

# The emissions of heavy metals and persistent organic pollutants from modern coal-fired power stations

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## Abstract

Extensive research for establishing the emissions of heavy metals from coal-fired power stations is performed in the Netherlands for the past 25 years. In the Netherlands coal is fired from all over the world. This means that the emissions are established for coal of various origins. In the eighties, the emissions of installations equipped with ESPs (electrostatic precipitators) were measured. In the nineties, the influence of wet FGD (flue gas desulphurisation) on the emissions was studied. The effect of co-combustion of biomass and other secondary fuels is the main item for the last 10 years.

Fifty-five elements were measured in the solid state and eight elements in the gaseous phase. It appeared that at low particulate concentration the influence of calcium containing evaporated water droplets downstream the wet FGD on the emissions of heavy metals is bigger than the composition of the coal. Also it appeared that at modern coal-fired power stations the emissions are hardly influenced by co-combustion of biomass. All the results are used for modelling, resulting in the KEMA TRACE MODEL<sup>®</sup>, by which the emissions can be predicted. The established emission factors are for most elements in good agreement with literature values for comparable modern installations.

Persistence organic pollutants (POPs) that were detected in the flue gases of coal-fired power stations are polycyclic aromatic hydrocarbons (PAH) and dioxins/furans. Measurements during full coal-firing and during co-firing of biomass have indicated that these emissions are negligible.

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**Keywords:** Emission factors; Coal-fired power stations; Co-firing; Heavy metals; PAH; Dioxins

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## 1. Introduction

Currently electricity in the Netherlands is mainly generated using natural gas and coal; only imported bituminous coal is fired. The contribution of coal increased from about 1% in 1974 to about 45% in 1995 (from about 0.1 million metric tons to about 10 million metric tons). Today the coal consump-

tion for the central generated electricity is about  $8.5 \times 10^6$  metric ton and coal is partly replaced by biomass (13.5%). The Dutch government promotes the co-combustion of biomass or other secondary fuels in order to reduce CO<sub>2</sub> emissions. The electricity companies have agreed with the government to reduce CO<sub>2</sub> emissions by 3 million metric tons by 2008. In practice this means that about 13% of the coal in terms of energy, or about 20% in terms of dry mass, will be replaced by secondary fuel. Typical values for the coal today are a calorific value of 25 MJ kg<sup>-1</sup>, an ash content of about 13%

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and a sulphur content of 0.8%. Most of the coal used is imported from South Africa, Colombia and Indonesia. But also coal is imported from Australia, Russia, USA, Poland and China. Only pulverised coal-fired dry bottom boilers are installed in the Netherlands, with one exception of a CGCC-plant (coal gasification combined cycle) that will not be discussed in this paper. The flue gases are cleaned by high-efficiency cold-side electrostatic precipitators (ESPs) and by wet flue gas desulphurisation (FGD) installations of the lime(stone)/gypsum process. SCR type of deNO<sub>x</sub> is present in 85% of the installed capacity; it will be 100% in 2008.

Following the reintroduction of coal after the oil crisis in 1973 as a fuel for power plants in the Netherlands, the environmental consequences for electricity generation have been thoroughly studied; for instance in the Dutch National Coal Research Programme (NOK). A rather important environmental aspect is the fate of the trace elements, present in the fuel. The concentrations and distributions of trace elements in coal, ash, and flue gas vapour phase were determined in 42 mass balance studies in coal-fired power plants. The information from these studies was used to calculate enrichment factors for the trace elements in ash and the vaporisation percentage of the macro, minor and trace elements in the flue gases. These enrichment factors and vaporisation percentages, combined with trace element analyses of the coals are used to predict the concentrations of trace elements in the ash and vapour phase of flue gases.

Trace elements are emitted into the air in solid (fly ash) and gaseous states. The emissions in the solid state are low due to their high degree of removal in ESPs. The emissions in the gaseous phase are relatively more important. In a plant with equipped with FGD both emissions are further diminished.

Since 1993, KEMA has researched the effect of direct co-combustion in 55 test series. In the first three years, seven tests were performed at the KEMA 1 MW test boiler, followed by 24 tests on a real scale at all seven Dutch coal-fired power stations in the following seven years. In these tests, secondary fuels are co-combusted in proportions up to 10% in terms of dry mass. In 2001, test series were started in which secondary fuels were co-combusted in proportions of more than 10% in terms of dry mass. At first, three test series were conducted in the KEMA 1 MW test boiler, followed by 11 tests on a real scale at three different power stations.

The ash released from a coal-fired power station is generally referred to as fly ash or coal fly ash (CFA). However, this term can be confusing, for two reasons. First, “fly ash” is a generic term, which can be applied to residues from the combustion of various substances. Second, the properties of the ash produced by the combustion of coal depend on the combustion technique used and to a considerable extent upon the precise part of the plant in which the ash is produced. These matters are considered in more detail below.

