady state	3
300	no	steady state	<1
108	no	steady state	3

**Table 20 Impact of operating conditions on total hydrocarbon emissions from full-scale coal-fired power plants (Owen and others, 1997)**

Unit size, MWe	Type	Fuel	Operating conditions	THD emissions, g/min
500	conventional	coal	base load (2.55 t/h)	150
			4 hours off line	192
			8 hours off line	197
			12 hours off line	202
500	low NOx	coal	base load (2.88 t/h)	190
			4 hours off line	213
			8 hours off line	228
			12 hours off line	241
90 MWth	CFBC 50:50	coal/RDF	1 hour transient operation	25
			2 hour transient operation	24
			4 hour transient operation	21
			6 hour transient operation	19

removal efficiency varied with temperature. The PCDD/F removal efficiency began to decrease from around 97% or more at 160°C to below 80% at 240°C.

As mentioned in Section 5.1, de novo synthesis of PCDD/F may occur in flue gases at 250–450°C (UNECE, 1999a). ESP in full-scale coal-fired power plants are generally maintained around 150°C and therefore it is unlikely that de novo synthesis would occur.

No information has been found on the effect of FGD systems on emissions of organic compounds.

It has been noted that adsorbers and dedusting installations upstream of SCR catalysts can lead to PCDD/F laden residues in waste combustion systems (UNECE, 1999a). There are no data relating to this effect in coal combustion systems. It has also been suggested that SCR systems may oxidise organic species but, again, no information has been found on this phenomenon.

### 5.3 Comments

Coal combustion in coal-fired power plants is not a major source of organic emissions. Although fuel type can affect the formation and release of organic compounds, in general it is those factors which control the combustion efficiency, such as fuel mixing, which are more important. Chlorine in the feed coal can potentially promote the formation of PCDD/F but, again, it is combustion conditions which play a greater role in controlling the release of these compounds than any variation in the coal characteristics.

It is interesting to note that, because of its efficient combustion properties, coal can help reduce organic emissions from the combustion of waste materials, even those containing high concentrations of chlorine. The elevated combustion temperatures induced by the addition of coal can have an 'after-burner' effect on the release of organic compounds from waste materials. Further, the sulphur present in coal can inhibit the formation of PCDD/F from waste combustion. This means that coal has the potential to reduce emissions of organic compounds from waste incineration. This is discussed in more detail in Chapter 7.

## 6 Emissions from industrial and residential coal use

As mentioned in Chapters 2 and 5, the combustion of coal in industrial and residential systems is generally less efficient than in full-scale coal-fired plants. This leads to higher concentrations of organic emissions. There are a good deal of old data which were reviewed in the previous reports on organic compounds by the Clean Coal Centre (Sloss and Smith, 1993; Smith, 1984). The following sections concentrate on recent data on organic emissions from different combustion systems, including FBC units, and also from industrial uses of coal such as coke making and the aluminium, iron and steel industries.

Coal gasification processes, such as that operated by Shell, produce syngas from coal. The syngas itself has been shown to contain concentrations of organic compounds which are either very low or below the detection limit (ppb levels). Emissions from coal fired power stations are predicted to very low. It is perhaps for this reason that no recent data have been found relating to organic emissions from coal gasification.

### 6.1 Industrial coal combustion

Table 21 gives examples of NMVOC emissions from different industrial coal-fired units (CEC, 1998a). From the table it is clear that the VOC emission concentrations can be higher from the smaller, more inefficient systems than from the larger units however, there is no real discernible

trend. In general the VOC emission were all low, below 0.2 g/kg, for the large-scale plant and industrial units. This is lower than the emissions from residential coal combustion in the open grate system (14.0 g/kg, *see also* Section 6.3 *below*).

There was no significant change in VOC emission factors with changes in the firing rate for the smaller units, the 0.9 MW underfeed, the 1 MW reciprocating grate and the 5 MW top feed boiler. The only significant variation in emissions was observed following manual de-ashing of the top feed boiler which caused an order of magnitude increase in the VOC emission factor. During de-ashing the induced draft fan was switched off causing an increase in emissions on re-start. Again this highlights the clear link between combustion efficiency and organic emissions. This is further confirmed by data from Owen and others (1997) who measured total hydrocarbon emission factors for different stoker fired units in the UK. The THC emission factors, shown in Table 22, were all quite similar and there were no firm conclusions to be drawn. However, the data did suggest that kindling periods and periods of decreasing load may give rise to greater THC emissions than steady combustion conditions.

Table 23 shows PCDD/F emission concentrations and emission factors for different combustion systems including several industrial boilers. Although it is clear that emissions from smaller, less efficient systems, are lower than those

**Table 21 NMVOC emissions from coal combustion (CEC, 1998a)**

Plant type	Rating, % max	Output, mg/m <sup>3</sup>	Fuel	VOC concentration, g/k g fuel	Emission factor
PF	500 MWe	100	bituminous coal	2.7	0.0 3
				21	0.2 *
PF cement kiln	90 MW	100	bituminous coal	61	1.4†
travelling grate	48 MW	100	bituminous coal	7.9	0.1 4
CFBC	43 MW	100	bituminous coal	7.7	0.0 5
FBC	19 MW	100	bituminous coal	2.6	0.0 3
top feed	4.9 MW	50	bituminous coal	3.5	0.0 9
		75	bituminous coal	3.2	0.0 5
		75	bituminous coal	47	0.8‡
		90	bituminous coal	3.4	0.0 5
		100	bituminous coal	3.4	0.0 5
reciprocating grate	1 MW	60	bituminous coal	2.1	0.0 3
		80	bituminous coal	0.1	<0.01
underfeed	0.9 MW	60	bituminous coal	3.2	0.0 2
		100	bituminous coal	0.8	0.0 1
underfeed	17 kW	n/a	bituminous coal	15	0.6
gravity feed	13 kW	n/a	anthracite	43	1.7
open grate	n/a	n/a	bituminous coal	91	14.0
			smokeless fuel	29	4.9

PF pulverised fuel  
 \* sample taken during soot blowing  
 † increased emissions due to heating of kiln material  
 ‡ sample taken after manual de-ashing



from larger systems, no conclusions could be drawn on differences between the different industrial units studied (Brain and others, 1995).

## 6.2 Fluidised bed combustion

A previous study by the Clean Coal Centre (Sloss and Smith, 1993) concluded that emissions of organic compounds from FBC appear to be higher than those from pulverised coal combustion due to the lower combustion temperatures: 800–900°C in FBC compared with >1200°C in pulverised coal fired plants. Table 24 shows measured total hydrocarbon emissions from different FBC units in different operating conditions. Although the emissions varied slightly from one plant to the next, they were all within the same order of magnitude and no firm conclusions could be drawn as there were too many variables to be considered (variation in fuel, combustion conditions and so on). The following sections discuss each of the variable factors and their effect on organic emissions in more detail.

Unit size, MWth	Type	Combustion conditions	THC emissions, g/GJ
53	travelling grate	?	<1
1.4	underfired	kindle	9
1.4	underfired	increasing load	2
1.4	underfired	decreasing load	11
0.6	underfired	overfire air	<1
0.6	underfired	no overfire air	2

### 6.2.1 Effect of fuel type

FBC is a popular system for the combustion of coal along with low grade fuels and waste. The inclusion of waste products as fuel in FBC combustion can have a distinct effect on organic emissions. For example, Mastral and others (2000b) fired 1:1 coal and tyres in a pilot-scale 2.8 kW AFBC unit. The tyres were found to be an ideal fuel with respect to their high calorific value. However, PAH emissions increased dramatically with the inclusion of tyres in the fuel. Coal combustion alone produced PAH emissions in the range of 10–20 g/kg whereas coal and tyres 1:1 produced PAH emissions in the range of 140–180 g/kg, depending on the temperature of combustion.

The co-combustion of MSW with low grade coal in a 700 kWth stationary fluidised bed released PCDD/F

Unit size, MWth	Type	Fuel	Combustion conditions	THC emissions, kg/TJ net
43	?	coal/bark	not detailed	1.5
	80:20			
19	AFBC	coal	not detailed	1
19	AFBC	coal	not detailed	2
90	CFBC	coal	low fire	9
90	CFBC	coal:RDF	low fire	8
	50:50			
90	CFBC	coal:RDF	high fire	4
	50:50			

RDF refuse derived fuel

System	Fuel	MCR, %	Emission, ng/m <sup>3</sup> TEQ	Emission factor, ng/kg TEQ
500 MWe pulverised	coal	100	0.005	0.06
380 MWe pulverised	coal	105	0.031	0.25
43 MW CFBC	coal	100	0.007	0.07
36 MW CFBC	coal	28	0.001	0.01
19 MW FBC	coal	100	0.004	0.05
5.0 MW tipping grate	coal	80	0.008	0.15
5.0 MW travelling grate	coal	100	0.034	0.57
		100	0.023	0.39
4.6 MW top feed	coal	100	0.014	0.20
1.4 MW underfeed	coal	100	0.10	1.68
1.0 MW reciprocating grate	coal	100	0.05	0.54
0.7 MW gravity feed	coal	100	0.09	0.74
17.5 kW underfeed	coal	100	0.08	1.5
15 kW underfeed	coal	85	0.09	1.1
PF burner/cement kiln	coal	100	0.004	0.06
domestic open fire	bituminous coal	n/a	0.75	5.7
	anthracite	n/a	0.08	2.1
	smokeless fuel	n/a	0.25	4.7

MCR maximum combustion rate, % of capacity  
 PF pulverised fuel  
 n/a not applicable

concentrations of less than 0.1 ng/m<sup>3</sup>. This PCDD/F was almost entirely bound to the dust which was captured in the bag filter. Concentrations in the cleaned flue gas downstream of the bag filter were 0.05 ng/m<sup>3</sup> (Sundermann and others, 1995).

Emissions from the co-combustion of shredded wastes (10–20 th%) with a peat and coal mixture (55:45) in a 65 MW CFBC also gave low emissions, below 0.1 ng/m<sup>3</sup>. No correlation was found between PCDD/F emissions and the chlorine content of the feed (Frankenhaeuser and others, 1994). Similarly the proportion of mixed plastics incorporated into the plastics/coal fuel blend combusted in a 7 MW BFBC at 850°C did not affect the emission levels of PCDD/F (Frankenhaeuser and others, 1993).

The formation of PCDD/F in the mixed combustion of coal with waste plastic in FBC was studied using principal component analysis (Ruuskanen and others, 1994; 1995). The PCDD/F concentrations were clearly dependent on the CO concentration in the flue gas and also on the concentration of PCBs and PAHs. No correlation between HCl and PCDD/F in the flue gas was found suggesting that HCl concentration is not a limiting factor for the formation of PCDD/F. The lack of correlation in the flue gas differed significantly from the positive correlation in the fly ash, indicating a different formation mechanism. Different results were obtained in a study of the co-combustion of 45 th% RDF with peat, wood chips and coal in multi-fuel FBC boilers (15–117 kWth) by Huotari and Vesterinen (1996). This second study showed that PCDD/F emissions increased with the chlorine content of the fuel. However, the emission levels varied by three orders of magnitude at the same chlorine content of the fuel and were all below 0.1 ng/m<sup>3</sup>. Vesterinen and Flyktman (1996) also showed a clear correlation between the chlorine content of the wood chips and the PCDD/F emissions from a 4 MW BFBC. The correlation no longer applied when the wood chips were co-fired with peat and the total emissions were lower (all below 0.1 ng/m<sup>3</sup>).

Frankenhaeuser and others (1993) noted that **limestone injection** into their 65 MW CFBC system increased PCDD/F emissions whereas elemental sulphur injection lowered emissions.

A similar study in the 7 MW BFBC system confirmed that limestone injection increased emissions slightly although they still remained below 0.1 ng/m<sup>3</sup> (Frankenhaeuser and others, 1993). However, a more recent study by Tagashira and others (1999) showed that the addition of Ca compounds such as CaCO<sub>3</sub> or Ca(OH)<sub>2</sub> to a test-scale CFBC burning waste prevented the formation of PCDD/F.

## 6.2.2 Effect of combustion conditions

According to Liu and others (2000b), the distribution and relative abundance of PAH from FBC is a function of operating temperature and process conditions. Liu and others (2000b) studied PAH emissions in fly ash rather than in the gas phase from a laboratory-scale FBC reactor and a 0.1 MWth bench-scale FBC unit. Tests were performed in

triplicate and different temperatures and oxygen ratios using a high volatile bituminous coal (10.5% ash, 34.5% volatile matter, 50.4% fixed carbon, 5.2% hydrogen). Results from the laboratory-scale combustor indicated that three and four ring aromatic compounds were the major products from pyrolysis conditions whereas naphthalene (two rings) was the major PAH in fly ash from oxygen rich combustion. Only naphthalene was detected in the bed ash of the laboratory-scale FBC system. Results from the laboratory-scale unit are shown in Table 25. The total amount of PAH obtained at 800°C is almost twice that obtained at 900°C under pyrolysis conditions. This may be due to the greater amount of energy at higher temperatures being able to break more bonds in the PAH molecules. This theory is supported by the fact that no five ring compounds are determined when the temperature is increased to 900°C. There was almost 80 times more PAH produced at 800 °C than PAH extracted from the raw coal. Liu and others (2000b) conclude from this that the majority of PAH are formed in breakdown reactions with condensation and cyclisation mechanisms playing less important roles.

