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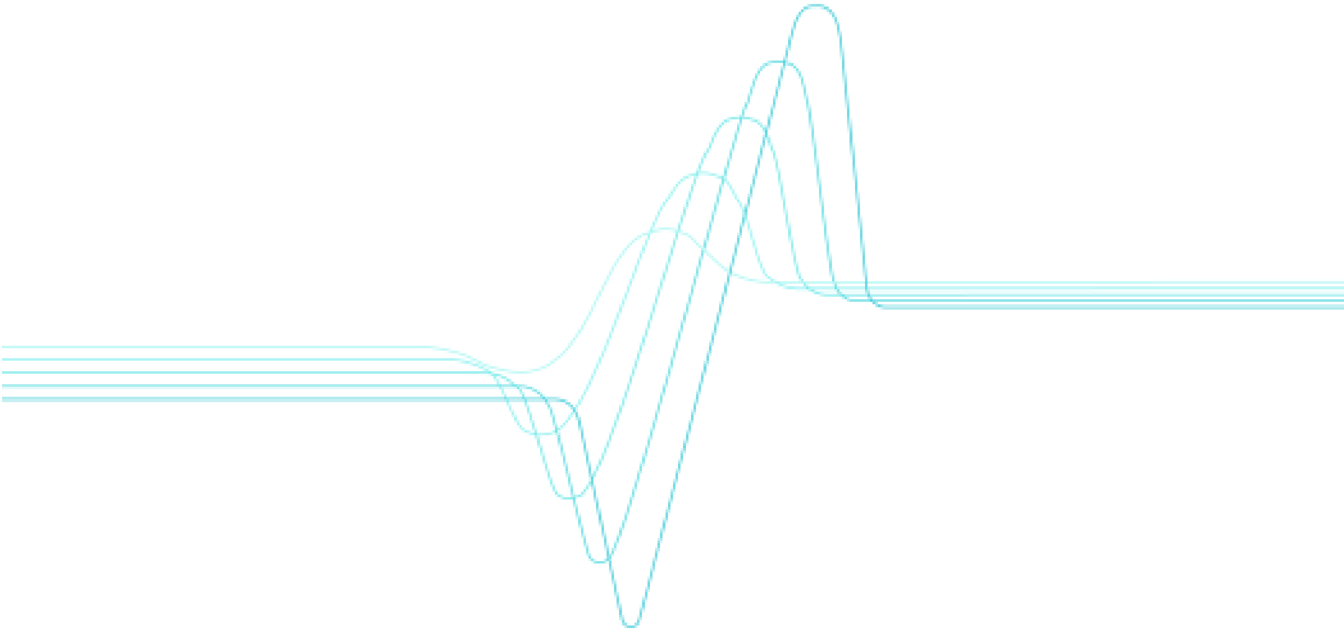

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Mass balance determination for trace elements at coal-, peat- and bark-fired power plants

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Academic dissertation

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Abstract

Determining the distribution of trace elements in a large-scale power plant is a challenge for both sampling and analysis. Besides the accuracy determination of the element content, the quantity flow rate of each stream of the plant is also a challenge because there are many streams without any flow recorders. This thesis describes a method to determine the steady-state mass balance of trace elements with highly satisfactory closures. When the method first developed for coal-fired power plants is applied to bark- and peat-fired power plants equipped with a fluidised bed, in order to attain a high closure of balance, some critical factors must be considered (running parallel tests, analysing parallel samples, sampling the main fuel and added fuel separately, including at least one element that is determined well above the detection limit in all the streams, waiting a long time to start sampling after the fuel supplying change etc.).

This thesis presents the results and evaluation of the mass balances for 14 trace elements (i.e. As, Be, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Tl, Se and Zn) determined in three coal-fired, three peat-fired power plants, and one bark-fired power plant in Finland. Each plant is equipped with specific low-NOx burning technology (i.e. low-NOx burners, staged over-fire air suppliers, selective catalytic NOx reduction or fluidised bed combustor) and an electrostatic precipitator. In addition, the coal-fired power plants were equipped with SO_2 control technology including a fabric filter or gypsum production unit. Some of the results pertain to the co-combustion of peat and bark with wooden waste material or sludge from the wastewater treatment plant.

The outcoming trace element flows of the power plants were low. Most of the trace elements exit the plant via the pulverised fly ash, removed by electrostatic precipitator, except for mercury. The collection efficiency of the electrostatic precipitators (ESP) was from 92 % to over 99 % for As, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn at the coal-fired power plants. In respect of the atmosphere

though, the ESP is followed by a flue gas desulphurisation plant (FGD), which removes the majority of the penetrated trace elements. The collection efficiency of the ESPs were from 94 % to over 99 % for As, Cd, Cr, Mn, Mo, Ni and Pb at the fluidised bed plants. The mercury in the flue gases was removed effectively by a semi-dry flue gas desulphurisation plant in the coal-fired power plants, but it was released mainly in the vapour phase to the atmosphere in the other plants.

The results of multivariate data analysis showed that the plants operating at maximum load was able to run well repeatable. The low-NOx burning technique had no significant effects on the enrichments of the trace elements in the outcoming streams compared to those of the conventional burning technique reported in the literature. No significant differences were found in the relative enrichment of trace elements in the outcoming streams of the plants between the coal-fired power plants equipped with semi-dry and wet flue gas desulphurisation. The case fluidised bed plants demonstrate appropriate techniques for co-combustion. The co-combustion tests revealed differences between pure bark and peat combustion according to the differences in the contents of Cd, Cr, Ni and Pb in the outcoming streams of the plant and in the relative enrichment factors of these trace elements. In addition to the relative enrichment factor of trace elements, the ratio of trace element content in the ash samples to the content in the fuel was found to be useful for element characterisation. The peat-fired power plants equipped with bubbling and circulating fluidised beds showed differences in the ratio of Cd, Hg and Pb in the outcoming streams compared to the contents in the fuel.

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Contents

Appendices

Acronyms

AFBC	atmospheric fluidised bed combustion
BFB	bubbling fluidised bed
CAAA	the Clean Air Act Amendments (USA)
CFB	circulating fluidised bed
CVAAS	atomic absorption spectrometry with cold vapour technique
EPA	Environment Protection Agency (USA)
ESP	electrostatic precipitator
FAAS	atomic absorption spectrometry with flame technique
FBC	fluidised bed combustion
FGD	flue gas desulphurisation plant
GFAAS	atomic absorption spectrometry with graphite furnace
HB	symbol for the case coal-fired power plant equipped with semi-dry desulphurisation plant
ISO	the International Organisation for Standardisation
m	missing data, not analysed
MB	symbol for the case coal-fired power plant equipped with wet desulphurisation plant
Mean	the average value (e.g. U13Mean: the average value of the results of the tests 1, 2 and 3 at plant UB)
n.c.	not counted
n.d.	not detected/determined
o.c.	out of classification
PAH	polyaromatic hydrocarbons
PCA	principal component analysis (chemometrics tools)
PCDD	polychlorinated dipenzo-p-dioxin
PCDF	polychlorinated dipenzofuran

PFA	pulverised fly ash separated by flue gas control device (i.e. electrostatic precipitator in the case plants in this thesis)
PFBC	pressurised fluidised bed combustion
PLS	partial least squares projections to latent structures (chemometrics tools)
RE	relative enrichment factor
RB	symbol for the case peat-fired power plant equipped with bubbling fluidised bed
SB	symbol for the case coal-fired power plant equipped with semi-dry desulphurisation plant
SCR	selective catalytic reduction
SDev	standard deviation value (e.g. U13SDev: the standard deviation value of the results of the tests 1, 2 and 3 at plant UB)
SFS	Finnish Standards Association
SNCR	selective non-catalytic reduction
UB	symbol for the case bark- and sludge-fired power plant equipped with bubbling fluidised bed
TB	symbol for the case peat- and wood-chips-fired power plant equipped with circulating fluidised bed
VB	symbol for the case peat- and sawdust-fired power plant equipped with circulating fluidised bed
VDI	Verein Deutcher Ingenieure

1 Introduction

This thesis was motivated by the need for public information about the distribution of trace elements in Finnish power plants. The different types of plant facilities and the fuels supplied do not permit the relevant and direct utilisation of the results obtained in other countries, e.g. in Germany (Rentz *et al*. 1996), the Netherlands (Meij 1989, 1997, 1999), Japan (Yokoyama *et al*. 1991) or the USA (Tillman 1994). Besides the results of the trace element flows, a reliable procedure is needed to determine further mass balances of trace elements in Finnish power plants, because the co-combustion of different waste materials with main fuel, e.g. peat is becoming more common.

The goal of this thesis is to define the ability (e.g. accuracy and reliability) of the methods developed for coal-fired power plants in bark- and peat-fired power plants and to identify the critical actions, which create the greatest uncertainties in the results and weaken the closure of the steady-state mass balance. In addition, the goal of this thesis is to study if by applying chemometrics tools, i.e. Principal Component Analysis (PCA) and Partial Least Squares Projections to Latent Structures (PLS), the results of large measurement campaigns can be more widely implemented.

All solid fuels are composed to varying degrees of organic matter (carbon, hydrogen, oxygen and other heteroatoms), inorganic material, and moisture. A part of the inorganic material (ash) consists of trace elements that are mobilised during combustion and released to the environment in ashes, wastewater and flue gases associated with particles or as vapours. Some of these elements are essential for healthy plant and animal life, whilst others are toxic for the environment and human health if present in sufficient quantities (Clarke & Sloss 1992). Some of these elements directly affect the performance of the boiler (Tillman, 1994). The alkali metals influence the performance of boilers by causing concerns like a high base/acid ratio, a high propensity for slagging and fouling, and related ash characteristics such as pH. These metals include silicon, aluminium, magnesium, iron, sodium, calcium, and potassium. Trace metals, which are of concern for environmental and health risk reasons, have toxic, carcinogenic and mutagenic properties.

The environmental effects and health effects of trace elements are governed, to some extent, by the chemical and physical form in which they are found. The effects may occur due to the action of an individual element and its compounds, or as a result of a combination of elements and/or compounds. Stringent environmental regulations have been implemented in Europe, in the USA, and in many other countries. The European Council directive concerning the SO_2, NOx and particle emissions in large-scale power plants came in force in 2004. The regulation includes strict limits for emissions of certain substances like trace elements and other hazardous air pollutants as well. The US Clean Air Act Amendments (CAAA) of 1990 defines 189 air toxics for which special abatement measures are required. The CAAA identifies eleven trace elements and their compounds commonly found in coal as potentially hazardous air pollutants. These elements are As, Be, Cd, Co, Cr, Hg, Mn, Ni, Pb, Sb and Se. (Except for Sb, all of these elements as well as Cu, Mo, Tl and Zn, are studied in this thesis.) The German Air Quality Guidance (the TA Luft regulations, 1986) and the European Council directive on the incineration of hazardous waste (1994) and waste (2000) also contain directives on the emission of trace elements into the atmosphere.

Owing to their toxic, carcinogenic and mutagenic properties, the environmental and health risks of the trace elements are the reasons why authorities are interested in the outcoming trace element flows from the power plants and other industrial facilities. This means that the content and the quantity of the trace elements significant to the environment or health must be known in all the outcoming flows of the plant. The outcoming flows of the plant are, e.g. bottom ash withdrawn from the boiler, fly ash separated by particulate control devices, solid and effluent products of the flue gas desulphurisation plant, and flue gases emitted from the stack.

On the other hand the owner and the operator of the power plant are interested in the ingoing trace element flows and further in the behaviour of trace elements during and after combustion, because some elements influence the performance of the boiler and the flue gas cleaning systems. This means that the ingoing flows of the trace elements as well as the flows from the boiler to the stack must be known. The owner of the plant is also interested in outcoming flows of trace elements because of potential commercial utilisation of the ash and end-products of the flue gas desulphurisation plants.

Determining the distribution of trace elements in a large-scale power plant is a challenge for both sampling and analysis. The contents of each trace element in different streams can have variations of several magnitudes. In determining the quantity of all the ingoing and outcoming flows of each element, the low contents of the elements must also be determined. The high determination limit of trace elements increases the uncertainty of the distribution and makes it even impracticable to determine the steady-state element balance without using some recovery factors. This was recognised by, e.g. Kouvo (2003), Meij (1989, 1997, 1999) and Rentz *et al*. (1996). Besides the accuracy determination of the element content, the quantity flow rate of each stream of the plant is also a challenge, because there are many streams without any flow recorders.

This thesis presents the results and evaluation of the mass balances for 14 trace elements determined in seven typical Finnish power plants including three coal-fired and three peat-fired power plants, and one bark-fired power plant. Each plant was equipped with specific low-NOx burning technology (i.e. low-NOx burners, staged over-fire air suppliers, selective catalytic NOx reduction or fluidised bed combustor) and with an electrostatic precipitator. Besides this, the coal-fired power plants were equipped with SO_2 control technology including a fabric filter or gypsum production unit. Some of the results pertain to the co-combustion of peat and bark with wooden waste material or sludge from the wastewater treatment plant. The results from each plant are analysed and presented as relative enrichment factors of trace elements and as the removal effects of particulate control devices. Not many reports on experimental tests for mass balance studies have been published, and especially not to such a large extent as reported in this thesis.

The background of the thesis with a summary of the measurement campaigns is presented in Chapter 2. The typical burning and flue gas control technology used in modern Finnish power plants is briefly described in Chapter 3. The literature of the trace elements in combustion processes and particulate control systems is reviewed at the end of Chapter 3, where the relative enrichment factor and the classification of elements according to their behaviour in installations are defined. The burning and flue gas control technology of the case study power plants with nominal parameters is described in Chapter 4. Chapter 5 presents the methods used in this thesis. The methods for sampling, determination of flow rate for each stream of the plant, pre-treatment, digestion and analysis of samples, which were used in the measurement campaigns, are described in detail first. The measurement campaigns produced many parallel results, which are compared, evaluated and concluded in section 5.4 giving the data for the mass balance calculations. The calculation procedure for steady-state mass balance with the methodology to determine the closure of the element balance of high grade without using any recovery factors in the calculations are presented in section 5.5. Chapter 5 concludes with a brief review of the principle of the chemometrics tools, i.e. PCA and PLS.

The results of the experimental studies are presented and discussed in Chapter 6. The process parameters, the contents and the main routes of the trace elements and the closure of the mass balances are introduced. The trace element contents in different streams of the plant are examined by ratio of the content in the sample to the content in the fuel, and by relative enrichment factors. The mass balance is determined using the procedure described in section 5.5. The collection efficiencies of flue gas control devices for each trace element are also presented. The results of the multivariate analysis are also presented and discussed. The main results are discussed further in Chapter 7. The conclusions of this thesis are presented in Chapter 8. The Appendix provides more detailed information concerning Chapters 5 and 6.

2 Scope of the investigation

The experimental work of this thesis was carried out in the mass balance project, which was jointly conducted by VTT, IVO and some other Finnish power companies in 1992−1998. "The mass balance determination for trace elements" project was partly financed by Tekes. The reason for starting this long-term project arose from the stringent environmental regulations.

Since 1992, the new power plants in Finland have had to assess the environmental impacts of their operations according to the combined environmental permission law (Finnish law 735/1991), and since 2000, according to the law of environment protection (Finnish law 86/2000). The mass flows of the plant and the occurrence of the significant elements must be reliably known to carry out systematic assessment. This means that all the different kinds of sampling and analyses of the streams of the plant must be well qualified and quantified.

"The mass balance determination for trace elements" project covered seven typical Finnish power plants. The results of the measurement campaigns in these power plants are now evaluated and concluded all together for the first time. In addition, the details of the methodology to determine the closure of the element balance of high grade are presented for the first time. These aspects contribute to making this thesis unique.

The measurement campaign of the mass balance project was first conducted in a coal-fired power plant because comparison data was available, e.g. Meij (1989), Maier (1990), Maier *et al*. (1992) and Klein *et al*. (1975) have experimentally studied the pathways of trace elements through coal-fired power plants in Holland, Austria and the USA. The sample preparation and analysis methods for the samples were developed and optimised before the first measurement campaign for mass balance determination of the whole power plant. The digestion procedures and analysis methods were qualified by using commercial reference materials as presented and discussed in detail in Hatanpää *et al*. (1997). Before the first measurement campaign for the mass balance determination, the relevant sampling method for flue gas fractions – especially for the particle fraction at a low particle concentration level – was developed, and the representative sampling period with the number of samples for the whole plant was optimised. The mass balances were experimentally determined first in two coal-fired power plants equipped with semi-dry flue gas desulphurisation units. The results of these two experimental mass balance determinations have been presented in Tolvanen *et al*. (1995), and in Aunela-Tapola *et al*. (1998).

In the next step of the project, the methods developed for coal-fired power plants equipped with semi-dry flue gas desulphurisation units were applied for a coal-fired power plant equipped with wet flue gas desulphurisation units. The distribution of the trace elements in the streams of this coal-fired power plant is presented in Hatanpää *et al*. (1995).

The coal-fired power plants were followed by three peat-fired power plants, which burn peat and peat mixed with waste wood material in the fluidised bed combustor. Peat is a common domestic fuel in Finland and there are many peat-fired power plants all around the country.

One measurement campaign was carried out for the mass balance determination of trace elements in the bark-fired power plant. Bark is a by-product of the pulp mill process. Typically, the energy obtained by burning bark is utilised to produce heat and power for the mill. The bark can be burned in a fluidised bed combustor also mixed with the sludge coming from the wastewater treatment plant.

The mass balance studies carried out at the peat- and bark-fired power plants are presented in Harju *et al*. (1998) and Tolvanen *et al*. (1998). A summary of these results was published by Harju *et al.* (2001).

Not many reports on experimental tests for mass balance studies have been published, and especially not to such a large extent as reported in this thesis. The type of the plants, including the fuel, burning technology and flue gas control technology reported by Meij (1989), Maier (1990), Maier *et al.* (1992), Rentz *et al.* (1996) or Klein *et al.* (1975) for examples do not correspond the type of the plants in Finland. This yields difficulties in applying the data to trace element flows in Finnish plants. Besides the results of the mass balance project of VTT named above, the trace elements in Finnish power plants have not been reported much in publicly. Manninen (1996) and Vesterinen (1997) have determined trace element concentrations in fuel, in fly ash and in flue gases, although the main focus of their work was on the formation of organic compounds like PAH, PCDD and PCDF during co-combustion in fluidised bed combustion. The trace element concentrations coming from the fluidised bed combustion in Finland have been reported also by Latva-Somppi (1998), who studied pulp and paper mill sludge ash behaviour. Kouvo (2003) has studied the formation and control of trace elements in the co-combustion of biomass, peat and wastes in fluidised bed combustion. Itkonen & Jantunen (1986) have reported on the emissions of trace elements determined in a peat-fired power plant equipped with front-wall burners. Mojtahedi *et al.* (1990) have studied partitioning of trace elements in pressurised fluidised bed combustion for both peat and coal burning.

In this thesis, the contents of trace elements in different streams of seven typical Finnish power plants are presented and discussed for the first time all together. Regarding the environmental aspect, the relative enrichment factors of trace elements in the outcoming streams of the plants and the main outcoming routes of trace elements are introduced. In addition, the removal effects of electrostatic precipitators and flue gas desulphurisation plants for trace elements are defined and discussed.

The sampling procedures and methods, the sample treatment and analysis methods and the method to determine the mass flows of the plant are described in detail and evaluated. The closures of the mass balances for trace elements are determined without using any recovery factors in the calculations. The critical actions, which increase the uncertainties of the results and render the closure of the element balance poorer, are identified and the methodology to determine the closure of the element balance of high grade is presented.

The large measurement campaign places heavy demands on personal resources, time and money. The chemometrics tools, i.e. Principal Component Analysis (PCA) and Partial Least Squares Projections to Latent Structures (PLS), are applied in this thesis to obtain further information about the plants and results to improve the utilisation possibilities.

The chemometrics tools are used in the following respects:

i) to observe the repeatability of the tests in respect of ingoing and outgoing trace element flows, which extend the representativeness of the results of one individual test
ii) to identify any substantial differences among the tests of each plant and among the different kinds of plants in respect of the relative enrichment of trace elements
iii) to express any significant effects on the outcoming trace element flows from the co-combustion of wood-chips or sawdust with peat, and from the co-combustion of bark with sludge.

In this thesis, the term trace element refers to the elements typically present in fuel at concentrations below 0.1 wt %. Manganese (Mn) of the major elements was included in the mass balance studies acting as the magnitude control of the mass flows. Table 2.1 briefly describes the case plants and identifies the experimental tests. The analysed trace elements are given in Table 2.2.

Table 2.1. Summary of the configuration of a) the coal-fired power plants and b) the bark- and peat-fired power plants with the identifying codes for the experimental tests.

a)

Power Plant		HB	SB	MB
Nominal fuel effect	MW	370	490	1300
Nominal gross load	MW_e	113	160	560
	MW_h	182	280	0
Boiler type:				
Single chamber with				
- cross-sectional area	m^2	6 x 4	11.4 x 11.7	20 x 15
- furnace height	m	20.5	31.1	55
Low-NOx burners, staged over-fire air (OFA) supply		12 (3 in 4 levels) front-wall fired	16 (4 in 4 levels) tangential fired	30 (10 in 3 levels) opposite-wall fired
Particulate control:				
Cold-side ESP upstream of the FGD:				
- hoppers		2 x 2	2 x 4	4 x 4
- nominal efficiency		99.2 %	99.6 %	99.5 %
Fabric filter downstream of the FGD:				
- nominal efficiency		> 99.5 %	99.7 %	No filter
External NOx control		none	none	catalytic converter
SO_2 control		semi-dry FGD	semi-dry FGD	wet FGD
Measurement campaign:				
Fuel (in dry basis):				
Origin of pulverised coal		Poland	Poland	Columbia & Poland
Supply rate	kg/h	58 400	62 800	153 000
Ash content	w-%	22.6	11.7	12.4
Sulphur content	w-%	1.2	0.8	0.7
Test ID		H1,H2,H3, H4,H5,H6	S1, S2, S3, S4, S5, S6	M1, M2, M3, M4

b)

Power plant		UB		RB	TB		VB	
Nominal fuel effect	MW	105		295	314		299	
Nominal gross load	MW_e	21.5		87	113		125	
	MW_h	50		140	170		100	
Boiler type:								
Fluidised bed		bubbling		bubbling	circulating		circulating	
- bed grate area	m^2	56		122	53		55	
- chamber volume	m^3	1400		2800	4680		4190	
Particulate control:								
Cold-side ESP								
- hoppers		2 x 2		2 x 3	3 x 3		2 x 4	
- nominal efficiency		over 99 %		over 99 %	99.8 %		99.9 %	
Measurement campaign:								
Fuel (in dry basis):								
Supply rate		bark:	bark:	peat:	peat	peat:	peat:	peat:
- main fuel	kg/h	15 000	12 000	48 000	60 000	43 000	64 000	49 000
			sludge			wood:		sawdust
- added fuel	kg/h	0	900	0	0	19 000	0	18 000
Ash content	w-%	1.8	3.4	8.7	6.1	3.9	4.1	2.6
Sulphur content	w-%	0.03	0.08	0.43	0.22	0.14	0.14	0.11
Test ID		U1,U2, U3	U4, U5, U6	R1,R2,R3 R4,R5	T1,T2, T3	T4,T5, T6	V1,V2	V3,V4

Table 2.2. Experimentally determined trace element flows in the coal- (HB, SB, MB), bark- (UB) and peat- (RB, TB, VB) fired power plants.

Power plant	**As**	**Be**	**Cd**	**Co**	**Cr**	**Cu**	**Hg**
HB	a	a	a	m	a	m	a
SB	a	a	a	a	a	a	a
MB	a	a	a	m	a	m	a
UB	a	m	a	m	a	m	a
RB	a	m	a	m	a	m	a
TB	a	m	a	m	a	m	a
VB	a	m	a	m	a	m	a

Power plant	**Mn**	**Mo**	**Ni**	**Pb**	**Se**	**Tl**	**Zn**
HB	a	m	a	a	m	a	a
SB	a	m	a	a	a	a	m
MB	a	m	a	a	a	m	m
UB	a	m	a	a	m	m	m
RB	a	m	a	a	m	m	m
TB	a	a	a	a	m	m	m
VB	a	a	a	a	m	m	m

a: analysed
m: missing, not analysed

3 Typical modern power plants and their trace element emissions

3.1 Modern burning technology in Finland

3.1.1 Pulverised combustion

Coal is typically burned in pulverised form in Finland, as in the HB, SB and MB, case power plants of this thesis. The fed coal is bunkered from the ferries and then pulverised in bullet mills. The coal is supplied with air to several burners from each mill. Conventional coal combustion in utility power plants takes place in furnace operating at temperatures above 1400 ^{o}C. The pulverised coal is typically injected into the furnace and ignited while in suspension. The burners can be located in a raw on the wall(s) of the furnace (i.e. front-wall or opposite wall fired) or in a raw in the corner(s) of the furnace (i.e. tangential fired).

To control the formation of NOx-emissions, modern power plants use low-NOx burners with staged over-fire air supply in the furnace, which yield lower temperature in the burning area and produce sufficient longer residence time for burning. The low-NOx burner itself includes a primary, secondary and tertiary air supply. The staged over-fire air supply directs a part of the burning air through the upper levels in the furnace. The temperature in the furnace is typically 1200 ^{o}C.

Besides combustible organic matter, coal includes some non-combustible inorganic material. Part of the inorganic material is retained in the furnace as bottom ash. Another part of the inorganic material exits in the flue gases in the fly ash. Some of the fly ash in the flue gases is separated in the economiser or even by the cyclone before the heat exchanger. This coarse fraction of fly ash can be conducted and cooled into the same quenching basin as the bottom ash or circulated back into the furnace.

3.1.2 Fluidised bed combustion

To formation of NOx-emission can also be controlled by fluidised bed combustion (FBC), where finely divided particles such as sand and ash form the main combustion place. The combustion air entering below lifts these particles until they form a turbulent bed at some 800 ^{o}C, after which any combustible material fed into the bed ignites almost immediately.

A large variety of fuels such as coal, peat, bark, municipal waste and oil can be burned in fluidised bed. This domestic fuel, e.g. peat, bark and sawdust, which is typically transported in trailers by trucks to the bunkers, is fed into the bed without any special pre-treatment. Bark, sludge, peat, wood-chips or sawdust are burned in the fluidised bed of the UB, RB, TB and VB, case power plants of this thesis.

Some of the non-combustible bed material is retained in the furnace in the bottom ash. Some of the non-combustible material exits in the flue gases in the fly ash. Most of this part is separated by the cyclone alongside or as a compact part of the furnace and circulated back to the burning area in circulating fluidised bed (CFB) combustion. In bubbling fluidised bed (BFB) combustion, a part of the exiting portion of bed material in the flue gases is separated by the economiser.

3.2 Air pollution control technology

3.2.1 Reduction technique for NOx emissions

NOx emissions may be controlled by decreasing the formation of NO_x during combustion, by cleaning the flue gases, or by a combination of both. Different technologies to reduce NOx emissions from the boiler include, for example, operational measures (decreased excess air), air staging (fire air through low-NOx burners or over-fire air supplied to the top level of the furnace), fuel staging (reburning) and flue gas recirculation (Clarke & Sloss, 1992). The NOx emissions are reduced with low-NOx burners and over-fire air supply at plants HB, SB and MB.

Flue gas treatment by processes such as selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) can reduce NO_x further. One process is also to supply ammonia into the flue gas at a high temperature (350 ^oC) before the heat exchanger. Ammonia reacts with NO and produces pure nitrogen and oxygen from reactive NO instead of NO_x. Plant MB is equipped with an SCR.

3.2.2 Reduction technique for SO_2 emissions

The emissions of SO_2 form when the sulphur contained in fuel is released and burned with oxygen in the fire air. The emissions of SO_2 can be reduced by a flue gas desulphurisation system of two broad types: regenerable and non-regenerable. The SO_2 sorbent can be re-used when the regeneration step that produces liquid SO_2, sulphuric acid or elemental sulphur is employed. In the systems using non-regenerable processes the SO_2 remains permanently bound with the sorbent to form a new compound/compounds. The non-regenerable FGD systems are most commonly fitted to coal-fired power plants, and these can be conveniently subdivided into wet scrubber systems and spray-dry (also called semi-dry) systems. (Clarke & Sloss, 1992)

Wet scrubbers commonly use limestone, slaked lime, or a mixture of slaked lime and alkaline fly ash as sorbent. The sorbent is sprayed into the flue gases where it reacts with SO_2 to form an insoluble calcium compound. The residuals from the processes are a mixture of calcium sulphite and sulphate. Gypsum may be produced through the use of an oxidation and drying step, either as an integrated part of the scrubbing processes, or externally. (Clarke & Sloss, 1992)

In wet scrubbers, the flue gases are first washed in a prescrubber with water. Most of the fly ash and gaseous inorganic compounds such as HCl, HF, SeO_2 and Hg are removed in the prescrubber. A part of the circulating liquid is drained off continuously to the wastewater treatment plant to prevent an accumulation of the compounds removed from the flue gas. After the addition of polyelectrolyte, the solids in the wastewater are coagulated and flocculated in a thickener. The sludge (i.e. wastewater cake) is dewatered on a belt filter and sent back to the furnace with coal. (Meij, 1989)

In spray-dry scrubbers, a solution or slurry of alkaline material is mixed with the flue gases. The flue gases are humidified by finely dispersed droplets. The solution or slurry is evaporated, the salts are precipitated, and the remaining solids are dried. The precipitated solids and particles are entrained in the flue gas and carried away from the spray-dry scrubber to a particle control device (e.g. fabric filter). Slaked lime or sodium carbonate solution can be used as sorbent, resulting in an end-product consisting of a mixture of calcium sulphite/sulphate and fly ash or sodium sulphite/sulphate, respectively. To produce a separate portion of fly ash and FGD waste stream (i.e. FGD end-product) a particle control system upstream of the spray-dry scrubbers is needed. (Clarke & Sloss, 1992)

The end-product accumulating at the bottom of the reactor is used to produce sludge, and the necessary amount of end-product separated by the fabric filter is added to it. Together with seawater, these form the base of sludge, and to which lime (CaO) in the form of lime milk is added to the degree that is needed for desulphurisation. The amount of sludge pumped from the feeding tank into the reactor is controlled so that all the water in the sludge evaporates and the flue gas going to the fabric filter is dry. Because the chemical reaction occurs partly in the wet state and partly in the dry state, the method is called half-wet or semi-dry. Plants HB and SB are equipped with a semi-dry FGD with a fabric filter, whilst plant MB is equipped with a wet FGD producing gypsum.

The emissions of SO_2 from the fluidised bed combustion at peat-fired power plants can be reduced by the co-combustion of peat with some low-sulphur-content fuel, e.g. wooden material, as in case of plants TB and VB. The addition of limestone to the bed also proceeds to reduce emissions of sulphur dioxide in fluidised bed combustion. (This aspect was not included in the case plants of this thesis.)

3.2.3 Particle control devices

The flue gas is introduced to some form of particulate control systems soon after the boiler. Typically, the particulate fraction is separated with electrostatic precipitators (ESP) or fabric filters. Mechanical collectors, such as cyclones, may be used after small boilers, where the emission limit required is more lenient. Cyclones are used also as a part of circulation fluidised bed combustion.

The ESPs can be classified into two types according to the flue gas temperature. The cold-side ESP operates with a flue gas temperature below 150 ^{o}C, as in all the case plants of this thesis, whilst the hot-side ESP operates at higher temperatures of up to about 350 ^{o}C. The collection efficiency depends on a range of parameters such as area of the electrostatic fields, the number of fields, size of the flue gas particles, ash receptivity, flue gas temperature, and moisture content. The overall collection efficiency can be over 99.9 %. The efficiency is lowest for the 0.05−1.0 μm particle-size range, and a fraction of fly ash will therefore penetrate the ESP (Hinds, 1982). The fly ash collected on the electrostatic fields of the ESP is shaken off to the hoppers. The hoppers are exhausted via channels and combined to the silo. This collected portion of fly ash can be called pulverised fly ash, i.e. PFA.

Fabric filter systems have similar overall particulate removal efficiency to ESPs (greater than 99 %) in combustion systems, but are superior at controlling fine particulate matter and less sensitive to particulate loading and fly ash characteristics (Clarke & Sloss, 1992). The fabric filters can be cleaned by a reverse air system, in which the gases are reversed through isolated cleaning compartments in a predetermined cycle, with the reverse air directed to those compartments still on line. A shake/deflate system may also be employed (bag shaking and reverse air). Pulse-jet cleaning can be used on the systems in which the flue gas is directed from the outside of the fabric through to the inside. Cleaning is carried out using short bursts of compressed air directed into the mouth of each bag, which, by combination of the shock wave sent down to the filter and the expansion of the bag, removes the dust cake, as in the case of plants HB and SB.