The composition of the ash produced depends on numerous parameters, which are summarised in Table 1. While the term “fly ash” is applied to all the materials produced, these materials are in fact quite different from one another, with divergent physical, chemical and consequently toxicological properties. It should be born in mind that a great deal of the research into the toxicological properties of fly ash, for instance, makes no reference to the process in which the fly ash was produced.

There can be considerable variations in the composition and morphology of CFA produced from the combustion of different coals. Since different combinations of flue gas cleaning devices are used in other countries, it cannot be assumed that the (fly) ashes produced in the Netherlands have a similar composition to the ashes described in the literature. Even in cases where the plant is comparable, the ash produced may differ on account of the type of coal used. Coal can be

Table 1  
Parameters influencing the composition of collected ash

Primary parameter	Secondary parameter
Fuel	Coal (subdivided according to type, origin and ash content), brown coal, peat, industrial waste, domestic waste, paper, etc.
Combustion technique	Grate boilers, pulverised coal boilers with dry ash removal, pulverised coal boilers with wet ash removal, cyclone boilers, gasification, fluidised bed combustion, fluidised bed gasification, etc.
Temperature and period of residence	During combustion and in the flue gas ducts
Type of particle filter	ESPs (high-temperature, low-temperature, dry and wet systems), cyclones, baghouses, wet systems; also filter efficiency
Other flue gas clean-up systems	deNO <sub>x</sub> , carbon injection, etc.

categorised on the basis of volatility due to variations in the degree of carbonisation.

The ash content of the coal fired in the Netherlands varies between 5% and 20%, with the average being around 13% (2004). Different types of coal, and even coals of the same type from geographically different sources, can differ considerably in composition. For this reason, KEMA has been conducting a systematic study on behalf of the electricity sector since 1978 to determine the composition of coals fired in the Netherlands and the associated ash types and flue gases.

The various ash flows in Dutch coal-fired power stations are listed in Table 2 together with their principal properties and relative distribution. The largest ash flow is that from the ESP. This CFA is referred to as pulverised fuel ash (PFA), partly to make it clear that it comes from pulverised coal boilers and partly to distinguish it from the material released into the atmosphere from the stack. The latter is referred to fly ash or fly dust. The term “fly ash” is used to refer to material from plants without FGD systems (of which there are no longer any in the Netherlands), while the term “fly dust” is applied to material from plants with FGD systems.

It will be apparent from Table 2 that the various ash types differ from one another greatly in terms of particle size. The concentrations of certain elements in the various ash types also differ considerably.

## 2. Methodology

All in- and out-going streams of the power station were sampled during the day. Composite samples were made of the solid and liquid streams. The flue gases were sampled either by CEMs or by wet and dry sorption methods. Besides fly ash or fly dust were sampled on plane filters. Next, the samples

were analysed at the laboratory and finally, mass balances were determined. Relative independent parameters, which describe the behaviour of the elements, were also established. The sampling methods and chemical analyses are described elsewhere (Meij, 1989, 1991; Meij et al., 1989).

## 3. Results and discussion

### 3.1. Definition of relative independent parameters

The behaviour of elements during combustion can be described by independent parameters. The relative independent parameters were distracted from 42 test series during full coal firing in the eighties. Parameters for chemical elements in the ash and for chemical elements in the vapour phase have been formulated.

The term “relative enrichment” was introduced to properly describe the observed behaviour of elements that end up in the ash. The relative enrichment (RE) factor is defined as (Meij et al., 1983):

$$RE = \frac{\text{conc. in ash}}{\text{conc. in coal}} \cdot \frac{\% \text{ ash content in coal}}{100}.$$

There are different types of ashes, each with their own characteristics (see Table 2). The enrichment in the ash depends on the type of ash and the particular element. This means that the RE factor for a certain element can be different for each ash type. Different names for each of the ashes are therefore necessary to avoid misunderstandings.

Based on the RE factor, elements can be grouped into three classes. The background of the classification is the behaviour of the elements during combustion in the boiler and further behaviour in the ducts, air preheater and ESP. The three classes are shown in Table 3. Class II is further divided into

Table 2  
Nomenclature applied in The Netherlands to ash flows from coal-fired power stations

Term	Definition	% of all ash produced	Particle size
Bottom ash	Collected at bottom of the boiler	12	Coarse
Pulverised fuel ash (ESP ash)	Removed from flue gases by ESP	87.8	50% of the overall mass made up of particles under 30 µm
Fly ash	In flue gases after passing through ESP and (in plants without FGD system) in the stack	0.25	50% of the overall mass made up of particles under 3 µm
Fly dust	In flue gases in the stack (after passing through FGD system)	0.05	50% of the overall mass made up of particles under 0.3 µm

three subclasses. These subclasses refer to the degree of volatility of the element (compound) in question.

For the different types of ashes the RE factors of each element studied have been established in the 42 studies mentioned earlier. All these RE factors are combined in a database. The elements are classified into the three classes as mentioned in Table 3 and presented in Table 4.