When the excess air ratio was below 1 (partial thermal decomposition) the total amount of PAH produced in the fly ash of a laboratory-scale combustor decreased with an increase in the level of excess air. The amount of PAH produced decreased significantly when the excess air was above 1. The results confirm the theory that incomplete combustion is the main reason for emissions of PAH. The PAH content of the fly ash was, at minimum, seven times greater than that in the raw coal. This suggests that the formation of PAH is mainly through the conversion of coal macromolecular aromatic structures into different size fragments and then further decomposition and cracking of the fragments into lower molecular weight PAH. In oxygen rich conditions the PAH will undergo oxidation reactions and produce more CO<sub>2</sub> and H<sub>2</sub>O. In oxygen deprived conditions more PAH are emitted (Liu and others, 2000b).

The results for PAH in the gas phase, as collected by filter, condenser and Tenax, are shown in Table 26. Naphthalene was the dominant PAH below 700°C, possibly due to its lower boiling point and higher stability amongst the PAH. As the pyrolysis temperature increased the amount of smaller PAH such as naphthalene and fluorene decreased whilst the emission of larger molecules increased with an increase in temperature. The lowest PAH concentrations were produced at around 600°C. At lower temperatures the major pathway for PAH formation is degradation, emitting smaller products during the devolatilisation process. As the temperature increases intermolecular cyclisation becomes more important and larger PAH are produced. Large PAH may also be produced by the deep degradation of char.

Having studied this PAH behaviour at lab scale, Liu and others (2000b) then performed some similar studies on a 0.1 MWth FBC bench-scale unit. These studies confirmed that incomplete combustion of coal is the main factor resulting in PAH in fly ash from FBC systems. The concentration of PAH in fly ash was much greater than that in bed ash, with little or no PAH being detected in the bed ash. Bed ash has a long residence time (30–60 min) with high temperatures and thorough mixing with oxidant gas, thus

**Table 25 US EPA specified PAH identified in the ash from a laboratory-scale FBC reactor, µg/g ash (Liu and others, 2000a)**

PAH	Coal	800°C pyrolysis	900°C pyrolysis	800°C 0.50 air†	800°C 1.00 air†	800°C 1.14 air†
<b>PAH in fly ash</b>						
<i>two-rings</i>						
naphthalene	2.78	65.82	20.28	23.81	19.91	6.50
<i>three-rings</i>						
acenaphthene	1.36	4.18	2.30	*	*	*
acenaphylene	*	75.21	b	76.42	15.01	3.53
fluorene	*	48.02	27.14	54.89	13.80	2.39
phenanthrene	1.46	60.04	42.11	70.02	30.08	6.01
anthracene	*	27.03	15.39	31.39	15.02	2.51
subtotal	2.82	214.48	86.94	232.72	73.91	14.44
<i>four-rings</i>						
fluoranthene	*	49.08	42.08	48.02	41.70	5.80
pyrene	*	32.61	28.22	29.31	30.23	4.22
benzo[a]anthracene	*	21.82	27.21	b	37.28	5.59
chrysene	*	19.28	11.30	13.39	20.71	2.01
subtotal		122.79	108.81	90.72	129.92	17.62
<i>five-rings</i>						
benzo[e]pyrene	*	36.20	*	*	*	*
total	5.60	439.29	216.02	347.25	223.74	38.56
<b>PAH in bed ash</b>						
naphthalene		b	b	10.31	9.43	12.71

\* below detection limit – 0.1 ppb  
† excess air ratio

**Table 26 PAH in coal and collected by filter, condenser and Tenax in the pyrolysis process in a lab scale FBC unit at different temperatures, µg/g (Liu and others, 2000b)**

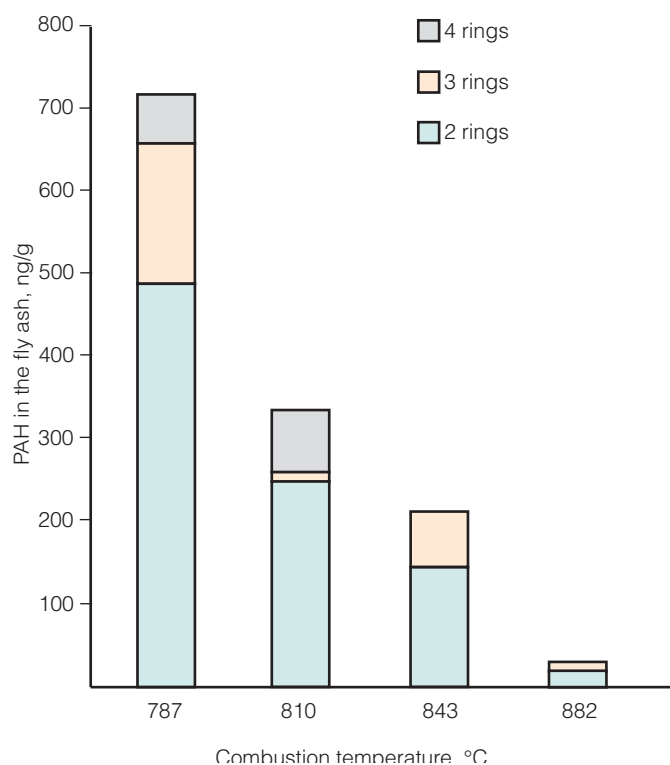
PAH	Coal	400°C		500°C		600°C		700°C		800°C	
		F/C	T	F/C	T	F/C	T	F/C	T	F/C	T
<i>two-rings</i>											
naphthalene	1.34	1.10	0.22	1.26	0.31	0.63	0.40	0.39	0.45	0.16	0.85
<i>three-rings</i>											
fluorene	0.13	0.29	0.03	0.80	0.61	0.33	b	0.28	0.66	0.30	0.79
anthracene	0.05	0.51	0.07	*	*	0.32	0.47	0.95	0.45	0.77	0.65
phenanthrene	0.07	0.77	*	1.10	0.16	0.37	0.30	*	*	*	*
<i>four-rings</i>											
chrysene	*	0.28	0.04	0.61	0.12	0.20	0.09	0.35	0.06	0.35	0.13
pyrene	0.01	0.12	0.03	0.32	0.04	0.22	0.15	0.43	0.22	0.53	0.27
Subtotal	1.60	3.07	0.37	4.09	1.24	2.07	1.41	2.40	1.84	2.11	2.69
Total			3.47		5.30		3.48		4.24		4.80

F/C PAH collected in the filter and condenser  
T PAH collected in the Tenax trap  
\* below detection limit

removing all combustible compounds. The actual PAH concentrations in the fly ash were much lower in the bench-scale unit than in the laboratory-scale unit (µg/g at laboratory scale, ng/g at bench scale). This was due to the efficient solid and gas mixing at bench-scale and the addition of limestone to the bench-scale unit. The relationship between the PAH content of the fly ash and the combustion temperature in the bench-scale unit is shown in Figure 11. An increase in combustion temperature causes a significant decrease in the PAH content of the fly ash. The major

reductions occur in the two and three ringed PAH whereas the four ringed PAH remained fairly constant. When the temperature was above 843°C no PAH with more than three rings were detected. Increases in the three ringed compounds may come from decomposition of the four ringed compounds.

A similar study by Mastral and others (1996; 1999a) provided very similar results, confirming the link between PAH emissions and temperature in FBC systems. However,

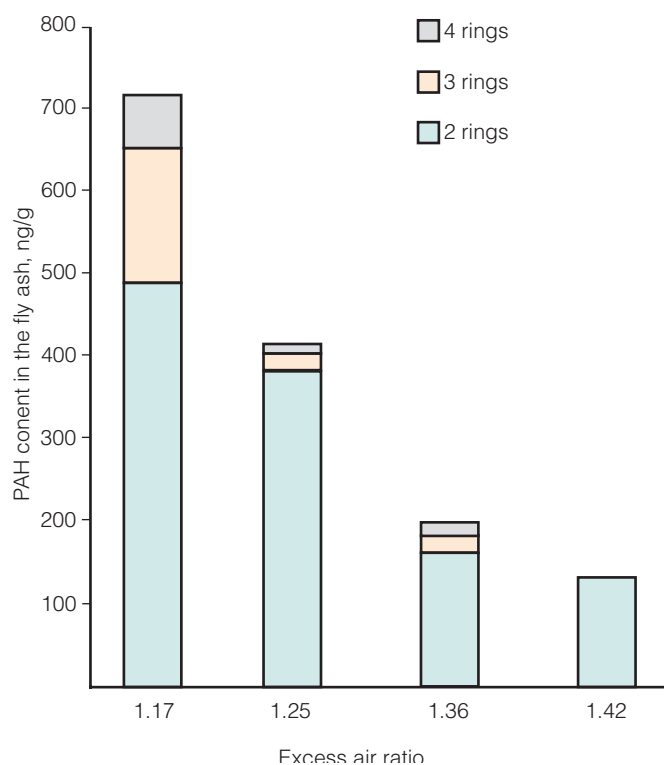


**Figure 11** Effect of combustion temperature on the number of fused rings in the PAH in fly ash from FBC (Liu and others, 2000b)

Mastral and others (1996) also showed that PAH emissions from FBC systems were dependent on both the combustion efficiency and the combustion conditions (temperature, flow and so on) at the outlet from the reactor. For low rank coals, the temperature of combustion did not affect efficiency as much as it did for high rank coals. The study showed that incomplete combustion was not the main factor responsible for PAH emissions but rather the temperature at the top of the reactor and the flow velocity. Pyrolytic reactions between the radicals emitted and formed at the top of the reactor are more important than those in the combustion zone.

Figure 12 shows the effect of the excess air ratio on the PAH measured. In this test the FBC bed temperature was maintained at 810°C and the excess air ratio was adjusted by the coal feeding rate. As the excess air ratio increased the PAH content of the fly ash decreased. Larger ringed PAH were reduced first. At the same time, the combustion efficiency was increased from 99.1% to 99.4% (Liu and others, 2000b).

Zhao and others (1999a) confirmed a link between the excess air ratio and PAH production in FBC. The excess air ratio in a laboratory-scale FBC at 700–900°C was varied between –50% and 14.4%. Bituminous coal was combusted and the PAH content of the fly ash was measured. PAH emissions were found to be generally lower during combustion than during pyrolysis. Pyrolysis at 800°C resulted in total PAH in the fly ash of 531.7 mg/kg. When the pyrolysis temperature was increased to 900°C the PAH in the ash dropped to 251.3 mg/kg. Combustion conditions of 800°C and –50% excess air produced ash PAH concentrations of 393.3 mg/kg. This



**Figure 12** Effect of excess air ratio on the number of fused rings in PAH in fly ash from FBC (Liu and others, 2000b)

dropped to 252.1 mg/kg when the excess air ratio was increased to 0% and dropped even further to 42.5 mg/kg when the excess air was increased to 14.4%.

Mastral and others (1999a) also confirmed that the excess air ratio in AFBC systems was important with respect to PAH emissions. The highest PAH emissions were measured when working at lower percentages of excess oxygen. Combustion efficiency in an experimental AFBC system increased from 98.7% at 5% excess oxygen to 99.6% at 40% excess oxygen. The amount of PAH emitted decreased from around 250 µg/kg at 5% excess oxygen down to less than 20 µg/kg at 20% excess oxygen but then increased again slightly to around 50 µg/kg at 40% excess oxygen.

The study by Liu and other (2000b) showed a strong correlation between bed height in the bench-scale FBC unit and the PAH in the fly ash. As the bed height increased from 0.5 m to 0.7 m the PAH concentration in the fly ash was reduced from around 700 ng/g to around 200 ng/g. Above this height there was very little further effect on the PAH.

Liu and others (2000b) concluded that the effects of FBC conditions on PAH could be ranked as follows: combustion temperature > excess air ratio > bed height where the combustion temperature in both the bed area and the freeboard area are equally as important. A correlation between fly ash particle size and PAH concentration was also indicated. Fine particles with diameters smaller than 0.1 mm contained five times as much PAH as coarser particles (0.1–0.3 mm). This effect would be caused by differences in combustor residence time and surface area. More condensed

PAH can be adsorbed onto larger surface areas (Liu and others, 2000b).

Mastral and others (1999a; 2000a) showed that sand was a more suitable fluidising agent than limestone for FBC systems when considering PAH emissions. With sand the effect of the excess oxygen on PAH emissions was greatly reduced. At 5% excess oxygen PAH emissions from a limestone bed were almost 12 times greater than those from a fluidised sand bed.

### 6.3 Residential coal combustion

Residential coal combustion is very much a batch process with a characteristic combustion cycle consisting of three stages:

- ignition/refuel;
- flame breakthrough;
- red fire.

The initial ignition and/or refuel may involve fire lighters or similar products which themselves contain VOC and contribute to the overall emissions. As would be expected, combustion is more efficient at the red fire stage and VOC emissions decrease from start-up through to this stage. Table 27 shows VOC emission concentrations and emission factors for the different stages of combustion in an open grate fire burning bituminous coal, as measured in the UK (CEC, 1998a). The concentrations and emission factors are both higher for the less efficient stages of combustion. Table 27 also includes emission data for 'smokeless' fuel. Smokeless fuel was first produced in the UK in 1950s. Briquettes producing little or no visible emissions were produced by processes such as carbonisation and controlled oxidation. In general the organic emissions from smokeless fuel were lower than those for coal, although emission during start-up

were higher with the smokeless fuel. This was attributed to the greater quantity of firelighters used to ignite the fire. The study, performed by the Coal Research Establishment in the UK, also compared emissions from an underfeed stoker and gravity feed boiler used for residential heating. Although the results were more variable and less easy to reproduce, the emissions were lower than those for the open grate fire due to the higher combustion efficiency of the enclosed appliances. The range of emission factors for the underfeed stoker was 0.1–1.7 g/kg and was 0.4–3.3 g/kg for the gravity boiler, both of which were firing anthracite.

Jaszczur and others (1995) compared the VOC emissions from a standard residential tile stove burning examples of both the 'best' and the 'worst' coals available in Poland. It has been estimated that there are 100,000 traditional coal-fired stoves in Kraków alone with an annual coal consumption of 130 kt and a total of 7 million stoves in the whole of Poland. A comparison of the VOC emissions from the fuels studied is shown in Table 28.