3.3 Trace elements in combustion processes and particulate control systems

As the solid fuel particles are heated, volatile matter, including pyrolysed organic species, is vaporised and combustion occurs. During burning the inorganic, mineral material in the fuel is exposed to rapid heating and high temperatures. As combustion proceeds, relatively non-volatile trace elements, which are trapped in the organic matrix material or bonded in organic compounds, may be transferred to the gas phase. Under these conditions minerals undergo thermal decomposition, fusion, disintegration, and even agglomeration. A portion of the non-combustible material falls down onto the bottom of the furnace as either slag or bottom ash. The bottom ash is cooled with water in the convenient quenching basin when necessary (e.g. hot slag from dry bottom furnace). The rest of the inorganic material in the furnace exits in the flue gases as fly ash and vapour. (Clarke & Sloss, 1992)

The majority of the available data relating to the partitioning of trace elements between ash, fly ash and flue gas comes from power plants using pulverised bituminous coal, i.e. a high-temperature (1250–1500 ^{o}C) combustion regime characterised by fine particles and short residence times. The corresponding data relating to fluidised bed combustion, where the temperatures are lower (800–950 ^{o}C), but residence times are much longer have been published much less (Clemens *et al.* 1999).

Trace element emission studies in fluidised bed combustion units have been carried out at 750–900 ^{o}C in AFBC (CRE, 1987) and at 800–900 ^{o}C in PFBC (Mojtahedi *et al.*, 1990). Trace element enrichment on fine particles is generally taken as evidence of volatilisation; so there has been an obvious assumption that it will be reduced by the lower temperatures in fluidised bed (CRE, 1987). This means that the small particles, which penetrate through the particle control devices, are expected to contain a lower concentration of trace elements than the small particles from conventional boilers. The flue gas emissions of trace elements from FBC units are also expected to be reduced because the volatilisation of elements occurs to a lesser extent at the lower operating temperatures. This reduction could be partially offset by the longer residence times at a relatively high temperature in FBC, allowing more volatilisation to occur (Mojtahedi *et al.*, 1990). Mojtahedi *et al.* (1990) have experimentally found the PFBC of solid fuels such as coal and peat is environmentally more acceptable than pulverised coal combustion with respect to trace element emissions. Significant amounts of the trace elements remain in the bed and are removed with the bottom ash. A larger proportion exits with the flue gas in the vapour phase and/or as solid particles. Some of the volatilised elements will condense and/or nucleate to form aerosols, which can be removed by an efficient particle control device (i.e. ceramic filter) (Mojtahedi *et al.*, 1990).

Clemens *et al.* (1999) have experimentally studied partitioning behaviour of As, Hg, Se and S during stoker and fluidised bed combustion of alkaline sub-bituminous coal. They found that a major influence on the volatile trace element and sulphur partitioning behaviour is the calcium oxide formed from the calcite present in high concentration in the mineral matter of the alkaline sub-bituminous coal. At the higher temperatures, i.e. 950–1000 ^{o}C, in an underfed stoker boiler furnace As volatility may be reduced by the formation of calcium arsenate and the inclusion of arsenic into developing calcium and alumino-silicate matrices. Se may be expected to form calcium selenates, and calcium oxide has the ability to trap SO_2. When combustion is characterised by lower temperatures and long residence times (e.g. in the fluidised bed boiler), the calcite breakdown still occurs and As, Se and S capture is observed. In all cases, the majority of Hg is recovered from the flue gas.

Meij (1997) has classified three types of ashes, which remain after pulverised combustion of the coal:

- ash collected on the down side of the boiler, called *bottom ash*
- ash collected in flue gases by gas control devices, such as an electrostatic precipitator (ESP) or fabric filter. This is called *pulverised ash* (PFA) in the UK, and *pulverized ash* or *fly ash* in the USA.
- ash that escapes the flue gas control devices and is emitted through the stack, called *fly ash*.

The ratio between the three types of ashes depends on the type of boiler, operating conditions and the efficiency of the flue gas cleaning devices.

The emissions of elements into the air depend on (Meij, 1997):

- the concentration in the coal
- the type of boiler
- the efficiency of flue gas control devices
- the distribution between the three types of ashes, which depends on the previous parameters
- the distribution between the particulate and gaseous phase.

In general, the ash contains the same elements as were present in the coal but they are enriched in the ash by a factor equal to 100/(ash content in %). This factor is called the “coal/ash ratio”. However, the enrichment in the ash also depends on the type of ash and the particular element. The behaviour can be described by the "relative enrichment factor" (RE), which has been defined by Meij (1989) as follows:

$$RE = (c_{i,a})/(c_{i,c}) \cdot (c_{a,c})/100 \qquad (3.1)$$

where $c_{i,a}$ = element concentration in ash
$c_{i,c}$ = element concentration in coal
$c_{a,c}$ = ash content in coal (%).

Based on the RE-factor, Meij (1989, 1997) has classified the elements into three classes in the case of dry bottom boilers in the Netherlands as follows:

Class	Bottom ash	PFA(1	Fly ash(2	Behaviour in installation
I	≈ 1	≈ 1	≈ 1	not volatile
II c	< 0.7	≈ 1	1.3 < ..≤ 2	volatile, but condensation
II b	< 0.7	≈ 1	2<..≤ 4	
II a	< 0.7	≈ 1	≥4	within the installation on the ash particles
III	<<1	<1	-	very volatile, hardly any condensation

[1] pulverised fly ash, precipitated by ESP
[2] RE(emitted fly ash) + RE(PFA of last hopper of ESP)

Meij (1997) has derived examples of the classification of elements from the Dutch test series while burning Australian coal in dry-bottom pulverised-coal-fired boilers:

Class	Elements
I	Al, Ca, Ce, Cs, Eu, Fe, Hf, K, La, Mg, Sc, Sm, Si, Sr, Th and **Tl**
II c	Ba, **Cr**, **Mn,** Na and Rb
II b	**Be, Co, Cu, Ni**, P, U, V and W
II a	**As, Cd**, Ge, **Mo, Pb**, Sb, **T**l and **Zn**
III	B, Br, C, Cl, F, **Hg**, I, N, S and **Se**

The test series performed in Austria in lignite-fired boilers (Maier, 1990) and in coal-fired boilers (Maier *et al.*, 1992) shows similar behaviour of As, Cd, Co, Cr, Hg, Ni, Pb, Se, V and Zn to the results of Meij (1997).

Yokoyama *et al.* (1991) have classified the trace elements into groups I, II and III, by comparing their thermodynamic data with the furnace temperature (1200–1600 ^{o}C) and the FGD temperature (50–60 ^{o}C) as follows:

Group	Behaviour of the elements (1	The elements
I	Non-volatile elements (remain in the coal ash)	Al, Ca, **Co, Cr**, Fe, Mg, **Mn, Ni**, Si
II	Volatile and condensable elements (mostly condensed and collected within the temperature ranges of ESP and of FGD)	**As**, B, **Be, Cd, Cu, Mo, Pb**, Sb, **Se**, V, **Zn**
III	Volatile and non-condensable elements (mostly present in gaseous form)	Cl, F, **Hg**

[1] behaviour in the combustion process in the furnace and the migration process to the downstream of the flue gas desulphurisation plant

Clarke and Sloss (1992) have reviewed the classification of elements in the groups corresponding to the classes listed above as follows:

Group	Partitioning during coal combustion	Examples
1	Elements concentrated in the coarse residue (i.e. bottom ash) or partitioned equally between coarse residues and particulates, which are generally trapped by particulate control device	Ba, Ce, Cs, Mg, **Mn**, Th (lithophylic elements)
2	Elements concentrated more in particulates compared with coarse slag/ash, enriched on the fine particles	**As, Cd, Cu, Pb,** Sb, **Se, Zn** (chalcophylic elements)
3	Elements volatilising most readily, concentrated in the vapour phase	Br, **Hg**, I

The group 1 elements do not vaporise during combustion. Their concentrations in all ash types are the same and they have been noted quite evenly distributed between different size fractions (Meij, 1997).

The group 2 elements do volatilise in the boiler. On the route of flue gases through the boiler, duct, air preheater and ESPs, the temperature decreases from

800–1600 °C to about 120 °C. Depending on the chemical composition, the dew point will be passed somewhere on this route and condensation on the surface of the fly ash particles will start. On the route of the flue gas, particles can form through the nucleation of vaporised material and growth through coagulation and heterogeneous condensation, as well (Meij, 1997, Clarke & Sloss, 1992). Data obtained from cascade impactor samples have shown that enrichments of group 2 elements increase with decreasing particle size (Gladney *et al.* 1976, Natusch *et al.* 1974), which is noted also by Meij (1997). A volatilisation-condensation mechanism has been invoked to explain the observed behaviour of enriched elements in a coal-fired power plant. The enrichment can be due to the volatilisation-condensation mechanism or to surface segregation within the particles (Germanni & Zoller, 1988). (Note: the smaller particles have a greater surface area to volume ratio.)

The group 3 elements occur in compounds with a low dew point. They condense only partly during combustion and, in the absence of an FGD plant, they are totally or partly emitted in the vapour phase (Meij, 1997, Clarke & Sloss, 1992). The mass balance calculations given by Klein *et al.* (1975) and Gladney *et al.* (1976) indicate that at least a portion of Br, I, Hg and Se are present in the vapour phase upon release from the stack.

Clarke & Sloss (1992) have compared classification of the trace elements present in the feed coal based on their thermodynamic data with typical furnace temperatures (1200–1600 °C) and flue gas cleaning temperatures studied by Yokoyama *et al.* (1991) with classification done by Meij (1989). The results are largely consistent, which shows that it is possible to predict the group to which element belongs based on the boiling points of the elements and their compounds, and the temperatures at which phase the changes occur.

Clarke & Sloss (1992) have reviewed the partitioning behaviour for different combustion systems with different operating conditions. The review is shown in Figure 3.1. Some elements (e.g. Be, Co, Cu, Mo, Ni) in some cases have been reported as intermediate between group 1 and group 2, and the relatively volatile elements B and Se have been reported as intermediate between group 2 and group 3.

Ratafia-Brown has (1994) concluded the three basic classes determined by several other authors (including Clarke & Sloss, 1992; Kaakinen *et al.* 1975; Meij, 1989; Yokayama *et al.*, 1991; Klein *et al.* 1975) as follows:

Class I	Elements which are approximately equally distributed between the bottom ash and fly ash or show no significant enrichment or depletion in the fly ash.
Class II	Elements which are enriched in the fly ash and depleted in the bottom ash, or show increasing enrichment with decreasing fly ash particle size.
Class III	Elements, which are volatised, but are not enriched on the fly ash. They are emitted fully in the vapour phase.

Rizeq *et al.* (1994) and Berger & Krabbe (1998) have used the element classification data for bituminous-coal-fired power plants for favourable simulation models of trace element partitioning.

From the environmental aspect, the Council of the European Communities gave the first limits for trace element emissions covering European countries in the directive on the incineration of municipal waste in 1989 (European Council Directive 89/369/EC). It was followed by the directive on the incineration of hazardous waste in 1994 (European Council Directive 94/67/EC). The most recent one concerning trace element emissions is the directive on the incineration of waste (European Council Directive 2000/76/EC), which will come in force in 2005 for existing power plants.

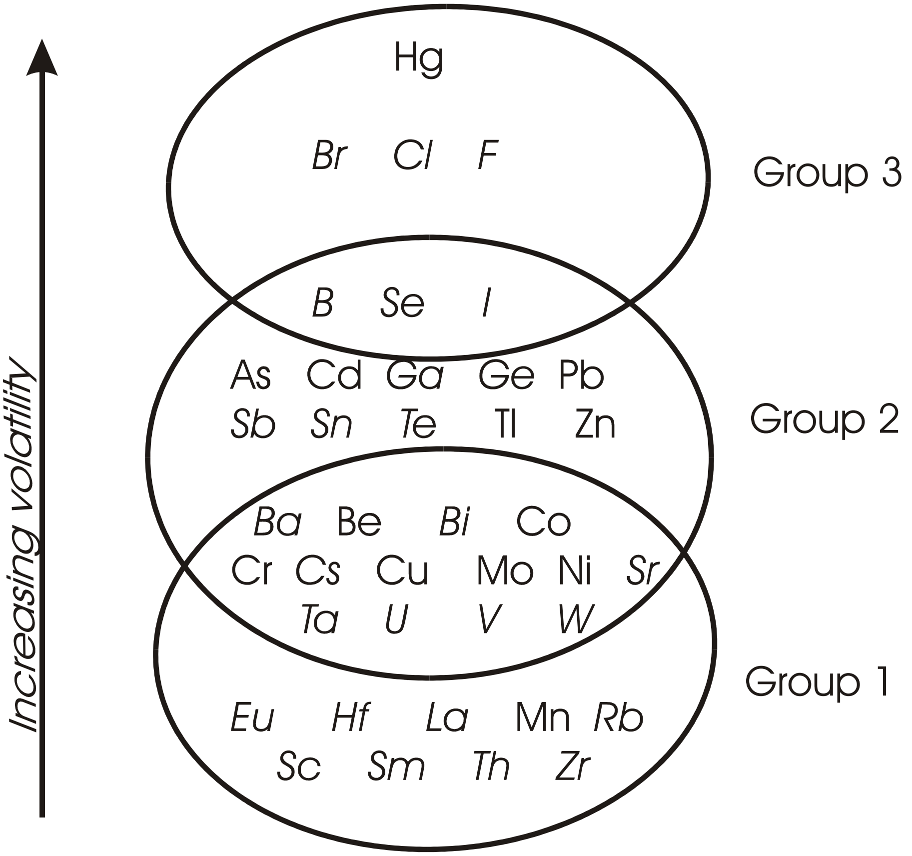


Figure 3.1. Classification of trace elements by their behaviour during combustion and gasification (modified after Clarke & Sloss, 1992, Figure 7, p. 37).

4 Description of the case study power plants

4.1 The coal-fired power plants HB, SB and MB

The measurement campaigns were carried out in three coal-fired power plants. Two of them, named HB and SB in this thesis, were equipped with a semi-dry FGD after the ESP, and the third plant, named MB in this thesis, was equipped with a wet FGD. Each plant is located on the coast of Finland, where the imported bituminous coal is transported by sea and unloaded from the ship straight to the open-air coal field of the plant. Crushed and sieved coal is first conducted to the bunkers. Then the required coal amount is pulverised by coal mills, which supply coal into the furnace via each specific burner level. The boilers are equipped with low-NOx burners and over-fire air suppliers on the upper level to control NOx emissions. During full load, the temperature is about 1200 ^{o}C in the high levels in the furnace. The technical details of the plants are given in Table 4.1 and the flow diagrams in Figure 4.1.

The maximum production capacity of the boiler of plant HB is 113 MW of electricity and 182 MW of district heating. The maximum production capacity of the boiler of plant SB is 160 MW of electricity and 280 MW of district heating. The maximum production capacity of plant MB is 560 MW of electricity. During the measurements, the plants were operated at the full capacity in steady-state condition using pulverised Polish coal as fuel at all the plants. Plant MB also used Columbic coal during the measurement campaign. The boilers were cleaned some hours before the measurements, which meant no cleaning was needed at plants HB and SB during the sampling period.

The bottom ash of the boiler is conducted to the quenching basin with seawater. The flue gases are directed to the economiser from the furnace. The flue gases of 400 ^{o}C are conducted to the heat exchanger (i.e. the air preheater) after the economiser. The flue gases cool to 120–140 ^{o}C and come up to the electrostatic precipitator (ESP), which functions as the preliminary remover of fly ash for the desulphurisation plant. The particle concentration is above 10 g/m^3 (in NTP) upstream of the ESP, and below 120 mg/m^3 (in NTP) downstream of the ESP, i.e. the removal capacity is over 99 %. The pulverised fly ash is pneumatically conveyed from each hopper to the intermediate reservoir and further to the ash silo. The economiser ash is also pneumatically conveyed to the same ash silo. Bottom ash is conveyed to another silo. The ashes are periodically transferred from the silos to trucks and sold as a by-product or transported to a landfill.

At plant MB ammonia is injected into the flue gases right after the economiser and a catalytic converter is used to control further NOx emissions.

Plants HB and SB have the spray-dryer-type reactor of the FGD. Flue gases of 132 ^{o}C come to two reactors with 9 suppliers from above and are mixed with lime sludge (CaO with seawater at plant SB and with seawater and tap water at plant HB) using compressed air. The particles of sludge and sulphur dioxide molecules are partly mixed in the reactor and reaction products fall to the bottom of the reactor silo. They are separated from the process as a coarse fraction of FGD at plant HB, while they are circulated back to the reactor at plant SB. The flue gases flow out from the reactor to the fabric filter at a temperature of 74 ^{o}C, where the reaction of lime and SO_2 continues. The flue gases go through the filter's textile tubes and over 99.5 % of the particles remains on its walls. The tubes are blown to remove the end-product of FGD and direct it to the FGD silo. The reaction product mainly consists of a mixture of $CaSO_3$, $CaSO_4$ and $CaCl_2$. There is no wastewater produced, because the water is evaporated during the reaction. Because the chemical reactions occur partly in the wet state, partly in the dry state, the method is called half-wet or semi-dry. From the fabric filter, the flue gases go via the fans into the stack and out in the air. The temperatures of the flue gases are 74 and 85 ^{o}C and the particle concentration is below 5 mg/m^3 in a 150-m high stack.

Pulverised fly ash and seawater are added to the outcoming end-product of the FGD, and it is formed into a mass, which is used for filling ditches, for strengthening man-made hills, and under dumping areas, etc.

Plant MB is equipped with a wet desulphurisation plant. Flue gases after the ESP flow in the reactor from down to up. Alkaline washing liquor made up of powdered limestone and water is mixed with the flue gases and the process water runs in the opposite direction. SO_2 in the flue gas reacts with the washing liquor and oxidising air addition and to form a slurry in the bottom of the reactor. The temperature is 50 ^{o}C in the reactor. The slurry is fed to hydro cyclones, which increase the solid matter content from about 10 % to 50 %. The reaction product is conducted to the gypsum dewatering (i.e. a vacuum belt filter) to produce pure gypsum (about 2.2 kg/s) of a solid content of about 90 %, wastewater and effluent, which are recycled back to the furnace with coal. The gypsum is used either in the construction industry or transported to a dumping ground.

The flue gases go via the fans and the reheater into the stack and out in the air. The temperature of the flue gases is 72 ^{o}C and particle concentration is below 50 mg/m^3 (in NTP) in a 150-m high stack.

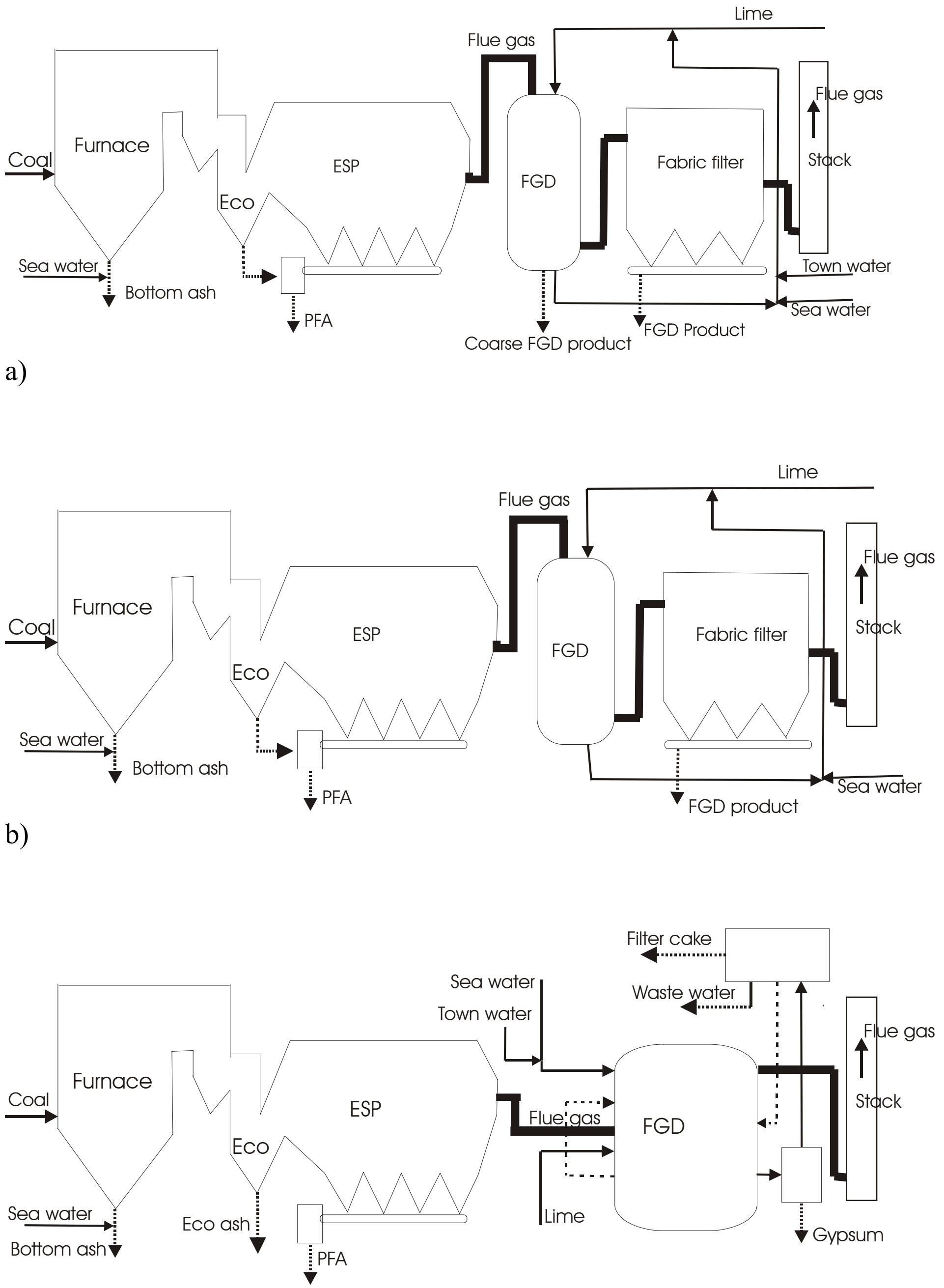


Figure 4.1. Simplified flow diagram of the coal-fired power plants a) HB b) SB and c) MB.

Table 4.1. The technical description of the coal-fired power plants: HB, SB and MB.

Power plant		**HB**	**SB**	**MB**
Nominal fuel effect	MW	370	490	1300
Nominal gross load	MW_e	113	160	560
	MW_h	182	280	0
Furnace (single chamber):		natural-circulation	natural-circulation	once-through, supercritical
- cross-sectional area	m^2	6 x 4	11.4 x 11.7	20 x 15
- furnace height	m	20.5	31.1	55
- Low-NOx burners		12 (3 in 4 levels) front-wall fired	16 (4 in 4 levels) tangential fired	30 (6 in 5 levels) opposite-wall fired
- over-fire air (OFA) suppliers		3	4	6
Coal mills (ball-ring)		4 x 17 000 kg/h	4x 25 000 kg/h	5 x 45 000 kg/h
Needed supply rate of coal for full capacity	kg/h	53 000	66 000	180 000
Flue gas cleaning systems:				
External NOx control		none	none	catalytic converter
Cold-side ESP upstream of the FGD:				
- hoppers		2 x 2	2 x 4	4 x 4
- nominal efficiency	%	99.2	99.6	99.5
Flue gas upstream of the ESP				
- temperature	°C	140	133	120
- particle concentration(1	g/m^3	15	14	17
Flue gas downstream of the ESP, i.e. upstream of the FGD				
- temperature	°C	140	132	120
- particle concentration(1	mg/m^3	115	50	below 100
- SO_2 concentration	ppm	710	460-504	860
SO_2 control technique		semi-dry FGD	semi-dry FGD	wet FGD
- nominal SO_2 removal efficiency	%	77-87	87	88
- nominal particle removal efficiency with fabric filter	%	over 99.5	99.7	no filter
Flue gas downstream of the FGD, i.e. in the stack				
- temperature	°C	74	85	72
- particle concentration(1	mg/m^3	5	< 5	< 50
- SO_2 concentration	ppm	95	83-100	130
Test ID		H1,H2,H3, H4,H5,H6	S1, S2, S3, S4, S5, S6	M1, M2, M3, M4

1 in normalised dry gas (t = 0oC, p = 101.325 kPa)

4.2 The fluidised bed (BFB and CFB) plants

4.2.1 Plants UB and RB with bubbling fluidised bed combustor

The first measurement campaigns in the fluidised bed combustors were carried out at the plants named UB and RB. The plants burn bark, sludge or peat in a bubbling fluidised bed (BFB). The technical details of the plants are given in Table 4.2 and the flow diagrams in Figure 4.2.

The main fuel at plant UB is bark. The bark comes from the pulp mill just beside the plant, when the conifers for the pulp process are peeled. The bark is fed by conveyor belt, which is loaded with the sludge that is coming from the wastewater treatment plant of the pulp mill. The water content of the sludge is depressed with a vacuum belt filter before the path of sludge crosses the bark. The distributing conveyors feed the fuel to the furnace above the fluidised bed via four suppliers. The maximum production capacity of plant UB is 21.5 MW of electricity and 50 MW of heating.

Plant RB is located in central Finland. The plant uses milled peat as fuel, which comes from the nearby peat fields. The maximum production capacity of plant RB is 87 MW of electricity and 140 MW of district heating. To produce the full capacity about, 50 000 kg/h peat (fuel effect of 295 MW) is needed, which is transported in trucks to the unloading station where it is unloaded onto a screen to separate the stumps and other large elements. A magnet separates the metal elements contained in the peat while the peat is conducted to the next screen with a grinder to crush the stumps. After the second screen, the peat is conducted to a storage of 2500 m^3. A screw unloader feeds the peat to two fuel bunkers of 60 m^3 alongside the conveyors. The distributing conveyors take the peat to the furnace above the fluidised bed via six suppliers.

The sand bed located in the bottom of the furnace is approximately 60 cm high. It contains screened natural sand with grain size of 0.5–1.5 mm. The temperature of the bed is 850 ^{o}C at plant UB, and 800 ^{o}C at plant RB. A part of the bed material is temporally removed from the furnace as bottom ash. It is conducted through six ducts to the transport container at plant UB and through three ducts to the quenching basin with water from the nearby lake at plant RB.

The flue gases, with temperature of about 400 °C, are conducted to the economiser from the furnace. Ash separated in the economiser is supplied and combined with bottom ash. The flue gases are conducted to the heat exchanger after the economiser. The temperature of the flue gases cools down to 170 and 130 °C before being led to the ESP. The particle concentration is about 5 g/m^3 (in NTP) upstream of the ESP and about 20 mg/m^3 (in NTP) downstream of the ESP, i.e. the separation efficiency is over 99 %. The pulverised fly ash is collected from the hoppers and combined in the ash silo.

The flue gases go via fans into the stack and out into the atmosphere. The temperature of the flue gases in an 80-m high stack is 170 °C at plant UB and 130 °C at plant RB. The maximum particle concentration in stack is 20 mg/m^3 (in NTP).

4.2.2 Plants TB and VB with circulating fluidised bed combustor

The measurement campaigns were also carried out in two circulating fluidised bed (CFB) combustors, which were equipped with an ESP. Both plants use milled peat as the main fuel. The technical details of the plants are given in Table 4.2 and the flow diagrams in Figure 4.2.

Plant TB is located in northern Finland. The plant occasionally uses a mixture of peat and wood-chips besides pure peat as fuel. The maximum production capacity of plant TB is 113 MW of electricity and 170 MW of district heating. Plant VB, which is located in western Finland, occasionally uses a mixture of peat and sawdust besides pure peat as fuel. The maximum production capacity of plant VB is 125 MW of electricity and 100 MW of district heating.

Wood-chips and sawdust are transported by lorries from the mechanical wood industry near the plants to their specific unloading stations. Peat is transported by trucks from the peat field near each plant and unloaded onto a coarse screen to separate the stumps and other large elements. A magnet separates the metal elements contained in the peat, while the peat is conducted to the next screen with grinder to crush the stumps. After the second screen the peat is conducted into intermediate storage, where a screw unloader feeds the peat to fuel bunkers along the conveyors. The distributing conveyors conduct the fuel to the furnace.

The wood-chips and sawdust are loaded onto the peat right after the intermediate storage.

The circulating fluidised bed contains screened natural sand with a grain size of 0.1–0.6 mm. The temperature of the bed is 750–920 °C. Solid fuel enters the fluidised bed via 3 suppliers on the front wall and via another 3 (at plant TB), and 6 (at plant VB) suppliers on the back wall above the bed. The primary burning air follows the fuel via the suppliers. The solids fill the entire furnace, and the hot combustion gases carry the particles right out the top of the furnace into a heavy-duty cyclone. The cyclone separates out the particles, which are re-circulated into the furnace via the suppliers on the back wall of the furnace. A part of the burning air, secondary air, is supplied into the furnace some meters above the fuel supply.

A part of the bed material is temporally removed from the furnace as bottom ash, which is conducted through 3 ducts to the transport container. The flue gases with a temperature of 420 °C are conducted to the economiser from the furnace. Ash separated in the economiser is put in the pulverised fly-ash silo.

The flue gases are conducted to the heat exchanger after the economiser. The flue gases cool to 145 °C at plant TB, and to 135 °C at plant VB, before being led to the ESP. The particle concentration is about 11 g/m^3 (in NTP) upstream of the ESP and 20–30 mg/m^3 (in NTP) downstream of the ESP at plant TB, i.e. a removal efficiency of 99.8 %. The particle concentration is about 15 g/m^3 (in NTP) upstream of the ESP and below 10 mg/m^3 (in NTP) downstream of the ESP at plant VB, i.e. a removal efficiency of 99.9 %. The pulverised fly ash is collected from the hoppers and combined into the fly-ash silo. The pulverised fly ash is transported to a dumping ground or used for land filling. The bottom ash is transported to a dumping ground.

The flue gases go via fans into a stack and out into the atmosphere. The temperature of the flue gases in a 130-m high stack is 145 °C at plant TB and 135 °C at plant VB, where the stack is 78.5-m high.

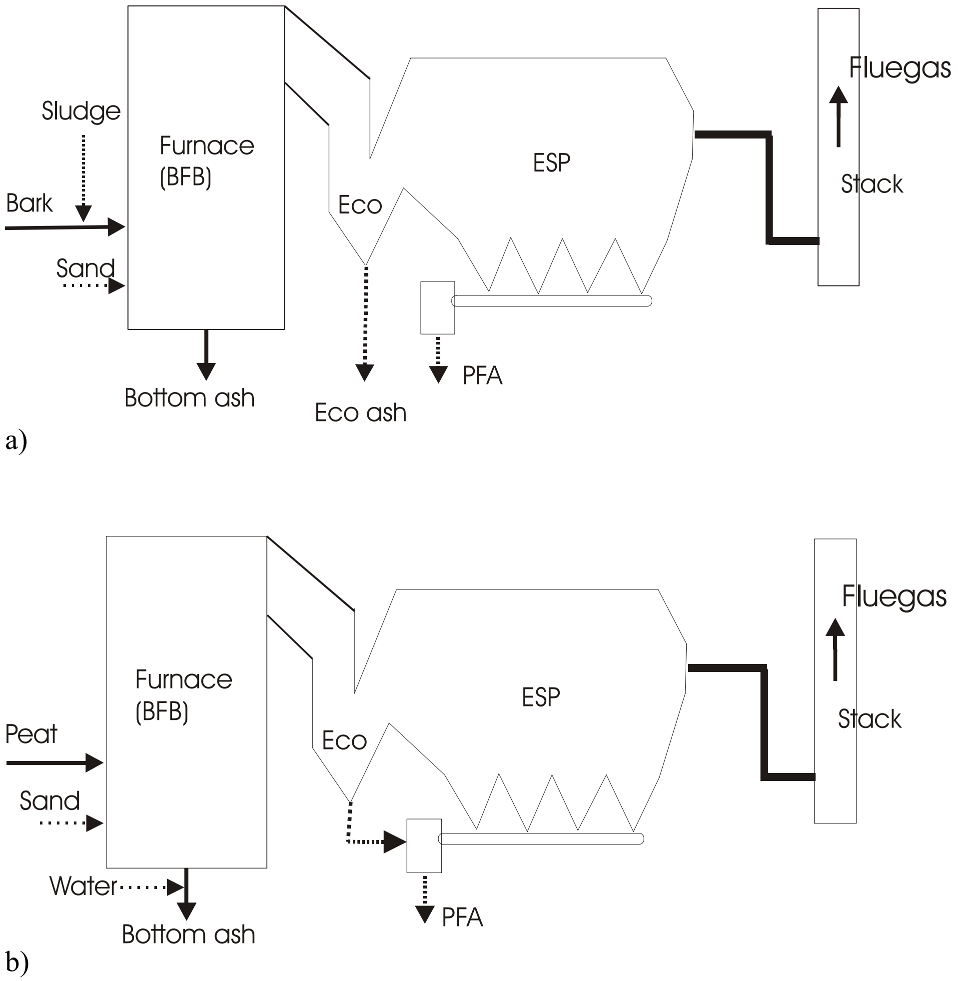


Figure 4.2. Simplified flow diagram of the fluidised bed plants: a) UB (BFB), b) RB (BFB), c) TB (CFB) and d) VB (CFB).