*Class I elements* are defined as elements that do not vaporise during combustion. Their concentration is the same in all ash types (see Table 3). The RE factor is about one.

However, for some elements there is redistribution among the various ash types, i.e. bottom ash, PFA (collected) and fly ash (in the flue gases downstream ESP). Those elements are vaporised in the boiler. Concomitantly with the route of the flue gases through the boiler, ducts, air preheater and ESPs, the temperature decreases from about 1600 °C to about 120 °C. Depending on the chemical compound, the dew point will be passed somewhere on this route and condensation will start. Condensation occurs on the surface of the fly ash particles and surface reactions take place. Particles can also be formed through nucleation of vaporised material and growth through coagulation and heterogeneous condensation. The smallest particles have the largest specific areas. Therefore, on a weight basis, the condensing elements have been found in greatest concentrations on the smallest particles. All elements that condense within the installation are grouped in *class II*. The RE factor of the bottom ash is less than 0.7 because elements originally present in the vapour phase have no chance of condensing on the bottom ash particles. The RE factor of the PFA from the collection tank is about one for elements of class II; the RE factor for the smaller particles exceeds 1.3. The smaller particles have been found in the last two hoppers of the ESP and in the flue gases downstream of the

ESP. Elements that occur in compounds with a low dew point condense only partly within the installation and, in the absence of an FGD plant, are totally or partly emitted in the vapour phase. They are grouped as *class III*. Their RE factor is very small ( $\ll 1$ ), especially in the bottom ash and to a lesser extent in the PFA of the collection tank. The RE factor of the smallest fly ash particles, as found in flue gas downstream of the ESP, can be high.

Class III elements are generally present in ash to a small degree. The largest part is present in the vapour phase. Just as for RE factors, a parameter was introduced for these elements to describe their behaviour: the vaporisation percentage (Meij, 1994). However, since the introduction of FGD, the major part of the class III elements are removed by the FGD. Another relative parameter was introduced: the degree of removal in the FGD (Meij, 1994). Concentrations of gaseous minor and trace elements in the flue gases downstream of the ESP were measured in all full coal-firing series, together with concentrations in the coal and, if present, also downstream from the FGD plant. All these factors have also been combined in a database.

Table 4  
Classification of elements based on research performed by KEMA in The Netherlands

Class	Classified elements
I	Al, Ca, Ce, Cs, Eu, Fe, Hf, K, La, Mg, Sc, Sm, Si, Sr, Th and Ti
Iic	Ba, Cr, Mn, Na and Rb
Iib	Be, Co, Cu, Ni, P, U, V and W
Iia	As, Cd, Ge, Mo, Pb, Sb, Tl and Zn
III	B, Br, C, Cl, F, Hg, I, N, S and Se

Table 3  
Classification of elements based on their behaviour during combustion in boiler and ducts with their relative enrichment (RE) factor

Class	FBA	PFA	Fly ash <sup>a</sup>	Behaviour in installation
I	~1	~1	~1	Not volatile
Iia	<0.7	~1	>4	Volatile in boiler, but complete condensation in ESP on the ash particles
Iib	<0.7	~1	2<–≤4	
Iic	<0.7	~1	1.3<–≤2	
III	≤1	≤1		Very volatile: some to hardly any condensation on ash particles in ESP

<sup>a</sup>Fly ash present in the flue gases downstream ESP and PFA from last hopper of ESP (finest fraction).

### 3.2. Speciation

The speciation of the elements present in the ash was determined on the basis of thermodynamic calculations, measurements (As, Cr, P, Si) and estimated on the basis of insight. The most common speciation is their oxide and/or sulphate. Elements present in the vapour phase are most likely to occur as the following compounds: HCl, HF, HBr, HI, Hg, HgCl<sub>2</sub>, HgBr<sub>2</sub>, SeO<sub>2</sub>, B<sub>2</sub>O<sub>3</sub> and As<sub>2</sub>O<sub>3</sub> (Meij, 1995).

### 3.3. Enrichment of elements in various types of ashes

The behaviour of the chemical elements in the installation is demonstrated in Fig. 1. The examples given in Fig. 1 originate from test series performed in 2003 in which 12.5% of biomass was co-combusted, mainly meat and bone meal. The RE factors of 55 elements were calculated for six different ashes collected through the installation: furnace bottom ash (FBA), ash collected in the hopper under de economiser (eco ash), CFA collected in the ESP in the collection vessel (PFA-C), CFA collected in the fifth hopper of the ESP (PFA-5, which is a very tiny fraction of the CFA), fly ash collected in the flue gases downstream ESP and fly dust collected in the flue gases downstream a wet FGD.