In the review by Mastral and Callan (2000), it is reported that emissions of PAH from residential coal combustion are three orders of magnitude greater than from industrial combustion. The use of the stoves indoors can lead to potentially high levels of PAH exposure. For example, rural houses in developing countries were found to have PAH concentrations in the range of 100–10,000 ng/m<sup>3</sup> which is exceptionally high when compared with concentrations in traffic areas (20 ng/m<sup>3</sup>) and in cigarette smoking areas (20–100 ng/m<sup>3</sup>) (Oanh and others, 1999). PAH from inefficient residential combustion of 'smoky coal' in China are believed to contribute to the high incidence of esophageal and lung cancers (Finkelman, 1999).

Coal-burning stoves emit lower quantities of organic species than wood burning ones because of their higher combustion

**Table 27 NMVOC emissions from an open grate fire burning bituminous coal (CEC, 1998a)**

Test no	Test status	VOC concentration, mg/m <sup>3</sup>	Emission factor, g/kg fuel
coal combustion			
1	start-up	233	38.1
2	start-up	255	41.6
3	flame breakthrough	107	16.7
4	flame breakthrough	87	13.6
5	flame breakthrough	76	11.8
6	flame breakthrough	56	8.5
7	flame breakthrough	57	8.6
9	red fire	14	2.2
10	red fire	16	2.4
11	re-fuel	194	28.7
12	re-fuel	205	30.5
	average for cycle	91	14.0
smokeless fuel combustion			
1	start-up	333	60.4
2	flame breakthrough	38	6.5
3	red fire	1	0.1
4	re-fuel	51	8.6
	average for cycle	2.9	4.9



**Table 28 Coal stove test fuels (Jaszczur and others, 1995)**

Fuel properties as-fired	Boleslaw Smialy coal*	Wujek coal†	Zabrze briquette‡	Wood briquettes§
Water, %	2.11	2.72	3.30	5.6
Ash, %	21.7	3.20	10.9	1.8
Volatiles, %	30.3	32.1	8.1	71.6
Sulphur, %	0.28	0.29	0.22	0.0
HHV, kJ/kg	25450	32440	28030	19520
Cost	\$60/t	\$80/t	?	\$30-40/t
Baseline test results:				
Efficiency, %	59	65	54	71
Semi-VOC, g/kg	0.9	0.9	0.4	2.2
g/GJ	34	280	140	100
VOC, g/kg	3.4	1.8	2.4	6.0
g/GJ	130	52	86	310
HHV higher heating value				
* 'poor' coal				
† 'good' coal				
‡ produced in Poland at a pilot-scale facility, smokeless fuel from fluidised bed gasifier char and preheated coking coal				
§ wood waste, proposed as an option to coal for the Polish stoves				

temperatures and more consistent fuel quality (UNECE, 1999a). However, coal combustion in some domestic combustion units may give rise to higher organic emissions than other fuels such as biomass, simply because coal combustion can be inefficient in such systems. For example, Jones and others (2000) compared coal combustion with oak wood combustion in a 30 kW bottom fired domestic boiler in Poland. Typical PAH emissions from the boiler burning bituminous Julian coal were:

benzene	12.7 µg/m <sup>3</sup>
toluene	7.7 µg/m <sup>3</sup>
xylene	1.7 µg/m <sup>3</sup>

The total organic matter amounted to 0.07–0.1 g/m<sup>3</sup> at standard temperature and pressure. As would be expected, the PAH emissions were found to be very sensitive to the secondary air ratios. A comparison of emission factors for different PAH from two tests with Julian bituminous coal (poor quality) and one with oak wood are shown in Table 29. In test 2, where the secondary air ratio was higher (unspecified), PAH emissions were much higher. Whilst the coal was found to emit more total PAH than wood, coal produces mainly two and three ringed species whereas wood produces more four and five ringed compounds. Jones and others (2000) noted that the PAH concentrations in this study are higher than those normally measured from boilers of this type and suggest that this is due to the greater sensitivity of their analysis method (pyrolysis GC and FTIR). However, they concluded that coal emits more total organic organic compounds than wood but that wood emits proportionally more as larger molecular weight material.

Oanh and others (1999) have compared PAH emissions from three common fuel-stove systems used in Southeast Asia. These were:

- a coal briquette stove (coal briquettes: 50% anthracite, 40% peat, 10% clay, by weight);
- Eucalyptus wood sticks, open burning;
- a charcoal (mangrove) stove.

**Table 29 PAH emission factors from combustion of Julian coal and oak wood in a 30 kW residential boiler, µg/MJ (Jones and others, 2000)**

Compound	Test 1* coal	Test 2* coal	Test 3 wood
naphthalene	897	14100	5.3
2-methylnaphthalene	405	10200	-
1-methylnaphthalene	295	7860	-
acenaphthylene	153	2220	6.20
acenaphthene	14	655	1.20
fluorene	118	2050	1.70
phenanthrene	357	3600	1.70
anthracene	24	1200	3.20
fluoranthene	49	2200	13.4
pyrene	94	1970	6.50
benzo[a]anthracene	37	848	6.60
chrysene	32	659	9.00
benzo[b]fluoranthene	37	285	13.2
benzo[k]fluoranthene	21	152	-
benzo[e]pyrene	42	163	5.70
benzo[a]pyrene	26	255	7.10
perylene	3.8	5.50	11.8
dibenzo[a,h]anthracene			
+ indeno[1,2,3]pyrene	19.1	133	17.5
benzo[g,h,i]pyrene	5.30	26.7	7.8
Total	2580	48700	118
* test 2 had higher secondary air (not specified)			

Emission factors for individual PAH from the three fuels are shown in Table 30. On a fuel-weight basis, the average total PAH emission factors for the coal briquette and wood burning were almost the same at around 110 mg/kg. However, on an energy basis the emission factor for wood burning (5.6 mg/MJ) is higher than that for coal briquettes (4.4 mg/MJ), although the ranges of values overlapped. Naphthalene, acenaphthylene and acenaphthene made up



**Table 30 Emission of total PAH (18 compounds) and genotoxic PAH (11 carcinogen and non-carcinogenic PAH) from residential fuel combustion (Oanh and others, 1999)**

Fuel	Emission factor, mg/kg		Emission factor, mg/MJ		Emission rate, mg/h		Emission concentration, µg/m <sup>3</sup>	
	total	genotoxic	total	genotoxic	total	genotoxic	total	genotoxic
wood vapour/total	43–192 95%	6.7–18.3 59%	2.2–9.7	0.34–0.93	66–386	13.5–28.2	295–1790	62.3–125
coal briquettes vapour/total	33–191 99.9%	1.2–9.3 99.7%	1.4–8.3	0.05–0.4	10.1–47.6	0.35–2.4	52–247	1.8–12.2
charcoal vapour/total	15–35 99.6%	1.1–3.2 96.8%	0.47–1.14	0.035–0.103	6–14.6	0.43–1.3	25.1–68.6	1.8–6.1

most of the emissions from all three stoves. The PAH emissions were found to correspond to the volatile content of the fuel. A large percentage of most of the PAH measured were emitted from the stoves in the vapour rather than the particulate phase.

Peat fires may cause severe haze episodes, for example in south east Asia. Muraleedharan and others (2000) combusted peat samples from Brunei Darussalam at 480°C and 600°C in a closed chamber to identify the organic emissions by GC/MS. The temperatures were assumed to be characteristic of the smouldering combustion which would occur in residential fires. Alkanes of low molecular mass (C<sub>2</sub>–C<sub>4</sub>) were detected at both temperatures. The proportion of the alkanes of lower molecular mass (methane, ethane) increased as the temperature increased and the concentration of the longer chained alkanes decreased. No PAH were detected at either temperature as they were below the detection limit (the detection limit was not specified).

Biofuels (such as wood, agricultural residues and cattle dung) may have higher emission factors for PAH than fossil fuels due to the high volatile content of the biofuels which leads to a higher possibility of incomplete burning. The high volatile content of biofuels results in more gas-phase combustion for which the oxygen contact time is short. This is a common problem in small furnace volumes where the small reactor area contributes to incomplete combustion. It has been estimated that around 50% of the world households use biofuels for daily cooking and/or heating. The burning of fuel wood on simple tripods or three stone stoves can have efficiencies as low as 8–12%. A wide range of traditional and improved cookstoves, such as portable metal and ceramic wood stoves, have efficiencies in the range of 25–30%. This is still low compared to modern kerosene stoves (50%) and LPG stoves (>60%) (Oanh and others, 1999).

Thuss and others (2000) compared thiaarenes, sulphur containing PAH (PASH – polycyclic aromatic sulphur heterocycles), emissions from lignite briquettes with different sulphur contents. The emissions were measured from lignite-fired residential heating systems in Germany. Emission concentrations for individual PASH compounds were in the range of 0.01 (triphenylene [2,3-b]thiophene) to 20.0 µg/m<sup>3</sup> (C<sub>22</sub>H<sub>12</sub>S-thiaarenes such as triphenylene[1,14-bcd]thiophene). The results indicated that emissions from the briquettes varied because of the variation in the way the

different briquettes burned. Variations were also noticed between different burns of the same briquette type. Despite these differences, there was a positive correlation between the sulphur content of the briquettes and the PASH/PAH ratio. One of the briquettes contained calcium additives to reduce SO<sub>2</sub> emissions. This calcium also reduced the thiaarene emissions.

Within the 1998 UNECE protocol on POPs, the emission rate of 0.1–0.7 ng TEQ/m<sup>3</sup> PCDD/F was given for residential fireplaces burning wood and coal. It was emphasised that this increased when packing material or other household wastes were added. For example, wood combustion alone can produce emissions of PCDD/F at 0.06 ng/m<sup>3</sup> whereas this can increase to 8 ng/m<sup>3</sup> (relative to 11% O<sub>2</sub> by volume) with the addition of waste packing material. Investigations in several countries show values up to 114 ng/m<sup>3</sup> (with respect to 13% O<sub>2</sub> by volume) in residential combustion appliances burning waste materials (UNECE, 1999a).

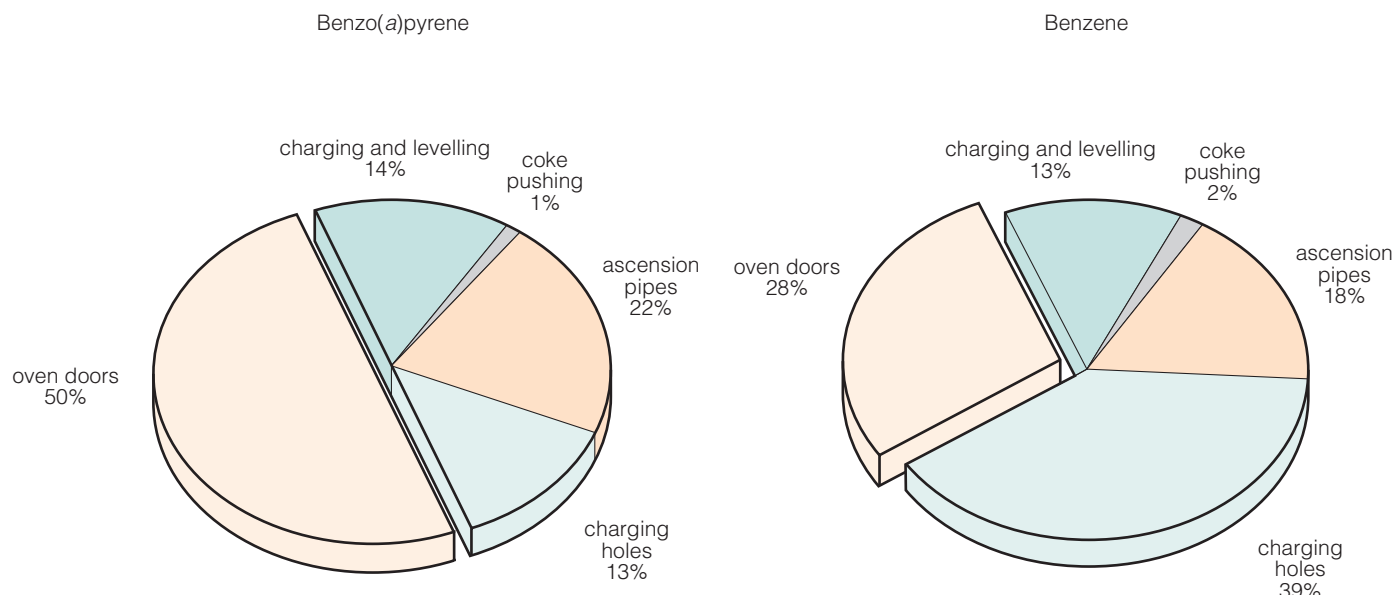
## 6.4 Industrial coal use

Coal can be used in several industrial manufacturing processes such as coke manufacture, metal smelting and cement production. The following sections give a brief overview of potential organic emissions from these sources.

### 6.4.1 Coke production

The production of coke involves the heating of coal in an oxygen-deprived atmosphere. In such conditions secondary reactions of carbon compounds such as aromatisation and cyclisation are promoted. PAH from coke production are released into the ambient air mainly through the charging holes, through leakages from the over door, pipes and lids and during coke pushing and cooling (UNECE, 1999a).