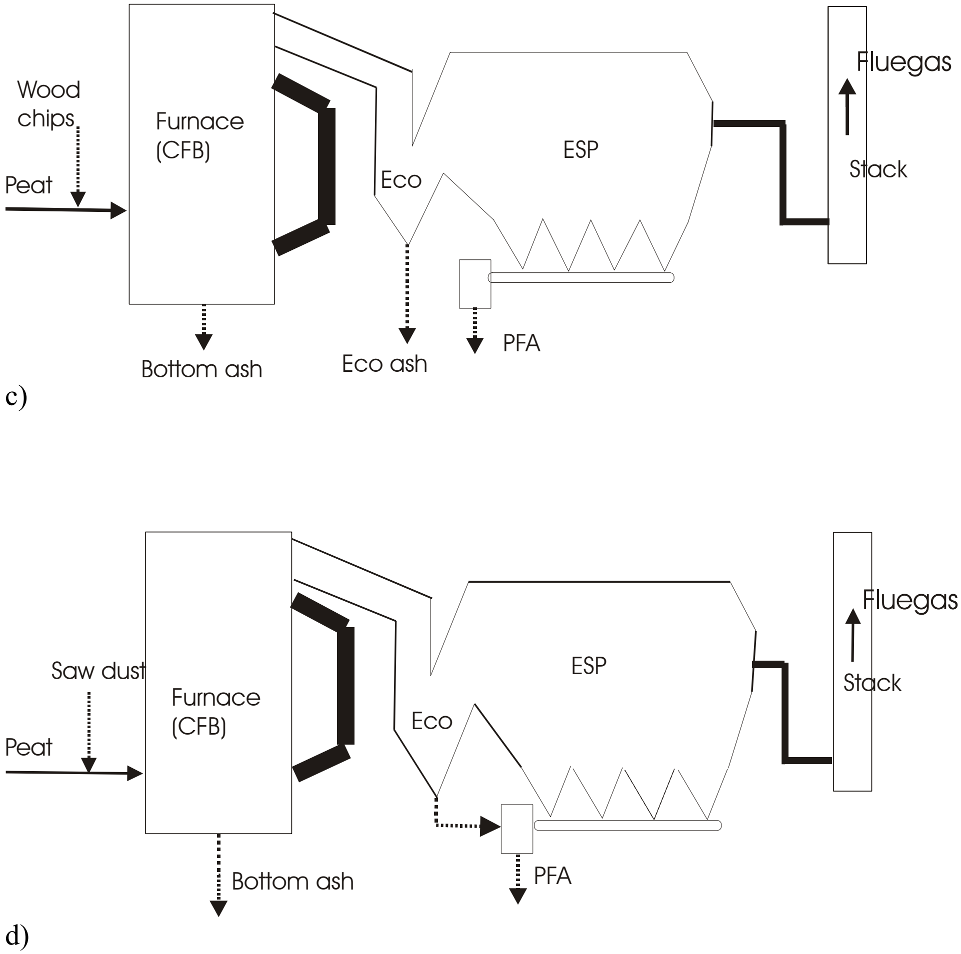


Figure 4.2. Continued.

Table 4.2. Technical description of the fluidised bed plants UB (BFB), RB (BFB), TB (CFB) and VB (CFB).

Power plant		**UB**	**RB**	**TB**	**VB**
Nominal fuel effect	MW	105	295	314	299
Nominal gross load	MW_e	21.5	87	113	125
	MW_h	50	140	170	100
Furnace:					
Fluidised bed		bubbling	bubbling	circulating	circulating
- furnace height	m	29	31	36	30
- chamber volume	m^3	1 400	2 800	4 680	4 190
- bed grate area	m^2	56	122	53	55
- bed height	m	0.6	0.4–0.6	-	-
- furnace temperature	°C	850	800	850	750–920
- number of air suppliers in the bottom of the furnace		2 622	4 000	1 300	7 800
- number of fuel suppliers		4 above the bed	6 above the bed	3 on the front wall and 3 on the back wall[2]	3 on the front wall and 6 on the back wall[2]
- number of the ash removing ducts in the bottom of the furnace		6	3	3	3
Sea-sand in bed					
- amount	kg	40 000	120 000	80 000	100 000
- grain size	mm	0.5–1.5	0.5–1.5	0.1–0.6	0.14–0.63
Fuel mixtures in the case studies		i) bark ii) bark and sludge	peat	i) peat ii) peat and wood-chips	i) peat ii) peat and sawdust
Flue gas cleaning system:					
Cold-side ESP					
- hoppers		2 x 2	2 x 3	3 x 3	2 x 4
- nominal efficiency	%	over 99	over 99	99.8	99.9
Flue gas upstream of the ESP					
- temperature	°C	170	130	145	135
- particle concentration[1]	g/m^3	5	5	11	15
Flue gas downstream of the ESP, i.e. in the stack					
- temperature	°C	170	130	145	135
- particle concentration[1]	mg/m^3	13–20	20	20	below 10
Test ID					
- pure bark/peat combustion		U1,U2, U3	R1,R2,R3, R4,R5	T1,T2,T3	V1,V2
- co-combustion		U4, U5, U6	none	T4,T5,T6	V3,V4

[1] in normalised dry gas (t = 0°C, p = 101.325 kPa)

[2] including re-circulation

5 Methods used for sampling, analysing and data processing

5.1 Sampling procedure for bulk samples

5.1.1 General aspects

The sampling procedure was based on one approach in all the plants: to collect the samples from all ingoing and outgoing flows in such a way that they represent the specific burning process at each plant. Whenever it was possible, the samples were taken from the flowing stream instead of a stock or a bunker to confirm the relation to the process under study. The sampling places were selected together with the operators and the staff of the plants to ensure the safety for the sampling personnel and to prevent interruptions in process operations. The ash silos at each plant were completely unloaded before the measurement campaign started. The fuel mixture under study was supplied to the furnace well before the sampling started. The length of the sampling period was determined with preliminary tests at plant SB: i) the sampling period must be long enough to measure even low concentrations in the flue gases and to obtain reliable measurements of the large mass streams, ii) from the economic point of view, the sampling period must be on the other hand short enough to run the plant in a steady state with selected parameters. The sampling time was 6 hours for the coal-fired and peat-fired power plants, and 5 hours for the bark-fired power plant. Each test was repeated from two to six times on different days.

5.1.2 Flue gases

The concentrations of NOx, SO_2 and combustion gases (O_2, CO, CO_2) as well as the flue gas temperatures were measured continuously in the stack during the measurement campaigns. The measurements were carried out according to the Finnish Standards SFS 3869 (1982) and SFS 5624 (1990). Three net-point filter samples according to the Finnish Standard SFS 3866 (1990) were taken during each test to determinate the particle concentration and moisture content of the flue gas. The particle concentration was measured according to the EPA Method 29 and EPA Method 5 in plants MB and RB. The particle concentrations were used to check the representativeness of the one-point sampling of the trace elements. The net-point velocity of the flue gas was measured a couple of times in each test to determine the flue gas flow rate. The dynamic pressure in the duct was monitored during the trace element sampling period with an S-type Pitot-tube at one point or periodically with a zero pressure nozzle from the particle measurement device at several points of the sampling level.

Isokinetic trace element samples from the flue gases going into the atmosphere were taken in all the measurement campaigns. In the coal-fired power plants, the simultaneous samples were taken upstream (i.e. downstream of the ESP) and downstream of the FGD.

The particulate and the gaseous fraction of the elements were sampled simultaneously with the sampling train made of glass and Teflon®. The sampling train was developed at VTT in co-operation with IVO. The construction of the sampling device is adapted from the German VDI Method 3868:1 (1994). The train was designed such that the sampled flue gases have contact with the glass only before particle separation and with the glass and Teflon® after the in-stack filter holder. Plane filters made of Teflon® (Fluoropore®, pore 0.5 µm, diameter 47 mm) were used to sample the particles upstream and downstream of the FGD in plants SB and MB, and in the stack of plant HB, where the particle concentration was 5 mg/m^3 (in NTP) or below. Thimble filters made of quartz fibre (Munktel MK360) were used in all the other measurement places because of the higher particle concentrations. After the particle separation, the sample gas was divided via Teflon® lines to the absorption units outside the flue gas duct. The flow rate of the sampling gas was controlled with critical orifices in plants SB and MB. The volume was calculated using the calibration curve of the orifice and the measured sampling time. The flow rate of the sampling gases was controlled with the needle valve and rotameter in all the other places. The volumes of the sampling gas in these places were determined with dry gas meters.

The absorption units were placed in cold water (ice-bath) during the sampling. A series of two absorption bottles containing a solution of 4 w-% $K_2Cr_2O_7$/20 w-% HNO_3 was used to absorb gaseous mercury (Hg), with collection efficiency of more than 99 % (Dumarey *et al.*, 1981). A series of two absorption bottles containing 38 w-% HNO_3 was used to collect the other gaseous elements. Each bottle contained 50–75 ml of absorption solution. There was one clean empty bottle upstream of the absorption solutions whenever it was expected to have flue gas condensation of more than 10 ml during the sampling. This was done to avoid any changes to the collection effect of the absorption solution.

At plants UB, TB and VB, the sampling line was heated up to the stack temperature to reach condensation of the sampling gas into the first, empty, absorption bottle and not on the inside of the sampling probe.

Before sampling started, the sampling probe was warmed up to the stack temperature. The sampling train was plugged into the end of the train and the nozzle was turned on so as not to point against the flow during warming. Any leakage of the sampling train was checked and eliminated before starting the sampling.

The masses of the moisture-free filters were determined before the sampling procedure. Some of these pre-handled filters were used as field blank filters, i.e. those filters that were taken to the measurement place but without any sampling in plants SB, HB and MB. In the rest of the plants, some of the pre-handled filters went through the whole sampling procedure without any sucking of flue gas. These filters, with some filters left in the laboratory, were used as check filters for mass determination and for blank filters for trace element analysis.

After each test, the whole sampling train was rinsed with 38 w-% HNO_3 and distilled water. The nozzle and the front inside of the filter holder were rinsed into one bottle and the train after the filter into another bottle. The field blanks were made like the real sampling without any sucking to check for any contamination of the sampling line for the gaseous fraction, as well. The solution blanks were made of 50–75 ml of the absorption solution, which was prepared for the measurement campaigns.

At plant RB, the flue gas sampling and analysis were also done according to the EPA Method 29. A flue gas sample was withdrawn isokinetically from the stack. The particulate fractions were collected in the probe and on a heated quartz fibre thimble filter, and the gaseous fraction was then collected in an aqueous acidic solution of hydrogen peroxide (analysed for all metals including Hg) and an aqueous acidic solution of potassium permanganate (analysed only for Hg). The recovered samples were digested, and appropriate fractions were analysed for Hg by cold vapour atomic absorption spectroscopy (CVAAS) and for other elements by atomic absorption spectroscopy (AAS).

5.1.3 Other mass streams (solid and liquid)

Samples of other mass streams were taken with a plastic bucket at regular intervals, i.e. one hour, over the period when the flue gases were being sampled and combined to the bulk sample of each test. There were some exceptions, which are mentioned below. All the ingoing and outcoming streams were studied.

The coal from each supplier of coal mills was sampled with a mechanical sampling device made of stainless steel and later combined. The total amount of coal collected was about 200 kg during one test.

The peat and bark were sampled from the conveyors supplying fuel to the boiler. During co-combustion, the sludge was sampled at plant UB from the conveyor after the filter press before it was combined to the bark stream. The fuel/fuel mixture samples were also taken from just in front of the fuel shutoff valve of the boiler at plant UB. The wood-chips samples at plant TB and sawdust samples at plant VB were taken from the output stream of the screwfeeder just before falling and combining with the peat stream. The total amount of each fuel was 30–50 litres during one test.

The samples of bottom ash were taken from the front end of the ash conveyor downstream of the quenching basin in the coal-fired power plants and at plants RB and TB. There was no quenching at plants UB and VB. The samples at plant UB were taken from the top of the ash hill in the transportation container right after the ash had fallen. The samples at plant VB were taken from the hopper before the ash was supplied to the transportation container. The total amount of bottom ash collected was 7–10 litres during one test.

At the MB, TB and VB plants, the ash samples coming from the economiser were taken from the hoppers and combined after each test. At plant UB the samples were taken when ash was falling down into the transportation container.

The total amounts of ash collected were 1–5 litres during one test. In the other plants (HB, SB and RB), ash fell to the quenching basin and was mixed with bottom ash.

The samples of fly ash precipitated by the ESP (so-called PFA samples) were collected from the intermediate reservoir in plants HB and SB and from the conveyor to the silo in plant UB. The ashes coming from all the hoppers of ESP combined upstream of the sampling place. The total amount of PFA collected was 10 litres during one test.

At plant MB, the PFA samples were collected from the first eight hoppers and combined after each test. The total amount of PFA collected was 7 litres during one test.

At plant RB, two PFA samples of 10 litres were collected from the landfill of pulverised fly ash when the ash silo was unloaded. The samples taken after test periods 1–3 and after test periods 4 and 5 were later combined into one sample.

At plant TB, the PFA samples were taken from each of the ESP hoppers at one-hour interval. The amount of the sample was 0.2–3 litres per test depending on the ESP field.

At plant VB, the PFA samples were taken with a mechanical sampling device made of stainless steel from one of two series of hoppers. The hourly samples from each hopper during one test were combined. The amount of sample was 0.6–7 litres per test depending on the ESP field.

Lime was sampled from the end of the screw conveyor above the slurry feed tank during a three-hour quenching period (a total of 2 kg) in the coal-fired power plants.

Samples of the end-product from the semi-dry FGD were collected from the transmitter of the fabric filter. At plant HB, samples of the coarse fraction of the FGD product were collected from the pre-separator of the by-product. The total amounts of each of the FGD products were 5 litres during one test.

At plant MB, the sample of pure gypsum was taken hourly from the conveyor supplying the gypsum to the storage. The total amount of gypsum was 7 litres during one test. The sample of wastewater treatment sludge was taken while the cake was falling from the filter press. The total amount of sample was 7 litres during one test.

One sea-sand sample of 10 litres was collected at plant RB when the sand silo for the fluidised bed was loaded. The results from plant RB were also used for plant UB. During the measurement tests, no sand was added to the bed at plants TB and VB.

Two 1-liter samples of sea- and tap water used in the spray-dryer and in the quenching basin for the bottom ash were taken once per test at the coal-fired power plants, and similar samples of lake water were taken at plant RB. (There were no water streams at plants UB, TB and VB).

In plant MB, the samples of untreated and treated wastewater were collected once per hour and combined, giving a sample of 7 litres per test.

5.2 Method description for mass flow determinations

In addition to the element content in each mass stream, the flow rates of all the streams are necessary data for mass balance calculations. The estimation of their magnitudes during each sampling period (i.e. each test) was made according to the information given by the plant operating records. The main process parameters of the plant including the flows of the coal, lime, gypsum and pulverised fly ash at the coal-fired power plants were continuously measured and recorded in the database. The weighing procedures for the other ash streams and end-products of FGD were agreed with the plant staff. The silos and transporting containers were unloaded before the test period started and unloaded and weighed after each test period as well as during the test if needed. The weighing procedure was agreed also at the bark- and peat-fired power plants, where the flows of the fuels are based on the results of the weighbridge, as well. The flow rate of sea- sand was recorded from the level transmitter in the sand silo at plants UB and RB. In the case of the coal-fired power plants and plant RB, the water content of the bottom ash was determined in the laboratory to calculate the dry flow rate. The flow rate of water coming to the quenching basin was approximated based on the knowledge of the technical staff and on the moisture analysis of the bottom ash.

The measurement group determined experimentally only the flue gas flow rate during each test at all the plants. The flow rates of the flue gases were determined with a Pitot-tube, according to the Finnish standards SFS 3866 (1990) and SFS 5624 (1990). The gaseous components and the flue gas temperatures were measured continuously with analysers, according to the standards SFS 3869 (1982) and SFS 5624 (1990). The dynamic pressure in the duct was monitored during the trace element sampling period with an S-type Pitot-tube at one point or periodically with a zero pressure nozzle from the particle measurement device at several points of the sampling level. The experimentally measured flow rate corresponded well with the theoretical calculations, according to the standard SFS 5624.

The flow rates of coal at plants HB, SB and MB were measured and recorded continuously from the suppliers of the coal mills. The data records also included very similar flow rates calculated from the produced power, whose values were used in the mass balance calculations.

The recorded flow rate of peat came from the weighing results of the trailer lorries. The process parameters gave the flow rate of the live steam produced at the plant, the total energy for utilisation (gross load), and the coefficient of utilisation. Based on these values, the fuel effect in peat supplied can be calculated. The heat value and the moisture of the fuel were analysed, then the flow of the peat could be calculated.

In the case of co-combustion, more information is needed to determine the flow rate of the fuel components. This is described and discussed here, as well as the flow rate of the pulverised ash streams at the bark- and peat-fired power plants.

The flow rate of the fuel was determined in the following way at plant UB. The conveyor belt scale of the plant recorded the mass of the fuel during the measurements. The heat value and moisture of the fuel components were analysed. The fuel energy calculated from these parameters was far too low compared to the produced energy during the pure bark combustion in tests U1–

U3. The flow rate of bark was determined based on the results from the heat value of the fuel, the gross load of the boiler and the utilisation efficiency. In the case of tests U4–U6, the results obtained from these two different ways were close to each other during co-combustion, so the flow rate used in the mass balance studies is based on the recorded mass from the conveyor belt scale. The flow rate of the sludge was recorded hourly at the plant, which gave the mass fractions of bark and sludge in the total flow rate of the fuel supplied.

The contents of nitrogen and sulphur in the sludge, bark and PFA were analysed and the concentration of SO_2 in the flue gas was measured. The flow rate of the bark and sludge determined by the balance sulphur did not make any corrections to the flow rate.

The bottom ash and ash from the economiser were removed into the same ash transporting container at the UB plant, which was unloaded daily just before and after the tests and weighed on the weighbridge. The ash container was supposed to contain 80 % bottom ash and 20 % ash from the economiser.

The pulverised fly ash silo at plant UB was unloaded just before tests U1 and U4, and unloaded and weighed after tests U3 and U6. During the first test, the technical staff in the control room of the plant noticed that the ESP shakers were not working after the summer down-time. The shakers were put on working, which produced a large amount of ash in the ash silo. The PFA mass data from the weighbridge was not suitable to use in tests U1–U3. The mass of PFA in tests U1–U3 was approximated on the analysed ash content of fuel, on the analysis of unburned content of PFA and on the mass data weighed during tests U4–U6.

The pulverised fly ash silo at plant RB was unloaded just before tests R1 and R4, and unloaded and weighed after tests R3 and R5. The pulverised ash was dumped on the ash disposal site beside the plant. The samples of PFA were collected and combined from the disposal site right after tests R3 and R5. All the tests were peat-firing, and it was supposed that there are no changes in contents of peat. Afterwards, it was found that the heat value of the peat was lower, and the sulphur content of the peat was higher during tests R4 and R5 compared to tests R1–R3. The trace element contents in the peat (e.g. Cd, Mn, Ni and Pb) during tests R4 and R5 differed also clearly from tests R1–R3 (see Table 6.4), which means that the mean contents analysed in the combined PFA sample are unrepresentative for these tests.

The flow rates of the fuels at plants TB and VB were checked with the mass balance calculation of sulphur. The sulphur contents in the fuel and in the PFA were analysed and the concentration of SO_2 was measured in the stack. During the co-combustion of peat and wood-chips/sawdust, the flow rates of each component were determined based on evaluations of sulphur flow calculations, on the total amount of wood-chips/sawdust, and on the rotational frequency of the screw feeder.

The ash separated in the economiser and the PFA was transferred to one ash silo at plant TB. The silo was unloaded just before tests T1 and T4 and it was unloaded and weighed after tests T3 and T6. The ash silo also contained the ash from another boiler on the same site. The flow rate was calculated based on the flow rate fractions of the ashes and the ash content of the fuel supplied in each boiler. The flow rate of the ash from the economiser was approximated to be 5 % of the total flow of the case boiler, and the flow rates of the ash from three ESP serial hoppers were approximated as 80 %, 15 % and 5 % of the total 95 % flow of the case boiler.

The ash separated in the economiser and the PFA was transferred to one ash silo at plant VB, which was unloaded just before tests V1 and V4, and unloaded and weighed after tests V2 and V4. The weighed mass gave only the approximation of true mass because some water was added to the ash during unloading to prevent dust nuisance. The flow rate of water supplied was measured. The flow rate of ash from the economiser and from four ESP serial hoppers were determined with pre-tests given the following ratio: economiser 0.7 %, PFA1 66.7 %, PFA2 28.9 %, PFA3 3.5 % and PFA4 0.2 %. The flow rate used in mass balance calculations corresponded with the flow rate of ash, which was calculated based on the ash content in fuels analysed and on the flow rate of fuel determined.

5.3 Sample treatment and analysis

5.3.1 Main principles

The main target of sample treatment and analysis was to measure very low element contents reliably in different power plant samples. Whenever the content of trace element is measured below the determination level, the mass balance calculations have greater uncertainties, which give poor closures. The low element content of solid samples requires the use of a sensitive analytical technique such as atomic absorption spectrometry (AAS) and inductively coupled plasma mass spectrometry (ICP-MS). These techniques require digestion of the sample before the determination. In mass balance calculations, the determination of only easily leachable fractions cannot be accepted. Instead, methods to determine the total concentration of each element are needed. Therefore, the digestion should be capable of bringing all the elements into solution. These problems are comprehensively discussed by Laitinen *et al.* (1996) and Hatanpää *et al.* (1997). The papers describe the developments and optimisation of trace element analysis of power plant samples, which were done before undertaking the mass balance measurement campaign at the coal-fired power plant.

Of the major elements, manganese (Mn) was analysed to act as the magnitude control of the mass flows. The content of Mn was intended to be measured over the determination level in all flows.

The coarse solid samples were ground and divided into smaller laboratory samples. One part of each solid sample was used for the moisture content determination. One part of the fuel samples was used for fuel analysis (i.e. heat value, ash, volatile material, S and N content) and one part of bottom ash, Eco ash and PFA were used for analysis of S and unburned fractions. The laboratory samples were digested with acids before the trace element analysis, as well as the filter samples. Graphic furnace atomic absorption spectrometry (GFAAS) was mainly used for the trace element determinations. Mercury was determined using cold vapour atomic absorption spectrometry.

A part of the samples from the parallel tests was left as reserve in the trace element analysis.

The analyses were performed mainly in three independent laboratories (Lab1, Lab2 and Lab3), which all have long experience in analysing samples from power plants. For the sake of improved quality assurance, a part of the samples (fuel and ash) were digested in parallel in two laboratories, and a part of the resulting two solutions were analysed by both laboratories. To recognise possible sources of errors in the case of large deviations, a few digested samples were also analysed by some other laboratories. Commercial reference materials (coal, fly ash from coal burning, limestone, gypsum) were added to the digestion batch in each digestion campaign. The commercial reference samples of coal and fly ash from coal burning were used with the digestion campaign of all the samples, because there was no commercial reference material available for peat- and bark-fired power plants. A known amount of the commercial reference fly ash was added also onto the blank filter when the filters of the flue gas samples were digested.

5.3.2 Pre-treatment and analysis methods of the samples

The coarse solid samples in large containers were first mixed, dried, ground and divided into smaller laboratory samples. The gross samples (about 200 kg) of coal were first ground to a grain size less than 5 mm. Then the samples were dried in air. Laboratory samples of 3–5 kg were taken from this gross sample. They were then ground to a grain size of less than 0.1 mm before being mechanically divided into smaller samples.

The gross samples (about 50 l) of peat were first mixed and then divided into two by a rifling divider. One part was divided into two samples a further two times and dried in an oven at 30 ^{o}C. The air-dried peat samples from plants RB and TB were first ground first to a grain size of less than 1 mm and then to less than 0.5 mm before being divided by a revolving divider into four smaller laboratory samples. The air-dried wood-chip samples followed the same procedure with a grain size of 10 mm in the first step. The air-dried peat samples from plant VB were ground to a grain size of less than 1 mm before being divided into four smaller laboratory samples by a revolving divider. The laboratory samples were still ground to a grain size less than 0.5 mm. The gross samples of sawdust also followed the same procedure but with a grain size of 10 mm in the first step.

The gross samples of bark and sludge were first divided into smaller samples by means of the manual "cone-to-squares" method and dried at 30 ^oC (sludge) and 20 ^oC (bark). The air-dried bark samples were first ground to a grain size of less than 10 mm and then to a grain size of less than 4 mm before being divided into four smaller laboratory samples by revolving divider. The laboratory samples were still ground to a grain size less than 0.5 mm. The sludge samples were directly ground to a grain size less than 4 mm.

The samples of bottom ash from the coal-fired power plants were dried and homogenised by means of grinding to a grain size of 0.1 mm. The bottom ash samples from the bark- and peat-fired power plants were first weighed and sieved. The fraction with a grain size of over 2 mm including mainly stones was removed and stored separately. The fraction with smaller particles was divided into four smaller laboratory samples by a revolving divider.

Samples of PFA, end-products of FGD, gypsum and wastewater cake from the coal-fired power plants were divided into smaller samples by means of the manual "cone-to-squares" method.

The PFA samples from plants UB and RB were divided into four laboratory samples by a revolving divider. PFA samples with ecoash samples from plants TB and VB underwent special pre-treatment because the samples were collected separately from the economiser hopper and from the four ESP hoppers. The samples from each hopper from plant TB were not combined, but divided into three laboratory samples. The samples from plant VB were weighed and combined according to the ratio of separation. The plant operators had determined the following ratios of separation: ecoash 0.7 w-%, first ESP hopper 66.7 w-%, second ESP hopper 28.9 w-%, third ESP hopper 3.5 %, and fourth ESP hopper 0.2 %. The combined samples were divided into four smaller laboratory samples.

The solid laboratory samples were digested with specific acids before analysis in two to five different laboratories (see Appendix 1). The digestion method used for the samples from the coal-fired power plants has been described by Hatanpää *et al.* (1997). The flue gas particle samples collected on quartz fibre filters at plants HB, SB and RB were digested according to the procedure described by Laitinen *et al.* (1996). The papers discuss the problems in reliably measuring low element contents in power plant samples and describe the developed and optimised analysis methods used for coal-fired power plants and plant RB for the quartz fibre filter samples. For the coal and ash samples, nitric acid and hydrofluoric acid were used in Teflon® PFA vessels under microwave heating. In Lab2 and Lab3, saturated boric acid was added to all these samples after digestion. Microwave oven digestion was not used for mercury determination. The coal samples were digested by refluxing with nitric acid and hydrochloric acid in Lab2 and Lab3. Nitric acid and sulphuric acid were used for ash samples in both laboratories. Limestone, end-products of FGD, filter cake and gypsum samples were digested in the microwave oven using nitric acid alone by Lab2 for other than Hg determination. Some of these samples were digested in Lab5 with nitric acid, hydrochloric acid and hydrofluoric acid in Teflon® PFA vessels under microwave heating. After digestion, saturated boric acid was added to the samples. For mercury determination, the samples were digested by refluxing with nitric acid and sulphuric acid in Lab2.

In the case of the coal-fired power plants, Teflon® filter samples from flue gases were digested in Lab2, similarly to the ash samples. Quartz fibre filter samples from flue gases upstream of the FGD of plant HB were digested in Lab2 by refluxing with nitric acid and hydrochloric acid for mercury analysis. For the other trace element analysis, quartz fibre filters were digested in Lab5 with nitric acid, hydrochloric acid and hydrofluoric acid under microwave heating with boric acid addition.

In the case of the bark-fired power plant and peat-fired power plants, the fuel and ash samples were digested in Lab1 with nitric acid, water and hydrofluoric acid under microwave heating for other trace element analysis but not for mercury. Lab2 used nitric acid and hydrofluoric acid under microwave heating with boric acid addition for all the trace element analyses of the peat, wood-chip and sawdust samples. This digestion method was also used in Lab3 for the fuel and ash samples without following any mercury analysis. For mercury analysis, the bark, sludge and ash samples from plants UB, RB and TB were digested in Lab2 by refluxing with nitric acid and sulphuric acid. In case of plant VB, the samples were digested in Lab2 under microwave heating with nitric acid, hydrogen peroxide and hydrofluoric acid under microwave heating with boric acid addition. Quartz fibre filter samples from the flue gases at plants UB, TB and VB were digested in Lab2 by refluxing with nitric acid and hydrochloric acid. The blank filters were followed the quartz fibre filter samples during the whole digestion and analysis procedure to quantify the trace element contents in the filter material. The filter samples from plant RB were digested in Lab5, as in the case of the coal-fired power plants.

The pulverised fly ash samples from plant RB were also digested and analysed in Lab4. The samples were digested with nitric acid and hydrochloric acid in room temperature and analysed using the ICP-MS technique.

The absorption liquids, probe rinsing acids and water samples were analysed with the same technique as the digested solid samples. Most of the metals were analysed by graphite furnace atomic absorption spectrometry (GFAAS). For Cr, Cu, Mn and Ni, the flame atomic absorption technique (FAAS) was used instead of GFAAS in Lab1, Lab2 and Lab3, if the element concentration of the sample was high enough. The mercury samples were analysed using the cold vapour atomic absorption method (CVAAS) in Lab2, or by a gold film mercury analyser in Lab3. Inductively coupled plasma emission spectrometry was used in Lab2 to measure beryllium concentrations in the case of the coal-fired power plants.

5.4 The procedure to weed the data used in mass balance calculations

5.4.1 Overall criteria

The individual laboratory samples from the same bulk sample of each measurement period were treated and analysed in several laboratories (see Appendix 1). The procedure gave two to three independent analysis results of the same bulk sample. On the other hand, each measurement period was repeated from two to six times. The plants were operated in the same way at a steady-state during every measurement period of each specific fuel supply. This procedure produced two to six independent measurement results from specific fuel mixtures from each measurement campaign.

In order to calculate the trace element balance for each measurement test and for each firing condition (specific fuel supplying), all the analysis and measurement results had to be evaluated very carefully. It was necessary to determine the criteria for handling the parallel results in the further calculations.

The successfully analysed commercial reference material (i.e. highly satisfactory element recovery) was one of the criteria to include in the analysis results of the real samples for the mass balance calculations. The average of all three parallel results was used in subsequent calculations if there had been no problems in digestion or the analysis procedure. When two results were close to each other, and the third was more than 10 % less or greater, it was not included in the average calculations. During co-combustion tests, it was necessary to compare and evaluate the analysis results of the fuel mixture and of each fuel component. The element contents and their enrichments in the ash were reported later with their respective contents given in the literature.

The contents of trace elements after evaluation of all the analysis results and after weeding out inappropriate results are shown in Appendix 7 and Appendix 9. These values are further used in the mass balance calculations.

5.4.2 Fuel samples

The digestion and analysis method for the coal samples in the case plants were comprehensively tested in several independent laboratories with commercial reference material. The method was highly satisfactory at producing element recoveries (Hatanpää *et al.*, 1997) and was used successfully with low detection limits in the case of plants HB and SB (Aunela-Tapola *et al.*, 1998). The high repeatability and reliability of the method was also confirmed in plant MB. The parallel coal samples of plant MB were digested in Lab2 and Lab3. The contents of As, Cd, Cr, Ni, Pb and Se were analysed in both laboratories, giving analysis results close to each other. The average of two independent element contents was selected for the mass balance calculations.

The trace element contents analysed in each fuel component at the bark- and peat-fired power plants, i.e. bark, peat, sludge, wood-chips and sawdust and their mixture are discussed in detail in Appendix 2. There was no sample of the fuel mixture in tests V3 and V4; the value for the mass balance calculations (i.e. “Mba”) in these tests was calculated based on the peat and sawdust analyses and on their mass fractions in the fuel mixture.

The contents of As, Cd, Cr, Mn, Ni and Pb in the fuel samples of plant UB were analysed in Lab1 and Lab3. The Hg content was analysed only in Lab2, which was employed the method accredited according to the EN 45001 and the ISO Guide 25 standard. Lab2 and Lab3 analysed fuel samples with certified reference material NBS1633a, NIST. The Hg content in the reference material analysed was well within the limits of the certified value. Lab1 analysed fuel samples with certified reference bituminous coal, NBS1632b, NIST. Based on the high element recoveries of commercial reference material, the analysis results of Lab3 were chosen for further calculations in the case of Cd, Cr, Mn, Ni and Pb with the following note: the content of Cd and Mn in the fuel of test U4 can be somewhat actually higher. The detection limit for As was lower in Lab1, which was chosen for the further calculations.

The contents of As, Cd, Cr, Mn, Ni and Pb in peat from plant RB were analysed in three laboratories (i.e. Lab1, Lab2 and Lab3). The content of Hg was analysed only in Lab2. There were no significant systematic differences in the analysis results, and therefore the average values of each test were chosen for the mass balance calculations. The contents of As, Cd, Cr, Mn, Ni and Pb in the peat in tests R3 and R4 were also analysed in Lab4, which used a totally different method for digestion and analysis (see Appendix 1). The results of the method used in Lab4 matched well the results from the other laboratories.