Aluminium and calcium are class I elements, and the RE factor in all types of ashes should be equal to about one. However, some exceptions were found. Aluminium in fly dust has been depleted and

calcium shows enrichment in the coarser particles, such as FBA and eco ash. The calcium and phosphorous in the coarser particles originate from the bones and teeth as a part of the bone and meat meal. It has nothing to do with a volatilisation/condensation mechanism. Calcium in the fly dust is enriched with respect to the fly ash. Sodium and chromium are class IIc elements, with a slight increase of enrichment in the smaller particles. The RE factor for sodium is about one in this example for all the ashes, except fly dust. In this case it acts more like a class II element. Arsenic, selenium and zinc are typically class IIa elements, showing an increase from coarser to finer particles, with the exception of the fly dust. Twenty-three elements show elemental concentrations in the fly dust with an average of 50% of the values found in the fly ash, just like aluminium, arsenic and zinc. Only a few elements show an increase in concentration from fly ash to fly dust; e.g. Ca and Mg by a factor of two, sodium by a factor of 10. The origins of Ca and Mg are the unreacted lime and/or the gypsum particles. The explanation is that the original fly ash has been diluted with other dust sources: evaporated droplets and gypsum and/or limestone particles. On average 50% of the fly dust consists of fly ash. Therefore, one can no longer speak of fly ash; the term “fly dust” has been introduced for this purpose (Meij, 1994). Sodium, as a very water soluble compound, is a representative for the influence of evaporated droplets. These results are almost similar to those obtained in 1986 during a detailed mass balance study for full coal firing (Meij, 1989).

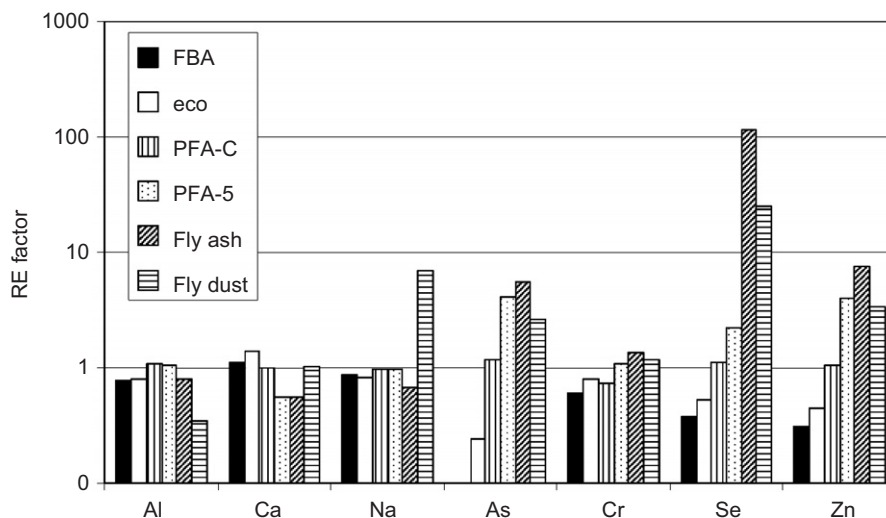


Fig. 1. Relative enrichment factors of various coal ash streams produced from co-combustion of coal and biomass.



### 3.4. Removal of elements

#### 3.4.1. Gaseous components

The gaseous elements are removed in the ESP between 1% (chlorine) and 80% (selenium), however, they are removed considerably in the wet FGD. The total slip of the gaseous elements for full coal firing and co-combustion is presented in Table 5. The slip has been defined as the part of the element that leaves the installation via the stack in a percentage of what was originally present in the fuel. No significant differences between full coal firing (A) and co-combustion (C) are observed. There are some differences found for Br and I, but they are less reliable due to the low number of observations and inaccuracy of the chemical analyses.

It appears that co-firing has no direct influence on the removal of gaseous components in a wet FGD. However, the existence of a gas–gas heat exchanger (GGHE) determines the emissions for fluorine to a large extend. This is illustrated in Table 6. The flue gases, which leave the FGD plant at a temperature of about 50 °C, are reheated to about 80 °C in a rotating GGHE. The reheating takes place through the transfer of heat from the incoming flue gases of the FGD plant (about 120 °C). Adsorption and

Table 5  
Slip of the gaseous elements for full coal firing (A) co-combustion (C)

%	Cl		B		Br		F	
	A	C	A	C	A	C	A	C
av	11	7	5	8	14	4	14	16
std	11	6	3	6	17	1	11	15
<i>v</i>	10	82	59	75	12	38	78	93
min	1	1	1	1	1	2	1	1
max	41	16	8	17	38	5	34	44
<i>n</i>	19	12	7	7	4	5	18	12
%	Hg		I		Se		SO <sub>2</sub>	
	A	C	A	C	A	C	A	C
av	22	22	36	10	1	5	9	9
std	12	8	13	6	1	5	3	2
<i>v</i>	55	36	38	62	64	99	36	29
min	7	15	26	5	0	0	4	5
max	50	43	45	16	2	13	18	12
<i>n</i>	17	10	2	3	7	5	21	10

A, full coal firing; C, co-combustion of biomass; av, average value; std, standard deviation; *v*, coefficient of variation in %; min, lowest value; max, highest value; *n*, number of observations.