A separate report by the Clean Coal Centre (Reeve, 2000) deals with coke oven emissions. Emission factors were cited ranging from 62 mg/t coke in NordRhein-Westfalen to 40 mg/t coke in newer plants in Kaiserstuhl, Germany. It was noted in the review that the battery itself is the main source of emissions, with a relatively small contribution from the by-products plant. Measurements at an old 4.5 m battery



**Figure 13** Diffuse emission sources of benzo[a]pyrene and benzene around coke ovens (Reeve, 2000)

showed that 48% of the PAH and BTX emissions came from the oven doors and 42% from the charge-hole lids. Figure 13 shows the relative contributions to total B[a]P emissions from various sites at the August Thyssen coking plant of Thyssen Krupp Stahl AG (TKS) in Germany. It has been established that the majority of emissions are released during the early part of the coking cycle. PAH emissions can drop from over 3000  $\mu\text{g}/\text{m}^3$  at the beginning of the cycle to below 500  $\mu\text{g}/\text{m}^3$  within the first five hours of the cycle (Thomas, 1991). Reeve (2000) discusses the problems with maintaining coke oven emissions of B[a]P below the allowable ambient levels (2.5  $\text{ng}/\text{m}^3$ ) in neighbourhoods surrounding six Bruckhausen coke oven batteries of TKS in Duisburg, Germany. New batteries are projected to come on stream in 2003 which will be further away from the residential areas and the older batteries will be closed. It is expected that these changes will bring B[a]P concentrations within the legislated limit.

Khalili and others (1995) measured PAH emissions from different sources in the Chicago, USA, area. Naphthalene was by far the most concentrated of the PAH measured, accounting for 22.4  $\mu\text{g}/\text{m}^3$  of the total of around 25  $\mu\text{g}/\text{m}^3$  PAH emitted. Most other individual PAH compounds were at concentrations of around 0.5  $\mu\text{g}/\text{m}^3$  or less.

Non-recovery coke making emits significantly less PAH than the more conventional by-product recovery process since the ovens work under negative pressure. The ovens are not designed to recover chemical by-products and so the off-gases are burned efficiently at high temperatures and with long residence times. At the moment there is one plant of this type in the USA and one in Australia (UNECE, 1999a). No data were found on organic emissions from these plants.

PCDD/F may form during coke production due to the high temperatures and the presence of suitable carbon structures and chlorine impurities in the coal (Dyke and others, 1997). No data were found on emissions from these plants.

## 6.4.2 Aluminium, iron and steel production

Aluminium is produced from aluminium oxide ( $\text{Al}_2\text{O}_3$ ) by electrolysis in pre-bake or Soederberg cells connected in series. PAH are emitted during the preparation and baking of the pastes involved in the making of the carbon anodes, mainly from the coal tar pitch and petroleum coke used as an anode binder. The concentrations of PAH emitted from this process can be 'very high' (UNECE, 1999a). The iron and steel industry can also be a significant source of PAH in some areas. For example, in Norway the iron and steel industry is responsible for 12% of the total annual PAH emissions (Lee and others, 1999).

Lee and others (1999) measured PAH emissions from steel and iron works in Taiwan. The sources were classified into three groups: Group 1 used coal as a fuel; Group 2 used heavy oil and Group 3 used an electric arc furnace. The total PAH emission factors for the three groups were as follows:

Group 1	coal	4340 $\mu\text{g}/\text{kg}$ coal
Group 2	heavy oil	6050 $\mu\text{g}/\text{l}$ oil
Group 3	electric arc	2670 $\mu\text{g}/\text{kWh}$

It is difficult to compare these emission factors as the units are not the same. Average emission concentrations in the stack for the three groups give a clearer result – emissions from Group 3 sources, those with electric arcs, were the most concentrated with an average PAH concentration of 5430  $\mu\text{g}/\text{m}^3$ . Group 2 sources gave lower concentrations of 1990  $\mu\text{g}/\text{m}^3$  and Group 1 lower still at 583  $\mu\text{g}/\text{m}^3$ , on average. These average emission concentrations are to be based on plants with the same emission control technologies, which may explain some of the differences in values. A comparison of the particulate control technologies on the sources showed that baghouses had higher PAH removal efficiency than cyclones since they captured smaller particles

which had proportionally higher amounts of PAH adsorbed to the surface.

Halogenated compounds may enter sinter plants in the feed as coke breeze or salt content in the ore and in added recycled material (blast furnace top gas dust, filter dust and sludges from waste water treatment). These compounds can lead to the formation and release of PCDD/F. According to the UNECE (1999a) there is no clear link between the chlorine content of the feed materials and the emissions of PCDD/F. PCDD/F emissions from smelting plants in the secondary aluminium industry are around 0.1–14 ng TEQ/m<sup>3</sup>. The actual emissions depend on the type of smelting aggregates, materials used and the waste gas purification systems used (UNECE, 1999a). According to UNECE data, PCDD/F emissions from sinter plants in the iron and steel industry are around 0.4–4 ng TEQ/m<sup>3</sup>. Buekens and others (2001) say the range is greater at 0.3–30 ng TEQ/m<sup>3</sup>. Concentrations as high as 43 ng/m<sup>3</sup> have been measured at one plant with no pollution control measures present. Emissions of PCDD/F from steelworks, hot blast cupola furnaces, electric furnaces and electric arc furnaces are commonly lower than 0.1 ng TEQ/m<sup>3</sup>. However, cold-air furnaces and rotary tube furnaces have higher emissions (unspecified) (UNECE, 1999a).

### 6.4.3 Cement kilns

Few data were found relating to organic emissions from cement and concrete manufacture suggesting that emissions are low and not of concern. Cement kilns rarely appear on national inventories for organic compounds and, when they do, their contribution to the total is small. For example, data from Environment Canada (EC, 2001a) suggest that, of the 3.5 Mt of VOC emitted in 1995, only 438 t (<<1%) arose from the cement and concrete industry. Although there are requirements for monitoring organic emissions from cement kilns in countries such as the USA, it is recognised that most of these emissions result from the combustion of waste at these facilities, rather than coal (Willis and Sweeney, 1997).

Table 21 in Section 6.1 included VOC emissions from a 90 MW pulverised unit used for cement manufacture. The mineral feedstock to the kiln was known to have a high carbonaceous content. This feedstock is preheated by the flue gases as part of the cement making process and therefore is an additional source of VOC release into the stack.

PCDD/F emissions from cement kilns in Canada have been reported to range between 0.01 and 0.14 g TEQ/y (EC, 2001b).

## 6.5 Comments

Emissions of organic species from industrial coal combustion are higher than those from full-scale coal-fired power plants simply because the combustion in the former is less efficient. Further, since industrial systems are more batch-based systems, there are greater emissions during less efficient start-up and refuelling stages.

Fluidised bed combustion systems operate at lower temperatures (800–900°C) than pulverised coal fired plants. Numerous studies have confirmed that the combustion temperature is by far the most important factor with respect to PAH emissions from FBC units. For example, in one system the PAH emission was halved by increasing the combustion temperature from 800 to 900°C. The excess air ratio was the next most important factor, followed by the bed height.

Residential combustion is the least efficient form of combustion and therefore leads to the highest relative emissions of organic compounds – almost three orders of magnitude greater than emissions from industrial combustion systems. In some situations, residential combustion of poor quality coal can lead to more concentrated PAH emissions than fuels such as dry wood and can result in detrimental health effects in humans. This suggests that coal is not an ideal fuel for residential use and is far more suited for large-scale combustion systems.

Industrial uses of coal, such as coke production, aluminium, iron and steel production and cement manufacture, tend to give rise to significant concentrations of some organic species, although the coal feed is not the only cause of these emissions. Practices to reduce and control these emissions are discussed in Chapter 7.

## 7 Practices to reduce emissions

International agreements to reduce emissions of organic compounds, such as those discussed in Chapter 3, specify reduction targets and minimum time periods for groups of organic species rather than actually specifying how such reductions are to be achieved or which sources should be targeted. For example, the EU VOC directive states that, within the framework of ‘national plans’, adherence to limit values is not binding. With respect to VOC emissions it is clear that industrial chemical sources must be where adjustments are made initially as these are the greatest sources of emissions. VOC emissions from industrial processes and hazardous waste incineration are much higher than those from coal-fired power stations. This makes emission control on such sources more important and easier to apply than on minor sources. Emissions from industrial sources such as chemical plants can be controlled by means such as regenerative thermal oxidisers, high-energy corona discharge, biofiltration, steam reforming, membrane separation and bioscrubbing/biofiltration (Traister and Hamel, 1996; Moralee, 1994). Pre-concentration technologies such as those involving fluidised beds of suitable adsorption materials are also being developed (Biedell and Cowles, 1996) but it is unlikely that such technologies would be applied to coal-fired power units.

As yet there is no legislation applicable to PAH or PCDD/F emissions from coal utilisation at either international or national level. However, ambient legislation may be set or tightened on these compounds and this may, in turn, lead to moves towards reducing emissions of these compounds from all sources.

The following sections look at each of the individual source categories discussed throughout the report and summarise those strategies and practices which can and/or are being used to reduce emissions of organic compounds.

### 7.1 Coal-fired power plants

As shown in previous chapters, it is well recognised that coal-fired power plants are not a significant source of organic emissions to the atmosphere. The 1999 UNECE protocol on VOC emissions acknowledged that ‘*for most countries, the VOC reduction potential for power plants is negligible*’. The protocol included the requirement for ‘best available techniques’ for reducing VOC emissions from stationary sources. Control measures were suggested for other combustion sources, including industrial and residential use of coal, and not for coal-fired power plants. Within the 1998 UNECE protocol on POPs there is a recommendation that, in utility and industrial boilers over 50 MWt, improved energy efficiency and energy conservation will reduce emissions. However, this is a recommendation and not a requirement. The protocol also acknowledged that, although techniques to reduce emissions of particulate, SO<sub>x</sub> and NO<sub>x</sub> from coal-fired plants may also remove PCDD/F emissions in some

situations, this effect was not guaranteed. No best available technique was identified for the specific purpose of PCDD/F removal (UNECE, 1999a).

Although it is established that control for organic compounds from coal-fired power plants is currently not necessary, the following sections describe situations where emissions can be or have been reduced by alterations to the operation of the plant.

#### 7.1.1 Combustion conditions

As suggested throughout this report, by far the greatest reductions in organic emissions from almost all combustion sources are achieved by ensuring complete and efficient combustion. This should be by the optimisation of factors such as combustion temperature, fuel mixing, oxygen ratio and so on. These are all factors which the operators of combustion systems would try to maximise anyway to produce maximum power output.

The 1998 UNECE POPs protocol acknowledged that it would not be cost-effective to remove chlorine from oil or coal to reduce emissions of PCDD/F. With respect to the potential for increased PCDD/F resulting from the co-combustion of waste in coal-fired plants, the protocol recommended that this should only be undertaken in installations using gas purification systems with appropriate flue gas controls.

The formation of organic compounds such as PCDD/F can be minimised in waste incineration systems by careful management of the feed material to reduce the content of halogenated substances and the promotion of recycling. Further formation can be avoided by ensuring that combustion is complete and takes place at temperatures above 850°C (UNECE, 1999a). Such controls would be unnecessary on large-scale coal-fired power plants as the fuel and combustion conditions do not normally promote the formation of these compounds. However, these methods for reducing emissions may be more relevant during the co-combustion of waste materials with coal in smaller-scale industrial units and in residential systems.

#### 7.1.2 Pollution control systems

De novo synthesis of PCDD/F can occur in flue gases in areas such as ESP systems at 250–450°C. As discussed in Chapter 5, the ESP systems in coal-fired power plants are generally operated at temperatures below those which are suitable for PCDD/F formation. This formation can be avoided in waste incineration systems by several means including (UNECE, 1999a):

- quenching of flue gases;
- using high temperature dust collection systems (such as ceramic filters and cyclones at 800–1000°C);



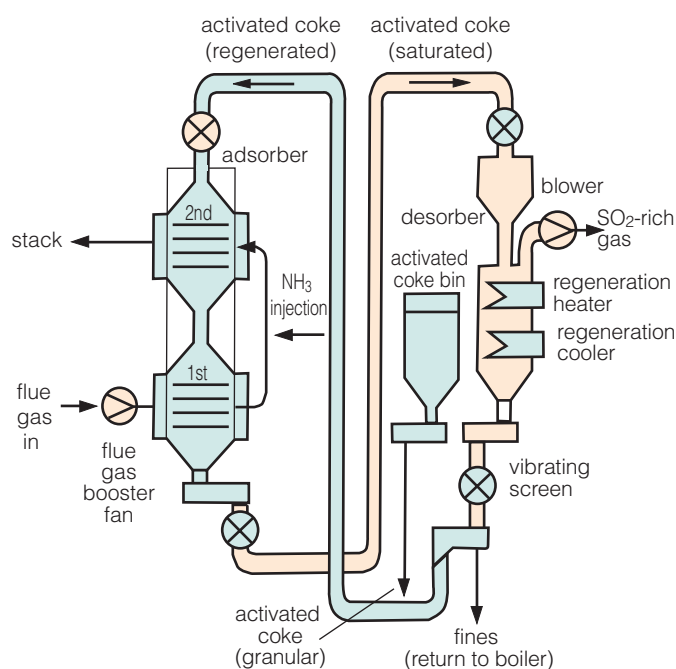
- the operation of bag filters below 150°C;
- the operation of ESP above 450°C;
- avoiding fly ash deposition in the flue gas exhaust system.

The UNECE document stresses that the reduction of PCDD/F in waste incineration flue gases is very complex and that there is no single clear method for the control of these emissions.

Wet flue gas desulphurisation (**FGD**) is used on many coal-fired power plants for the control of SO<sub>2</sub> emissions. As shown in Chapter 5, there are very few data on the effect of FGD on the control of organic emissions. Bendig (1995) emphasises the importance of the gas/liquid contact between flue gas and scrubbing systems suggesting that selection of nozzle type can enhance or reduce pollution control for many volatile pollutants, which may include VOC.