The contents of As, Cd, Cr, Mn, Mo, Ni and Pb in fuel samples from plant TB were analysed in two laboratories (i.e. Lab1 and Lab2). The content of Hg was analysed only in Lab2. The results showed significant differences in the contents of As, Cr, Mn, Mo and Ni analysed in the two laboratories. No relevant arguments were found from the quality control checks on the analysis. Therefore, the element contents analysed in the fuel mixture samples were compared to the combined values of the individual contents in the peat and wood-chips in proportion to their flow rate. The mass balance was calculated first with the values determined in one laboratory (Lab1) and when ever the ratio between outcoming and ingoing flow was not within the criterion limit (i.e. 0.7–1.3), the mass balance was calculated again with the analysis results determined in another laboratory.

The analysis results from Lab1 instead of Lab2 were selected for further calculations of Cd, Cr, Mo and Pb. The results from Lab2 were used for test T4, because the results from Lab1 were absent. The contents of As, Mn and Ni that were analysed in Lab1 instead of Lab2 were chosen for the element balance calculations for peat combustion, but not for co-combustion. In the case of As, the analysis results from Lab2 gave the most acceptable closure to the element balances for the co-combustion tests. The contents of Mn and Ni in the fuel mixtures analysed in Lab2 were closest to the combined values of peat and wood-chips in proportion to their flow rate.

The contents of As, Cd, Cr, Mn, Mo, Ni and Pb in the fuel samples of plant VB were analysed only in Lab1. The content of Hg in the fuel was analysed in Lab2. Because there was no relevant fuel mixture sample available, the contents of trace elements in peat and sawdust were determined individually, and a combined value was calculated in proportion to their flow rate. In addition to common quality control checks (determination of method blanks, etc.), the analysis results of the samples of fuel mixtures collected a week before (Vc1) and after (Vc2) the measurement campaigns were utilised in data evaluation. No argument was found to eliminate any analysis results in tests V1–V4.

5.4.3 Sea-sand and water samples

The sea-sand used in the fluidised bed was analysed only at plant RB. The contents of As, Cd, Cr, Mn, Ni and Pb used in further calculations are the average values of two laboratories (Lab1 and Lab3), because there was no commercial reference sea-sand sample available. The content of Hg in sea-sand was analysed below the detection limit in Lab2. Because the flow rate of the sand was very low compared to the flow rate of the fuel, these values were used also in the mass balance calculations of plant UB.

The flow rates of the waters at all the plants were low compared to the flow rates of the fuel; as expected, the element concentrations were also low. The water samples were analysed only in one laboratory, i.e. Lab2 or Lab3, depending on the case plant.

5.4.4 Ash and other solid samples

The digestion and analysis methods used for coal fly ash, lime and gypsum samples were detailed and satisfactorily tested in several independent laboratories with commercial reference materials, as in the case for coal. The methods were used successfully with low detection limits in plants HB and SB (Aunela-Tapola *et al.*, 1998). The high repeatability and reliability of the method was found also in the case of plant MB for bottom ash, ecoash, pulverised fly ash, lime, gypsum and filter cake samples, which were digested in both Lab2 and Lab3. The contents of As, Cd, Cr, Ni, Pb and Se were analysed in both laboratories, giving analysis results close to each other except in the following cases: the determining complexity of Cr and Ni in the bottom ash, Ni in lime and Cr in filter cake could be observed. The average of two independent element contents was selected for the mass balance calculations.

The trace element contents analysed in bottom ash and in pulverised fly ash (i.e. PFA) samples at plants UB, RB, TB and VB are discussed in detail in Appendix 3.

The contents of As, Cd, Ni and Pb in the bottom ash and PFA samples of tests U1–U2 and U4–U5 were analysed in Lab1 and Lab3. The contents of Cr and Mn were also analysed in Lab3 and the content of Hg was analysed in Lab2. Lab2 employed the method accredited according to the EN45001 and the ISO Guide 25 standard. Lab2 and Lab3 analysed ash samples with certified reference material NBS1633a, NIST. The content of Hg in the reference material analysed was well within the limits of the certified value. Lab1 analysed the ash samples with certified reference bituminous coal, NBS1632b, NIST. Based on the data evaluation with the results of reference material samples, the analysis results of Lab3 were selected for further calculations of As, Cd, Cr, Mn, Ni and Pb with the following note: the content of Ni and Pb in PFA can be actually somewhat higher.

The contents of As, Cd, Cr, Mn, Ni and Pb in the bottom ash and in the PFA samples of plant RB were analysed in Lab1 and Lab3. The content of Hg was analysed in Lab2. The contents of trace elements in the PFA were determined also in Lab4. The results of the method used in Lab4 matched well the results from the other laboratories except for the content of Mn in peat in test R3, which was analysed somewhat higher (i.e. 65 mg/kg) compared to the average of the other laboratories (i.e. 59 mg/kg). The averages of the analysis results from Lab1 and Lab3 were selected for the mass balance calculations, with the following remarks: the contents of As, Mn, Ni and Pb in the bottom ash were determined as systematically low in Lab1 compared to Lab3, as well as most of the Cd contents. The content of As in the PFA was analysed in Lab3 below the contents determined in Lab1 and Lab4. The content of Ni determined in Lab3 was somewhat higher than the contents determined in Lab1 and Lab4.

In the case of plant TB, the contents of As, Cd, Cr, Mn, Mo, Ni and Pb in all the bottom ash samples and the PFA samples from three ESP hoppers were analysed in Lab3. The samples of tests T2–T3 and T5–T6 were digested and the trace elements were analysed in Lab1 as well. The content of Hg was determined only in Lab2. The contents of the trace elements in the PFA samples from three ESP hoppers met expectations. The contents were lowest in the first hopper, which removes the coarse particulate fraction from the flue gases, and the contents were highest in the third hopper, which removes the fine particulate fraction. The trace element contents in the PFA for the mass balance studies were calculated based on the flow rate ratio of each PFA stream (i.e. 80 % PFA(ESP1), 15 % PFA(ESP2), 5 % PFA(ESP3)). These combined values are shown in Appendix 9. Based on the data evaluation described in Appendix 3, the analysis results of Lab3 were selected with the following remarks for further calculations of As, Cd, Cr, Mn, Mo, Ni and Pb: the contents of Mn and Pb in the bottom ash and the PFA samples of plant TB could be actually somewhat higher. The true contents of Mo and Ni in the PFA samples could be somewhat lower than the values determined in Lab3.

The contents of As, Cd, Cr, Mn, Mo, Ni and Pb in the bottom ash samples from plant VB were analysed in Lab1. The content of Hg was analysed in Lab2. The contents of As and Cd were determined low compared to plant RB or TB. All the other contents were close to the contents determined in the case of plants RB and TB.

Ash samples collected from the economiser and from four ESP hoppers at plant VB were combined before sample pre-treatment in ratio to their flow rate (i.e. 0.7 % PFA(ECO), 66.7 % PFA(ESP1), 28.9 % PFA(ESP2), 3.5 % PFA(ESP3), 0.2 % PFA(ESP4)). The combined sample was recorded as the PFA sample. The contents of As, Cd, Cr, Mn, Mo, Ni and Pb in the PFA samples were analysed in

Lab1. The content of Hg in the PFA samples was determined in Lab2. To control the content levels, the sample of test V3 was digested and analysed in Lab3. The contents of Cd and Pb were determined quite equal in both laboratories. The contents of As, Mo and Ni in PFA determined in Lab1 were low compared to the contents determined in Lab3. The contents of Cr and Mn were determined higher in Lab1 than in Lab3. The content of Hg was determined somewhat higher in Lab2 than in Lab3.

In addition to this, the samples from the two first ESP hoppers in tests V2 and V3 were digested and analysed separately in Lab1 to control the content level. The element contents were lower in the first ESP hopper during both tests, as expected. All the contents in the PFA determined in Lab1 and Lab3 fitted well between the contents of the PFA(ESP1) and PFA(ESP2), but not Mo. Subsequent examinations indicated that the samples had been combined approximately in the correct ratio and the true content of Mo in the PFA could be somewhat higher in tests V1–V4.

The contents of As, Cd, Cr, Mn, Ni and Pb in the ecoash samples from plants UB and TB were analysed in Lab1, as well as the content of Mo in the case of plant TB. The content of Hg was analysed in Lab2. The results are shown in Appendix 9. In plants RB and VB, the ash from the economiser is a part of the ash precipitated by the ESP.

5.4.5 Flue gas samples

The trace element concentrations in the particulate and gaseous fractions of flue gases are shown in Appendix 7 and Appendix 9. Some of the pre-handled filters stored in the laboratory during the measurement campaign were used as laboratory blank filters. Some of the pre-handled filters taken to the measurement place, mounted in the sampling line and in the sampling point in the channel/stack were used as field blank samples. The blank filters were digested and analysed with the real samples. The field blank samples were made also for the absorption solutions and rinsing solutions of the sampling probe. The solution blanks were made of 50–75 ml of the absorption solution, which was prepared for the measurement campaigns. Each of the solutions was analysed with the real samples. When the element contents in the blank samples were repeatable over the detection limit, the element content was first deducted from the values analysed in the real samples before further calculations.

In the case of plants UB, TB and VB, the quartz fibre thimble filters were digested with the acid solutions of HNO_3 and HCl, which resulted in incomplete dissolution of some trace elements, especially Cr and Nil. This can be seen, and is discussed, in detail in Appendix 4. This has been widely studied experimentally earlier in the pre-tests of plant SB and published by Laitinen *et al.* (1996). The acid solutions of HNO_3 and HCl enabled the analysis of all the element contents, including mercury, from each sample. However, it must be kept in mind that some of the real contents can be higher.

The trace element concentrations in the flue gases of plant RB were measured with two different methods. The results of these two methods are discussed in detail in Appendix 5.

One sampling method employed was the method developed by VTT and IVO for the mass balance studies (i.e. method MV, referred to in section 5.1.2), which was used in all the measurement campaigns of this thesis. Another method used in plant RB was according to the EPA Method 29 with specific sampling, digestion and analysis methods (i.e. method ME). The results of these two methods are discussed in Appendix 5. For the mass balance calculations, the results of the MV method were chosen, for the following reasons: the detection limit of the ME method was high for the particulate As, Cr, Mn and Ni compared to the concentrations detected with the MV method. The MV digestion and analysis method was successfully verified with reference fly ash samples from coal burning in the pre-tests of the coal-fired power plant.

5.5 Procedure for mass balance calculations

The flow rate of each trace element can be calculated based on the trace element content analysed in each ingoing and outgoing stream, and on the flow rate of each stream according to the following equation:

$$Q_{i,j} = c_{i,j}\, q_j \tag{5.1}$$

Where $Q_{i,j}$ = the flow rate of the element i in the ingoing or outcoming material stream j of the plant (mg/h)
$c_{i,j}$ = the content of the element i analysed in the representative sample of the material stream j of the plant (mg/kg in dry basis for solid samples, $\mu g/Nm^3$ in NTP for dry flue gas samples, mg/m^3 for water samples)
q_j = the flow rate of the material stream j of the plant (kg/h in dry basis for solid streams, Nm^3/h in NTP for dry flue gases, m^3/h for water streams).

The sum of all the ingoing and outcoming flow rates of each element gives the total ingoing ($Q_{i,in}$) and outcoming ($Q_{i,out}$) streams of each element, respectively.

$$Q_{i,in} = \Sigma(Q_{i,j}), \text{ when } j = 1\ldots n \tag{5.2a}$$

$$Q_{i,out} = \Sigma(Q_{i,j}), \text{ when } j = n+1\ldots n+m \tag{5.2b}$$

where n = number of the ingoing streams of the plant
m = number of the outcoming streams of the plant.

The steady-state mass balance of each element means that

$$Q_{i,\, in} - Q_{i,\, out} + r_i = 0 \tag{5.3}$$

where r_i = recovery factor.

In this thesis the recovery factor is zero (0) in the calculations in order to reveal information about the success of the experimental tests and the ability of the experimental methods. This is studied based on the closure of each element mass balance.

The closure of each element mass balance, $(Out/In)_i$, means the ratio between outcoming and ingoing streams of the element.

$$(Out/In)_i = Q_{i,out}/Q_{i,in} \tag{5.4}$$

When the ratio $(Out/In)_i$ is close to 1.0, the mass balance has been determined successfully. When the ratio is below 1.0, the outcoming stream is too low compared to the ingoing stream. This results when all the ingoing streams of the element have not been detected in the outcoming streams, or the real ingoing stream of the element is lower than the determined one. On the other hand, when the ratio is more than 1.0, the outcoming stream is too high compared to the ingoing stream. This results when the real outcoming flow of the element is lower than the determined one, or the ingoing stream of the element has been detected too low. The criterion for the applicability of the results was the range of closure, 0.7–1.3.

The mass balance was calculated first for manganese (Mn) in all the case plants. Mn was chosen to act as the magnitude control of the mass streams, because the content of Mn was intended to be measured over the determination level in all the streams of the plants. The closure of Mn indicated whether there was something wrong in the determined flow rate of the ingoing or outcoming streams. When the closure of Mn was not between 0.95 and 1.05, the reasons were sought, and the mass streams were corrected using additional data concerning the plant (see section 5.2).

The mass balances were then calculated for the other elements using data of the element contents ($c_{i,j}$) presented in section 5.4 and the flow rate of the material stream of the plant (q_j) was determined according to the method described in section 5.2. If the results gave poor closure, the element balance was recalculated using only the analysis results of one laboratory (e.g. As in peat at plant VB).

5.6 Tools for multivariate data analysis

Multivariate data analysis, such as Principal Component Analysis (PCA) and Partial Least Squares Projections to Latent Structures (PLS), has been used successfully to predict the approaching process drift, which was caused by sludge bulking in the wastewater treatment plants of the paper and pulp mills (Mujunen *et al.*, 1998). The average purification efficiency could be predicted, but the models for effluent quality indicated an obvious lack of relevant information. Aarnio (1985) has used chemometrics tools to analyse the data concerning 33 elements in the peat and ash samples from four peat-fired power plants. The results revealed significant differences in the element contents according to the combustion technology and according to the size of the power plants. Manninen (1996) have analysed the combustion results of the RDF and PDF in a fluidised bed by multivariate data analysis. The calculations showed the correlation of total PCDD/Fs with some trace element contents in fuel, when combustion was efficient.

PCA and PLS were used in this thesis to study whether applying the chemometrics tools widens the implementation of the results of the large measurement campaigns. The tools were used in the following respects:

i) to observe the repeatability of the tests in respect of ingoing and outgoing trace element flows, which extend the representativeness of the results of one individual test
ii) to identify any substantial differences between the tests of each plant and between the different kind of plants in respect of the relative enrichment of trace elements
iii) to express any significant effects on the outcoming trace element flows from the co-combustion of wood-chips or sawdust with peat, and from the co-combustion of bark with sludge.

The limited information of the process was known as restricting factor for the data analysis and there was no aim to predict the characterisation of the trace elements. Multivariate data analyses calculations were carried out using the Unscrambler 6.11 program.

5.6.1 Principal Component Analysis (PCA)

Principal Component Analysis (PCA) is a multivariate data analysis method designed to analyse and interpret a set of data with a large number of measurements but a limited number of samples (Beebe *et al.*, 1998, Wold *et al.*, 1987, Wold, 1978). PCA helps to determine in what respect one sample is different from another, which variables contribute most to this differentiation, and whether those variables contribute in the same way (i.e. are correlated) or are independent of each other.

The underlying idea in PCA is to replace a complex multidimensional data set by a simpler version involving fewer dimensions, but still fitting the original data closely enough to be considered a good approximation.

PCA is based on a data matrix **X** composed of objects (e.g. test runs) and variables (e.g. analytical results). This data matrix **X** is partitioned into two smaller matrices, a score matrix (**T**) and loading matrix (**P'**) by principal component (PC) decomposition. In matrix representation, the model has the following equation:

$$\mathbf{X} = \mathbf{TP'} + \mathbf{E} \tag{5.5}$$

where score matrix **T** contains information about the objects, the loading matrix **P'** contains the information about the variables and error matrix **E** contains the part of the data not accounted for in the model. The error or residual matrix **E** represents the fraction of variation that cannot be interpreted.

The principle of PCA is the following: find the directions in space along which the distance between the data points is the largest. The directions, or combinations, are called principal components (PCs). The first PC is the one that carries most information (i.e. most explained variance). The second PC is calculated orthogonally to the first PC and it will carry the maximum share of the residual information (i.e. not taken into account by the previous PC). The process continues until all the systematic variation is exhausted. The number of significant PCs is determined by cross validation (Wold, 1978).

To interpret the results, loading plots and score plots can be presented. The loading plot shows variable correlations which reflects both how the variables are related to each other and how they influence the PCs.

The score plot describes the properties of the samples, and the sample differences and similarities. The samples with close scores along the same PC are similar. The score values from the PCA are useful in describing the systematic variation between the test runs.

5.6.2 Partial Least Squares Projections to Latent Structures (PLS)

The regression method fits a model to the observed data in order to quantify the relationship between two groups of variables. Partial Least Squares or Projection to Latent Structures (PLS) is a regression method which models both the **X**- and **Y**-matrices simultaneously to find the latent variables in **X** that will best predict the latent variables in **Y** (Beebe *et al.*, 1998, Wold *et al.*, 1987). These PLS-components are similar to the principal components, and will also be referred to as PCs. PLS decomposes two matrices, **X** and **Y**, simultaneously and interdependently into new latent variables (PLS components), which are correlated to each other through an inner relation between **T** and **U**. In matrix representation, the model has the following equation:

$$\mathbf{X} = \mathbf{TP'} + \mathbf{E}$$

$$\mathbf{Y} = \mathbf{UC'} + \mathbf{F} \qquad (5.6)$$

$$\mathbf{U} = \mathbf{bT} + \mathrm{H}$$

Analogous to PCA, the significant number of PLS components is determined by cross validation (Wold, 1978). Interpretation of PLS results can be done using score plots, loading plots and weight plots. PLS scores have the same interpretation as PCA scores. PLS loadings express how each of the variables is related to the model component, and PLS loading weights express the importance of the variable.

6 Results of the experimental studies and multivariate analysis

6.1 Process parameters of the plants during the measurement campaigns

The experimental tests have been coded according to Table 6.1. The supplied fuel at the HB and SB coal-fired power plants is pulverised Polish coal. Plant MB uses coal that is mined and shipped from both Poland and Columbia. Plant UB uses wood bark as a main fuel and sludge as an added fuel. The plant is located in the pulp mill area. The bark comes from the timber barking part and sludge from the wastewater treatment plant of the pulp mill. Milled peat used at plants RB, TB and VB comes from the peat bogs at a maximum distance of 100 km from the plant. Plant TB uses peat as a main fuel and wood-chips as an added fuel. The wood comes from the small mechanical forest industry plants nearby. Plant VB uses peat as the main fuel and sawdust as an added fuel. The sawdust comes from the sawmills nearby.

The idea for carrying out the measurement campaigns was to produce six repeatable tests at plants HB and SB, four repeatable tests at plant MB and five tests at plant RB. The aim was three repeatable tests both for main pure fuel and for co-combustion at the UB and TB plants, and two repeatable tests in the case of plant VB. The process parameters during each test at the power plants are shown in Appendix 6. The principle component analysis (PCA) was used to determine the main differences of the case plants and of the variations of the processes during the measurement campaigns at each plant. The PCA studies are presented and discussed in Appendix 13.

It can be seen in Appendix 6 that the coal supplied had no significant variations between the tests in each plant. The dry coal flow was approximately 58 t/h at plant HB, 62 t/h at plant SB and 153 t/h at plant MB. The ash content in dry coal was 22.6 %, 11.7 % and 12.41 % respectively. The energy production parameters (fuel effect, gross load and live steam) were also close to each other in the different tests. The gross load was 312 MW during the tests at plant HB, 454 MW at plant SB and 587 MW at plant MB.

The variations in the flow rate of the outcoming mass streams at the coal-fired power plants were maximum 10 %. The main outcoming streams were ashes from the ESP (i.e. PFA), which were 10 t/h at plant HB, 8 t/h at plant SB and 16 t/h at plant MB. The flow rate of the FGD product was approximately 2 t/h at plant SB, and as high as 5 t/h at plant HB. Plant HB had a higher flow rate of outcoming solid streams, because of the high ash and sulphur contents and the low heat value of the coal supplied. The gypsum production at plant MB was approximately 9 t/h.

The flow rate of the flue gases was 495 000 Nm^3/h in the stack of plant HB, 638 000 Nm^3/h at plant SB and 1560 000 Nm^3/h at plant MB. The NOx concentration in dry flue gas was 116 ppm in the first test (H1) at plant HB and approximately 200 ppm in the tests H2–H6. The CO concentration at plant HB was lowest in tests H4–H6 (200–300 ppm) and highest in test H3 (1500 ppm). The flue gas contents at plant SB had no remarkable variations between each test. The CO concentration upstream of the FGD was 70–90 ppm at plant SB. The particle concentrations in the stack were below the determination limits of the measurement methods, which was 2 mg/Nm^3 at plant HB and 5 mg/Nm^3 at plant SB. The particle concentration was approximately 6 mg/Nm^3 in the stack of plant MB.

As the result of the PCA for the process parameters of plants HB, SB and MB given in Appendix 6 show, it can be concluded that tests H1–H6, S1–S6 and M2–M4 had good repeatability. No significant differences were found between the tests of each plant. Plant MB has higher mass flows and fuel effect than other plants. The moisture and ash content in the coal is high, and the heat value of the coal is low at plant HB. The particle concentration in the flue gases upstream of the FGD is highest at plant HB.

Table 6.1.The identifying codes for the experimental tests.

		Fuel	Test ID
Coal-fired power plants			
HB	semi-dry FGD	pulverised Polish coal	H1
		pulverised Polish coal	H2
		pulverised Polish coal	H3
		pulverised Polish coal	H4
		pulverised Polish coal	H5
		pulverised Polish coal	H6
SB	semi-dry FGD	pulverised Polish coal	S1
		pulverised Polish coal	S2
		pulverised Polish coal	S3
		pulverised Polish coal	S4
		pulverised Polish coal	S5
		pulverised Polish coal	S6
MB	wet FGD	pulverised Columbic and Polish coal	M1
		pulverised Columbic and Polish coal	M2
		pulverised Columbic and Polish coal	M3
		pulverised Columbic and Polish coal	M4
Bark-fired power plant			
UB	bubbling fluidised bed	bark	U1
		bark	U2
		bark	U3
		bark + sludge	U4
		bark + sludge	U5
		bark + sludge	U6
Peat-fired power plants			
RB	bubbling fluidised bed	peat	R1
		peat	R2
		peat	R3
		peat	R4
		peat	R5
TB	circulating fluidised bed	peat	T1
		peat	T2
		peat	T3
		peat + wood-chips	T4
		peat + wood-chips	T5
		peat + wood-chips	T6
VB	circulating fluidised bed	peat	V1
		peat	V2
		peat + sawdust	V3
		peat + sawdust	V4

Appendix 6 shows that the fuel characteristic parameters had no remarkable variations between different tests during pure peat or bark burning at each plant. The dry bark flow was 15 t/h at plant UB. The dry peat flow was 48 t/h at plant RB, 60 t/h at plant TB and 64 t/h at plant VB. The ash content of the bark was 1.8 %. The ash content in the dry peat was 8.7 % at plant RB, 6.1 % at plant TB, and 4.1 % at plant VB. The ash contents in the dry added fuels were 14.5 % in sludge, 0.4 % in wood-chips, and 0.3 % in sawdust. The heat values of the added fuels were 5–15 % less than the heat values of the main fuel. The ash contents in the dry fuel mixtures were between 2.7 % and 3.8 % at plant UB, 3.3–4.7 % at plant TB and 2.5–2.7 % at plant VB. The variations can help explain the problems of the representative sampling during co-combustion or real variations of the element content in fuel. To minimise the effect of the sampling problems, the trace element contents of the fuel mixtures were calculated based on the separate analysis results of the main and the added fuels and weighting the results in ratio to their flow rate (see Chapter 5). The variation in the energy production parameters was maximum 10 % of the mean values. The gross load was 68 and 65 MW during the tests at plant UB, 199 MW at plant RB, 287 MW at plant TB, and 299 MW at plant VB.

The large variations in the flow rate of the outcoming mass streams at the fluidised bed plants can be clearly seen, especially in the case of bottom ash, which includes a part of the bed material. The main outcoming stream was pulverised ash from the ESP, which was 0.3 and 0.4 t/h at plant UB, 4.4 t/h at plant RB, 4.4 and 4.8 t/h at plant TB and 1.8 and 2.1 t/h at plant VB. The flow rates of the bottom ash were 110 and 140 kg/h at plant UB (low compared to the other plants), 200 kg/h at plant RB, 750 and 420 kg/h at plant TB and 870 and 460 kg/h at plant VB. The total flow rate of ashes (bottom ash, ash from the economiser and from the ESP) compared to the energy production was high during co-combustion at plant UB. The higher ash content and lower heat value of the sludge compared to bark explain this. The co-combustion increased the total flow rate of ashes also at plant TB in spite of the decreasing flow rate of the bottom ash. This must result from less effective burning of the fuel mixture, which is indicated by higher CO and particle concentrations in the flue gases. The co-combustion decreased the total flow rate of ashes at plant VB, which is explained by the effective burning of the fuel mixture and low ash content of the added fuel.

The flow rates of the dry flue gases were 150 000 and 140 000 Nm^3/h at plant UB, 500 000 Nm^3/h at plant RB, 450 000 and 400 000 Nm^3/h at plant TB and 470 000 Nm^3/h at plant VB. The SO_2 concentration was below 10 ppm and the NOx concentration below 100 ppm in the dry flue gases at plant UB, which is much less than the concentrations at the peat-fired power plants. The particle concentration was below 15 mg/Nm^3 at plant UB, 17–70 mg/Nm^3 at plant RB, 25 and 35 mg/Nm^3 at plant TB, and 5–6 mg/Nm^3 at plant VB.

From the results of the PCA for the process parameters of the fluidised bed plants, it can be concluded that besides the highest fuel effect, gross load and live steam production, plants TB and VB had higher flow rates of bottom ash compared to the others. Plant RB had the highest ash and sulphur content in fuel as well as the highest SO_2, NOx and particle concentrations in dry flue gases. Plant UB had low SO_2 and NOx concentrations and a high CO concentration in the dry flue gases of high temperature compared to the other plants. The content of volatile compounds in dry bark was high compared to the other fuels.

In plant UB, co-combustion with bark and sludge from the wastewater treatment plant decreased the gross load by 5–6 % and increased the outcoming ash flows by 30 %, which results from the high moisture and ash content of the sludge. In spite of the increasing ash flows, co-combustion utilises the solid sludge stream's energy effect (lower heat value of 18.5 MJ/kg) and deforms solid sludge into flue gases and solid ash by 15–30 % of the origin sludge stream. The NOx concentration in dry flue gases increased from 70–80 ppm to 70–110 ppm and the CO concentrations decreased from 230–400 ppm to 100–200 ppm during co-combustion. The particle concentration, O_2 concentration or low SO_2 concentration had no significant changes during co-combustion. The mass flow of bottom ash and ecoash varied a lot between each test, especially during co-combustion. The flow rate of sand supplied was stable, so the extra material to the bed came in with the fuel. The results of the PCA confirmed well that the pure bark-combustion tests differentiated clearly from the co-combustion tests. The repeatability of the tests U1–U3 and U4–U6 was good if the random value of coarse ash (bottom ash and ecoash) flow and high NOx concentration in the flue gases in test U5 are accepted.

The co-combustion of peat and wood-chips had no effect on the gross load at plant TB compared to the combustion of peat alone, although it increased the outcoming ash flows less than 5 %. This must be the result of less effective burning of the fuel mixture, which was indicated by higher CO and particle concentrations in the flue gases, as well. In spite of the slightly increased ash flows, co-combustion utilises the energy content (lower heat value of 19.4 MJ/kg) of the solid wood stream and deforms solid wood into flue gases and solid ash to the amount of less than 1 % of the origin wood stream. The NOx concentration in the dry flue gases decreased from 95–115 ppm to 80–95 ppm, the SO_2 concentration decreased from 175–190 ppm to 160–175 ppm, the CO concentrations increased from 70 ppm to 130 ppm, and the particle concentration increased from 20–35 mg/Nm^3 to 25–50 mg/Nm^3 during co-combustion. The results of the PCA confirmed that the pure peat-combustion tests differentiated clearly from the co-combustion tests. The repeatability of tests T1–T3 and T4–T6 is rather good if the random value of bottom ash flow and high particle concentration in flue gases in the test T6 are accepted.

Co-combustion with peat and sawdust had no significant effect on the gross load at plant VB compared to the combustion of peat alone. The co-combustion decreased the total flow rate of ashes, which is explained by the effective burning of the fuel mixture and the low content of ash (0.3 %) in the added fuel, i.e. sawdust. The lower heat value of sawdust was 19.3 MJ/kg. The NOx, CO or particle concentrations in dry flue gases had no significant changes during co-combustion. The SO_2 concentration in flue gases decreased from 120 ppm to 94 ppm during co-combustion. The results of the PCA confirmed that the pure peat-combustion tests differentiated from the co-combustion tests. The repeatability of tests V1–V2 and V3–V4 is excellent.

The highest content of sulphur in the fuel and SO2 concentration in dry flue gases were found at plant RB, especially during the tests R4 and R5. The repeatability of the tests R1–R5 was not good. This was clearly seen in the results of the PC analysis. Tests R1, R2 and R3 differed obviously from tests R4 and R5. The flow rate of flue gases, particle concentration, NOx and SO_2 concentrations in dry flue gases, as well as the flow rates of bottom ash and PFA were higher in tests R4 and R5 than in tests R1 and R2. Test R3 was closer to tests R1 and R2 according to those parameters and according to the content of ash in the fuel and the low heat value of the fuel.

When the principle component analysis was made for the process parameters given in Appendix 6 for the peat-fired power plants, it was seen that the tests of plant RB differentiated from the tests of plants TB and VB. Plant RB, which is equipped with a bubbling fluidised bed, had a lower fuel effect, a lower gross load, cooler flue gases and a lower flow rate of the bottom ash than plants TB and VB. The significant difference of tests R1–R5 compared to the other tests was high SO_2 and NOx concentrations in the flue gases. Plants TB and VB are equipped with circulating fluidised bed, which produces a higher flow of bottom ash.

As a conclusion of the process parameters, it can be summarised that tests U1–U3, U4–U6, T1–T3, T4–T6, V1–V2 and V3–V4 have good repeatability. Tests R1–R3 and R4–R5 are better to study separately in the case of plant RB. The flow rate of bottom ash is significantly higher in the circulating fluidised bed plants (TB, VB) than in the bubbling fluidised plant (RB) during peat combustion.

If the process parameters given in Appendix 6 are used as the arguments, plants UB, TB and VB have an appropriate technique for co-combustion. The energy contents in different fuels were utilised effectively during pure bark or peat combustion as well as during co-combustion of bark and sludge or peat and wood-chips/sawdust. The higher ash content of fuel was seen only in the increased stream of pulverised ash, not in the particle concentration in the flue gases in the stack. From the environmental aspect, the concentration of SO_2 decreases during co-combustion of peat and wood-chips or sawdust because of the low content of sulphur in wood. In the case of the bark-fired power plant, the higher content of sulphur in the sludge did not increase the SO_2 concentration in flue gases even close to the requirement of environmental authorities (i.e. 70 ppm; 1017/2002). NOx concentrations in the flue gases in the stack were also well below the requirements of environmental authorities in all cases.

6.2 The concentrations of trace elements in the coal-fired power plants

Each trace element marked with “a” in Table 2.2 was analysed from the samples of all the tests (H1–H6) at plant HB, from the samples of the tests S1, S2, S5, S6 at plant SB, and from the samples M2–M4 at plant MB. The rest of the samples were saved in the storage as reserve.

The trace element contents in different solid streams calculated on a dry weight basis, as well as the element concentrations in the dry flue gases and in the process waters are given in Appendix 7 and they are discussed in detail in Appendix 8. The trace element contents in the fuel (i.e. coal) are shown in Table 6.2.

The contents of mercury (Hg) and cadmium (Cd) were below 0.26 mg/kg in all the coal samples of plants HB, SB and MB. The mean content of thallium (Tl) was 0.9 mg/kg in the samples of plant HB, and it was analysed below the detection limit at plants SB (0.5 mg/kg) and MB (2 mg/kg). The content of selenium (Se) was approximately 1 mg/kg at plants SB and MB (no analysis was done at plant HB). The contents of beryllium (Be) were 1–3 mg/kg and the contents of arsenic (As) were 4–7 mg/kg at the case plants. The contents of cobalt (Co) were 7–10 mg/kg and the contents of copper (Cu) were 20–25 mg/kg at plants SB and MB (no analysis was done at plant HB). The contents of lead (Pb) and nickel (Ni) were 20–30 mg/kg at plants HB and SB. The content of Pb was at the same level at plant MB, but the mean content of Ni was 60 mg/kg. The contents of zinc (Zn) analysed only at plant HB, were approximately 70 mg/kg. The contents of chromium (Cr) were 30–40 mg/kg at plants HB and SB. The content of Cr was 90–150 mg/kg at plant MB, which is higher than the values, i.e. 0.5–60 mg/kg given in the literature. The contents of manganese (Mn) have the highest values, which were approximately 200 mg/kg at plant HB and 100 mg/kg at plants SB and MB. All the element contents analysed in the coal samples are inside the content ranges reported in the literature (Maier et al. 1992; Clarke and Sloss, 1992; Meij, 1989, 1997) with the exceptions of Cr and Ni at plant MB.