Table 6

Influence of gas–gas heat exchanger on the removal of gaseous components in a wet FGD

%	F		Cl		B	
	Yes	No	Yes	No	Yes	No
mean	73	99	92	98	78	93
std	12	1	4	3	14	7
<i>v</i> (%)	17	1	5	3	17	8
min	43	97	82	91	43	77
max	97	99	98	100	95	98
<i>n</i>	21	6	18	7	10	7

Yes, GGHE; no, no GGHE present.

desorption processes in the ingoing and outgoing flue gases of the GGHE are in decreasing order of importance for fluorine > boron > chlorine, resulting in higher emissions of the elements involved. In The Netherlands two coal-fired power stations only have a GGHE, resulting in lower emissions of fluorine, chlorine and boron.

#### 3.4.2. Aerosol-bound components

On average the particulate matter (PM) concentrations downstream ESP are about 25 mg m<sup>−3</sup>. Another 80% of the remaining fly ash is removed in the wet FGD, yielding in a final average fly dust concentrations of about <5 mg m<sup>−3</sup> with a maximum of 20 mg m<sup>−3</sup> (Meij and Te Winkel, 2005). The actual removal of fly ash in the FGD is higher because about 50% of the fly dust consists of unreacted limestone and gypsum particles. The removal of the aerosol-bound elements is at first-hand similar to that of the total PM, however, due to differences in enrichment minor differences are found (see next section).

The particle size of the emitted PM is such that all belongs to PM<sub>2.5</sub> (Meij and Erbrink, 2001; Meij and Te Winkel, 2005; Meij et al., 2007). PM<sub>2.5</sub> is the fraction with a mass medium aero dynamical diameter (MMD) of 2.5 μm.

#### 3.4.3. Total removal

The total average removal of the elements is given in Table 7, thus the sum of the removal of gaseous and aerosol-bound elements. It is assumed that all fly dust downstream FGD is 100% fly ash, thus in practice the removal rates are for most elements higher. Separate figures for F, Cl and S are given for installations with a GGHE (indicated with #) and for Hg for installations without a deNO<sub>x</sub> (indicated

Table 7

Average removal of the gaseous and aerosol-bound elements together in ESP, wet FGD and combined ESP+FGD

	ESP (%)	FGD (%)	Total (%)
Al	99.8	80.0	99.96
As	98.3	75.0	99.59
B	49.8	90.0	94.96
Ba	99.7	80.0	99.93
Be	99.6	80.0	99.92
Br	39.8	90.0	93.95
Ca	99.8	80.0	99.96
Cd	98.5	80.0	99.71
Cl#	0.9	90.0	90.09
Cl	0.9	95.0	95.04
Co	99.5	80.0	99.91
Cr	99.7	80.0	99.94
Cs	99.8	80.0	99.96
Cu	99.5	80.0	99.91
F#	19.7	70.0	75.94
F	19.7	94.9	95.94
Ge	98.5	80.0	99.70
Hf	99.8	80.0	99.96
Hg\$	49.6	50.2	74.92
Hg	49.6	80.0	89.92
I	3.0	80.0	80.60
K	99.8	80.0	99.96
Mg	99.8	80.0	99.96
Mn	99.7	80.0	99.94
Mo	99.2	80.0	99.83
Na	99.7	80.0	99.94
Ni	99.4	80.0	99.88
P	99.5	80.0	99.89
Pb	99.1	80.0	99.82
PM	99.8	80.0	99.96
Rb	99.8	80.0	99.96
S#	2.0	90.0	90.20
S	2.0	92.0	92.16
Sb	98.9	82.1	99.81
Se	82.4	65.6	93.95
Si	99.8	80.0	99.96
Sn	99.1	80.0	99.83
Sr	99.8	80.0	99.96
Te	99.1	80.0	99.83
Th	99.8	80.0	99.96
Ti	99.8	80.0	99.96
Tl	99.1	80.0	99.83
U	99.5	80.0	99.89
V	99.4	80.0	99.88
W	99.4	80.0	99.88
Zn	98.9	80.0	99.79

PM, particulate matter; #, installation with gas–gas–heat exchanger; \$, no deNO<sub>x</sub>.

with \$). Detailed information about the behaviour of mercury is discussed in Meij et al. (2002), Meij and Te Winkel (2003) and Meij and Te Winkel (2006). The removal of mercury depends mainly on the speciation of mercury; elemental mercury is

hardly removed. The oxidation of mercury is in a deNO<sub>x</sub> enhanced, so in the presence of a deNO<sub>x</sub> the average total mercury removal increases from 75% up to 90%. The results can be compared with the results of an inventory done for the Department of Energy (DOE) of the USA at nine coal-fired power stations in the USA (Miller et al., 1996). Wet FGD was present at four stations and dry FGD was present at one station. The reported removal rates for 11 heavy metals of >95% in the particulate control (ESP or FF) and >99% in ESP (or FF) plus FGD is lower than our findings (>99% and ~99.9%).