**Activated carbons** are used for the control of toxic emissions from sources such as waste incinerators in Europe. Although the target species are generally HCl and mercury, VOC may also be captured. An activated carbon process for the combined removal of SO<sub>x</sub>, NO<sub>x</sub> and air toxics has been designed by MET-Mitsui – BF (Marsulex Environmental Technologies- Mitsui-Bergbau Forschung) and is currently installed in two coal-fired boilers and two fluidised catalytic cracker units in Japan. Installations on a further utility boiler were planned to start in 1999–2000, also in Japan (Olson and others, 2000). The system uses activated carbon at 100–200°C. The activated carbon moves continuously from top to bottom through the adsorber unit. In the first stage the NO<sub>x</sub> is reduced with addition of NH<sub>3</sub> and in the second stage most of the SO<sub>x</sub> and air toxics removal occurs. A schematic of the system is shown in Figure 14. Once the activated carbon has passed through both stages it travels to the regeneration section where the trapped pollutants are thermally decomposed at 400°C producing a pollutant loaded gas. The activated carbon is either recycled to the adsorber or burned in the furnace as fuel while the polluted gas is scrubbed and the air toxics are collected in the waste water. Recent tests have shown the process to be effective in removing up to 99% of both PCDD and PCDF emissions from inlet concentrations of around 8 µg/m<sup>3</sup> for PCDD and 23 µg/m<sup>3</sup> for PCDF. Actual emission data from the Takehara Unit 2 power plant (combusting waste) show that with the activated carbon process running at 180°C, the inlet concentration of PCDD/F (TEQ) was reduced from 2.5 to 0.24 ng/m<sup>3</sup>, a removal efficiency of 90.4%. When the adsorber was run at 150°C, the inlet concentration was reduced from 3.30 to 0.06 ng/m<sup>3</sup>, a reduction of 98.2%. The process was also noted to be efficient in removing chlorobenzene, a precursor of PCDD/F, and is likely to be efficient at removing other volatile organic compounds, although no removal data were given. No data were given for PCDD/F or any other VOC removal for units firing coal, although it was suggested that the removal efficiencies would be similar.

The MET-Mitsui-BF process removes the PCDD/F from the flue gas into the activated carbon and then ultimately into waste water. Olson and others (2000) state that subsequent



**Figure 14 MET-Mitsui-BF dry DeSO<sub>x</sub>/DeNO<sub>x</sub>/air toxics removal process (Olson and others, 2000)**

treatment of this highly concentrated contaminant stream from the regenerator makes ultimate collection and disposal less costly.

**Urea injection** has been tested for PCDD/F control in waste incinerators. Ruokojarvi and others (2001) describe the testing of urea injection at a pilot-scale waste incineration plant in Finland firing RDF. The results indicated that the injection of urea can successfully inhibit PCDD/F formation if the correct conditions are used. The urea must be injected into the incineration system at an early stage and must be present long enough to create metal-inhibitor complexes to arrest PCDD/F and precursor formation. The combustion conditions and fuel are also important. Ruokojarvi and others suggest that the effect may also be successful on full-scale incinerators. However, whether such treatment would be successful, or even necessary, on coal-fired power plants, remains to be seen. Urea is commonly used in conjunction with SCR systems where the effect of the urea is enhanced by the oxidation effect of the catalyst.

In some areas of the USA, new oil and gas fired boilers may need to install controls for VOC. This control will not apply to coal-fired power plants in the foreseeable future. For the oil and gas plants, **oxidation catalysts** based on heated platinum, chromium or other precious metals can reduce VOC emissions by up to 80% (Lausman and Lavelly, 1997).

## 7.2 Industrial and residential coal combustion

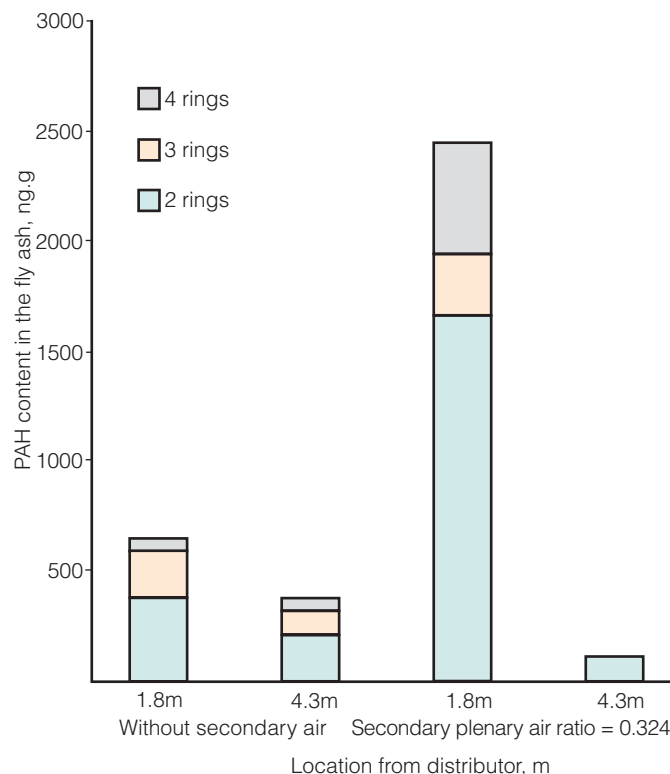
Although there is no legislation which is applicable specifically to organic emissions from industrial or residential



coal combustion systems, the emissions can be reduced by best practices which increase general efficiency. The 1999 UNECE protocol on VOC emissions included the requirement for 'best available techniques for reducing emissions from industrial and residential combustion sources. The suggested measures were as follows (UNECE, 1999b):

- industrial and commercial sources
  - energy savings
  - better maintenance
  - fuel-type modification
  - change of furnace and load
  - change of burning conditions
- small-scale combustion sources
  - energy savings (for example, insulation)
  - regular inspection
  - replacement of old furnaces
  - natural gas and fuel oil instead of solid fuels
  - central heating systems
  - district heating systems

Liu and others (2000b) studied the effect of air staging on a 0.1 MWth bench-scale FBC unit firing high volatile bituminous coal. It was noted that the use of secondary air for NO<sub>x</sub> control also had an effect on PAH emissions. High vortex secondary air injected into the freeboard of the FBC system was found to minimise the PAH in the fly ash as a result of more complete combustion. Figure 15 shows the effect of the use of secondary air. Although secondary air resulted in much lower PAH emissions, the actual PAH content on the fly ash 1.8 m from the distributor was actually higher than that without the use of secondary air. This was



**Figure 15** The effect of secondary air on the PAH content in the fly ash in FBC (Liu and others, 2000b)

because of the reduction of primary air when secondary air is being used. Thus the actual excess air ratio in the fluidising zone (below the second set of air nozzles) is lower than when secondary air is not being used. Liu and others (2000b) concluded that air staging was an effective method to reduce PAH emissions but also emphasised the importance of bed temperature, freeboard temperature and excess air ratio to reduce the production of PAH (*see* Chapter 6).

Liu and others (2000a) studied the behaviour of chlorine in a simulated FBC system and concluded that the temperature is of primary importance to PCDD/F formation in these systems. They suggest that PCDD/F formation can be minimised in FBC by maintaining combustion temperatures at around 850°C in the combustion area, 600°C in the freeboard area. They also suggested that oxygen concentrations should be kept low and that the residence time for particulates in the freeboard should be as long as possible.

With respect to emissions from **residential combustion**, the UNECE 1998 POP protocol recommended that emissions of POP could be reduced by restricting the input of materials to good quality fuel and avoiding the burning of waste, halogenated plastic and other materials. This will be achieved by passing suitable information to the public through the appliance manufacturers. Emissions of PAH from residential combustion could be reduced by switching from wood combustion to coal combustion and by ensuring the efficiency of boiler systems. Improvements in the combustion conditions of residential boilers and the use of ceramics in the combustion zone can reduce PAH emissions by up to 55%. For this to be adopted on a large scale, negotiations would have to be held with stove manufacturers to introduce approval schemes for stoves. It is recognised that low emissions of CO and total hydrocarbons result in lower emissions of PAH. Therefore limit values for CO and total hydrocarbons from residential boilers up to 300 kW, as set in the 1997 draft CEN standards, should result in lower emissions of PAH (UNECE, 1999a).

In their study of PASH emissions from lignite briquettes, Thuss and others (2000) noted that the emissions were reduced (no value given) when the briquettes contained calcium additives for SO<sub>2</sub> reduction.

## 7.3 Industrial coal use

As discussed in Chapter 6, industrial uses of coal, such as coke production and metal smelting, can be significant sources of organic compounds to the atmosphere. They are therefore becoming the target for legislation and control.

### 7.3.1 Coke production

Within the 1998 protocol on POPs, the UNECE recommended that PAH emissions from old coke ovens be reduced by technical measures aimed at reducing fugitive emissions from lids, doors and pipes. It was also recommended that, where possible, old coke plants were replaced and iron and steel plants should be technically

improved to avoid or reduce the requirement for coke. By ensuring efficient monitoring of leaks and doors, fugitive emissions can be kept to a minimum. Increasing coke oven volumes increases productivity whilst reducing the relative amount of PAH escaping from leaks and doors. Retrofitting existing coke batteries to allow condensation of flue gases from all sources (with heat recovery) can result in a decrease in PAH production of 86–90% in air (without regard to waste water treatment) (UNECE, 1999a).

Control of emissions from coke ovens is discussed in greater detail in a complementary report from the Clean Coal Centre (Reeve, 2000).

### 7.3.2 Aluminium, iron and steel making

PAH emissions from the Soederberg process in aluminium production can be reduced by 70–90% (to around 0.015 kg B[a]P/t Al) with primary abatement measures such as modernisation of the plants and optimisation of the process. Replacing Soederberg cells (using carbon blocks with petroleum coke and coal tar pitch as binders) with prebaked ones would require major reconstruction but could potentially almost eliminate all PAH emissions from this sector. The capital costs for such replacement would be high (UNECE, 1999a).

Sole and others (1999) report on the use of low softening point coal tar pitches, produced from thermal treatment, for the manufacture of electrodes for the aluminium industry in Brazil. These alternative pitches gave rise to lower PAH emissions (unspecified).

The UNECE protocol on POPs (UNECE, 1999a) suggests several methods for the reduction of PCDD/F from sinter plants. These include recirculating waste gas, the installation of fabric filters (in combination with ESP in some situations, with the injection of activated carbon) and high performance scrubbing. The latter can reduce emissions to 0.2–0.4 ng/m<sup>3</sup> and the additional use of adsorption agents such as lignite coal cokes can reduce emissions further to 0.1 ng TEQ/m<sup>3</sup>. Uncontrolled emissions are normally up to 4 ng TEQ/m<sup>3</sup> but can be over 40 ng TEQ/m<sup>3</sup> in some plants. For steel making, the separate collection of emissions from loading and discharging and the use of a baghouse or ESP with coke injection can reduce emissions to below 0.1 ng TEQ/m<sup>3</sup> with reduction efficiencies of 99%. Sorting, de-oiling and de-coating of scraps in the feedstock can also reduce emissions. Similar results are seen in the secondary aluminium industry. A state-of-the-art nitrogen/chlorine gas injection system for the removal of magnesium and other undesired components has been shown to reduce PCDD/F emissions further to around 0.3 ng TEQ/m<sup>3</sup>.

Buekens and others (2001) studied PCDD/F formation in an iron ore sintering plant and found that de novo synthesis took place during sintering and cooling as well as in the off-gas passages and collector ducts to the ESP. They suggest the use of inhibitors such as triethanolamine which can reduce de novo synthesis of PCDD/F in sintering plants by 50%.

Lowering the O<sub>2</sub> concentration in the gas stream was also found to reduce PCDD/F formation.

A report by the Commission of the European Communities (CEC, 1998b) gave results of a preliminary investigation into methods to reduce PCDD/F emissions from steel plants. Several options were considered:

- existing particulate control devices;
- catalysts used for NO<sub>x</sub> control also used as a PCDD/F control;
- coke injection for adsorption of PCDD/F;
- an incineration chamber with a natural gas source for high temperature destruction of PCDD/F.

The study showed that the capture of PCDD/F in the existing particulate control devices varied from 53% to 98.5% depending on the conditions. Most of the PCDD/F was present on smaller particles and more PCDD/F were found to pass through the filter at higher temperatures. The NO<sub>x</sub> catalyst was not successful for PCDD/F control in a high dust position because of the heavy dust load. It was suggested that the installation of a NO<sub>x</sub> catalyst in a low dust position would be too costly due to the large gas flow and the necessity of reheating the flue gas to the reaction temperature of around 350°C.

Coke injection as a sorbent showed an average PCDD/F reduction efficiency of 93%. The efficiency of the system actually decreased with increasing temperature, which was unexpected. Although the coke injection was effective, with an average PCDD/F reduction efficiency of 93%, it was costly and hazardous. The optimal method for PCDD/F control was found to be the introduction of an incineration treatment prior to the fabric filter, although no details of the system were given.

The CEC report concluded that the optimal condition for minimising PCDD/F production during scrap melting is to avoid the use of fossil fuel (CEC, 1998b).

### 7.3.3 Cement kilns

In the USA, new emission limits are expected for cement kilns. These limits would be for new and reconstructed kilns only and existing sources are exempt. The limit for total hydrocarbons, taken as a surrogate for hazardous VOC, would be 50 ppmv where previously there was no standard. The emission limit for PCDD/F would be 0.2 ng/m<sup>3</sup> TEQ or would take the form of a requirement for heating of the exhaust gases to 400°F (200°C) prior to any air pollution control devices and a then limit of 0.4 ng/m<sup>3</sup>. This limit applies to all plants, existing and new (Brubaker and others, 1997). Activated carbon treatment is used for PCDD/F control in some cement kilns in the USA (Willis and Sweeney, 1997).