Table 6.2 shows that the contents of Tl and Pb in the fuel samples of test H1 and the contents of Hg and Zn in the fuel samples of tests H2 and H3 were high compared to the other tests of plant HB. The content of Co in the fuel sample of test S6 and Se in the fuel sample of test S1 were low compared to the other tests of plant SB. The high contents of As, Cd, Co, Cr, Hg, Ni, Pb and Se in the fuel samples of test M2 at plant MB can be explained by the inhomogeneous fuel mixture of coal originating from two different countries.

Table 6.2. Trace element contents in the fuel samples (i.e. coal) at plants HB, SB and MB (mg/kg in dry basis). Two bottom lines shows the values reported in literature (Maier et al. 1992; Clarke and Sloss, 1992; Meij, 1989 , 1997).

Test ID	As	Be	Cd	Co	Cr	Cu	Hg
H1	5.5	3.6	0.22	m	39	m	0.16
H2	5.1	3.2	0.22	m	39	m	0.19
H3	7.0	3.1	0.26	m	40	m	0.21
H4	6.7	2.8	0.24	m	39	m	0.11
H5	6.7	2.6	0.20	m	40	m	0.10
H6	6.6	2.7	0.25	m	38	m	0.10
HMean[1]	**6.3**	**3.0**	**0.23**	**m**	**39**	**m**	**0.15**
HSDev[2]	***0.8***	***0.4***	***0.02***	***m***	***1***	***m***	***0.05***
S1	4.3	1.1	0.13	10.0	31	25	0.10
S2	4.1	1.4	0.13	9.4	29	23	0.09
S5	4.0	1.3	0.19	9	24	22	0.07
S6	4.1	1.5	0.25	6.7	31	23	0.07
SMean	**4.1**	**1.3**	**0.18**	**8.8**	**29**	**23**	**0.08**
SSDev	***0.1***	***0.2***	***0.06***	***1.5***	***3***	***1***	***0.01***
M2	3.8	1.8	0.11	8.1	86	20	0.13
M3	10	1.8	0.23	8.8	152	22	0.19
M4	4.0	1.8	0.11	8.4	111	22	0.12
MMean	**5.9**	**1.8**	**0.15**	**8.4**	**116**	**21**	**0.15**
MSDev	***3.6***	***0.0***	***0.05***	***0.4***	***33***	***1***	***0.04***
Typical	10	2	0.5	5	20	15	0.1
range	0.5–80	0.15–15	0.1–3	0.5–30	0.5–60	0.5–50	0.02–1

m: missing, not analysed

[1] mean value of tests H1–H6

[2] standard deviation of tests H1–H6

Table 6.2. Continued.

Test ID	Mn	Ni	Pb	Se	Tl	Zn
H1	190	25	44	m	1.50	67
H2	210	30	33	m	0.69	72
H3	200	25	34	m	0.89	84
H4	180	28	29	m	0.91	66
H5	180	24	30	m	0.81	59
H6	180	25	29	m	0.76	64
Hmean(1	**190**	**26**	**33**	**m**	**0.93**	**69**
HSDev(2	***13***	***2***	***6***	***m***	***0.29***	***9***
S1	95	34	17	0.6	< 0.5	m
S2	77	31	18	1.0	< 0.5	m
S5	96	30	18	1.0	< 0.5	m
S6	100	28	20	1.0	< 0.5	m
SMean	**92**	**31**	**18**	**0.9**	**< 0.5**	**m**
SSDev	***10***	***3***	***1***	***0.2***	***n***	***m***
M2	102	49	18	1.3	< 2	m
M3	121	74	22	1.2	< 2	m
M4	119	53	17	0.8	< 2	m
MMean	**114**	**58**	**19**	**1.1**	**< 2**	**m**
MSDev	***10***	***14***	***3***	***0.4***	***n***	***m***
typical	70	20	40	1	< 1	50
range	5–300	0.5–50	2–80	0.2–10	m	5–300

m: missing, not analysed
[1] mean value of tests H1–H6
[2] standard deviation of tests H1–H6

Based on the results of the PC analysis, the coal supplied at plant HB differed from the coal supplied at plants SB and MB according to its somewhat high contents of Be, Cd, Mn and Pb. The contents of As and Hg were higher in the coal supplied at plants HB and MB than at plant SB (see Appendix 14 for further details).

The trace element contents in different streams of the plant were examined in the following two ways:

i) the trace element content in each solid mass stream was divided by the trace element content in the fuel
ii) the relative enrichment factor of each element in the solid material was calculated according to the formula (3.1).

The results are shown and discussed in detail in Appendix 8.

The trace element contents in lime were low compared to their contents in coal with some exceptions. The content of Mn in lime and coal were approximately equal at plants HB and MB. In the case of plant SB, the lime was richer in Mn and Tl than coal. The concentrations of trace elements in the seawater and tap water were also very low, of course. Mechanically filtered seawater comes from the Baltic Sea beside the plants, and tap water used at plants HB and MB is supplied by the municipal water utility.

Most of the trace element contents in the bottom ash were high compared to their contents in the coal, especially Cr and Ni with enrichment factors of 3–7. The contents of As and Cd in the bottom ash were on an equal level with the coal samples for all the plants, as well as the contents of Tl at plant HB. These trace elements had the lowest enrichment factors, i.e. 0.1–0.2. The content of Pb in bottom ash in all the plants and the content of Zn at plant HB were twice as high as the one in the coal. The contents of Be, Co, Cu and Mn were 4–10 times higher in the bottom ash samples than in the coal samples. Their relative enrichment factors were 0.7–1.2. The content of Hg in bottom ash was 0.26 mg/kg at plant HB, which is much higher than in the cases of plants SB and MB. The enrichment factor was 0.4, which is high compared to 0.01 in the case of plant MB. Mercury had obviously different values in the bottom ashes of the different plants.

The trace element values in the ash coming from the economiser at plant MB were very similar to the bottom ash samples for As, Be, Mn, Pb, Se and Tl. The ecoash of plant MB had a higher content and enrichment of Cd and Hg and lower contents and enrichments of Co, Cr, Cu and Ni compared to the bottom ash.

The contents of As, Be, Cd, Co, Cu, Pb Se, Tl and Zn in the PFA were 4–10 times higher than the one in the coal. Their relative enrichment factors were approximately 1.0, which are high compared to the bottom ash with one exception: the PFA was not as rich as bottom ash in the case of Co and Cu at plant MB. The relative enrichment factor of Mn was near 1.0 in both the bottom ash and PFA at all the plants. The content of Cr in the PFA at plant MB, and Ni at plants HB and MB were 2–3 times higher than the one in coal, and much less than in the bottom ash. All the relative enrichment factors for Cr and Ni were much lower for the PFA than for the bottom ash. The content of Hg was the lowest at all the plants representing the relative enrichment factor of 0.5–0.6, which is high compared to the one for bottom ash. The content of Hg in the PFA was significantly higher at plant MB compared to plants HB and SB. This is coming most probably from behaviour of Hg after the SCR-installation. Very volatile, elemental Hg is oxidised to $HgCl_2$ in the SCR (Gutberlet *et al.* 1991, Meij 1997). $HgCl_2$ is less volatile and begins to condense on the fly ash particles if the temperature is below 140°C. The flue gas temperature downstream of the ESP was 128°C and the nominal collection efficiency for PFA of the ESP is 99.5 %, which results higher content of Hg in PFA at plant MB.

The relative enrichment factors of particles in the flue gases upstream of the FGD were high (i.e. 4–11) for As, Cd and Pb at all the plants, as well as for Se at plant SB. The enrichment of Se in flue gas particles was extremely high (i.e. 27) at plant MB. The enrichment of Be, Mn and Ni was 1.0 or somewhat over at all the plants, as well as Co and Cu at plant SB, and Zn at plant HB. The enrichment of Cr and Hg was below 1.0 at plant MB, and over 1.0 at plants HB and SB.

The trace element concentrations in the flue gases in the stack were low both in the particulate fractions and in the gaseous fractions of all the coal-fired power plants. The relative enrichment factors for the particulate fractions were low for most of the trace elements with the exception of Hg at plant SB, and of As and Se at plant MB. The enrichments of trace elements in the particles in flue gases of plant MB were typically higher than at plants HB and SB.

The concentrations of As, Be, Cd, Cr, Hg, Mn, Ni, Pb, Tl and Zn in the particulate fractions were much lower in the stack than upstream of the FGD at plant HB. The high content of Zn in the lime increased the concentration of Zn in the gaseous fraction.

The concentrations of As, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se and Tl in the particulate fractions were much lower in the stack than upstream of the FGD at plant SB. The concentration of Hg in the particulate fraction was at the same level in both cases. Higher concentrations of Cr, Cu, Ni and Pb in the gaseous fractions could be seen, which results from their content in the lime.

The trace element contents in the coarse fractions of the FGD and in the fractions removed by the fabric filter downstream of the FGD at plant HB were close to each other. The relative enrichment factors of other elements were 0.03–0.2, but 0.3 for Hg. The contents of As, Be, Cd, Cr, Hg, Mn, Ni and Pb in particulate fraction of flue gases upstream of the FGD were higher at plant HB than at plant SB. The trace element concentrations in the gaseous fraction were quite equal in both plants. The contents of As, Cd, Hg and Mn in the lime supplied to the FGD at plant HB were high compared to plant SB. These differences were seen in the trace element contents in the FGD products. The contents of As, Be, Cd, Mn, Ni and Pb in the FGD products of plant HB were higher than in plant SB. The contents of Hg in the FGD products were equal in both plants.

In plant MB, the concentrations of As, Be, Cd, Mn and Pb in the particulate fractions were lower in the stack than upstream of the FGD. The concentrations of Hg and Ni in the particulate fractions were at the same level at both locations. Higher concentrations of Cr in the particulate fraction could be found, as well as some higher concentrations of Se.

The contents of all the trace elements in the gypsum at plant MB were low compared to the FGD products at plants HB and SB. The contents of all the elements were significantly higher in the filter cake samples, as expected. The relative enrichment factors in the filter cake were higher than in the PFA for Cd, Mn and Se. The contents of As, Be, Cd, Ni and Pb in the wastewater were determined high compared to the contents in the seawater and tap water at plant MB. However, the contents of trace elements in the wastewater were typically lower than reported by Meij (1989).

Based on the PC analysis, it was recognised that the trace element contents in the particulate fraction of the flue gases compared to the contents in the coal were higher at plant HB than that at the other plants. The ratio of the element contents in all the other ash samples to that in coal was typically low at plant HB compared to plants SB and MB (more details are given in Appendix 14). The highest ratios of Cr and Ni contents in the PFA to that in coal were seen in plant SB. The PCA for relative enrichment factors did not express, unfortunately, any additional consistent information about the tests or about the plants.

The results for all of the coal-fired plants are summarised based on the relative enrichment factors in Table 6.3. Table 6.3 also includes the classes for Dutch coal-fired power plants equipped with ESPs (1997) and for a coal-fired power plant equipped with a wet FGD after the ESP in the Netherlands (1989) presented by Meij. The plot of the RE factors of the coal-fired HB, SB and MB power plants are shown with the RE factors of the fluidised bed plants UB, RB, TB and VB in Figure 6.1.

The relative enrichment factors determined for plants HB, SB and MB are mainly consistent with the values reported by Meij (1997). The trace elements in the case plants fell into the same classes as in the coal-fired power plants studied by Meij (1997, 1989), with some exceptions. The Mn fell into class I at all the plants. The enrichment of Mn in the particulate fraction of the flue gases was over 1.0 in plants SB and MB. This was also found in the Dutch coal-fired power plants reported by Meij (1997). The enrichments of As, Cr and Zn in the particulate fractions of the flue gases in the stack were found to be lower than those reported by Meij (1989). This can be explained by the high removal efficiency of the semi-dry FGD plant, which is equipped with the fabric filter at plants HB and SB. The enrichment of Be in the bottom ash at all the plants was 0.8, as reported also by Meij (1989). The intermediate behaviour between classes I and II has also been reported by Clarke and Sloss (1992). Significantly high enrichments of Cr and Ni were found in the bottom ash, which comes from such high contents of Cr and Ni determined in the bottom ash. The enrichments of Hg in the bottom ash and in the particulate fraction of the flue gases were also reported by Meij in 1997, but not in 1989.

In plant HB, the coal contained more ash, e.g. more calcium. This may lead to increased sorption of Hg, which was seen in the enrichment of Hg in the bottom ash, in the PFA and in the flue gas particles upstream of the FGD. In plant MB, the high enrichment of Hg in the PFA and in the flue gas particles upstream of the FGD is most probably resulting from the SCR.

The high contents of Cr and Ni determined in the coal samples of plant MB lead to very small enrichment factors in the PFA and in the particulate fraction of the flue gas. Consequently, these were omitted from the classification. The contents of trace elements in the gypsum, filter cake and in the wastewater samples of plant MB were typically lower than the values reported by Meij (1989).

Table 6.3. Classification of the trace elements in the coal-fired power plants according to the relative enrichment factors. The results upstream of the FGD are shown in the upper rows in the italics. The bottom line shows the results given by Meij (1997, 1989).

Power plant	**As**	**Be**	**Cd**	**Co**	**Cr**	**Cu**	**Hg**
HB	*IIa*	*IIc*(2	*IIa*	*m*	*IIc*(2	*m*	*III*(2,3
	II(1	II(2,4	IIb	m	II(1,2	m	III
SB	*IIa*	*IIc*(2	*IIa*	*IIb*	*IIc*(2	*IIb*	*III*(3
	II(1	II(2,4	IIc	II(4	II(1,2	IIc	III(3
MB	*IIa*	*IIb*(2	*IIa*	*m*	o.c.	*m*	*III*
	IIa	IIb(2	IIa	m	o.c.	m	III(3
Meij							
1997,	IIa	IIb	IIa	IIb	I/IIc	IIb	III(3
1989	IIa	IIc(2	IIa	IIc	I	IIc	III

Power plant	**Mn**	**Ni**	**Pb**	**Se**	**Tl**	**Zn**
HB	*I*	*IIb*(2	*IIa*	*m*	*II*	*IIb*
	I(1	IIb(2	IIc(1	m	II(4	IIc(1
SB	*I*	*IIc*(2	*IIb*	*III*	*II*(4	*m*
	I(3	IIc(2	IIc(1	III	II(4	m
MB	*I*(3	o.c.	*IIc*	*III*	*m*	*m*
	I(3	IIb(2	IIb	III(3	m	m
Meij						
1997,	I/IIc	IIb/IIc	IIa	III	IIa	IIa
1989	I(1	IIc(1	IIc(1	III(3	IIa	IIb

Notes to the classification

[1] low enrichment in particulate fraction

[2] high enrichment in bottom ash

[3] high enrichment in particulate fraction

[4] the element concentration in the particulate fraction of flue gases below the detection limit

m: missing value

o.c.: out of classification

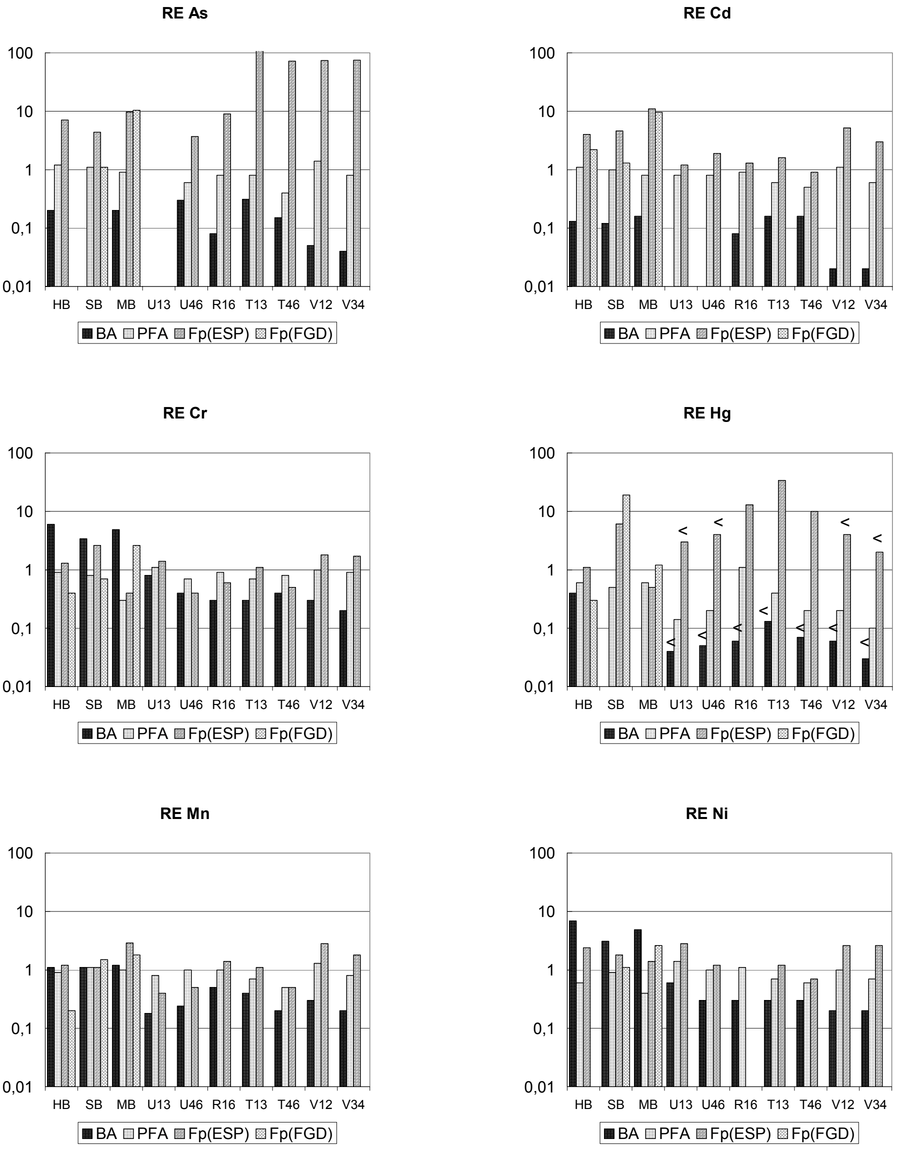


Figure 6.1. The relative enrichment factors of trace elements in the coal-fired power plants HB, SB and MB and in the fluidised bed plants UB (U13, U46), RB (R16), TB (T13, T46) and VB (V12, V34).

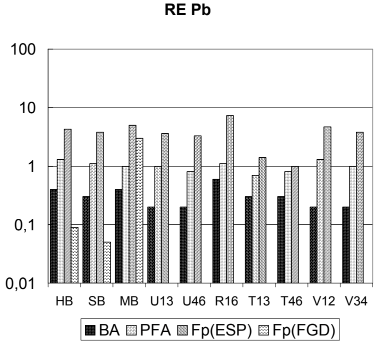


Figure 6.1. Continued.

6.3 The concentrations of trace elements in the bark- and peat-fired power plants

Each trace element marked with ”a” in Table 2.2 was analysed from the samples of all the tests (U1–U6, R1–R5, T1–T6, V1–V4) at plants UB, RB, TB and VB.

The trace element contents in different solid streams calculated on a dry weight basis, as well as the element concentrations in the dry flue gases and in the process waters are given in Appendix 9 and discussed in detail in Appendix 10. The plots of the RE factors are shown in Figure 6.1.

The trace element contents analysed in each fuel component, i.e. bark, peat, sludge, wood-chips and sawdust and in the mixture of them, are given in Table 6.4. There was no sample of the fuel mixture in the V3 and V4 tests; the value for the mass balance calculations in these tests was calculated based on the peat and sawdust analyses and their mass fractions in the fuel mixture supplied.

Bark, peat, wood-chips, sawdust and sludge

The contents of trace elements in the bark were low compared to the peat in the case of As, Cr, Hg, Ni and Pb. The content of As in the bark was analysed below the detection limit (0.1 mg/kg). The content of As in the fuel mixture of bark and sludge was analysed as 0.2 mg/kg in the sample U4 and below the detection limit in the sample U5. The content of Hg was 0.02 mg/kg in the bark and a little higher, i.e. 0.03 mg/kg, in the fuel mixture. All the other elements analysed at plant UB, i.e. Cd, Cr, Mn, Ni and Pb were also higher in the fuel mixture compared to the pure bark, because of higher element contents in the sludge. The contents of Cd and Mn in the fuels were higher at plant UB than in the peat fuels.

The contents of Hg in the peat were seen as an indication of the peat's origin bog. It was 0.03 mg/kg in tests R1–R5 and T1–T3. The content of Hg in the peat was higher, i.e. 0.05–0.07 mg/kg, in tests T4–T6 during co-combustion. The Hg content in the wood-chips was 0.01–0.02 mg/kg, which led to a mean Hg content in the mixture of peat and wood of 0.04 mg/kg. The highest content of Hg in the peat (0.07 mg/kg) was analysed in test V3. The content of Hg in the peat was 0.04 mg/kg in test V4. The content of Hg in sawdust was determined equal to and below the detection limit, i.e. 0.04 mg/kg, during the tests. These values were reflected in the contents of Hg in the fuel mixture, 0.05 mg/kg and 0.04 mg/kg during tests V4 and V5.

The content of Cd in the peat was highest, i.e. with a mean value of 0.22 mg/kg, at plant RB. The content of Cd in the peat, wood-chips and sawdust were analysed close to each other, at 0.08–0.1 mg/kg at plants TB and VB in the peat and in the fuel mixture.

The Mo content in the peat was 0.6–0.7 mg/kg in tests T1–T3. The content of Mo in the peat was analysed some higher (i.e. 0.7–0.8 mg/kg) in tests T5–T6 and the content of Mo in the wood-chips was analysed below the detection limit of 0.5 mg/kg. These values led to the content of 0.5 mg/kg Mo in the mixture of peat and wood-chips at plant TB. The contents of Mo in peat and sawdust were analysed below the detection limit of 0.5 mg/kg at plant VB. (Note: no Mo analysis was performed at plants UB and RB).

The origin bog and analytical difficulties were obviously seen from the content of As in the fuel, which was 13−15 mg/kg at plant RB, where the peat is supplied from the bogs in central Finland. The peat and wood-chip samples from plant TB were analysed in two different laboratories. The analysis result of the peat from Lab1 was 1.4−1.5 mg/kg in the tests T1–T3 and 0.7−1.0 mg/kg in tests T4–T6. The analysis results from Lab2 were much higher, 2.5−2.7 mg/kg and 2.2−2.8 mg/kg, respectively. The content of As in the wood-chips was determined below the detection limit at 0.3 mg/kg by Lab1, and 1.1 mg/kg by Lab2. The results from Lab1 were obtained based on the mass balance calculations being too low.

The content of As in the peat was 0.9 mg/kg at plant VB, which is close to the As content in the peat in tests T5–T6 at plant TB. The As content in the wood-chips was analysed below the detection limit at 0.5 mg/kg. Based on these results, the content of As in the fuel mixture supplied at plant VB was 0.7 mg/kg.

The mean contents of Pb in the peat were 2.7–2.9 mg/kg. The Pb content in the fuel mixture is lower (1.9 and 1.6 mg/kg) owing to the lower content of Pb in the wood-chips (0.5 mg/kg) and in the sawdust (below 0.5 mg/kg). The results from two different laboratories were very similar.

Table 6.4. Trace element contents in the main fuel, added fuel and fuel mixture samples at plants a) UB and b) RB, TB and VB (mg/kg in dry basis).

a) Plant UB

Test ID	As	Cd	Cr	Hg
U1 Bark	< 0.1	0.41	0.88	0.02
U2 Bark	< 0.1	0.35	0.86	0.02
U3 Bark	m	0.35	0.67	0.02
U13Mean(1	**< 0.1**	**0.37**	**0.80**	**0.02**
U4 Mixture	0.2	0.53	3.2	0.02
U4 Bark	<1.1	0.24	1.1	< 0.04
U4 Sludge	< 5.6	6.4	42	0.05
U5 Mixture	< 0.1	0.84	3.2	0.03
U5 Bark	< 1.1	0.32	0.58	< 0.04
U5 Sludge	< 5.4	8.0	57	< 0.04
U6 Mixture	m	0.64	3.2	0.03
U46Mean	**0.1**	**0.67**	**3.2**	**0.03**

Test ID	Mn	Ni	Pb
U1 Bark	450	0.63	0.83
U2 Bark	430	0.58	0.69
U3 Bark	420	0.51	0.87
U13Mean	**433**	**0.57**	**0.80**
U4 Mixture	580	2.3	1.2
U4 Bark	390	0.66	0.78
U4 Sludge	5600	22	6.2
U5 Mixture	800	2.5	1.3
U5 Bark	490	0.33	0.59
U5 Sludge	5850	26	7.4
U6 Mixture	760	2.0	1.3
U46Mean	**713**	**2.3**	**1.3**

m: missing, not analysed,[1] mean value of tests U1–U3

Table 6.4. Continued.

b) Plants RB, TB and VB

Test ID	As	Cd	Cr	Hg
Plant RB				
R1 Peat	13.4	0.22	10	0.029
R2 Peat	15.1	0.19	9.4	0.026
R3 Peat	15.3	0.21	9.0	0.033
R4 Peat	13.3	0.25	10	0.031
R5 Peat	15.1	0.23	11	0.033
RMean[1]	**14.4**	**0.22**	**9.9**	**0.030**
Plant TB				
T1 Peat	1.4	0.10	7.9	0.03
T2 Peat	1.4	0.10	9.6	0.03
T3 Peat	1.5	0.10	9.5	0.04
T13Mean	**1.4**	**0.10**	**9.0**	**0.03**
T4 Mixture	1.9	0.09	5.6	0.04
T4 Peat	2.8	0.09	8.7	0.06
T4 Wood	< 1.1	0.10	< 0.2	0.02
T5 Mixture	1.6	0.09	5.4	0.04
T5 Peat	2.4	0.09	9.3	0.07
T5 Wood	< 1.1	0.10	< 0.5	0.01
T6 Mixture	1.8	0.10	5.6	0.04
T6 Peat	2.2	0.10	9.0	0.05
T6 Wood	< 1.1	0.10	< 0.5	0.01
T46Mean	**1.8**	**0.09**	**5.5**	**0.04**
Plant VB				
V1 Peat	0.86	0.08	3.9	0.04
V2 Peat	0.93	0.08	4.3	0.04
V12Mean	**0.90**	**0.08**	**4.1**	**0.04**
V3 Mixture	0.66	0.09	2.9	0.05
V3 Peat	0.90	0.08	4.0	0.07
V3 Sawdust	< 0.5	0.11	< 1.0	< 0.04
V4 Mixture	0.66	0.08	2.8	0.04
V4 Peat	0.89	0.07	3.8	0.04
V4 Sawdust	< 0.5	0.11	< 1.0	0.04
V34Mean	**0.66**	**0.09**	**2.9**	**0.05**

[1] mean value of tests R1-R5

Table 6.4. Continued.

b) Plants RB, TB and VB (continued)

Test ID	Mn	Mo	Ni	Pb
Plant RB				
R1 Peat	51	m	4.4	3.3
R2 Peat	59	m	3.9	2.8
R3 Peat	59	m	4.0	3.0
R4 Peat	42	m	5.3	2.4
R5 Peat	41	m	5.9	2.2
RMean	**51**	**m**	**4.7**	**2.7**
Plant TB				
T1 Peat	111	0.55	3.8	2.9
T2 Peat	99	0.59	4.2	2.9
T3 Peat	100	0.68	4.3	2.9
T13Mean	**103**	**0.61**	**4.1**	**2.9**
T4 Mixture	121	m	4.0	2.0
T4 Peat	135	m	5.9	3.0
T4 Wood	101	m	< 0.5	0.5
T5 Mixture	115	0.50	3.0	1.5
T5 Peat	124	0.79	5.7	2.9
T5 Wood	119	< 0.5	< 0.5	0.5
T6 Mixture	122	0.50	3.2	2.3
T6 Peat	117	0.66	5.4	3.4
T6 Wood	108	< 0.5	< 0.5	< 0.5
T46Mean	**119**	**0.50**	**3.4**	**1.9**
Plant VB				
V1 Peat	31	< 0.5	3.3	3.2
V2 Peat	39	< 0.5	3.6	2.6
V12Mean	**35**	**< 0.5**	**3.5**	**2.9**
V3 Mixture	49	< 0.5	2.7	1.6
V3 Peat	38	< 0.5	3.7	2.2
V3 Sawdust	79	< 0.5	< 0.5	< 0.5
V4 Mixture	46	< 0.5	2.7	1.6
V4 Peat	33	< 0.5	3.6	2.2
V4 Sawdust	83	< 0.5	< 0.5	< 0.5
V34Mean	**47**	**< 0.5**	**2.7**	**1.6**

m: missing, not analysed

The mean content of Ni in the peat was 4.7 mg/kg at plant RB. The analysis results from Lab2 were systematically higher for Ni in the peat at plant TB. The results from Lab1 were chosen for the mass balance calculations, i.e. a mean value of 4.1 mg/kg. The real values are in all probability between the results of these two laboratories. The content of Ni in the wood-chips was analysed in both laboratories below the detection limit, 0.5 mg/kg. The contents of Ni in the fuel mixture analysed by Lab2 were closer to the combined values of peat and wood-chips in proportion to their flow rate analysed in both laboratories. The mean content of Ni in the peat was 3.5 mg/kg at plant VB. The content of Ni in sawdust was analysed below the detection limit, i.e. 0.5 mg/kg. These led to the content of Ni in the fuel mixture being 2.7 mg/kg.

The contents of Cr in the peat were 8–11 mg/kg at plants RB and TB and approximately 4.1 mg/kg at plant VB. The mean Cr content in the mixture of peat and wood-chips was 5.5 mg/kg, and in the mixture of peat and sawdust, 2.9 mg/kg.

The origin bog obviously had effect on the content of Mn in the peat. The lowest Mn content in peat was found at plant VB, with the mean value of 35 mg/kg. The value was 51 mg/kg in plant RB, and 103 mg/kg in the case of plant TB. The Mn contents in the peat-mixture were higher compared to the pure peat – 120 mg/kg at plant TB, and 47 mg/kg at plant VB.

The As content in the peat at plant RB was high compared to the content in coal used as fuel at plants HB, SB or MB. The As contents in fuel were significantly lower at plants UB, TB and VB. The content of Cd in the peat at plant RB was equal to the content in coal. It was low in the peat-fuel at plants TB and VB. The contents of Cd and Mn in the bark and in the mixture of bark and sludge were analysed as much higher than the contents in coal. The Mn contents in the fuels were low at plants RB and VB. The Mn content in the peat-fuels of plant TB was at the same level as in the coal at plants SB and MB.

The contents of Cr, Hg, Ni and Pb in the bark- and peat-fuels were low at plants UB, RB, TB and VB compared to the contents in coal at plants HB, SB and MB.

Based on the PC analysis (see Appendix 14) it can be concluded that the peat supplied at plants RB, TB and VB differed from according to the contents of As, Cd, Cr, Hg and Mn. The contents of Pb and Ni in the peat were close to each other. The mixture of peat and wood-chips differed from the peat supplied at plant TB in the contents of As, Cr, Hg, Mn, Mo, Ni and Pb. The content of Cd in the fuel mixture was close to its content in the peat at plant TB. The mixture of peat and sawdust differed from the peat supplied at plant VB in the contents of As, Cr and Pb. The contents of Cd, Hg, Mn and Ni in the fuel mixture were close to the contents in the peat at plant VB. The bark and the mixture of bark and sludge supplied at plant UB had significantly different contents of Cd and Mn compared to the fuels supplied at plants RB, TB and VB. The mixture of bark and sludge had higher contents of Cd, Cr, Mn, Ni and Pb than pure bark. The content of Hg in the bark was almost equal with the content in the mixture of bark and sludge.

The content of As in the bark supplied at plant UB was equal to the contents given by Latva-Somppi (1998). The contents of Cr, Mn, Ni and Pb were somewhat lower and the content of Cd was somewhat higher at plant UB than reported by Latva-Somppi (1998). Tillman (1994) has reported higher contents of As, Cr, Pb and Ni in bark.