### 3.5. Emission of inorganic substances

The yearly averaged emission of a 600 MW coal-fired power station into the air of inorganic substances is given in Table 8. It is assumed that no calcium-particles are present (thus worst-case scenario; most elements lie on 50% of the values due to dilution with Ca-particles). A distinction is made between the aerosol-bound elements (dust) and the gaseous components (gas). The results are presented in several units: in flue gas concentration, in emission per hour, in energy input and in electricity output. They apply to an installation without GGHE and with an SCR type of deNO<sub>x</sub>. The mercury emissions are somewhat higher when a deNO<sub>x</sub> is not present, which are indicated with a \$. The same applies for fluorine, chlorine and SO<sub>2</sub> when a GGHE is present, which are indicated with a #.

Model calculations by the KEMA TRACE MODEL<sup>®</sup> are the source of the results as presented in Table 8. They are based on the yearly averaged coal composition in 2004. Variation in coal composition from year to year is the cause for slightly different results from previous published figures (Meij and Te Winkel, 2004), however, the differences are negligible. In the Netherlands, as mentioned before, nowadays co-combustion is a daily practice. The emissions into the air on annual bases are hardly influenced by co-combustion and will be in the same order of magnitude as mentioned in Table 8.

The emissions lie well below the European limits for co-combustion (Sum of nine heavy metals is 75 µg m<sub>std</sub><sup>-3</sup> and for Hg + Tl 75 µg m<sub>std</sub><sup>-3</sup>; EU Waste Incineration Directive). The Dutch limits are 6 times lower. Stewart and Walker (1997) have reviewed trace element emission factors of coal-fired power stations in mg GJ<sup>-1</sup> of 15 heavy metals (As–Zn)

Table 8  
Emission factors of macro, micro and trace elements

	$\text{mg m}^{-3}$		$\text{kg h}^{-1}$		$\text{g GJ}_{\text{th}}^{-1}$		$\text{mg kWh}^{-1}$	
	Dust	Gas	Dust	Gas	Dust	Gas	Dust	Gas
PM	5		9.7		1.8		16	
CO <sub>2</sub>		2.63E+05		5.08E+05		9.40E+04		8.35E+05
NO <sub>x</sub>		200		386		71		636
SO <sub>2</sub>		124		239		44		393
SO <sub>2</sub> #		154		298		55		491
Al	0.73		1.4		0.26		2.3	
Ca	0.14		0.26		0.05		0.4	
Cl	0.002	1.0	0.004	2	0.001	0.4	0.01	3
Cl#	0.002	2.0	0.004	4	0.001	1	0.01	6
Fe	0.22		0.43		0.08		0.71	
K	0.05		0.09		0.017		0.2	
Mg	0.05		0.10		0.019		0.2	
Na	0.02		0.05		0.009		0.1	
P	0.05		0.09		0.018		0.2	
Si	1.2		2.3		0.43		4	
Ti	0.04		0.08		0.02		0.14	
	$\mu\text{g m}^{-3}$		$\text{g h}^{-1}$		$\text{mg GJ}_{\text{th}}^{-1}$		$\mu\text{g kWh}^{-1}$	
As	1.42		2.7		0.5		4.5	
B	2.0	254	3.8	490	0.7	91	6.2	807
Ba	14		28		5.2		46	
Be	0.12		0.2		0.04		0.4	
Br	0.09	11.8	0.2	23	0.03	4.2	0.3	37
Cd	0.03		0.1		0.01		0.1	
Co	0.59		1.1		0.21		1.9	
Cr	1.6		3.1		0.57		5.1	
Cs	0.04		0.1		0.01		0.1	
Cu	1.01		2.0		0.36		3.2	
F	7.9	548	15	1058	3	196	25	1741
F#	7.9	3287	15	6345	3	1175	25	10445
Ge	4.25		8.2		1.52		13.5	
Hf	0.06		0.12		0.02		0.2	
Hg	0.01	1.0	0.01	1.8	0.003	0.3	0.02	3.0
Hg\$	0.01	2.4	0.01	4.6	0.003	0.8	0.02	7.6
I		54		104		19		171
Mn	2.9		5.6		1.03		9.2	
Mo	0.46		0.9		0.16		1.5	
Ni	2.2		4.2		0.77		6.9	
Pb	1.2		2.3		0.42		3.7	
Sb	0.13		0.3		0.05		0.4	
Se	6.1	9.9	11.8	19	2.18	3.6	19.4	32
Sn	0.28		0.5		0.1		0.9	
Sr	8.0		15		3		25	
Te	0.21		0.4		0.1		0.7	
Th	0.18		0.3		0.06		0.57	
Tl	0.18		0.4		0.07		0.58	
U	0.15		0.3		0.06		0.49	
V	3.9		7.5		1.39		12.3	
W	0.10		0.2		0.04		0.32	
Zn	3.6		6.9		1.3		11	