## 7.4 Coal as a control option for waste incineration

Chapter 5 introduced the concept that coal can be added to

waste incineration to reduce organic emissions. The coal can increase the combustion efficiency of the waste material, raising the combustion temperature and therefore reducing organic emissions. Further, the sulphur in the coal can inhibit the formation of PCDD/F.

Liu and others (2000a) cite an example of lignite coal being added to paper recycling residues to decrease PCDD/F emissions from an FBC unit. They also cite the use of 60% coal in a municipal waste incinerator to 'drastically reduce' the formation of PCDD/F. Liu and others (2000a) suggest that FBC systems are best suited for the co-combustion of waste and coal with the concomitant reduction in PCDD/F emissions.

Gullett and others (2000b) report on the addition of small amounts of coal (<7% by weight) to municipal waste incineration to reduce PCDD/F emissions. Reductions in PCDD/F emissions of up to 80% were achieved. The rate of reduction of PCDD/F formation varied with the current fuel but also with past fuel burnt due to deposition on the combustor walls. The wall deposits act as sources and receptors of PCDD/F precursors, reactants and/or catalysts. The higher sulphur concentration provided by the co-combustion of coal displaces the sulphide/chloride equilibrium in the deposits, decreasing the chlorine contact with the active sites and/or reducing catalytic activity through formation of metal sulphates rather than metal chlorides. There was a two-hour lag in the increase in SO<sub>2</sub> concentration and the eventual decrease in PDDC/F emissions as the slower SO<sub>2</sub> increase overcomes the initial promotional effect of the coal feed.

Further research is needed to fully evaluate the potential for coal as a control measure for emissions from waste incineration. However, these initial results are promising. As mentioned in Chapter 5, it is likely that the optimum benefit would be obtained if waste were added to large-scale coal combustion systems where the destruction of organic species will be greatest and where any additional energy produced from waste can be utilised.

## 7.5 Comments

Since there is little or no legislation which applies specifically to organic emissions from coal combustion, any reductions made are being made voluntarily to help in the general reduction of air pollution. Organic emissions are generally products of incomplete combustion, and so many of the measures used to optimise plant performance result in a concomitant reduction in organic emissions. It is these improvements in general efficiency which are currently recommended as the most appropriate measures to reduce organic emissions from coal combustion. The improvements will be most beneficial on smaller, less efficient combustion systems such as industrial boilers and residential stoves.

Industrial uses of coal such as coke manufacture and metal production can lead to high concentrations of organic emissions. Again reductions can be achieved by increasing efficiency. However, in some situations the complete

replacement of old and inefficient systems is the best option. New control technologies, including the use of coke as a sorbent, are being developed specifically for the reduction of PCDD/F emissions from some metal smelting processes.

Waste incineration is a significant source of organic compounds, especially PCDD/F. It has been shown the co-combustion of coal with waste can reduce the release of organic compounds and inhibit PCDD/F formation. This effect would work best if waste were added to large-scale coal combustion systems.

## 8 Conclusions

The study of organic compounds from sources such as coal utilisation is hindered by the great number of compounds which may be released. Thousands of compounds may be formed, some of which are more important with respect to environmental problems than others. Although advanced sampling and analysis techniques can be used to distinguish and quantify these compounds, these methods would be too slow, complicated and expensive to perform routinely. And so emissions are commonly measured in terms of groups of compounds such as VOC, THC, PAH or PCDD/F.

Organic emissions from the clean and efficient use of coal are not of concern with respect to either human health effects or ground level ozone formation. Emission concentrations of VOC, PAH and PCDD/F from full-scale coal-fired power plants are so low that they rarely appear on national or international emission inventories. Emission factors, when available, are known to be inaccurate. This is partly because of the lack of accuracy at such low concentrations, and partly because these emissions are not considered to be of concern and are therefore not routinely measured. Because organic emissions from full-scale coal-fired plants are virtually negligible, there has been no requirement for legislative control and there is unlikely to be any such legislation in the foreseeable future.

Less efficient coal combustion results in the release of unburned organic material. Further, new organic compounds may be formed in the cooler areas of the combustion zone and downstream. Although emissions of organic compounds from industrial boilers are generally higher than those from utility plants, the emissions are still relatively low compared to sources such as chemical plants and the transport sector. There is currently no legislation which applies to organic emissions from industrial boilers. However, international agreements such as the UNECE VOC and POP protocols encourage practices which increase general efficiency at industrial boilers.

Fluidised bed combustion systems operate at lower temperatures (800–900°C) than pulverised coal fired plants. Many also combust lower grade fuels. This can mean higher emission factors compared to pulverised coal fired units. Maintaining a high combustion temperature (>900°C) is the most effective way to reduce organic emissions from FBC systems.

The combustion of coal in residential systems gives rise to concentrations of organic compounds which are several orders of magnitude greater than those from full-scale coal-fired power plants. Emissions from smoky coal combustion in residential stoves in countries such as China can directly contribute to human health effects. Although the emissions of organic compounds from coal combustion in residential stoves can be reduced by increasing their efficiency, this is one area where fuel switching from coal to more appropriate end-use fuels such as biofuels could be more appropriate.

In many countries industries such as coke manufacture and metal production are significant sources of organic emissions. Emissions from these sources are often difficult to evaluate accurately as the organic compounds may be released sporadically and from diffuse areas such as coke oven doors. Sampling these emissions is difficult and so obtaining a representative emission factor or average concentration over time is far more difficult than at the stack of a coal-fired power plant. Legislation on emissions of organic compounds from coke ovens may require major improvements in efficiency and, in some cases, the complete replacement of old coke oven batteries with new technologies is necessary. New flue gas treatment technologies such as activated carbon and flue gas heating systems are being suggested for the control of organic compounds from metal smelting.

This report has emphasised the fact that, when used efficiently, coal is not a significant source of organic compounds. In fact, coal combustion can be so efficient that it can remove organic compounds released and produced from the combustion of other materials such as waste. The sulphur released from the coal during combustion also acts as an inhibitor to the formation of PCDD/F from the chlorine in the fuels. Although more work is necessary, there is potential for coal-fired power plants to be used for co-combustion of waste in such a way that energy would be produced from both fuels and emissions of organic compounds would be reduced. Not only is efficient coal combustion a negligible source of organic emissions, it is also a potential solution to emissions of these compounds from waste incineration.



## 9 References

- Allen J O, Dookeran N M, Taghizadeh K, Smith K A, Sarofim A F (1997)** Measurement of oxygenated polycyclic aromatic hydrocarbons associated with a size-segregated urban aerosol. *Environmental Science and Technology*; 31 (7); 2064-2070 (1997)
- Altenstadt J, Pleijel K (2000)** An alternative approach to photochemical ozone creation potentials applied under European conditions. *Journal of the Air and Waste Management Association*; 50 (6); 1023-1036 (Jun 2000)
- Alvim Ferraz M C M, Moser S, Tonhaeuser M (1999)** Control of atmospheric emissions of volatile organic compounds using impregnated active carbons. *Fuel*; 78; 1567-1573 (1999)
- Agren C (2000)** Clashing over ceilings. *Acid News*; 3; 6-7 (Oct 2000)
- Aragon P, Atienza J, Climent M D (2000)** Analysis of organic compounds in air: a review. *Critical Reviews in Analytical Chemistry*; 30 (2&3); 121-151 (2000)
- Baker J I, Hites R A (2000)** Is combustion the major source of polychlorinated dibenzo-p-dioxins and dibenzofurans to the environment? A mass balance investigation. *Environmental Science and Technology*; 34 (14); 2879-2886 (2000)
- Bendig L (1995)** Wet scrubbers: match the spray nozzle to the operation. *Environmental Engineering World*; 1 (2); 12-17 (Mar 1995)
- Bertoni G, Tappa R, Allegrini I (2000)** Assessment of a new passive device for the monitoring of benzene and other volatile aromatic compounds in the atmosphere. *Annali de Chimica*; 90 (3-4); 249-263 (2000)
- Biedell E L, Cowles H (1996)** A novel pre-concentration technology for VOC and air-toxics control. In: *Emerging solutions to VOC and air toxics control*, Clearwater, FL, USA, 28 Feb-1 Mar 1996. Pittsburgh, PA, AWMA, pp 80-87 (1996)
- Bonfanti L, Cioni M, Riccardi J, Rossi C (1994)** PCDD/PCDF formation and destruction during co-firing of coal and RDF in a slag forming combustor. *Fresenius' Journal of Analytical Chemistry*; 348 (1/2); 136-140 (Jan 1994)
- Brain S A, Carr C E, Davies M, Rantell T (1995)** *Toxic organic compounds from coal combustion*. Rep COAL R037. Cheltenham, UK, Coal Research Establishment, 29 pp (1995)
- Brubaker D L, Bumpers W M, O'Hare A T (1997)** The Portland cement NESHAP rulemaking: a model for complex regulatory development. Paper presented at: *AWMA 90th annual meeting and exhibition*, 8-13 Jun 1997, Toronto, Ontario, Canada, 9 pp (1997)
- Buekens A, Stieglitz L, Hell K, Huang H, Segers P (2001)** Dioxins from thermal and metalurgical processes: recent studies for the iron and steel industry. *Chemosphere*; 42 (5-7); 729-735 (2001)
- Burg P, Fydrich P, Abraham M H, Matt M, Gruber R (2000)** The characterisation of an active carbon in terms of selectivity towards volatile organic compounds using LSER approach. *Fuel*; 79 (9); 1041-1045 (Jul 2000)
- Bursey J (2001)** *Risk burn guidance for hazardous waste combustion facilities. Appendix B: Sampling and analysis*. Morrisville, NC, Eastern Research Group, 130 pp (2001)
- CEC (1998a)** *Emission of volatile organic compounds (VOC) from coal-fired appliances*, EUR-17444-EN, Stoke Orchard, UK, Coal Research Establishment, 72 pp (1998)
- CEC (1998b)** *Optimisation of environmental and related energy utilisation on scrap-based steelmaking. Phase II*, EUR-18556-EN, Luxembourg, Commission of the European Communities, 88 pp (1998)
- Chagger H K, Jones J M, Pourkashanian M, Williams A (1997)** The nature of hydrocarbon emissions formed during the cooling of combustion products. *Fuel*; 76 (9); 861-864 (1997)
- Chagger H K, Jones J M, Pourkashanian M, Williams A, Owen A, Fynes G (1999)** Emission of volatile organic compounds from coal combustion. *Fuel*; 78 (13); 1527-1538 (1999)
- Chen M L, Mao I F, Wu M T, Chen J R, Ho C K, Smith T J, Wypij D, Cristiani D C (1999)** Assessment of coke oven emissions exposure among coking workers. *American Industrial Hygiene Association Journal*; 60 (1); 105-110 (Jan 1999)
- Chmielewski A G (1995)** Electron beam gaseous pollutants treatments. In: *IEEE conference record - abstracts: 1995 IEEE international conference on plasma science*. New York, NY, USA, Institute of Electrical and Electronics Engineers Inc, p 269 (1995)
- Chu P, Epstein M, Gould L, Botros P (1995)** Evaluation of air toxic emissions from advanced and conventional coal-fired power plants. Paper presented at: *Conference on new power generation technology*, San Francisco, CA, USA, 25-27 Oct 1995. 18 pp (1995)
- Coleman P (1993)** Stack sampling of toxic organic micropollutants. In: *Measurement of airborne pollutants*. S. Couling (ed), Oxford, UK, Butterworth-Heinemann, pp 242-259 (1993)
- Coleman W M, Dominguez L M, Gordon B M (1996)** A gas chromatographic continuous emission monitoring system for the determination of VOCs and HAPs. *Journal of the Air and Waste Management Association*; 46 (1); 30-34 (Jan 1996)
- Curran K J, Irvine K N, Droppo I G, Murphy T P (2000)** Suspended solids, trace metal and PAH concentrations and loadings from coal pile runoff to Hamilton Harbour, Ontario. *Journal of Great Lakes Research*; 26 (1); 18-30 (2000)
- Daughtrey E H, Oliver K D, Adams J R, Kronmiller K G, Lonneman W A, McClenny W A (2001)** A comparison of sampling and analysis methods for low ppbC levels of volatile organic compounds in ambient air. *Journal of Environmental Monitoring* 2001; 3 (1); 166-174 (2001)
- Davidson R M (1999)** *Experience of cofiring waste with coal*. CCC/15. London, UK, IEA Coal Research, 63 pp (Feb 1999)
- Davies M, Rantell T D, Stokes B J, Williamson F (1992)** *Characterisation of trace hydrocarbon emissions from coal fired appliances. Final report*. ECSC project no 7220-ED821. EUR-14866. Cheltenham, UK, Coal Research Establishment, 18 pp (Oct 1992)
- Delbrueck K (1998)** Mixing economic instruments with