The contents of trace elements in sewage sludge depend on the industrial/municipal activities around the source of the sludge. The contents of As, Cr, Hg, Ni and Pb in the sludge supplied at plant UB were low, and the content of Cd was somewhat high compared to the contents reported for municipal sewage sludge (e.g. Werther and Ogada, 1999). The content of As, Cr and Ni in sludge supplied at plant UB were at an equal level to the contents reported for paper-mill sludge by Latva-Somppi (1998). The content of Pb in the sludge of plant UB was somewhat low, and the contents of Cd and Mn were higher than the contents measured by Latva-Somppi (1998).

The contents of trace elements in the wood-chips supplied at plant TB and in the sawdust supplied at plant VB were analysed to be close to the contents given by Kouvo (2003). The content of Cd in this study was somewhat higher, and the contents of Ni and Pb lower than the contents determined by Kouvo (2003).

Siltaloppi *et al.* (1992) have measured trace element contents in 139 peat samples. The samples represented the peat used in numerous Finnish power plants. The content of As was typically 2.2–2.8 mg/kg. They measured individual contents in the range of 0.4–14.1 mg/kg. The highest contents were found in central Finland. The effect of the bog's location was seen also in the results of this thesis. The contents of Cd in the peat were close to the contents of Cd 0.12–0.13 mg/kg measured by Siltaloppi *et al.* (1992). The contents of Cr were measured at 10.2 mg/kg in central Finland, 4.2 mg/kg in western Finland and 7.4–8 mg/kg in northern Finland. The contents of Ni were measured at 5.5 mg/kg, 2.7 mg/kg and 3.9–5.0 mg/kg, respectively. The element contents determined in this thesis fell in a very similar way. The content of Pb was measured at 4.3–5.2 mg/kg by Siltaloppi *et al.* (1992). The contents of Pb in this thesis were somewhat lower. The typical content of Hg in Finnish peat used as fuel is 0.07 mg/kg with some variation depending on the area in Finland (Siltaloppi and Lehtovaara, 2003). The contents of Hg in this thesis were somewhat lower, but close to the contents given by Kouvo (2003). The contents of Cd, Mn and Pb in peat in this thesis were also close to the contents given by Kouvo (2003). The contents of As, Cr and Ni were slightly lower in this thesis, but close to the values given by Vesterinen (1997). The higher contents of Hg and Pb in the peat have been reported by Mojtahedi *et al.* (1990).

The trace element contents in different streams of the plants were examined in the following two ways:

i) the trace element content in each solid mass stream was divided by the trace element content in the fuel

ii) the relative enrichment factor of each element in the solid material was calculated according to the formula (3.1).

The results are shown and discussed in detail in Appendix 10.

Sea-sand and water

The trace elements in sea-sand were analysed only at plant RB. The contents of As and Cd in the sand were low compared to the contents in peat. The contents of Mn and Pb in the sand were twice as high as the content in peat. The contents of Cr and Ni were the same in the sand and peat. The Hg content in the sand was below the detection limit, i.e. 0.05 mg/kg.

Plant RB uses some mechanically sieved water from the lake beside the plant for the bottom ash quenching basin. The element concentrations in the water samples were low and below the detection limit for As, Cd and Hg. The mean concentration of Cr in the water was 0.5 mg/m^3, Ni 0.8 mg/m^3, Pb 0.4 mg/m^3 and Mn 150 mg/m^3.

Ashes

Most of the trace element contents in the bottom ash were high compared to their contents in the fuel at the bark- and peat-fired power plants. Only the contents of As, Cd, Hg and Mo were close to an equal level in the bottom ash and fuel samples. The relative enrichment factors of the trace elements in these cases were low, less than 0.1. The relative enrichment factor of Cr, Mn, Ni and Pb was typically 0.2–0.5, as shown in Figure 6.1.

The ash samples from the economiser had quite equal contents of trace elements to the bottom ash at plants UB and TB in the case of As, Hg and Pb. The contents of Cd, Cr, Mn, Mo and Ni in the ecoash as well as the relative enrichment factors of these elements were typically high compared to the bottom ash, especially during co-combustion.

The low enrichments of As, Cd and Pb in bottom ash at plant TB were close to the enrichments at the coal-fired power plants. The enrichments of all the other elements in bottom ash and ecoash were significantly low at the bark- and peat-fired power plants compared to the enrichments at the coal-fired power plants.

All the PFA samples at the bark- and peat-fired power plants had higher contents of trace elements than the fuel samples. The relative enrichment factors of the PFA were high for all the elements compared to the bottom ash or ecoash. Most of the relative enrichment factors in the PFA were close to 1.0. Significantly lower RE values were obtained for Hg at plants UB, TB and VB. The highest RE values (1.3–1.4) were found for Ni at plant UB during bark-combustion and for As, Mn and Pb at plant VB during peat-combustion. Plant TB did not have such a high enrichment of As, Cd, Hg, Mn and Pb in the PFA as the other peat-fired or the coal-fired power plants.

The contents of As, Cr, Hg, Ni and Pb in PFA at the bark-and peat-fired power plants were low compared to the coal-fired power plants with the exception of As content in the PFA at plant RB, which was determined high. The contents of

Cd and Mn in the PFA were high at the bark-and peat-fired power plants compared to the coal-fired power plants.

Flue gases

The trace element concentrations in the flue gases after the ESP, i.e. in the stacks at the bark- and peat-fired power plants were low. Cd, Mn, Ni and Pb occurred mainly in the particulate fraction at plant UB, where Hg was present only in the gaseous form. Cr and Ni were present at plant UB both in the particulate and gaseous fractions. The emissions of Cd, Hg and Mn appeared to be at a higher level and the emissions of Ni and Pb at a lower level during co-combustion of bark and sludge compared to pure bark-combustion. The relative enrichment factors of As, Hg and Mn in flue gas particles at plant UB were lower than those for peat-fired power plants during pure peat combustion. The enrichment factors of the other trace elements in the flue gas particles were quite equal in the bark- and peat-fired power plants.

The detection limit of the gaseous fraction of As was higher than the small concentrations measured in the particulate fraction at plants UB, TB and VB. Plant RB had a high As concentration in the flue gases (which results from the high As content in the peat) compared to the other plants.

A small amount of Cd was found in both flue gas fractions at plant RB and at plant TB during peat-combustion. The detection limits of Cd in the gaseous fraction were higher than the small concentrations measured in the particulate fractions at plants TB and VB. Cr occurred both in the gaseous and particulate form at all the peat-fired power plants. Hg was mainly present in the gaseous form. The concentrations became higher during co-combustion at plant TB, and decreased at plant VB. Mn occurred mainly in the particulate fraction at all the peat-fired power plants. Mo, Ni and Pb were found in the particulate fractions at plants TB and VB, where the detection limits of the gaseous fractions were too high to consider dividing. The detection limit of Ni in the particulate fraction was high compared to the low concentration measured in the gaseous fraction at plant RB.

The particulate fractions of the flue gases of the coal-fired power plants were not as rich in As and Hg as the peat-fired power plants. The enrichment was found to be higher for Cd and Pb in the particulate fraction of the flue gases in the coal-fired power plants than in the peat-fired power plants.

Based on the PC analysis, which is discussed in detail in Appendix 14, it was recognised, that the high ratio of Cd in the bottom ash, and Hg in the gaseous fraction of the flue gases, and the low ratio of Pb in the flue gas particles compared to the contents in the fuel made the test results of the circulating fluidised bed combustion different from the tests of the bubbling fluidised bed combustion. This difference was not found in relative enrichment factors. The tests for pure bark combustion in the bubbling fluidised bed were separated from the other tests because of the high ratio of Cr, Ni and Pb contents in the bottom ash, ecoash, PFA and flue gas particles to the contents in the fuel. The ratios of Cd and Mn in the PFA to the contents in the fuel were also high in the tests for pure bark combustion.

The results concerning the bark- and peat-fired power plants are summarised based on the relative enrichment factors in Table 6.5. The relative enrichment factors determined for plants UB, RB, TB and VB are consistent with the classes for coal-fired power plants equipped with ESPs reported by Meij (1997) for most of the elements and the plants. This is discussed further in Appendix 10. The plots of the RE factors of all the case plants are shown in Figure 6.1.

None of the trace elements under study fell into class I because the bottom ash had enrichment factors below 0.8 for all the elements. All the other trace elements fell into the classes IIa–IIc depending on the RE in the particulate fractions of the flue gases, except for Hg.

The high detection limit of Ni in the flue gas particles provided no possibilities for closer classification of the class II at plant RB.

The RE of Hg in the bottom ash samples was much below 1 as well as the RE in the PFA at plants UB, TB and VB. The flue gas particles were very poor for Hg at plants UB and VB, which led to the class III. A part of the Hg was enriched to the flue gas particles at plants RB and TB. The RE of Hg in the PFA was also high (i.e. 1.1) at plant RB, which meant that Hg fell to class IIa or III.

Table 6.5. Classification of the trace elements in the bark-fired power plant (UB) and peat-fired power plants (RB, TB, VB) according to the relative enrichment factors. The bottom line shows the results given by Meij (1997).

Plant	**As**		**Cd**		**Cr**		**Hg**	
	Only main fuel	Co-combustion	Only main fuel	Co-combustion	Only main fuel	Co-combustion	Only main fuel	Co-combustion
UB	n.c.	IIb	IIc	IIc	IIc	IIc	III	III
RB	IIa	m	IIc	m	IIc	m	IIa/III	m
TB	IIa	IIa	IIc	IIc	IIc	IIc	III	III
VB	IIa	IIa	IIa	IIb	IIc	IIc	III	III
Meij	IIa	m	IIa	m	I/IIc	m	III	m

Plant	**Mn**		**Mo**		**Ni**		**Pb**	
	Only main fuel	Co-combustion	Only main fuel	Co-combustion	Only main fuel	Co-combustion	Only main fuel	Co-combustion
UB	IIc	IIc	m	m	IIb	IIc	IIb	IIb
RB	IIc	m	m	m	II	m	IIa	m
TB	IIc	IIc	IIb	IIc	IIc	IIc	IIc	IIc
VB	IIb	IIc	n.c.	n.c.	IIb	IIc	IIa	IIb
Meij	I/IIc	m	IIa	m	IIb/IIc	m	IIa	m

m: missing value
n.c.: not calculated

Mo at plant TB was classified into class IIb during peat combustion and into class IIc during co-combustion. The differences resulted from the enrichment of Mo in the flue gas particles, which was not as high as reported by Meij (1997). The detection limit of the gaseous fraction was too high to draw conclusions if the particulate fraction was the dominating Mo flow in the flue gases.

In the case of Hg and Mn, the bark-fired and peat-fired power plants differed from the classes of the coal-fired power plants HB, SB and MB. In the case of Mo, plant TB differed from the Dutch coal-fired power plants.

6.4 The closure of the trace element mass balances

The ingoing flows and the outcoming flows of trace elements during each test at i) the coal-fired power plants HB, SB and MB and at ii) the bark-fired power plant UB and at the peat-fired power plants RB, TB and VB were calculated according to the formula (5.1, 5.2, 5.3 and 5.4). The results are shown in Appendix 11 and Appendix 12, with the closures of the mass balance (i.e. the ratio of the outcoming to the ingoing flows). When the ratio between the outcoming and ingoing flows is equal to 1.0, the mass balance closures are the best. The acceptable closure for utilisation of the results is 0.7–1.3. When the closure of the individual test was outside the criterion limit, it was omitted from the mean value calculations of the parallel results. The results after the data weeding procedure are summarised in Figure 6.2.

The mass balances of the trace elements in the coal-fired power plants were determined very successfully. Most of the trace element closures of different tests matched the criterion limit. The closures of As, Be, Cd, Cr, Hg, Mn, Ni, Pb, Tl and Zn at plant HB were determined acceptable, when the results for As, Cd, Ni, Pb and Tl of test H2, and for Cr and Hg of the three tests were omitted. In plant SB, the closures of As, Be, Cd, Co, Cr, Cu, Hg, Mn, Ni and Pb were within the criterion limit, when the results for Be, Cd, Cr, Hg, Mn and Pb of one test were omitted. Tests S5 and S6 do not include the flue gas fraction of Cu, therefore the outcoming flow of Cu in these tests was not relevant for the mass balance calculations. The ingoing flow of Tl and both flows of Se were too low to determine the mass balance at plant SB with the method in this thesis. The closures of As, Be, Cd, Cr, Hg, Mn, Ni, Pb and Se at plant MB were determined acceptable, when the results of test M3 for all the elements were omitted, as well as the results of one another test for Cr and Hg. The ingoing flow of Tl was too low to determine the mass balance at plant MB with the method in this thesis. The outcoming flows of Co and Cu were higher than the ingoing flows in most of the tests of plant MB, although the flue gas fractions were absent. Therefore, the outcoming flows of Co and Cu were not relevant for the mass balance calculations.

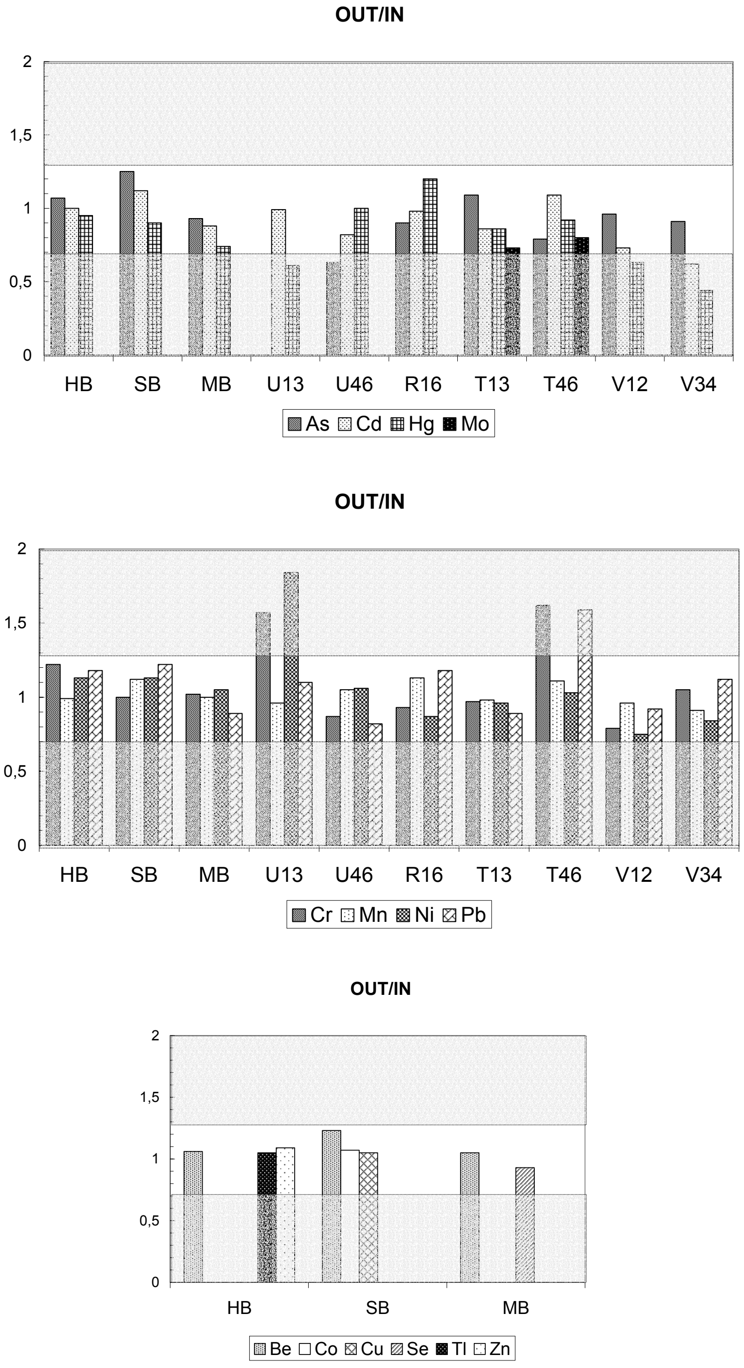


Figure 6.2. The mass balance closures of the case power plants.

The mass balances of Cd, Mn and Pb had acceptable closures at plant UB. The closures of As, Cr, Hg and Ni were acceptable during co-combustion tests at plant UB. In most of the tests, the ingoing flow of As was too low to determine with the method of this thesis; the poor closure (0.63) was obtained in one of the co-combustion tests. The outcoming flows of Cr and Ni were determined far too high compared to the ingoing flows during pure bark combustion, giving poor closures, i.e. 1.5–1.6 and 1.8. The high outcoming flows of Cr and Ni could originate from the bed material capturing substantial amounts of Cr and Ni during a typical combustion process (i.e. co-combustion of bark and sludge with higher contents of Cr and Ni) and releasing a part of them during pure bark combustion. Ho *et al.* (1992, 2001), Lind *et al.* (1999) and Kouvo (2003) have shown that the capture of certain trace elements in the bed material takes place depending on the combustion temperatures, fuel composition, combustion chemistry, and the bed material used. Kouvo (2003) has suggested that metals such as Cu, Mn, Ni, Pb and Zn may also be released from the bed where changes in the fuels and/or operational parameters are made. In the tests in this thesis, pure bark was supplied only during the test period and about an hour before.

The mass balances of trace elements in the peat-fired power plants were determined successfully in most of the cases. The closures of As, Cd, Cr, Hg, Mn, Ni and Pb were determined acceptable at plant RB, when the result for Pb in test R5 and the results for Hg and Ni in tests R1–R3 were omitted. The outcoming Hg and Ni flows were determined significantly higher than the ingoing flows in tests R1–R3, as well as the Pb flow in test R5.

The closures of As, Cd, Hg, Mn, Mo and Ni were acceptable during the peat and co-combustion tests at plant TB. The closures of Cr and Pb were acceptable during the peat combustion tests. The ingoing flow of Mo was determined too low compared to the outcoming flow in two peat combustion tests, as well as the flow of Cd in one test. The closures of Cr and Pb were poor, i.e. 1.6–1.7 and 1.4–2.0, during co-combustion of peat and wood-chips. The high outcoming flow of Cr and Pb can originate from the bed material capturing Cr and Pb during a typical combustion process (i.e. pure peat with higher contents of Cr and Pb) and releasing them during the test runs. The mixture of peat and wood-chips was supplied only during the test period and some hours before.

The mass balances of As, Cr, Mn, Ni and Pb were determined acceptable during peat and co-combustion of peat and sawdust at plant VB, as well as of Cd during peat combustion. The outcoming flows of Cd and Hg were determined far too low compared to the ingoing flows, giving the closures of 0.4 and 0.6. Typically, it is difficult to close the mass balance of mercury. It was recovered 0.59–0.68 in the fluidised bed combustion studies of Clemens *et al.* (1999), 0.21−1.12 in the studies of CRE (1987) and 0.66−1.70 in the studies of Kouvo (2003). The poor closures of mass balance for Cd, i.e. 0.32−1.27 have also been reported by CRE (1987), too. The ingoing flow of Mo at plant VB was too low to determine with the method used in this thesis.

6.5 The main routes of the trace elements in the coal-fired power plants

The main routes of the trace elements in the coal-fired power plants based on the mass balance studies in this thesis are shown in Tables 6.6–6.8. The results have been summarised as a relative distribution of the elements between outcoming streams in Figure 6.3.

The most important outcoming stream in the coal-fired power plants is that of PFA, which is consistent with the literature. In the case of Cr and Ni, the streams of bottom ash are also significant at plants HB and MB. A significant fraction of mercury and cadmium exit the plants also in the flue gases, mainly in the gaseous fractions. The streams of the FGD products represent 20 % of the outcoming stream of Hg at plant HB. This is not the case for the other coal-fired power plants.

The ash content of coal at plant HB was high compared to the other coal samples of this thesis. The content of Hg in the coal at plant HB was also high. The speciation of Hg in coal burning has been reported by e.g. Hower *et al.* (1999), Meij (1999, 1997) and Maier *et al.* (1992). Regardless of the form in which mercury is present in coal, elemental mercury is released during combustion. Elemental mercury is very volatile, and accordingly, only a little part will be removed by the ESP. The vaporisation percentage will be about 90 %. However, in the presence of HCl a part of Hg^o can be converted into $HgCl_2$ at temperatures between 300 and 400 ^oC (Maier *et al.*, 1992; Meij, 1994, 1997) (i.e. the flue gas temperature after the economiser, well upstream of the ESP). $HgCl_2$ is less volatile and begins to condense on the fly ash particles if the temperature is below 140 ^{o}C (i.e. the flue gas temperature upstream of the ESP and FGD). The particle concentration in the flue gases downstream of the ESP is high at plant HB compared to that of plant SB. The particle concentration in the flue gases in the stack is low at both plants. This means there is a higher collection efficiency of the fabric filter at plant HB than the one at plant SB. Along with the higher dust cake formation on the filter material, more $HgCl_2$ on the fly ash particles can be observed, which increases the relative fraction of Hg in the end-product of the FGD and decreases the fraction of Hg in the flue gases.

The fractions of As, Cd, Tl and Zn in the end-product of the FGD represent 5−10 % of the outcoming streams at plant HB. The fraction of Cd in the end-product of the FGD at plant SB is negligible, whilst the fraction in the flue gases represents 5 %.

Arsenic is rarely found in flue gases in the stack. However, it originates from the content of calcium in the coal and lime supplied to the FGD. Meij (1999 & 1994) has found gaseous arsenic only if coal with a low concentration of calcium was fired. The explanation is that calcium reacts with arsenic to form calcium arsenate, which is not volatile under these circumstances. The occurrence of this phenomenon has been demonstrated by Gutberlet (1988).

The volatility of As, Cd, Tl and Zn are close to each other during combustion (Clarke & Sloss, 1992). The contents of these elements were low especially in the flue gas fraction at plant HB. Along with the higher particle concentration upstream of the FGD and with the higher dust cake formation on the filter material, more condensation of the elements on the fly ash particles can occur. This increases the relative fractions of the elements in the end-product of the FGD and decreases the fractions in the flue gases.

The high detection limit compared to the concentration of Se in flue gases gives a great uncertainty to the relative fractions of outcoming streams at plant MB. Meij (1997) has reported that the flue gas fraction was 15 % of the outgoing Se streams from a Dutch wet FGD plant. If this is also the case at plant MB, the main outcoming stream of Se is the PFA.

The fractions of bottom ash are high for Cr and Ni, especially at plant MB. The fractions of 8–9 % for Cr and Ni, i.e. for plant SB, have been reported by Clarke & Sloss (1992) for a Danish coal-fired power plant equipped with a semi-dry FGD. The fractions reported by Meij (1989, 1997) are somewhat higher, but not as high as for plant HB or MB. The enrichment factors of Cr and Ni in the bottom ash were not consistent with the literature data. The deviations of Cr and Ni contents in bottom ash samples between the different tests indicated some difficulties associated with the determination of these metals. The difficulties may be caused by contamination owing to the construction materials used at the plants or by analytical problems.

The fractions of bottom ash for Be in the outcoming streams are high compared to other volatile elements such as As, Cd, Tl or Zn. This was also reported by Meij (1989, 1997).

Table 6.6. Trace element balances of plant HB.

	q_j		**As**	**Be**	**Cd**	**Cr**	**Hg**	**Mn**	**Ni**	**Pb**	**Tl**	**Zn**
Coal	58 400 kg/h	$Q_{i,j}$ (g/h)	326	150	12	2010	5.0	9500	1390	1670	49	3440
Lime	1 300 kg/h	$Q_{i,j}$ (g/h)	1.2	< 0.52	0.16	7.8	< 0.01	250	3.7	2.8	0.4	13
Sea water	12.4 m^3/h	$Q_{i,j}$ (g/h)	< 0.06	< 0.06	< 0.006	0.03	< 0.001	0.31	< 0.03	< 0.06	< 0.07	< 0.0001
Town water	5 m^3/h	$Q_{i,j}$ (g/h)	< 0.03	< 0.03	< 0.001	< 0.01	< 0.0005	0.02	< 0.01	< 0.03	< 0.03	< 0.0001
Total ingoing		$Q_{i.in}$ (g/h)	**330**	**150**	**12**	**2020**	**5.0**	**9750**	**1390**	**1670**	**49**	**3450**
Total outcoming		$Q_{i.out}$ (g/h)	**350**	**160**	**12**	**2480**	**4.8**	**9660**	**1570**	**1970**	**52**	**3750**
Closure		$Q_{i.out}/Q_{i.in}$	***1.07***	***1.06***	***1.00***	***1.22***	***0.95***	***0.99***	***1.13***	***1.18***	***1.05***	***1.09***
Ratio in total outcoming stream												
	q_j	$Q_{i,j}/Q_{i.out}$										
Bottom ash	1 130 kg/h	%	1.6	7.5	1.3	36	3.5	11	52	3.0	1.8	4.0
PFA	10 200 kg/h	%	90	90	89	63	74	83	46	93	89	91
Flue gas upstream of the FGD												
Particulate	*495 000 m^3/h*	*%*	*6.1*	*1.1*	*4.2*	*1.0*	*1.6*	*1.4*	*0.8*	*4.0*	*< 15*	*4.0*
Gaseous	*495 000 m^3/h*	*%*	*< 0.3*	*< 0.2*	*0.4*	*< 0.04*	*30*	*< 0.01*	*< 0.03*	*< 0.05*	*< 1.6*	*0.1*
FGD coarse	520 kg/h	%	0.6	< 0.2	0.8	0.1	2.0	0.6	0.2	0.3	0.6	0.4
FGD prod	4 680 kg/h	%	7.7	1.9	8.1	0.7	20	5.0	2.0	4.0	7.0	4.5
Flue gas downstream of the FGD												
Particulate	495 000 m^3/h	%	< 0.02	< 0.01	< 0.04	0.002	0.02	0.002	< 0.001	0.001	< 0.1	0.01
Gaseous	495 000 m^3/h	%	< 0.3	< 0.3	0.3	< 0.06	1.0	0.001	< 0.04	< 0.05	< 1.8	0.7

Table 6.7. Trace element balances of plant SB.

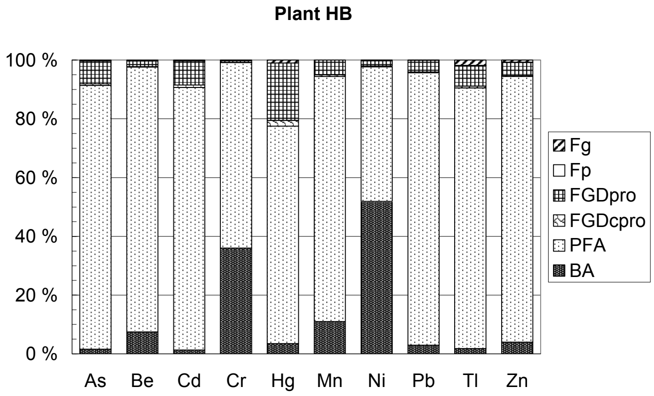
	q_j		**As**	**Be**	**Cd**	**Co**	**Cr**	**Cu**	**Hg**	**Mn**	**Ni**	**Pb**	**Se**	**Tl**
Coal	62 200 kg/h	$Q_{i,j}$ (g/h)	238	78	9.9	507	1620	1350	4.4	5610	1780	1075	52	< 29
Lime	1 100 kg/h	$Q_{i,j}$ (g/h)	2.8	< 0.11	0.10	1.7	10.6	15	< 0.01	180	5.8	2.3	< 22	0.8
Sea water	17 m^3/h	$Q_{i,j}$ (g/h)	< 0.070	0.001	0.003	< 0.013	0.008	0.03	< 0.017	0.12	< 0.013	0.080	0.035	0.029
Total ingoing		$Q_{i,in}$ (g/h)	**240**	**78**	**10**	**510**	**1670**	**1360**	**4.4**	**5790**	**1780**	**1080**	**< 80**	**< 30**
Total outcoming		$Q_{i,out}$ (g/h)	**300**	**96**	**11**	**550**	**1670**	**1430**	**3.9**	**6480**	**2010**	**1310**	**< 90**	**25**
Closure		$Q_{i,out}/Q_{i,in}$	**1.25**	**1.23**	**1.12**	**1.07**	**1.00**	**1.05**	**0.90**	***1.12***	**1.13**	**1.22**	***n***	***n***
Ratio in total outcoming stream														
	q_j	$Q_{i,j}/Q_{i,out}$												
Bottom ash	190 kg/h	%	< 0.7	2.0	0.3	1.9	11	1.6	< 0.05	3.0	7.5	0.6	n	n
PFA	7 500 kg/h	%	97	98	94	97	88	96	60	95	92	99	n	n
Flue gas upstream of the FGD														
Particulate	*627 000 m^3/h*	*%*	*0.7*	*0.3*	*0.8*	*0.3*	*0.4*	*0.4*	*1.2*	*0.1*	*0.3*	*0.5*	n	n
Gaseous	*627 000 m^3/h*	*%*	*0.3*	*0.3*	*3.4*	*0.1*	*0.1*	*0.1*	*65*	*0.5*	*0.05*	*0.1*	n	n
FGD prod	2 000 kg/h	%	2.0	< 0.2	1.7	0.5	0.8	1.4	8.9	2.6	0.3	0.6	n	n
Flue gas downstream of FGD														
Particulate	638 000 m^3/h	%	0.02	< 0.002	0.03	< 0.01	0.03	0.1	1.3	0.05	0.04	0.001	n	n
Gaseous	638 000 m^3/h	%	< 0.5	< 0.6	3.5	< 0.3	0.2	0.5	30	0.1	0.1	0.2	n	n

n: not calculated

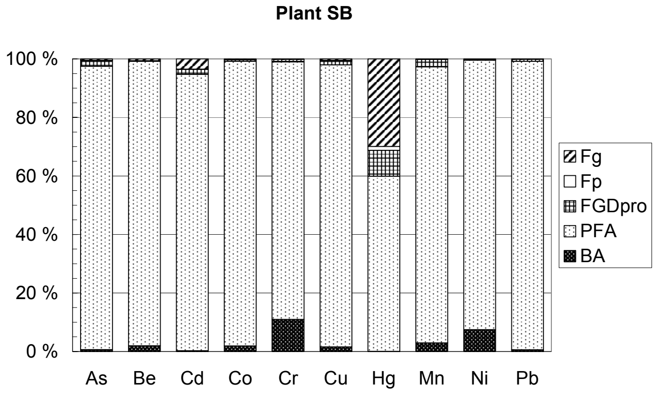
Table 6.8. Trace element balances of plant MB.

	q_j		As	Be	Cd	Cr	Hg	Mn	Ni	Pb	Se
Coal	153 000 kg/h	$Q_{i,j}$ (g/h)	593	276	16.3	13200	18.3	16900	7450	2680	194
Lime	5 500 kg/h	$Q_{i,j}$ (g/h)	5.9	< 5.4	0.31	17	0.3	620	12	8.9	< 9.6
Sea water	56 m^3/h	$Q_{i,j}$ (g/h)	< 0.56	< 0.11	0.015	0.067	< 0.007	0.49	< 0.14	< 0.56	< 5.6
Town water	7.4 m^3/h	$Q_{i,j}$ (g/h)	< 0.015	< 0.015	< 0.001	0.002	< 0.001	0.14	< 0.008	< 0.004	< 0.077
Total		$Q_{i,in}$ (g/h)	**600**	**280**	**17**	**13200**	**20**	**17500**	**7460**	**2690**	**194**
Total outcoming		$Q_{i,out}$ (g/h)	**560**	**290**	**15**	**13500**	**13**	**17500**	**7850**	**2380**	**180(a**
Closure		$Q_{i,out}/Q_{i,in}$	***0.93***	***1.05***	***0.88***	***1.02***	***0.65***	***1.00***	***1.05***	***0.89***	***0.93***
Ratio in total outcoming stream											
	q_j	**$Q_{i,j}/Q_{i,out}$**									
Bottom ash	1 890 kg/h	%	2.7	7.2	2.0	74	0.12	11	67	4.1	< 2
Ecoash	570 kg/h	%	1.3	2.4	1.3	0.9	0.06	3.0	0.9	1.3	< 0.5
PFA	16 000 kg/h	%	93	86	90	25	81	81	32	94	70
Flue gas upstream of the FGD											
Particulate	*1 560 000*	%	*0.9*	*0.2*	*1.0*	*0.03*	*0.1*	*0.2*	*0.1*	*0.5*	*n*
Gaseous	*1 560 000*	%	*< 0.8*	*< 3*	*7*	*0.02*	*9.0*	*0.02*	*< 0.04*	*0.3*	*n*
Gypsum	9 030	%	1.3	< 3	< 3	0.1	7.5	0.6	0.2	0.4	12
Waste	10 m^3/h	%	0.04	0.1	0.2	0.0001	< 0.01	0.4	< 0.001	< 0.02	< 3
Filter cake	160 kg/h	%	0.5	0.2	1.3	0.1	0.7	4	0.1	0.4	10
Flue gas downstream of the FGD											
Particulate	1 560 000	%	0.4	0.1	0.4	0.3	0.1	0.07	0.2	0.1	0.7
Gaseous	1 560 000	%	< 0.6	< 1.6	2.0	0.01	10	0.01	< 0.04	0.1	n

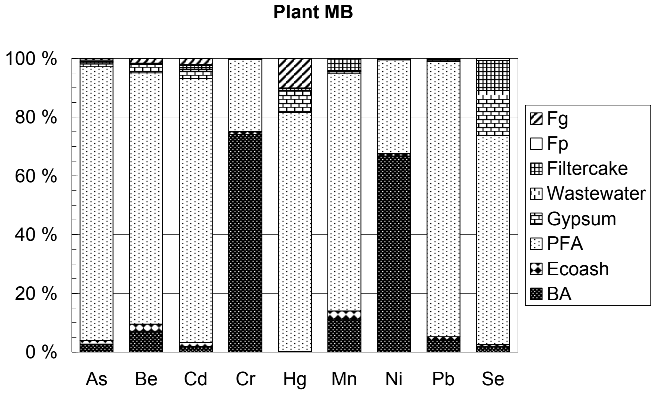
a flue gas/gaseous fraction excluded
n: not calculate



a)



b)



c)

Figure 6.3. The main outcoming routes of the trace elements at plant a) HB, b) SB and c) MB.