PM, total particulate matter; #, GGHE present; \$, no deNO<sub>x</sub> present.



for the UK, Europe and world wide (Sloss and Smith, 2000). It appears that the emissions factors found at the Dutch stations lie between 0.1% and 1% of the figures mentioned in the review. The Dutch figures apply to installations with wet FGD and the figures in the review applies to installations without FGD. The large ESPs in the Netherlands, designed for a wide range of coals, explains the differences. Selenium is an exception; the Dutch figures are in agreement with the figures mentioned in the review. The DEO inventory for installations equipped with FGD gives similar emission factors as we found (converted from lb/Btu in mg/GJ) for As, Sb, Co, Pb, Hg (if no  $\text{deNO}_x$  is present) and HF (if GGHE is present) (Miller et al., 1996). On average lower figures are found in our study for Be(5x), Cr(4x), Cd(40x), Mn(5x) and Ni(6x), but are comparable with some individual measurements mentioned in the DOE study. Chemical analytical problems explain the big average differences found for Cd, because in the DOE study large variations were found for Cd in the round robin study. The only big difference is found for Se. On average it is 5x higher than found in the DOE inventory, but again comparable with some individual measurements. Our findings are that a large part of the Se is released in the vapour phase (see Table 8) requiring special sampling approach and it is assumed that the figures mentioned in the literature most probably are based on aerosol-bound emissions. The emission factor for HCl varies enormously in the DOE study, but is mostly lower than our findings (if GGHE is present). The flue gas concentrations of heavy metals presented in a recent Japanese paper are in agreement with our findings, although the Japanese flue gas concentrations are somewhat lower (2x–7x) (Ito et al., 2006). The average results for both countries are almost identical for Hg (in the presence of a  $\text{deNO}_x$ ), F (if no GGHE is present) and Sb. Both Dutch and Japanese power stations are equipped with wet FGDs. Ito et al. sampled Hg, F and Se both in the gas phase and in the particulates. They confirm our finding that they are predominately present in the vapour phase.

### 3.6. Emission of organic substances

#### 3.6.1. Dioxins and furans

Incomplete combustion of fossil fuels and waste can lead to the formation of hydrocarbons. Under certain circumstances, some of the hydrogen atoms in these hydrocarbons can be replaced by atoms of

chlorine, fluorine or bromine to form substances called dioxins. There are 210 different types of dioxin and furans, of which a “congeneric” group of seventeen, the so-called “dirty seventeen”, are toxic.

In principle, any combustion process that takes place in the presence of chlorine can lead to dioxin formation. (Combustion in the presence of fluorine, bromine or a mixture of these halogens can also result in dioxin formation, but, since fluorine and bromine are much less common, they are much less significant in relation to emissions.) Two mechanisms of formation are known: homogeneous gas phase reaction at 850–1100 °C and de-novo synthesis. The latter can take place during cooling at temperatures of between 500 and 200 °C on the surface of fly ash particles. The level of dioxin formation depends on the fuel composition and the combustion conditions. The large-scale combustion of fossil fuels, as in power stations, results in very low levels of dioxin emission. This is mainly because combustion in modern coal-fired power stations is virtually complete.

Complete combustion is critical in this context. If combustion is complete, no soot is formed; this is significant because soot particles are believed to have the right carbon structure for the formation of dioxin. The presence of chlorine is also a determining factor, but the chlorine concentration does not significantly influence the amount of dioxin formed. Furthermore, the presence of  $\text{SO}_3$ , formed from  $\text{SO}_2$ , appears to inhibit dioxin formation via the low-temperature pathway. In this context too, coal combustion differs from waste incineration, since little  $\text{SO}_2$  is present in the waste incineration process, whereas coal combustion is associated with high  $\text{SO}_2$  concentrations. Together, the almost complete combustion and the presence of  $\text{SO}_2$  account for the very low levels of dioxin formation associated with coal combustion. Chlorinated dioxins and furans concentrations in flue gases emitted from the Dutch coal-fired power stations are low. Measurements made using the most accurate techniques available have put the concentration between 1.5 and 3.2 pg I-TEQ  $\text{m}_{\text{std}}^{-3}$  (0.5–1.1 µg I-TEQ  $\text{TJ}^{-1}$ ). These measurements were performed during co-combustion up to 20% by dry mass. This is 1% of the limit for waste incineration plants and co-combustion in coal-fired power stations (EU Waste Incineration Directive), which may be regarded as strict, at 0.15 ng I-TEQ  $\text{m}_{\text{std}}^{-3}$ . Emission factors mentioned in the DOE inventory are <3–<6 mg  $\text{GJ}^{-1}$ , but are difficult to compare

because they are not expressed in I-TEQ (Miller et al., 1996).