- other instruments such as regulations or voluntary agreements/self-commitments. In: *Role of economic instruments in integrating environmental policy with sectoral policies*. Series no. ECE/CEP/60. Becvar J, Kokine M G (eds) New York, NY, USA, United Nations, pp 23-28 (Jun 1998)
- DETR (1999)** *Expert panel on air quality standards: Polycyclic aromatic hydrocarbons*, 99/30949, London, UK, DETR - Department of the Environment, Transport and the Regions, 35 pp (1999)
- DETR (2000)** *The air quality strategy for England, Scotland, Wales and Northern Ireland: working together for clean air*, CM4548 SE2000/3 NIA 7, London, UK, DETR - Department of the Environment, Transport and the Regions, 192 pp (2000)
- Drivas P J, Hopkins P K, Angotti L D (1996)** Use of a relational database system to quantify and reduce hazardous air pollutant emissions. In: *Emerging solutions to VOC and air toxics control*, Clearwater, FL, USA, 28 Feb-1 Mar 1996. Piitsburgh, PA, AWMA, pp 53-62 (1996)
- DTI (2000)** *Digest of United Kingdom Energy Statistics 2000*. Scullion M (ed), London, UK, Department of Trade and Industry, 305 pp (2000)
- Dyke P H, Wenborn M J, Coleman P J, Woodfield M J, Rose C L (1997)** *A review of dioxin releases to land and water in the UK*. Bristol, UK, Environment Agency, 87 pp (1997)
- EA, Environment Australia (2001a)** *National Pollutant Inventory Guide. August 2000 (revised). Version 2.3*. www.npi.ea.gov.au (2001)
- EA, Environment Australia (2001b)** *Emission estimation technique manual for fossil fuel electric power generation*. www.npi.ea.gov.au (2001)
- EMEP (1996)** *Atmospheric emission inventory guidebook. Volume 1*. Technical Report no 30. Luxembourg, European Environment Agency, EMEP Programme, vp (Feb 1996)
- ENDS (2000)** Coalite dioxins enter human food chain via game birds. *ENDS Report*; 300; 14-15 (Jan 2000)
- Environment Canada (1997)** *Strategic options for the management of toxic substances from the steel manufacturing sector - report of the stakeholders consultations*. Environment Canada, 123 pp (Dec 1997)
- EC, Environment Canada website (2001a)** www.ec.gc.ca/pdb/apc (May 2001)
- EC, Environment Canada website (2001b)** www.ec.gc.ca/dioxin/english (May 2001)
- ES&T (2000)** PBT releases, including dioxin, will be captured on TRI reports. *Environmental Science and Technology*; 34 (3); 73A (Feb 2000)
- ES&T (2001)** Canada's ozone plan. *Environmental Science and Technology*; 35 (5); 181-182A (May 2001)
- Fan Z, Zhang J, Fan C, Pennise D (2001)** The MMT bag for emission source sampling: design and evaluation. *Journal of the Air and Waste Management Association*; 51 (1); 60-68 (Jan 2001)
- Finkelman R B (1999)** Health impacts of residential coal combustion in China. In: *Prospects for coal science in the 21<sup>st</sup> Century*. Li B Q, Liu Z Y (eds) Taiyuan, China, Shanxi Science and Technology Press, pp 1457- 1460 (1999)
- Fitz D R, Motallebi N (2000)** A fabric denuder for sampling semi-volatile species. *Journal of the Air and Waste Management Association*; 50 (6); 981-992 (Jun 2000)
- Frankenhaeuser M, Manninen H, Kojo I, Ruuskanen J, Vartiainen T, Vesterinen R, Vrikki J (1993)** Organic emissions from co-combustion of mixed plastics with coal in a bubbling fluidised bed boiler. *Chemosphere*; 27 (1/3); 309-316 (Jul 1993)
- Frankenhaeuser M, Hitunen H, Manninen H, Palonen J, Ruuskanen J, Vartiainen T (1994)** Emissions from co-combustion of used packaging with peat and coal. *Chemosphere*; 29 (9/11); 2057-2066 (1994)
- Friedrich R (1997)** European emissions - distribution and trends: invited contribution to subproject GENEMIS. In: *EUROTRAC symposium 96: transport and transformation of pollutants in the atmosphere*, Garmisch-Partenkirchen, Germany, 25-29 Mar 1996. Southampton, UK, Computational Mechanics Publications, pp 24-34 (1997)
- Gerasimov G Y (2000)** Emission of dioxins in burning of chlorine-containing coals. *Chemical Physics Reports*; 18 (6); 1173-1181 (2000)
- Goklany I M (1998)** Did federalisation halt a race to the bottom for air quality? *EM -Environmental Manager*; 12-18 (Jun 1998)
- Gould R (1998)** Turning the screw: tightening up air quality standards. *Environment Business Magazine*: pp 24-33 (Sep 1998)
- Gridin V V, Inoue T, Ogawa T, Schechter I (2000)** On-line screening of airborne PAH contamination by simultaneous multiphoton ionisation and laser induced fluorescence. *Instrumentation Science and Technology*; 28 (2); 131-141 (2000)
- Gullett B K, Touati A, Lee C W (2000a)** Formation of chlorinated dioxins and furans in a hazardous-waste- firing industrial boiler. *Environmental Science and Technology*; 34 (11); 2069-2074 (2000)
- Gullett B K, Dunn J E, Raghunathan K (2000b)** Effect of co-firing coal on formation of polychlorinated dibenzo-p-dioxins and dibenzofurans during waste combustion. *Environmental Science and Technology*; 34 (2); 282-290 (Jan 2000)
- Hahn D W, Hencken K R, Johnsen H A, Ross J R, Walsh P M, Christy R H, Ziman S D (1999)** Real-time measurements of particulate matter and polycyclic aromatic hydrocarbon emissions from stationary combustion sources used in oil and gas production. In: *Emission Inventory: Living in a Global Environment*, Vol II. Sewickley, PA, USA, Air and Waste Management Association, pp 1175-1193 (1999)
- Heger H J, Zimmermann R, Blumenstock M, Kettrup A (2001)** On-line real-time measurements at incineration plants: PAHs and a PCDD/F surrogate compound at stationary combustion conditions and during transient emission puffs. *Chemosphere*; 42 (5-7); 691-696 (2001)
- Holland M J, Linton R W, Steger J L, Merrill R G, Strossman G S, Fister T F, Odom R W (1996)** Imagine mass spectrometry of particulate-associated polynuclear aromatic hydrocarbons. In: *Measurement of toxic and related air pollutants*. Pittsburgh, PA, USA, Air and Waste Management Association, pp 604-612 (1996)
- Huotari J, Vesterinen R (1996)** PCDD/F emissions from co-combustion of RDF with peat, wood waste and coal in FBC boilers. *Hazardous Waste and Hazardous Materials*; 13 (1); 1-10 (Sep 1996)
- Jackson P M, King P G (1993)** *An emissions audit of a chain grate stoker burning coal*. ETSU B 1313-P3, London, UK, Department of Trade and Industry, vp (1993)

- Jaeger-Voirol A (2000)** VOC: volatile organic compounds: formation and emission. In: *Pollutants from combustion: formation and impact on atmospheric chemistry. Nato Science Series C: Mathematic and Physical Sciences volume 547*. Vovelle C (ed) Dordrecht, The Netherlands, Kluwer Academic Publishers, pp 241-261 (2000)
- Jaszczur T, Lewandowski M, Szewczyk W, Zaczkowski A, Butcher T (1995)** Coal-fired stoves - efficiency and emissions. *ASHRAE (American Society of Heating, Refrigeration and Air-conditioning Engineers) Transactions*; 101 (1); 573-584 (1995)
- Jansen A A, Blinksbjerg P (2000)** *Baggrundsdokument for fastsaettelse af emissionsgraensevaerdi for PAH i luft*. Soberg, Denmark, dk-Teknik Energy and Environment, www.dk-teknik.dk/ref-lab/rapporter/PAH.asp 35 pp, In *Danish* (Jun 2000)
- Jantzi B L, Haites E F (1998)** Industry initiatives in emission reduction trading for smog mitigation in eastern Canada and bordering airsheds. In: *Greenhouse gas mitigation. Proceedings of the 1st international conference on technologies for activities implemented jointly (AIJ)*, Vancouver, BC, Canada 26-29 May 1997. Oxford, UK, Elsevier Science Ltd, pp 367-370 (1998)
- Jones J M, Pourkashanian M, Ross A, Danos L, Bartle K D, Williams A, Kubica K, Anderson J, Kerst M, Danihelka P (2000)** The combustion of coal and biomass in a fixed bed furnace. In: *Proceedings of the 5th European conference on industrial furnaces and boilers. Volume II*. Reis A, Ward J, Leuckel W, Collin R (eds), pp 45-54 (2000)
- Kaiser J (2000)** Toxicology - dioxin sparks controversy. *Science*; 288 (5470); 1313-1214 (May 2000)
- Khalili N R, Scheff P A, Holsen T M (1995)** PAH source fingerprints for coke ovens, diesel and gasoline engines, highway tunnels and wood combustion emissions. *Atmospheric Environment*; 29 (4); 533-542 (1995)
- Klemm O, Stockwell W R, Schlager H, Krautstrunk M (2000)** NOx or VOC limitation in East German ozone plumes? *Journal of Atmospheric Chemistry*; 35 (1); 1-18 (2000)
- Koziel J A, Pawliszyn J (2001)** Air sampling and analysis of volatile organic compounds with solid phase microextraction. *Journal of the Air and Waste Management Association*; 51 (2); 173-184 (Feb 2001)
- Kubica K, Nowak Z, Sciazko M (1997)** Clean coal combustion in small boilers. In: *14th annual international Pittsburgh coal conference and workshop: clean coal technology and coal utilisation*, Taiyuan, China, 23-27 Sep 1997. Pittsburgh, PA, USA, Pittsburgh Coal Conference, 1 pp (1997)
- Lausman R, Lavelly L (1997)** Controlling air toxics emissions poses challenges. *Power Engineering*; 101 (8); 23-25 (Aug 1997)
- Lee C W, Lemieux P M, Gullett B K, Ryan J V, Kilgroe J D (1998)** Research on emissions and mitigation of POPs from combustion sources. In: *Air pollution in the 21st century: priority issues and policy. Studies in Environmental Science 72*. Schneider T (ed). Amsterdam, The Netherlands, Elsevier Science BV, pp 361-378 (1998)
- Lee W-J, Lai S-O, Chen S-J, Hsueh H-J (1999)** PAH emission from steel and iron industries. In: *Air Pollution VII*. Brebbia C A, Jacobson M, Power H (eds) Boston, MA, USA, WIT Press, pp 357-366 (1999)
- Lefevre T, Timilsina G R, Shrestha S (2000)** Techno-economic databases for environmental policy analysis in Asia: requirements and barriers. *Pollution Atmospherique*; 4; 79-88 (Oct 2000)
- Lemieux P M, Lee C W, Ryan J V (2000)** Prediction of dioxin/furan incinerator emissions using low- molecular weight volatile products of incomplete combustion. *Journal of the Air and Waste Management Association*; 50 (12); 2129-2137 (Dec 2000)
- Levendis Y A, Atal A, Courtmanche B, Carlson J B (1998a)** Burning characteristics and gaseous/solid emissions of blends of pulverised coal with waste tire-derived fuel. *Combustion Science and Technology*; 131 (1/6); 147-185 (1998)
- Levendis Y A, Atal A, Carlson J B (1998b)** Emissions from burning tire-derived fuel (TDF): comparison of batch combustion of tire chips and continuous combustion of tire crumb mixed with coal. In: *Proceedings of the 23rd international technical conference on coal utilisation and fuel systems*. Clearwater, FL, USA, 9-13 Mar 1998. Sakkestad B A (ed) Washington, DC, USA, Coal and Slurry Technology Association, pp95-106 (1998)
- Lewis A C (2000)** New directions: novel separation techniques in VOC analysis pose new challenges to atmospheric chemistry. *Atmospheric Environment*; 34; 1155-1156 (2000)
- Li H, Yang X, Tomes W, Pan W P, Riley J T (1997)** Chlorinated organic compounds evolved during the combustion of blends of refuse-derived fuels and coals. *Journal of Thermal Analysis*; 49 (3); 1417-1422 (1997)
- Liu K, Pan W-P, Riley J T (2000a)** A study of chlorine behaviour in a simulated fluidised bed combustion system. *Fuel*; 79 (9); 1115-1124 (2000)
- Liu K, Xie W, Zhao Z B, Pan W P, Riley J T (2000b)** Investigation of polycyclic aromatic hydrocarbons in fly ash from fluidised bed combustion systems. *Environmental Science and Technology*; 34 (11); 2273-2279 (2000)
- Lohmann R, Northcott G L, Jones K C (2000)** Assessing the contribution of diffuse domestic burning as a source of PCDD/Fs, PCBs and PAHs to the UK atmosphere. *Environmental Science and Technology*; 34 (14); 2892-2899 (2000)
- Luria M, Tanner R L, Imhoff R E, Valente R J, Bailey E M, Mueller S F (2000)** Influence of natural hydrocarbons on ozone formation in an isolated power plant flume. *Journal of Geophysical Research*; 105 (D7); 9177-9188 (Apr 2000)
- Maspero M, Rusconi M, Fiore A, Negri A, Sanavio D (2001)** Assessment of some organic pollutants from combustion processes. Preliminary results of laboratory and field tests. Paper presented at: *CEM 2001*, Arnhem, Netherlands, 25-27 April 2001. London, UK, IEA Coal Research, 15 pp (2001)
- Mastral A M, Callen M S (2000)** A review on polycyclic aromatic hydrocarbon (PAH) emissions from energy generation. *Environmental Science and Technology*; 34 (15); 3051-3057 (Aug 2000)
- Mastral A M, Callen M, Murillo R (1996)** Assessment of PAH emissions as a function of coal combustion variables. *Fuel*; 75 (13); 1533-1536 (1996)
- Mastral A M, Callen M S, Murillo R, Garcia T (1999a)** PAH emissions from coal atmospheric fluidised bed combustion. In: *Prospects for coal science in the 21st*