6.6 The main routes of the trace elements in the fluidised bed plants

The main routes of the trace elements in the bark- and peat-fired power plants based on the mass balance studies in this thesis are shown in Tables 6.9–6.12. The results have been summarised as a relative distribution of the elements between outcoming streams in Figures 6.4–6.7.

The most important outcoming stream in the fluidised bed plants is that of PFA for all other elements, but not for mercury. The gaseous fraction in the flue gases is the most important fraction of mercury in the outcoming streams. This was reported also by CRE (1987) for coal burning in the bubbling fluidised bed of 4 MW. The gas phase mercury was also dominant in the results of Kouvo (2003), who studied sawdust, peat and RDF in the bubbling fluidised bed of 6 MW. Clemens *et al.* (1999) have reported the majority of the mercury (85 %) in the flue gases in the tests, which were carried on a small-scale fluidised bed (50 kW) with sub-bituminous coal. Rentz *et al.* (1996) have reported 64 % of the mercury in the flue gases of the circulating fluidised bed plant, when coal was burned with sorbent injection to the bed for flue gas sulphur reduction.

The flue gas fraction was less than 20 % for the outcoming Hg stream at plant RB. Such results are not found in the literature. The unrepresentative sample of the PFA must be the reason for low flue gas fraction in the results of this thesis. The samples of PFA were not combined representatively before analysis. The content of Hg in the peat differed between the tests, giving variations in the ingoing Hg streams. These variations are seen in the stream of gaseous fraction of Hg in the flue gases, but only one result represents the PFA. Two samples of 10 litres were collected from the PFA landfill when the ash silo was unloaded. The samples taken after test period 1–3 and after test periods 4 and 5 were later combined into one sample. This procedure hid the information of varying contents during each test and distorted the average value of PFA. As a conclusion, it seems that the real relative flue gas fraction is larger in plant RB than shown in Figure 6.5.

The bottom ash is also a significant outcoming stream for all the trace elements, except for mercury and molybdenum. The contents of As, Cd, Cr, Hg, Mn, Ni and Pb in the bottom ash are consistent with the results given by CRE (1987), Clemens *et al.* (1999) and Mojtahedi *et al.* (1990). Significant amounts of trace elements can remain in the bed and are removed with the bottom ash. The fluidised bed combustion particles are irregular in shape and not fused (i.e. they are porous and have a large surface area), which can explain their adsorption potential for the vapour-phase constituents such as As and Cd (Mojtahedi *et al.* 1990). No reference results were found for Mo streams of the fluidised bed combustion in the literature. The volatility of Mo in combustion processes has been reported close to that of Ni. The relative fractions of outcoming streams of Mo and Ni were found to be approximately equal.

The co-combustion of bark and sludge or of peat and sawdust or wood-chips had no significant effects on the relative distribution of the outcoming streams.

Table 6.9. Trace element balances of plant UB.

	q_j		As	Cd	Cr	Hg	Mn	Ni	Pb
Bark	15 300	$Q_{i,j}$ (g/h)	< 1.5	5.6	12	0.31	6610	8.7	13
Sand	90 kg/h	$Q_{i,j}$ (g/h)	0.10	0.003	0.60	<	15	0.50	0.70
Total ingoing		$Q_{i,in}$ (g/h)	**< 1,5**	**5.6**	**13**	**0.31**	**6630**	**9.2**	**14**
Total outcoming		$Q_{i,out}$ (g/h)	**1.8**	**5.6**	**n**	**0.20**	**6390**	**n**	**15**
Closure		$Q_{i,out}/Q_{i,in}$	***n***	***0.99***	***n***	***0.61***	***0.96***	***n***	***1.10***
Ratio in total outcoming stream									
	q_j	$Q_{i,j}/Q_{i,out}$							
Bottom ash	110 kg/h	%	11	0.3	n	< 2	8	n	5
Eco ash	30 kg/h	%	2	1	n	< 0.6	2	n	2
PFA	310 kg/h	%	80	98	n	24	90	n	90
Flue gas	150 000 m^3/h								
Particulate		%	< 2	1	n	< 3	0.3	n	3
Gaseous		%	< 8	< 0.2	n	71	0.003	n	1
Co-combustion									
Bark+sludge	15 300	$Q_{i,j}$ (g/h)	1.6	7.6	43	0.33	9500	30	17
Sand	90 kg/h	$Q_{i,j}$ (g/h)	0.06	0.002	0.4	<	8.0	0.3	0.4
Total ingoing		$Q_{i,in}$ (g/h)	**1,6**	**7.6**	**43**	**0.33**	**9510**	**30**	**17**
Total outcoming		$Q_{i,out}$ (g/h)	**1.9**	**6.3**	**37**	**0.33**	**10000**	**32**	**14**
Closure		$Q_{i,out}/Q_{i,in}$	***1.20***	***0.82***	***0.87***	***1.01***	***1.05***	***1.06***	***0.82***
Ratio in total outcoming stream									
	q_j	$Q_{i,j}/Q_{i,out}$							
Bottom ash	110 kg/h	%	12	0.2	14	< 2	7	8	6
Eco ash	30 kg/h	%	3	1	7	< 0.5	5	7	2
PFA	310 kg/h	%	77	98	79	26	89	84	90
Flue gases	150 000 m^3/h								
Particulate		%	1.5	1.1	0.2	< 2	0.2	0.5	1.7
Gaseous		%	< 6.5	< 0.1	0.3	70	0.01	0.13	0.6

n: not calculated

Table 6.10. Trace element balances of plant RB.

	q_j		As	Cd	Cr	Hg	Mn	Ni	Pb
Peat	48 100 kg/h	$Q_{i,j}$ (g/h)	695	10.6	480	1.7	2 410	300	130
Sand	28 kg/h	$Q_{i,j}$ (g/h)	0.03	0.001	0.19	< 0.001	4.5	0.14	0.20
Water	90 l/h	$Q_{i,j}$ (g/h)	< 0.1	< 0.01	0.05	< 0.02	13	0.08	0.04
Total ingoing		$Q_{i,in}$ (g/h)	**700**	**11**	**480**	**1.7**	**2410**	**300**	**130**
Total outcoming		$Q_{i,out}$ (g/h)	**630**	**10**	**440**	**2.0**	**2720**	**260**	**160**
Closure		$Q_{i,out}/Q_{i,in}$	***0.90***	***0.98***	***0.93***	***1.21***	***1.13***	***0.87***	***1.18***
Ratio in total outcoming stream									
	q_j	$Q_{i,j}/Q_{i,out}$							
Bottom ash	200 kg/h	%	0.5	0.3	1	< 0.3	2	1	2
PFA	4 430 kg/h	%	97	98	99	83	97	93	94
Flue gas	504 000 m^3/h								
Particulate		%	2	0.8	0.4	3	0.7	6	3
Gaseous		%	< 0.5	1	0.1	15	< 0.4	< 0.2	< 1

Table 6.11. Trace element balances of plant TB.

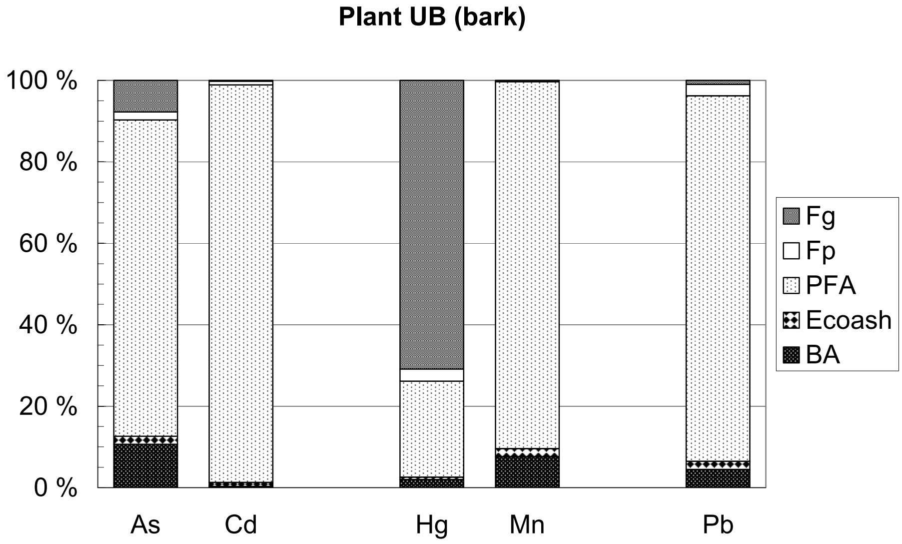
	q_j		As	Cd	Cr	Hg	Mn	Mo	Ni	Pb
Peat	59 700 kg/h	$Q_{i,j}$ (g/h)	86	6.0	540	2.0	6 180	35	250	170
Sand	0 kg/h									
Total ingoing		$Q_{i,in}$ (g/h)	**86**	**6.0**	**540**	**2.0**	**6180**	**35**	**250**	**170**
Total outcoming		$Q_{i,out}$ (g/h)	**93**	**5.1**	**520**	**1.7**	**6060**	**25**	**230**	**160**
Closure		$Q_{i,out}/Q_{i,in}$	***1.09***	***0.86***	***0.97***	***0.86***	***0.98***	***0.73***	***0.96***	***0.89***
Ratio in total outcoming stream										
	q_j	**$Q_{i,j}/Q_{i,out}$**								
Bottom ash	750 kg/h	%	6	5	8	3	8	< 2	7	7
Eco ash	230 kg/h	%	2	2	3	< 1	3	1	3	2
PFA	4 390 kg/h	%	90	92	89	48	89	91	90	90
Flue gas	450 000 m^3/h									
Particulate		%	0.5	0.6	0.4	12	0.3	1	0.4	0.5
Gaseous		%	1.5	2	0.1	36	0.01	5	< 0.6	< 1
Co-combustion										
Peat+ wood-chips	63 100 kg/h	$Q_{i,j}$ (g/h)	110	5.9	350	2.4	7 540	32	250	123
Sand	0 kg/h									
Total ingoing		$Q_{i,in}$ (g/h)	**110**	**5.9**	**n**	**2.4**	**7540**	**32**	**250**	**n**
Total outcoming		$Q_{i,out}$ (g/h)	**90**	**6.4**	**n**	**2.2**	**8370**	**26**	**250**	**n**
Closure		$Q_{i,out}/Q_{i,in}$	***0.79***	***1.09***	***n***	***0.92***	***1.11***	***0.80***	***1.03***	***n***
Ratio in total outcoming stream										
	q_j	**$Q_{i,j}/Q_{i,out}$**								
Bottom ash	420 kg/h	%	3	3	n	2	3	2	5	n
Eco ash	250 kg/h	%	2	2	n	< 1	3	2	4	n
PFA	4 830 kg/h	%	93	94	n	51	93	92	91	n
Flue gas	402 000 m^3/h									
Particulate		%	0.5	0.5	n	6	0.3	0.5	0.3	n
Gaseous		%	1.5	< 1	n	41	0.01	5	< 0.5	n

n: not calculated

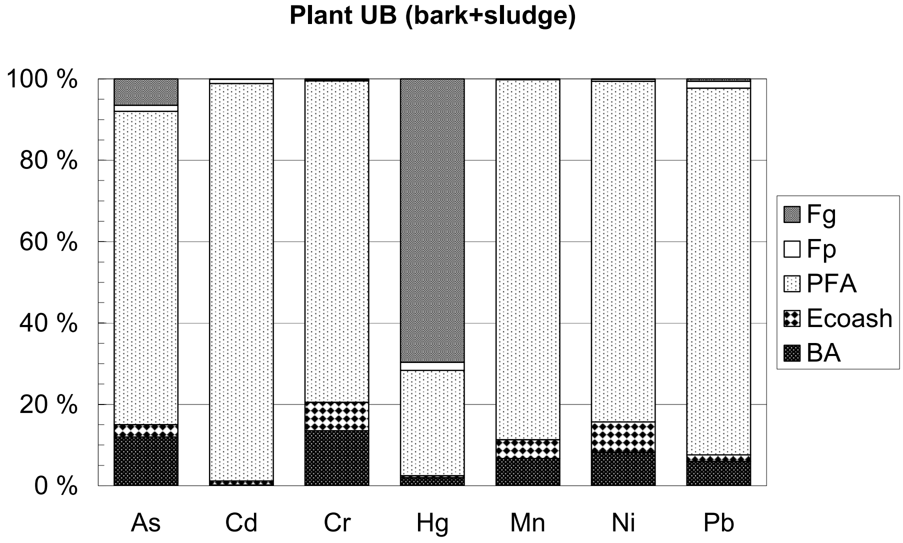
Table 6.12. Trace element balances of plant VB.

	q_j		**As**	**Cd**	**Cr**	**Hg**	**Mn**	**Mo**	**Ni**	**Pb**
Peat	64 200 kg/h	$Q_{i,j}$ (g/h)	57	5.1	260	2.6	2250	< 32	220	190
Sand	0 kg/h									
Total ingoing		$Q_{i,in}$ (g/h)	**57**	**5.1**	**260**	**2.6**	**2250**	**< 32**	**220**	**190**
Total outcoming		$Q_{i,out}$ (g/h)	**55**	**3.8**	**210**	**1.6**	**2170**	**12**	**170**	**170**
Closure		$Q_{i,out}/Q_{i,in}$	***0.96***	***0.73***	***0.79***	***0.63***	***0.96***	***n***	***0.75***	***0.92***
Ratio in total outcoming stream										
	q_j	**$Q_{i,j}/Q_{i,out}$**								
Bottom ash	870 kg/h	%	2	1	12	< 3	10	< 3	11	8
PFA	1 760 kg/h	%	96	95	86	19	90	90	88	92
Flue gas	466 200 m^3/h									
Particulate		%	1	0.5	0.2	< 0.5	0.3	0.5	0.3	0.5
Gaseous		%	< 1.5	< 4	1	78	< 0.02	< 7	< 0.5	< 0.5
Co-combustion										
Peat+ Wood-chips	67400 kg/h	$Q_{i,j}$ (g/h)	44	5.7	190	3.1	3200	< 34	180	110
Sand	0 kg/h									
Total ingoing		$Q_{i,in}$ (g/h)	44	5.7	190	3.1	3200	< 34	180	110
Total outcoming		$Q_{i,out}$ (g/h)	40	3.6	200	1.4	2920	11	150	120
Closure		$Q_{i,out}/Q_{i,in}$	*0.91*	*0.62*	*1.05*	*0.44*	*0.91*	*n*	*0.84*	*1.12*
Ratio in total outcoming stream										
	q_j	**$Q_{i,j}/Q_{i,out}$**								
Bottom ash	460 kg/h	%	1	1	7	< 2	5	< 2	6	6
PFA	1 950 kg/h	%	96	94	93	20	95	89	93	94
Flue gas	472 500 m^3/h									
Particulate		%	1	0.5	0.3	< 0.5	0.3	0.5	0.5	0.5
Gaseous		%	< 2	< 5	0.1	78	< 0.01	< 9	< 0.6	< 0.5

n: not calculated



a)



b)

Figure 6.4. The main outcoming routes of trace elements during a) bark combustion and b) bark and sludge co-combustion at plant UB.

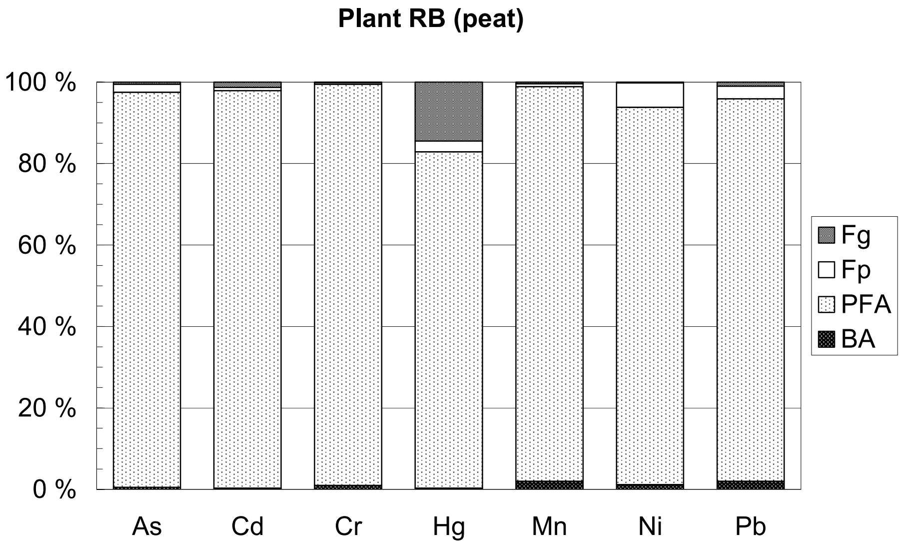
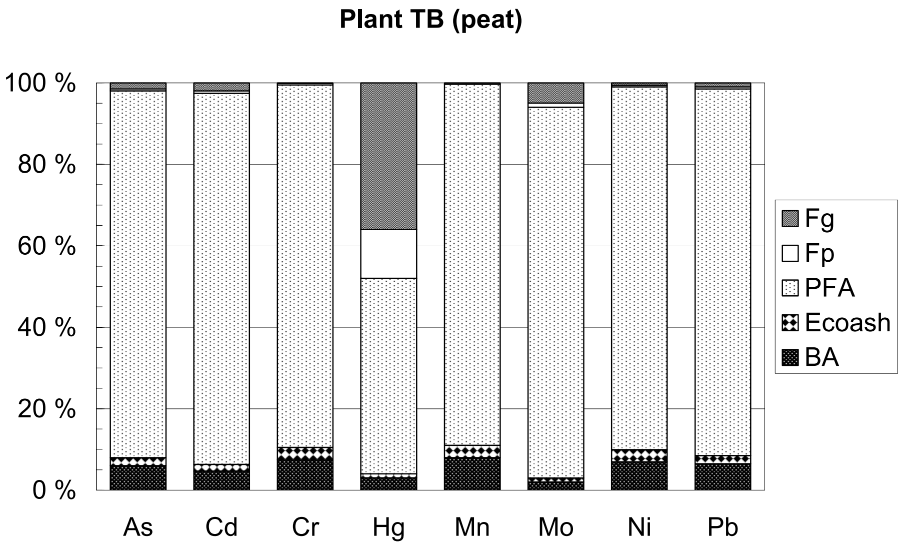


Figure 6.5. The main outcoming routes of trace elements during peat combustion at plant RB.



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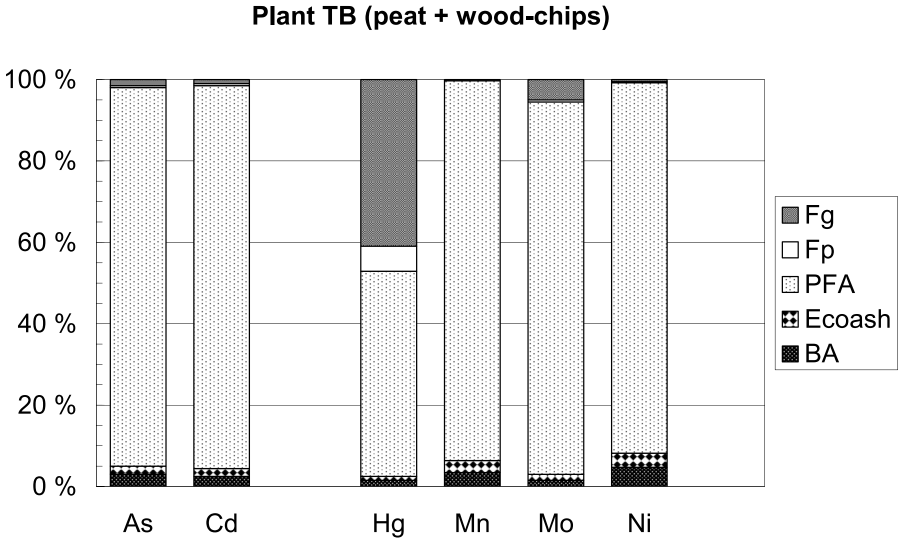
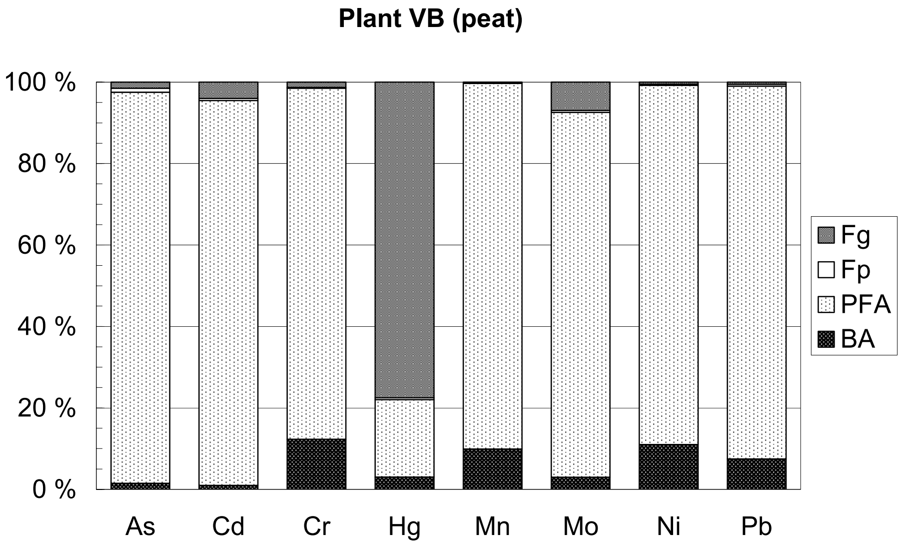
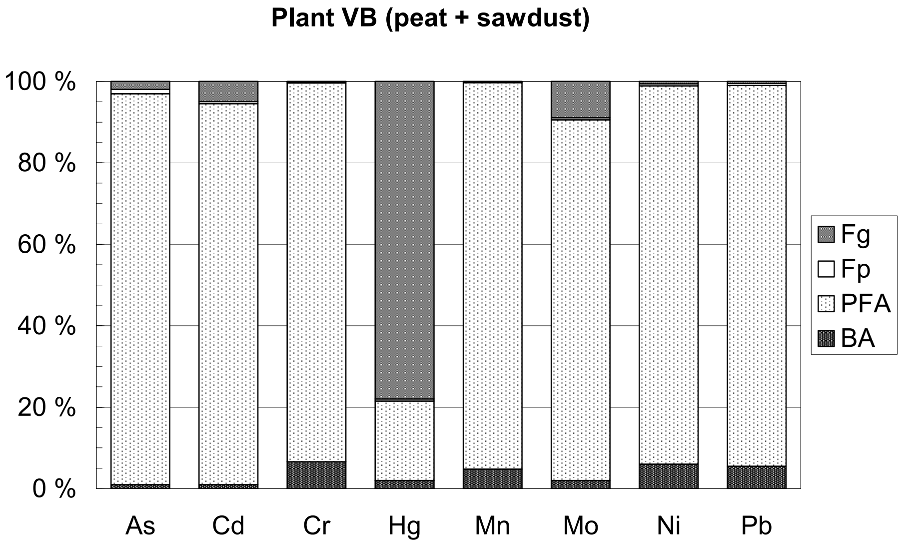


b)

Figure 6.6. The main outcoming routes of trace elements during a) peat combustion and b) peat and wood-chips co-combustion at plant TB.



a)



b)

Figure 6.7. The main outcoming routes of trace elements during a) peat combustion and b) peat and sawdust co-combustion at plant VB.

6.7 Control of trace elements by ESP and FGD

Electrostatic precipitators (ESP) are installed to remove particles from flue gases. ESPs also remove a part of the trace elements that has already sorbed onto or into the ash particles. The collection efficiencies of ESPs for trace elements in the case plants are shown in Table 6.13. The collection efficiency of the ESP at the coal-fired power plants was from 98 % to over 99 % for the elements of class I, IIb or IIc (i.e. Be, Co, Cr, Cu, Mn and Ni). The collection efficiency of the ESP was somewhat lower for the elements of class IIa, which was between 90 % and 99 % for As, Cd, Pb and Zn. The volatile elements of class III (i.e. Hg, Se) were poorly collected by the ESP. The collection efficiency for Hg was 40–93 % and for Se 80 %.

Meij (1989, 1997) has reported high removal efficiencies of ESPs for trace elements of classes I and II. The removal efficiency for aerosol-bound elements in the ESP was 99.6–9.9 % for the Dutch power plants, which burned bituminous coal with conventional burners. The combustion temperature was about 1400 °C. Maier *et al.* (1992) has reported such high removal fractions in similar burning conditions in Austria, as well. The results of this thesis gave lower removal efficiencies. This means that the low-NOx burning technique, i.e. low-NOx burners and staged over-fire air supplying, has significant effects on the collection efficiency of the ESP for trace elements. It is known that particles of sizes between 0.05 and 1.0 μm may penetrate the ESP (Hinds, 1982), because of their poor electrical mobility. The trace elements have been observed to have a tendency to enrich into this particle mode during coal combustion with a low NOx-burning technique (Ylätalo & Hautanen, 1998).

The collection efficiency of the ESP for Hg was significant higher at plant MB compared to plant HB and SB. This is most probably coming from the behaviour of Hg in the SCR installation (discussed further in section 6.2).

The collection efficiencies of the ESP at the fluidised bed plants for the trace elements were very close to the case coal-fired power plants. It was only mercury, which had an exceptional low removal in the fluidised bed plants. The collection efficiency of the ESP for Hg was only 25–79 %. At the bed temperatures of 800–900 °C, most of the mercury is in the vapour phase

(Mojtahedi *et al.* (1990), Clemens *et al.* (1999)). This was clearly seen in the results of plants UB, TB and VB.

The collection efficiencies of the ESPs for arsenic were 97 % or more for the other plants, except for plant HB. At plant HB, the particulate As fraction in the flue gases downstream of the ESP (i.e. upstream of the FGD) was determined to be higher than in the other coal-fired power plants. The relative enrichment factor in bottom ash at plant HB was lower than that at plant SB. These values both show that arsenic has reacted in different ways at plants HB and SB. The contents of arsenic and ash in the coal were higher than usual at plant HB during the measurement campaigns. The levels were also high compared to plant SB. Higher ash amounts and the quality of ash compared to the typical burning circumstances may cause growth of deposition on the ESP electrodes and decrease the overall fly ash removal efficiency (Kouvo, 2003).

Flue gas desulphurisation plants (FGD) are installed primarily to remove sulphur dioxide. However, during the process other flue gas components can also be removed. The collection efficiencies of the FGDs in the coal-fired power plants HB, SB and MB are shown in Table 6.13. The trace element concentrations determined upstream and downstream of the FGD are shown in Appendix 7. The collection efficiency of the FGD was high for all the trace elements at plant HB compared to that of plants SB and MB. At plant HB only Cd, Hg and Zn were found besides a minimum amount of Cr, Mn and Pb in the flue gases downstream of the FGD. Along with the higher particle concentration upstream of the FGD and with the higher dust cake formation on the filter material, more condensation of the elements on the fly ash particles can occur. This increases the relative fractions of the elements in the end-product of the FGD, as seen in the case of plant HB. Such high removals in a semi-dry FGD plant as in plant HB for As, Cd, Cr, Mn, Ni and Pb has been determined in a Swedish coal-fired power plant (Clarke & Sloss, 1992). The removal efficiency of Hg in Swedish studies was determined as 72 %.

Table 6.13. Collection efficiencies[1, 2] of the ESP and FGD (%) for trace elements a) at the coal-fired power plants HB, SB and MB and b) at the fluidised bed plants UB, RB, TB and VB.

a)	**HB**		**SB**		**MB**	
	ESP(%)	**FGD(%)**	**ESP(%)**	**FGD(%)**	**ESP(%)**	**FGD(%)**
As	90	>95	99	>48	97	n
Be	99	> 72	99	n	> 96	n
Cd	95	93	95	18	92	69
Co	n	n	> 99.5	> 38	n	n
Cr	98	> 92	99.5	38	99.8	n(a
Cu	n	n	99	0	n	n
Hg	69	96	40	54	93	0
Mn	97	99.8	99	81	99.7	70
Ni	98	> 93	99.6	65	99.6	n(a
Pb	95	> 98.5	99	73	99	59
Se	n	n	80	> 44	n	n
Tl	> 81	n	n	13	n	n
Zn	96	82	n	n	n	n

b)	**UB**		**RB**	**TB**		**VB**	
ESP (%)	bark	bark + sludge	peat	peat	peat + wood-chips	peat	peat + saw-dust
As	n	97	98	> 97	> 98	99	99
Cd	99	99	98	> 98	> 98	> 96	> 96
Cr	n	99	99.5	99.5	n	99	99.6
Hg	55	25	79	57	54	49	65
Mn	99.7	99.7	> 98	99.6	99.7	99.7	99.7
Mo	n	n	n	> 95	> 95	n	n
Ni	n	99	> 94	> 99	> 99	> 99	> 99
Pb	96	98	99	> 98	> 98	> 99	> 98

n: not determined/calculated

[a] trace element flow deviation in the flue gas downstream of the FGD was high between different tests

[1] collection efficiency of the ESP: 100 % ∗ (the ingoing trace element flow to the ESP – the outcoming trace element flow in the flue gas)/(the ingoing trace element flow to the ESP)

[2] collection efficiency of the FGD: 100 % ∗ (the trace element flow in the flue gas upstream of the FGD – the trace element flow in the flue gas downstream of the FGD)/(the trace element flow in the flue gas upstream of FGD)

The high determination level of Tl in the flue gas gave no possibilities for the calculation of the collection efficiency for Tl at plant HB. In the case of plant SB, the collection efficiencies of the FGD for Cd, Cu and Tl was low, i.e. 0–18 %. The high determination level of Be in the flue gas downstream of the FGD gave no possibilities for the calculation of the collection efficiency for Be at plant SB.

The collection efficiencies of the wet FGD for Hg, Mn and Pb were lower at plant MB compared to plant SB. The collection efficiency of the wet FGD was about 0 % for Hg. The deviations of particulate fractions in the flue gas downstream of the FGD were high for Cr and Ni in different tests giving the collection efficiencies of 0–80 %. The particulate flue gas fractions of trace elements after the wet FGD were measured higher at plant MB than the results given by Maier (1990). The concentrations of As, Be, Co, Se and Tl downstream of the FGD at plant MB were consistent with the results of the Dutch power plants reported by Meij (1997). The other trace element concentrations in the flue gases downstream of the FGD at plant MB were somewhat higher, and the collection efficiencies of the FGD for Cd, Mn, Ni and Pb were lower than the results of the Dutch plants. Meij (1997) has reported significant amounts of Cd in wastewater, which was not found in the studies of this thesis. The high determination levels of As, Be and Se in the gaseous fractions of the flue gas gave no possibilities for the calculation of the collection efficiencies at plant MB.

The trace elements concentrations in the flue gas fractions given in Appendix 7 show that the semi-dry FGD plant reduced effectively the total flue gas emissions of Hg at plant HB, as well as the particulate emissions of As, Be, Cd, Cr, Mn, Ni, Pb and Zn. In the case of plant SB, the semi-dry FGD reduced the total flue gas emissions of Mn and Se. The particulate fractions of As, Be, Cd, Co, Cr, Cu, Ni, Pb and Tl as well as the gaseous fraction of Hg in the flue gases were also removed effectively at plant SB. The FGD increased the gaseous fractions of Cr, Cu, Ni and Pb in the flue gases at plant SB. The wet FGD reduced the total flue gas emissions of Cd, Mn and Pb at plant MB. The particulate emissions of As and Be and the gaseous emissions of Cr and Hg in the flue gas were also reduced.

6.8 Multivariate analysis of relative enrichment factors and process parameters

Beside PCA, PLS was used in this thesis with the aim of extending the implementation of the results of the large measurement campaigns.

PLS was carried out for the data of i) relative enrichment factors and ii) values of flue gas temperature, NOx, SO_2 and particle concentrations in the flue gases upstream of the FGD (i.e. downstream of the ESP) and contents of moisture, volatiles, sulphur and ash in the fuel (described in more detail in Appendix 15). The contents of volatiles and moisture in the fuel correlate positively with the relative enrichment factors of As and Hg in the flue gas particles downstream of the ESP, and with the enrichments of Cr and Ni in the PFA, which were high at plants UB, TB and VP compared to the coal-fired power plants.