### 3.6.2. Polycyclic aromatic hydrocarbons

Incomplete combustion of fossil fuels and waste results in the formation of soot and tar. These materials contain all sorts of organic compounds (hydrocarbons), including polycyclic aromatic hydrocarbons (PAHs). Some PAHs are known to have carcinogenic properties, while others do not. When considering the health issues associated with PFA and other airborne particulate materials, it is therefore important to distinguish between carcinogenic and non-carcinogenic PAHs. PAHs consist of two or more benzene rings. At room temperatures, those with two or three rings possess a high vapour pressure and are therefore known as more volatile PAHs. PAHs with more than three rings are much less volatile. The carcinogenic PAHs all have four to six benzene rings, while most mutagenic PAHs have four or more rings. Hence, it is only the less volatile PAHs with four or more rings that represent a major health hazard. These PAHs are normally bonded to very fine particulate materials known as aerosols.

PAHs are products of incomplete combustion. In principle, therefore, coal combustion can lead to their formation. At modern pulverised coal-fired power stations, however, combustion is virtually complete. First, the coal is pulverised to form a fine powder. Furthermore, during firing, the temperatures, boiler residence times and fuel–air ratios are such that almost all the carbon is converted into carbon dioxide. Consequently, almost no hydrocarbons are formed. The low carbon content of PFA, in practice about 5%, is evidence of the near-complete conversion (99–99.5%). The introduction of low- $\text{NO}_x$  burners has not affected this situation. As their name suggests, low- $\text{NO}_x$  burners are designed to minimise the formation of  $\text{NO}_x$ . This is achieved by keeping the combustion temperature and oxygen surplus as low as possible. Such conditions might be expected to lead to the formation of PAHs, but an optimum balance has been struck so as to minimise  $\text{NO}_x$  formation while achieving high carbon conversion rates. Consequently, PAH formation remains minimal.

The flue gases formed by the combustion of coal contain very low PAH concentrations: only a few micrograms per cubic metre. Roughly 50% of these PAHs are then removed by the flue gas desulphurisation systems used at Dutch power stations.

The average concentration of the 16 EPA PAHs in the purified flue gases emitted by power stations is roughly  $1\text{--}3\text{ }\mu\text{g m}_{\text{std}}^{-3}$  ( $0.4\text{--}1.1\text{ g TJ}^{-1}$ ) (16 PAHs defined by the Environmental Protection Agency of the USA). These measurements were mostly performed during co-combustion up to 20% by dry mass. No limits are given for PAHs in the EU. The concentrations found downstream FGD during co-combustion are comparable to figures reported in the literature for firing South-African and Australian coal in power stations without FGD (for 12 PAHs 1.5, 3.4, 2.8 and  $17.8\text{ }\mu\text{g m}_{\text{std}}^{-3}$ ) (Masclet et al., 1987; Sloss and Smith, 1993). The DOE inventory reported the results for 11 PAHs:  $1.4\text{ }\mu\text{g m}_{\text{std}}^{-3}$  ( $0.4\text{ g TJ}^{-1}$ ), which are also in good agreement with our findings during co-combustion.

## 4. Conclusions

- The behaviour of heavy metals is well studied in Dutch coal-fired power stations during the last 26 years, both during full coal firing and during co-combustion.
- The particulates loadings (PL) in the flue gases lies between 1 and  $20\text{ mg m}_{\text{std}}^{-3}$ , with an average value of  $<5\text{ mg m}_{\text{std}}^{-3}$ . The removal in the ESP is on average 99.8%, in the wet FGD on average about 80% and their total removal is on average about 99.96%. The removal of the aerosol-bound elements lies in the same region, the lowest is found for arsenic with 99.6%.
- The particulate size of the emitted particulate matter (PM) at the Dutch coal-fired power stations is such that all belong to  $\text{PM}_{2.5}$ .
- At low PL 50% of the fly dust consist of fly ash and the other 50% consists of unreacted limestone and gypsum particles. This phenomenon is neglected in the presented figures, which are based on model calculation with RE factors of fly dust (downstream FGD) taken equal to fly ash (up stream FGD). Therefore, the presented figures overestimate the emissions of heavy metals.
- The total averaged removal of the gaseous components is  $\sim 81\%$  for I,  $\leq 90\%$  for Hg, 94% for Br and Se, 95% for B and Cl and 96% for F. When no  $\text{deNO}_x$  is present the average removal for Hg is 75% and when a GGHE is present the removal for Cl is 90% and F is 76%.
- The emissions of dioxins and furans lies in the region of  $1.5\text{--}3.2\text{ pg I-TEQ m}_{\text{std}}^{-3}$  ( $0.5\text{--}1.1\text{ }\mu\text{g I-TEQ TJ}^{-1}$ ).

- The emissions of the 16 EPA PAHs lies in the region of  $1\text{--}3\text{ }\mu\text{g m}^{-3}_{\text{std}}$  ( $0.4\text{--}1.1\text{ g TJ}^{-1}$ ).
- The removal rates and emission factors are during co-combustion and full coal firing comparable.

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