- Century. Li B Q, Liu Z Y (eds) Taiyuan, China, Shanxi Science and Technology Press, pp 1373-1376 (1999)
- Mastral A M, Callen M S, Murillo R, Garcia T (1999b)** Organic emissions from coal AFBC. In: *Proceedings of the 15<sup>th</sup> international conference on fluidised bed combustion, Savannah, Georgia, USA, 16-19 May 1999*. New York, NY, USA, American Society of Mechanical Engineers, paper no FBC99.0092, 10 pp (1999)
- Mastral A M, Callen M S, Garcia T (2000a)** Toxic organic emissions from coal combustion. *Fuel Processing Technology*; 67 (1); 1-10 (2000)
- Mastral A M, Callen M S, Garcia T (2000b)** Polyaromatic environmental impact in coal-tire blend atmospheric fluidised bed combustion. *Energy and Fuels*; 14 (1); 164-168 (Feb 2000)
- Moralee D (1994)** Air pollution abatement and treatment: technology guide. *Environmental Business Magazine*; 6; 13-29 (Sep 1994)
- Muraleedharan T R, Radojevic M, Waugh A, Caruana A (2000)** Emissions from the combustion of peat: an experimental study. *Atmospheric environment*; 34; 3033-3035 (2000)
- Oanh N T K, Reutergårdh L B, Dung N T (1999)** Emission of polycyclic aromatic hydrocarbons and particulate matter from domestic combustion of selected fuels. *Environmental Science and Technology*; 33 (16); 2703-2709 (1999)
- Ohlsson O O (1993)** Results of performance and emissions testing when cofiring blends of dRDF/coal in a 440 MWe cyclone fired combustor. In: *Proceedings of the 10<sup>th</sup> annual international Pittsburgh coal conference*. Pittsburgh, PA, USA, 20-24 Sep 1993. Chiang S-H (ed) Pittsburgh, PA, USA, University of Pittsburgh, pp 505- 510 (1993)
- Ohlsson O O (1994)** Results of performance testing and emission testing when co-firing blends of dRDF/coal in a 440 MWe cyclone fired combustor. In: *Alternate fuels IV conference*. New Orleans, LA, USA, 8-9 Feb 1994. Burke, VA, USA, Council of Industrial Boiler Owners, pp 39-52 (1994)
- Olson D, Tsuji K, Shiraishi I (2000)** The reduction of gas phase air toxics from combustion and incineration sources using the MET-Mitsui-BF activated coke process. *Fuel Processing Technology*; 65-66; 393-405 (2000)
- Options (1998)** RAINS: regional air pollution information and simulation. *IIASA Options*; 6-16 (1998)
- Oros D R, Simoneit B R T (2000)** Identification and emission rates of molecular tracers in coal smoke particulate matter. *Fuel*; 79 (5); 515-536 (Apr 2000)
- Owen A J, Fynes G, Sage P W (1997)** *Emissions of radiative gases and ozone precursors from coal use*. UK DOE Report EPG/1/1/1. Stoke Orchard, Cheltenham, CRE Group Ltd, vp (Jan 1997)
- Pease J (2000)** Meeting VOC directive requirements. *Environment Business Magazine*; 52-53 (May/June 2000)
- Perret R (2001)** *Project: organic micropollutants*. France, Inersis, remi.perret@inersis.fr (May 2001)
- Placet M, Mann C O, Gilbert R O, Niefer M J (2000)** Emissions of ozone precursors from stationary sources: a critical review. *Atmospheric Environment*; 34 (12/14); 2183-2204 (2000)
- Reeve D A (2000)** *Coke production and the impact of environmental legislation*. CCC/35. London, UK, IEA Coal Research, 74 pp (Aug 2000)
- Reichl D, Krage R, Krummel C, Gauglitz G (2000)** Sensing of volatile organic compounds using a simplified reflectometric interference spectroscopy setup. *Applied Spectroscopy*; 54 (4); 583-586 (2000)
- Reinmann J (2001)** Continuous monitoring of the dioxin/furan emission of nearly all waste incinerators in Belgium. Poster presented at: *CEM 2001*. Arnhem, The Netherlands, 25-27 April 2001. Sneek E (ed), Arnhem, The Netherlands, KEMA, 1 pp (2001)
- Ridge T, Seif J M (2000)** *Source testing manual revision 3.3. New Millennium edition*. Pennsylvania, USA, Dept of Environmental Protection, Bureau of Air Quality, 38 pp. www.dep.state.pa.us/dep/deutate/airwaste/qaq/source/sts.htm (Nov 2000)
- Riley C E (2001)** Method development and implementation for co-planar polychlorinated biphenyls (PCBs). Paper presented at: *Stationary source sampling and analysis for air pollutants XXV*, Destin, FL, USA, 25-30 Mar 2001, New York, NY, USA, Engineering Foundation, 19 pp (2001)
- Ruokojarvi P, Asikainen A, Ruuskanen J, Tuppurainen K, Mueller C, Kilpinen P, Yli-Keturi N (2001)** Urea as a PCDD/F inhibitor in municipal waste incineration. *Journal of the Air and Waste Management Association*; 51 (3); 422-431 (Mar 2001)
- Ruuskanen J, Vartiainen T, Kojo I, Manninen H, Oskanen J, Frankenhäuser M (1994)** Formation of polychlorinated dibenzo-p-dioxins and dibenzofurans in co-combustion of mixed plastics with coal: exploratory principal component analysis. *Chemosphere*; 28 (11); 1989-1999 (1994)
- Ruuskanen J, Halonen I, Frankenhäuser M, Manninen H, Vilokki H, Vartiainen T (1995)** Behaviour of polychlorinated dioxin and furan emissions from co-combustion of different waste materials: principal component analysis study. In: *Proceedings of the 10<sup>th</sup> world clean air congress. Emissions and control*. Espoo, Finland, 28 May - 2 Jun 1995. Tolvanen M, Anttila P, Kamari J (eds) Helsinki, Finland, Finnish Air Pollution Prevention Society, Paper 086, 4 pp (1995)
- Salway A G (1999)** *UK Greenhouse gas inventory, 1990 to 1997: annual report for submission under the framework convention on climate change. Report AEAT-5689*. Culham, UK, National Environmental Technology Centre, 105 pp (Nov 1999)
- Schleicher O (2001)** Soborg, Denmark, dk-Teknik Energy and Environment, Air Pollution Department, *personal communication* (May 2001)
- Shaw I A C (1999)** Environmental issues facing the coking industry into the 21<sup>st</sup> century. In: *Second McMaster cokemaking course*, McMaster University, Hamilton, Ontario, Canada, Volume 1, Lecture 7, pp 7.1-7.26 (May 1999)
- Sloss L L (1998)** *Sampling and analysis of PM<sub>10</sub>/PM<sub>2.5</sub>*. CCC/09. London, UK, IEA Coal Research, 38 pp (Oct 1998)
- Sloss L L, Gardner C A (1995)** *Sampling and analysis of trace emissions from coal-fired power stations*. IEACR/77. London, UK, IEA Coal Research, 74 pp (Feb 1995)
- Sloss L L, Smith, I M (1993)** *Organic compounds from coal utilisation*. IEACR/63. London, UK, IEA Coal Research, 69 pp (Oct 1993)
- Smith I M (1984)** *PAH from coal utilisation – emissions and effects*. ICTIS/TR29. London, UK, IEA Coal Research, 117 pp (Dec 1984)
- Sole R A, Vina J A, Bermejo J, Garcia R, Moineiro S R**

- (1999) Low volatile PAH coal tar pitches used in the aluminium production. In: *Prospects for coal science in the 21<sup>st</sup> Century*. Li B Q, Liu Z Y (eds) Taiyuan, China, Shanxi Science and Technology Press, pp 1001-1004 (1999)
- Solomon B D, Gorman H S (1998)** State level air emissions trading: the Michigan and Illinois models. *Journal of the Air and Waste Management Association*; 48 (12); 1156-1165 (Dec 1998)
- Stewart R, Walker D (1997)** *Emissions to atmosphere from fossil fuel power generation in the UK*. AEAT- 0746. Abingdon, UK, AEA Technology Plc, National Environmental Technology Centre, 89 pp (Jan 1997)
- Sun C, McRae C, Snape C E, Fallick A E, Taylor D (1999)** Use of coal compound specific stable isotope measurements to source coal-derived PAH in the environment. In: *Prospects for coal science in the 21<sup>st</sup> Century*. Li B Q, Liu Z Y (eds) Taiyuan, China, Shanxi Science and Technology Press, pp 1353-1356 (1999)
- Sundermann B, Rubach T, Rensch H P (1995)** Feasibility study on the co-combustion of coal/biomass/sewage sludge and municipal solid waste for plants with 5 and 20 MW thermal power rating using fluidised bed technology. In: *APAS Clean coal technology programme 1992-94. Volume II: Combined combustion of biomass/sewage sludge and coals. Final reports*. Bemtgen J M, Hein K R G, Minchener A J (eds) Stuttgart, Germany, University of Stuttgart, Institute for Process Engineering and Power Plant Technology, 30 pp, paper B21 (Sep 1995)
- Tagashira K, Torii I, Myouyou K, Takeda K, Mizuko T, Tokushita Y (1999)** Combustion characteristics and dioxin behaviour of waste fired CFBC. *Chemical Engineering Science*; 54 ; 599-5607 (1999)
- Thomas B (1991)** *Pollution at coke works: joint report of investigations into the measurement of polycyclic aromatic hydrocarbons (Project 7257-13) and benzene, toluene and xylene (Project 7257-14) in and around coke works*. Report no EUR 13196EN. Luxembourg, Commission of the European Communities, 61 pp (1991)
- Thuss U, Popp P, Ehrlich C, Kalkoff W (2000)** Identification and quantification of thiaarenes in the flue gas of lignite-fired domestic heating. *Journal of High Resolution Chromatography*; 23 (7/8); 457-473 (2000)
- Tian- Rui Li (1999)** Trend of coking industry in Shanxi, China. In: *Coke outlook 99, crisis or opportunity*. New Orleans, LA, USA, Gorham/Intertech Consulting, Gorham, Maine, USA (Feb 1999)
- Tolnai B, Gelencser A, Barko G, Hlavay J (2000)** Evaluation of the applicability of different adsorbents for the diffusive sampling of volatile organic hydrocarbons in ambient air. *Magyar Kemiai Folyoirat*; 106 (7); 270- 276 (2000) *In Hungarian*
- Traister M, Hamel T M (1996)** Overview of emerging control technologies for treating VOC emissions. In: *Emerging solutions to VOC and air toxics control*, Clearwater, FL, USA, 28 Feb-1 Mar 1996. Pittsburgh, PA, AWMA, pp 171-182 (1996)
- UKEA (2000)** *The state of the environment in England and Wales: the atmosphere*. M00/21069. Bristol, UK, Environment Agency, vp (Mar 2000)
- UNECE (1999a)** *1979 Convention on long-range transboundary air pollution and its 1998 protocols on persistent organic pollutants and heavy metals*, ECE/EB.AIR/66, Geneva, Switzerland, United Nations Economic Commission for Europe, 91 pp (1999)
- UNECE (1999b)** *Protocol to the 1979 convention on long-range transboundary air pollution concerning the control of emissions of volatile organic compounds or their transboundary fluxes*. GET FULL REF FROM CDROM
- US EPA (1998)** *USEPA national air pollutant emission trends update, 1970-1997*. EPA-454/E-98-007. Research Triangle Park, NC, USA, US EPA Office of Air Quality Planning and Standards, 116 pp (Dec 1998)
- Vesterinen R, Flyktmann M (1996)** Organic emissions from co-combustion of RDF with wood chips and milled peat in a bubbling fluidised bed boiler. *Chemosphere*; 32 (4); 681-689 (Feb 1996)
- Vovelle C, Delfau J L (2000)** Formation of aromatics from combustion systems. In: *Pollutants from combustion: formation and impact on atmospheric chemistry. Nato Science Series C: Mathematic and Physical Sciences volume 547*. Vovelle C (ed) Dordrecht, The Netherlands, Kluwer Academic Publishers, pp 183-203 (2000)
- Westlin P (2001)** Highlights of emission measurements development activities for 2000-2001. Paper presented at: *Stationary source sampling and analysis for air pollutants XXV*, Destin, FL, USA, 25-30 Mar 2001, New York, NY, USA, Engineering Foundation, 12 pp (2001)
- Wickert B, Friedrich R, Merten D (1998)** Emissions of air pollutants in the New Federal States of Germany. *Gefahrstoffe - Reinhaltung der Luft*; 58 (1/2); 51-55 (Jan-Feb 1998) *In German*
- Willis D A, Sweeney D M (1997)** MACT compliance in the cement industry. Paper presented at: *AWMA 90<sup>th</sup> annual meeting and exhibition*, Toronto, ON, Canada, 8-13 Jun 1997, 7 pp (Jun 1997)
- Winner D A, Cass G R (2000)** Effect of emissions control on the long-term frequency distribution of regional ozone concentrations. *Environmental Science and Technology*; 34 (12); 2612-2617 (2000)
- Xu J, Xie Y, Bowles J, Pan W-P, Riley J T (1998)** Studies of the mechanism for the formation of chlorinated organics during the combustion of MSW and coal. *American Chemical Society, Division of Fuel Chemistry, Preprints*; 43 (1); 173-179 (1998)
- Zevehoven R (2001)** [www.hut.fi/~rzevenho.gasbook](http://www.hut.fi/~rzevenho.gasbook) (2001)
- Zhao Z-B, Fant M, Liu K, Pan W-P, Riley J T, Xie K-C (1999a)** Analysis of polycyclic aromatic hydrocarbons in fly ash from a fluidised bed reactor. In: *Prospects for coal science in the 21<sup>st</sup> Century*. Li B Q, Liu Z Y (eds) Taiyuan, China, Shanxi Science and Technology Press, pp 1529-1532 (1999)
- Zhao Z-B, Fant M, Liu K, Pan W-P, Riley J T, Xie K-C (1999b)** Behaviour of polycyclic aromatic hydrocarbons from different types of coal. In: *Prospects for coal science in the 21<sup>st</sup> Century*. Li B Q, Liu Z Y (eds) Taiyuan, China, Shanxi Science and Technology Press, pp 1417-1420 (1999)