The contents of sulphur and ash in the fuel, as well as SO_2 concentrations in the flue gases upstream of the FGD (i.e. downstream of the ESP) was high at plant HB. These properties indicated positive correlation with the enrichment factors of As, Cd, Hg, Mn and Pb in the bottom ash and PFA.

The PLS was also performed for the data of the fluidised bed plants alone. The contents of ash and sulphur in the fuel and the concentrations of NO_x and SO_2 in flue gases had positive correlation to the enrichment factors of Mn and Pb in the bottom ash, as well as to the enrichment factor of Hg in the bottom ash, PFA and flue gas particles. These properties indicated a weak negative correlation with the enrichment factors of Cr in the bottom ash and Ni in the PFA.

PLS was used to determine any correlation between the contents of different trace elements in the case plants. If the correlation between two trace elements was obvious, another could be excluded from the experimental studies, which yields lower economical costs of the measurement campaign. Unfortunately, the results of PLS did not reveal any relevant correlation.

7 Discussion

7.1 Procedure for mass balance determination

The high closure of a steady-state mass balance for trace elements means that the measured ingoing flows are equal to the measured outcoming flows for each trace element. The objective of the Electric Power Research Institute (EPRI, USA) for the material balance closures in their research program, PISCES (Power Plant Integrated Systems: Chemical Emission Studies), is that the total outcoming stream for each element deviates less than 30 % from the total ingoing stream. When the experimental results deviate more than 30 %, the streams can be adjusted with recovery factors. In practice, it has been found that the evaluated recoveries of trace elements in different streams of the plant are subject to large errors (Clarke & Sloss, 1992).

In the tests of this thesis, the steady-state mass balances for trace elements were determined experimentally for three Finnish coal-fired power plants equipped with modern burning and flue gas control technology. Four fluidised bed combustion plants using peat and bark as the main fuels were also experimentally studied in this thesis. The closure of the mass balance was determined without using any recovery factors in the calculations to eval uate the procedures and the methods. The main task was to obtain the methodology to determine the relevant mass balance for trace elements with highly satisfactory results.

The high closure of the steady-state mass balance was found for i) As, Be, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Tl and Zn at the coal-fired power plants equipped with a semi-dry flue gas desulphurisation plant (plants HB and SB) and for ii) As, Be, Cd, Cr, Hg, Mn, Ni, Pb and Se at the coal-fired power plant equipped with a wet flue gas desulphurisation plant (plant MB).

The closures for Se and Tl at plant SB, and Co, Cu and Tl at plant MB could not be calculated, however. In the case of plant SB, the detection limits for low contents of Se in lime and in the end-product of the flue gas desulphurisation plant were so high that the determination limits of Se flows via the lime and end-product were much higher than the determined Se flows via the other streams of the plant. The detection limit for low contents of Tl in the coal was also so high that the determination limit of ingoing flow was well above the determined outcoming flows. This was also the case for Tl at plant MB. The mass balance for Co and Cu was not possible to calculate at plant MB – the ingoing flows were higher than the outcoming flows, although the results of the flue gas fractions of Co and Cu were not available.

In the case of the fluidised bed plants, high closures were determined for i) As, Cd, Cr, Hg, Mn, Ni, Pb at the bark- and sludge-fired power plant UB, and ii) As, Cd, Cr, Hg, Mn, Ni and Pb at the peat-fired power plant RB, which were equipped with bubbling fluidised bed (BFB). High closures were found also for iii) As, Cd, Cr, Hg, Mn, Mo, Ni and Pb at plant TB, which was burning peat and a mixture of peat and wood-chips and for iv) As, Cd, Cr, Mn, Ni and Pb at plant VB, which was burning peat and a mixture of peat and sawdust. Plants TB and VB were equipped with a circulating fluidised bed (CFB).

At plant UB, the mass balance closures were below 0.7 only for Hg during pure bark burning and for As during co-combustion of bark and sludge. The closures for Hg were also below 0.7 at plant VB. The low contents of Hg in outcoming streams at plants UB and VB were determined so low that the determined outcoming Hg flow was only 40–63 % of the ingoing flow. This happened also in the case of Cd at plant VB during co-combustion of peat and sawdust.

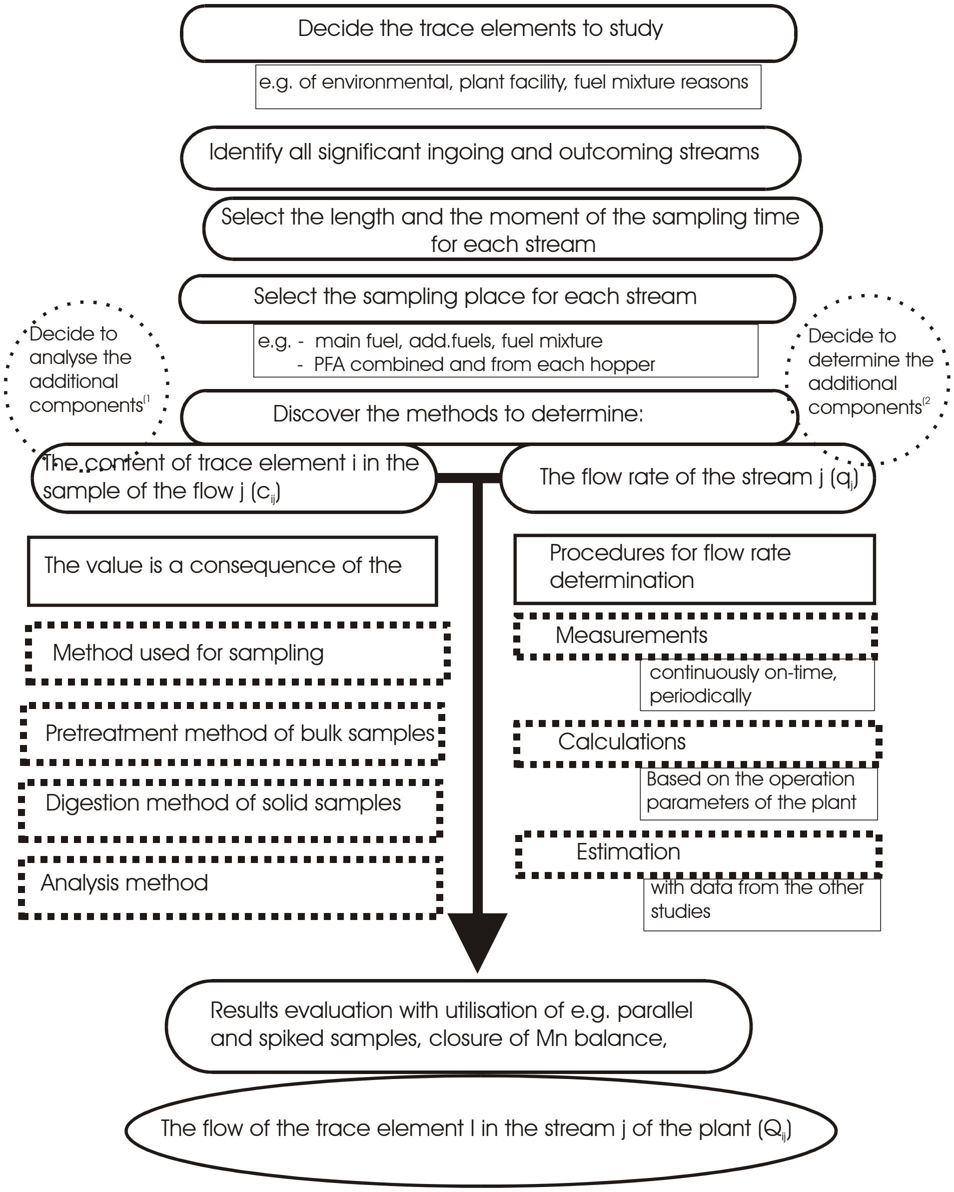
The closures for As during pure bark burning could not be calculated at plant UB, however. The detection limit for the low content of As in bark was so high that the determination limit of ingoing As flow at plant UB was much higher than the determined outcoming As flows. In the case of plant VB, the determination level of ingoing Mo flow was also high compared to the determined outcoming flows, giving no possibilities for mass balance calculations.

The outcoming flows of Cr and Ni at plant UB were 160–180 % of the ingoing flows during pure bark burning, giving poor closures. A part of the measured Cr and Ni was most probably released during the tests from the bed material, which had captured Cr and Ni during the typical combustion process of the plant, i.e. co-combustion of bark and sludge. The same effect was seen in outcoming Cr and Pb flows at plant TB during untypical co-combustion of peat and wood-chips.

As a conclusion, it can be summarised that the procedure and the methods described in this thesis for mass balance determination worked successfully. The results can be considered highly satisfactory. The procedure is illustrated in Figure 7.1. Representative sampling and accurate determination of the trace element contents and flow rate in all the ingoing and outcoming flows of the facilities were necessary for the success of the procedure.

The knowledge of the operational personnel at the plants was needed to determine the representative and safe sampling places. The flue gases were sampled during the whole test period, whilst the other streams were sampled periodically; the samples of each test were later combined. The samples from the flow instead of the pile were necessary. Besides the fuel mixture, the main fuel and added fuel had to be sampled separately during co-combustion tests. The pulverised fly ash was sampled from the first hoppers of the ESP separately besides the combined PFA of all the hoppers, which enabled to control of the PFA samples on the basis of the relative enrichment factors of the trace elements. To evaluate the total trace element flows, the results of parallel tests were necessary, especially in the case of Cr, Hg and Ni. To represent the specific combustion technology and fuel for purposes of public utility, the tests were repeated in the steady-state operation with the maximum load of the plant.

The accurate determination of the element content is a challenge especially for volatile elements, i.e. As, Be, Cd, Hg, Mo, Tl and Se, and for elements used in the raw material of stainless steel, i.e. Cr and Ni, both in respect of sampling and analysis. The sampling device for the flue gas sampling was made of glass and Teflon®. The consistency and volume of absorption solutions as well as the material and the size of the filter in the flue gas sampling method were optimised for the duration of the sampling time. The length of the sampling period of 5–6 h was long enough to determine the low concentrations in the absorption solutions and in the digested filters with the help of spiked and blank solutions and filters, as well as with the help of field blank samples. The samples of solid streams were carefully ground and divided among several laboratories. The samples were digested and analysed with procedures that were validated with certified reference material before and during the analysis of the measurement campaign samples.



1) Mn analysis to use as magnitude control of the mass flows; filter and solution blanks; commercial reference materials

2)fuel analysis: heat value, contents of ash, moisture, N, S, volatiles; PFA analysis: content of unburned; NO_x, SO_2, O_2, CO, CO_2 in flue gases

Figure 7.1. The procedure of relevant steady-state mass balance determination for trace elements.

The flow rate of the fuel was determined based on the measurement of the mass flow, on the process data of the power produced, on the analysis of the heat value and sulphur content in the fuel. The contents of ash and sulphur in the fuel were required to ensure the flow rate of the ash streams and the flue gases, especially during co-combustion. The outcoming ash and end-product streams of the flue gas desulphurisation plants were collected throughout the whole sampling period. The silos and containers were unloaded and weighed before and after the sampling period. The flow rates of the flue gases were continuously measured.

The content of manganese (Mn) was measured over the determination level in all the streams of the plant, as supposed in the hypothesis to control the mass flows with the closure of the Mn balance. The closure of the Mn balance was used to solve any problems in the determined flow rate of the ingoing or outcoming streams. The reasons were sought and the mass flows were corrected using additional data, i.e. sulphur and ash contents in the main fuel, in the added fuel and in the fuel mixture, the samples from separate ESP hoppers etc., besides the measured primary data.

7.2 Trace element contents

All the element contents in the pulverised Polish and Columbic coal samples of the case plants were determined to be inside the content ranges reported in the literature, with exceptions of high Cr and Ni contents at plant MB. The trace element contents in the lime supplied to the flue gas desulphurisation plants were typically low compared to their contents in the coal, with the exceptions of Mn and Tl.

The origin bog was obviously seen in the contents of As, Cd, Cr, Hg and Mn in domestic peat supplied to the fluidised bed plants. The trace element contents were typically lower in the bark, wood-chips and sawdust than the contents in the peat, with exceptions of Cd and Mn. The contents of Cd, Cr, Hg, Mn, Ni and Pb were somewhat higher in the sludge coming from the wastewater treatment plant of the pulp mill compared to their contents in bark.

In general the most of the trace element contents in the outcoming streams were determined to be low at all the case plants. The majority of trace elements exited the plant via pulverised fly ash, removed by the electrostatic precipitator, except for mercury. This fly ash, as well as the end-product of the flue gas desulphurisation plant, is collected separately for potential utilisation, e.g. in the construction industry and for fertilisers. Atmospheric emissions of trace elements were very low; most of them of a magnitude of much less than 5 μg/m^3 (NTP) - thanks to the high collection efficiency of the particle control devices.

The collection efficiency of the electrostatic precipitators (ESP) was from 98 % to over 99 % for Be, Co, Cr, Cu, Mn and Ni, and between 90 % and 99 % for As, Cd, Pb and Zn at the coal-fired power plants. The collection efficiency for Hg was 40–93 % and for Se 80 %. The removed fractions are low compared to the collection efficiencies reported in the literature (Meij, 1989, 1997; Maier *et al.* 1992) for the plants burning bituminous coal with conventional burners at higher temperature. The low-NOx burning technique, i.e. the low-NOx burners and staged over-fire air supplying at plants HB and SB, and the catalytic NOx converter at plant MB, had significant effects on the collection efficiency of the ESP for trace elements. In respect of the atmosphere though, these effects should not be exaggerated because the ESP is followed by the flue gas desulphurisation plant (FGD), which removes the majority of the penetrated trace elements. The collection efficiency of the semi-dry FGD equipped with a fabric filter was especially high, i.e. over 92 % for most of the elements at plant HB, where the particle concentration in the flue gases upstream of the FGD was high (coming from the high ash content of the coal). The wet FGD had somewhat lower collection efficiencies for trace elements compared to the semi-dry FGD. However, from the environmental aspect, the high-efficiency ESP followed by a wet FGD reduces effectively the flue gas emissions of trace elements at plant MB.

The collection efficiencies of the ESPs for trace elements at the fluidised bed plants were close to those at the coal-fired power plants with over 94 % for all the elements, except for mercury. The mercury in the flue gases was removed effectively by a semi-dry flue gas desulphurisation plant in the coal-fired power plants, but it was released in the vapour phase to the atmosphere in the fluidised bed plants.

Such high reductions of trace element emissions into the atmosphere mean that further reductions can only be accomplished if techniques capable of removing gaseous elements more effectively are available.

The relative enrichment factors determined for the coal-fired power plants HB, SB and MB were mainly consistent with the values reported by Meij (1997) for the Dutch power plants. The enrichments of the trace elements in pulverised fly ash separated by electrostatic precipitator were close to 1.0 for most of the elements, except for mercury. The enrichments in the flue gas particles were typically higher. No other significant differences were seen in the enrichments between plants HB, SB and MB, except for mercury. The enrichment of Hg in pulverised fly ash separated by electrostatic precipitator and in flue gas particles upstream of the flue gas desulphurisation plant were high at plants HB and MB compared to plant SB. The coal supplied at plant HB contained more ash, e.g. more calcium, which may lead to increased sorption of Hg, which was observed in bottom ash, as well. The plant MB is equipped with catalytic NOx converter, which effects on behaviour of Hg leading to increased sorption on the flue gas particles.

The relative enrichments of As, Cd, Cr, Mn, Ni and Pb in pulverised fly ash (i.e. PFA) separated by electrostatic precipitator were also close to 1.0 at the fluidised bed plants UB, RB, TB and VB. The relative enrichments of Hg and Mo in the PFA were typically below 0.5, as well as the typical relative enrichments of all the elements in bottom ash and ecoash. The relative enrichments of all the other elements in the flue gas particles were also low, except in the case of arsenic and mercury, which were even higher than the relative enrichments in the coal-fired power plants.

The co-combustion of bark and sludge or of peat and sawdust or wood-chips had no significant effects on the relative distribution of the outcoming streams. The relative enrichment factors of the elements are somewhat lower in the case of co-combustion of peat and sawdust or wood-chips compared to pure peat burning.

In spite of some lower control efficiencies of the electrostatic precipitator for trace elements, the low-NOx burning technology (i.e. low-NOx burners, staged over-fire air suppliers, catalytic converter for external NOx-reduction in the case of the coal-fired power plants, or fluidised bed in case of the peat- and bark-fired power plants) had no significant effects on the enrichments of the trace elements compared to the conventional burning technique reported and classified by Meij (1997).

From the environmental point of view, Mo entering the plant along with peat should be included in the environmental studies besides the potentially hazardous air pollutants identified by the CAAA (the USA Clean Air Act Amendments). The main part of this toxic element leaves the plant in the pulverised fly ash of the electrostatic precipitator.

7.3 The results of multivariate analysis

Chemometrics tools, i.e. Principal Component Analysis (PCA) and Partial Least Squares Projections to Latent Structures (PLS) were used to analyse the empirical data of the three coal-fired power plants and four fluidised bed plants.

Based on the PC analysis concerning the operation parameters and trace element flows of the plants, good repeatability of the parallel tests was observed. The plant operated at maximum load was able to run repeatable on successive days with the specific fuel supplied.

The PCA was used to clarify the differences in the trace element contents in the fuel supplied. The coal supplied at plant HB differed from the coal supplied at plants SB and MB according to its somewhat high contents of Be, Cd, Mn and Pb. The contents of As and Hg were higher in the coal supplied at plants HB and MB than at plant SB. The ratio of these element contents in the bottom ash and PFA to that in the coal was typically low at plant HB compared to plants SB and MB. In addition, the trace element contents in the flue gas particles upstream of the flue gas desulphurisation plant compared to the contents in the coal were higher at plant HB than that at the other plants. These differences were not found in the relative enrichment factors.

The PCA clearly determined out that the contents of As, Cd, Cr, Hg and Mn in the peat supplied in the fluidised bed plants differed from each other depending on the location of the plant. The distribution of the elements has been accordingly reported in the literature. The ratio of Cd in the bottom ash, Hg in the gaseous fraction of the flue gases, and Pb in the flue gas particles compared to the contents in the fuel divided the tests according to the combustion technology (i.e. between bubbling and circulating fluidised bed). The differences were not seen, however, in the relative enrichment factors.

In the case of coal-fired and peat-fired power plants, besides the relative enrichment factor, the ratio of trace element content in the ash samples to the content in the fuel can be a useful value to give further information on element characterisation.

Owing to a lack of information about the operation parameters, the PLS was not used successfully enough to produce any significant new information about the trace elements in the case plants. The contents of ash and sulphur in the fuel correlate positively with the enrichment factors of Hg, Cd, Mn, Pb in the bottom ash and of Hg in the PFA both at the coal-fired power plants and at the fluidised bed plants. The correlation of ash and sulphur contents in the fuel was negative to the enrichment of Cr and Ni in the PFA in both cases.

PLS was used to determine any correlation between the contents of different trace elements in the case plants. If the correlation between two trace elements was obvious, another could be excluded from the experimental studies, which yields lower costs of the measurement campaign. Unfortunately, the results of PLS did not reveal any relevant correlation.

8 Conclusions

The experimental results of the 14 trace elements considered in this thesis were analysed and evaluated with the help of chemometrics tools. All the outcoming trace element flows of three coal-fired, three peat-fired power plants, and one bark-fired power plant are low. Most of the trace elements exit the plant via the pulverised fly ash, removed by electrostatic precipitator, except for Hg. Atmospheric emissions of trace elements were very low - thanks to the high efficiency of the particle control devices (i.e. over 94 % for most of the trace elements).

The low-NOx burning technology has no significant effects on the enrichments of the trace elements in the outcoming streams compared to those of the conventional burning technique reported in the literature. No significant differences were found in the relative enrichment of trace elements in the outcoming streams of the plants between the coal-fired power plants equipped with semi-dry and wet flue gas desulphurisation.

The bark- and peat-fired fluidised bed plants considered in this thesis demonstrate appropriate techniques for co-combustion. The co-combustion tests revealed differences between pure bark and peat combustion according to the differences in the contents of Cd, Cr, Ni and Pb in the outcoming streams of the plant and in the relative enrichment factors of these trace elements. In addition to the relative enrichment factor of trace elements, the ratio of trace element content in the ash samples to the content in the fuel was found to be useful for element characterisation.

The method described in section 7.1 determines the steady-state mass balance of trace elements with highly satisfactory closures. In order to attain the high closure of balance in a large-scale power plant, the several critical factors must be considered.

Samples from the solid flow (e.g. fuel and pulverised fly ash), instead of the pile, and samples of a short enough regular interval (e.g. 1 h) over the whole sampling period are necessary. Although the peat is transported to the power plant from the bogs nearby, the content of trace elements in peat originating from even one bog can vary significantly (e.g. As, Hg). In the fluidised bed plant, the bed material captures a part of the trace elements (e.g. Cr, Ni, Pb) of the fuel and releases part of them later at an indefinite moment. This means that the waiting time to start sampling after the fuel supplying change must be long enough (i.e. several hours).

When the fuel mixture (e.g. milled peat and wood-chips) includes material of different physical characteristics, the main fuel and added fuel should be sampled and analysed separately. To confirm the flow rate of the solid streams, the content of sulphur and ash in the fuel should be analysed, especially during co-combustion. In order to control the mass flows of the whole plant, the content of some element, which is determined well above the detection limit in all the streams (e.g. Mn), is needed.

When pulverised fly ash (PFA) from the first hoppers of the electrostatic precipitator (ESP) is sampled and analysed separately besides the combined PFA, the relative enrichment factor of the trace element indicates contamination of the elements in the PFA samples, e.g. in the case of Cr and Ni.

The accurate determination of the low element contents for volatile elements (i.e. As, Be, Cd, Hg, Mo, Tl and Se) demands that that the content and the volume of absorption solutions, as well as the material and the size of the filter in the flue gas sampling method, is optimised throughout for the sampling time. In addition, field blank samples and samples spiked with the certified reference material are necessary for the accurate determination.

A large-scale power plant can be operated to run well repeatable with maximum load. To evaluate the total trace element flows and to represent the specific combustion technology and fuel, the results of parallel tests were necessary, especially in the case of Cr, Hg and Ni.

The method described in this thesis reliably determines the partitioning of the trace elements into different mass streams. The partitioning justifies a further quantitative analysis of the chemical form, and solubility, etc. This, in turn, facilitates the assessment of the environmental impacts and the optimisation of the operation of the whole power plant.

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Appendix 1. The digestion and analysis methods used in laboratories Lab1–Lab5

Plant HB, SB and MB	**Lab2**	**Lab3**	**Lab5**
Analysis methods	Hg: CVAAS Be: ICP-OES Mn: FAAS Rest: GFAAS	Hg: gold film Cr, Cu, Mn, Ni: FAAS Rest: GFAAS	All but Hg, Tl: GFAAS
Digestion methods:			
Coal			
All but Hg	HNO_3+HF; H_3BO_3	HNO_3+HF; H_3BO_3	
Hg	HNO_3+HCl	HNO_3+HCl	
Bottom ash and PFA			
All but Hg	HNO_3+HF; H_3BO_3	HNO_3+HF; H_3BO_3	
Hg	HNO_3+H_2SO_4	HNO_3+H_2SO_4	
Limestone			
All but Hg	HNO_3		HNO_3+HCl+HF; H_3BO_3
Hg	HNO_3+H_2SO_4		
End-product of FGD, gypsum and filter cake			
All but Hg	HNO_3		HNO_3+HCl+HF; H_3BO_3
Hg	HNO_3+H_2SO_4		
Flue gas filters (teflon)			
All but Hg	HNO_3+HF; H_3BO_3		
Hg	HNO_3+H_2SO_4		
Flue gas filters (quartz fibre)			
All but Hg			HNO_3+HCl+HF; H_3BO_3
Hg	HNO_3+HCl		

	Lab1	**Lab2**	**Lab3**
Plant UB			
Analysis methods	Hg: n.d. Cr, Mn, Ni: FAAS Rest: GFAAS	Hg:CVAAS Rest: n.d.	Hg: n.d. Cr, Mn: FAAS Rest: GFAAS
Digestion methods:			
Bark and sludge	HNO_3+H_2O+HF	Hg: $HNO_3+H_2SO_4$	HNO_3+HF; H_3BO_3
Bottom ash	HNO_3+H_2O+HF	Hg: $HNO_3+H_2SO_4$	HNO_3+HF; H_3BO_3
Ecoash	n.d.	Hg: $HNO_3+H_2SO_4$	HNO_3+HF; H_3BO_3
PFA	HNO_3+H_2O+HF	Hg: $HNO_3+H_2SO_4$	HNO_3+HF; H_3BO_3
Flue gas filters (quartz fibre)	n.d.	HNO_3+HCl	Dig. by Lab2
Plant TB			
Analysis methods	Hg: n.d. Cr, Mn, Ni,: FAAS Rest: GFAAS	Hg: CVAAS Mn: FAAS Rest: GFAAS	Hg: n.d. Mn: FAAS Rest: GFAAS
Digestion methods:			
Peat and wood chips	HNO_3+H_2O+HF	All: $HNO_3+H_2O_2+HF$; H_3BO_3	
Bottom ash	HNO_3+H_2O+HF	Hg: $HNO_3+H_2SO_4$	HNO_3+HF; H_3BO_3
Ecoash	HNO_3+H_2O+HF	Hg: $HNO_3+H_2SO_4$	
PFA	HNO_3+H_2O+HF	Hg: $HNO_3+H_2SO_4$	HNO_3+HF; H_3BO_3
Flue gas filters (quartz fibre)		All: HNO_3+HCl	
Plant VB			
Analysis methods	Hg: n.d. Cr, Mn, Ni: FAAS Rest: GFAAS	Hg: CVAAS Flue gas: Mn: FAAS and Rest: GFAAS	Hg: gold film Cr, Mn, Ni: FAAS Rest: GFAAS
Digestion methods:			
Peat and saw dust	HNO_3+H_2O+HF	Hg: $HNO_3+H_2O_2+HF$; H_3BO_3	
Bottom ash	HNO_3+H_2O+HF	Hg: $HNO_3+H_2O_2+HF$; H_3BO_3	
PFA	HNO_3+H_2O+HF	Hg: $HNO_3+H_2O_2+HF$; H_3BO_3	HNO_3+HF; H_3BO_3
Flue gas filters (quartz fibre)		All: HNO_3+HCl	

n.d.: no digestion/no determination

Plant RB	**Analysis methods**	**Digestion methods**
Lab1	Hg: n.d. Mn: FAAS Rest: GFAAS	
Lab2	Hg: CVAAS Mn: FAAS Rest: GFAAS	
Lab3	Hg: n.d. Mn: FAAS Rest: GFAAS	
Lab4	ICP-MS	
Lab5	Hg: n.d. Rest: GFAAS	
		Peat
Lab1		HNO_3+H_2O+HF
Lab2		HNO_3+HF; H_3BO_3
Lab3		HNO_3+HF; H_3BO_3
Lab4		HNO_3+HF in room temperature
		Bottom ash
Lab1		HNO_3+H_2O+HF
Lab2		Hg: HNO_3+H_2SO_4
Lab3		HNO_3+HF; H_3BO_3
		PFA
Lab1		HNO_3+H_2O+HF
Lab2		Hg: HNO_3+H_2SO_4
Lab3		HNO_3+HF; H_3BO_3
		Flue gas filters (quartz fibre)
Lab2		Hg: HNO_3+H_2SO_4
Lab5		HNO_3+HCl+HF; H_3BO_3
		Sand
Lab1		HNO_3+H_2O+HF
Lab2		Hg: HNO_3+H_2SO_4
Lab3		HNO_3+HCl

Appendix 2. The procedure to weed the element contents analysed in the fuel samples of the bark- and peat-fired power plants

The trace element contents analysed in the fuel samples of plants UB, RB, TB and VB are shown in Table 6.4 and in Appendix 9. The procedure to weed the element contents determined in the parallel fuel samples is presented in detail in this appendix.

Plant UB

The contents of As, Cd, Cr, Mn, Ni and Pb in the fuel samples of plant UB were analysed in Lab1 and Lab3. The content of Hg was analysed in Lab2. In addition to common quality control checks (determination of method blanks, etc.), commercial reference materials were added to the digestion batch. The contents of Cd, Cr, Mn, Ni and Pb in parallel fuel samples and in commercial reference materials are shown in Table A2.1.

The contents of Cd and Mn in the reference samples were analysed well within the acceptable limits of the certified value in both laboratories, i.e. Lab1 and Lab3. The results of both laboratories indicated some difficulties associated with determining of Cr, Pb and Ni.

The content of Hg in the reference material (i.e. NBS 1633a, NIST: fly ash from coal burning) was analysed by Lab2 well in the limits of the certified value. The content of Hg in bark was 0.2 mg/kg in tests U1–U3 and below the higher detection limit (0.04 mg/kg) in tests U4–U6. The content of Hg in sludge was also low, which led however, to a slightly higher content in the fuel mixture in tests U4–U6 compared to tests U1–U3.

All the contents of As in the fuel, except in test U4, were below the detection limit. The detection limit of As was much higher in Lab3 (1.1 mg/kg) compared to Lab1 (0.1 mg/kg) and no relevant arguments were found from the quality control checks to eliminate the results. Consequently, the results analysed in Lab1 were selected for use in the mass balance studies.

Table A2.1. The trace element contents in the parallel fuel samples of plant UB (i.e. tests U1, U2, U4 and U5) and the results of the commercial reference samples (i.e. Lab1: NBS 1632b, NIST, bituminous coal; Lab3:NBS 1633a, NIST, fly ash from coal burning) (mg/kg).

	Cd			**Cr**			**Mn**		
	Lab1	**Lab3**	**Mba(1**	**Lab 1**	**Lab 3**	**Mb a**	**Lab1**	**Lab 3**	**Mb a**
Bark									
U1	0.41	0.41	0.41	m	0.88	0.88	m	450	450
U2	0.39	0.35	0.35	1.2	0.86	0.86	440	430	430
Mixture (bark+sludge)									
U4	0.71	0.53	0.53	m	3.2	3.2	m	580	580
U5	0.89	0.84	0.84	3.4	3.2	3.2	830	800	800
Reference sample	0.060	0.89		10.3	186		12.3	173	
certified	0.0573 ±0.0027	1.00 ±0.15		(11)	196 ±6		12.4 ±1.0	179 ±8	

	Ni			**Pb**		
	Lab1	**Lab3**	**Mb a**	**Lab1**	**Lab 3**	**Mb a**
Bark						
U1	0.88	0.63	0.63	0.87	0.83	0.83
U2	0.87	0.58	0.58	0.75	0.69	0.69
Mixture (bark+sludge)						
U4	3.0	2.3	2.3	2.0	1.2	1.2
U5	2.7	2.5	2.5	1.5	1.3	1.3
Reference sample	6.8	110		3.1	51.9	
certified	6.10 ±0.27	127 ±4		3.67 ±0.26	72.4 ±0.4	

[1] the value used in mass balance calculations
m: missing, not analysed

The results for Cd in the bark and in fuel mixture from both laboratories were close to each other. The result of the fuel mixture analysed in Lab3 was somewhat lower in test U4 (0.53 mg/kg) compared to the combined value of bark and sludge in ratio to their flow rate (0.67 mg/kg). The analysis results in test U5 were almost equal (0.84 mg/kg and 0.82 mg/kg). In spite of the difference of test U4, the results analysed in Lab3 were selected for further calculations, keeping in mind that the real flow of Cd in the fuel in test U4 could be somewhat higher.

The content of Cr in certified reference material was determined below the certified high value in Lab3 and below the expected value in Lab1. The content of Cr in bark was analysed as1.2 mg/kg in Lab1 in test U2, which is higher than the analysis results of Lab3. The values were nearly equal in test U5, i.e. 3.4 mg/kg and 3.2 mg/kg, which are somewhat low, compared to the combined value of bark and sludge in proportion to their flow rate (4.0 mg/kg). These two results from Lab1 indicated that the results from Lab3 were well suited for further calculations.

The content of Mn in the bark in test U2 was analysed as quite equal in Lab1 (440 mg/kg) and Lab3 (430 mg/kg). The content of Mn in the fuel mixture was analysed as 830 mg/kg in Lab1 and 800 mg/kg in Lab3 in test U5. These values are close to the combined value of bark and sludge in ratio to their flow rate (840 mg/kg). The content of Mn in the fuel mixture in test U4, 580 mg/kg, was low compared to the combined value of bark and sludge in proportion to their flow rate, 750 mg/kg. The analysis results from Lab3 were selected for further studies with the note of the possible low content of Mn in test U4.

The content of Ni in certified reference material determined in Lab1 exceeded the acceptable limits. The contents of Ni in the bark and in fuel mixture were also analysed as consistently higher in Lab1 compared to Lab3. The analysis results from Lab3 in tests U4 and U5, 2.3 mg/kg and 2.5 mg/kg, were closer to the combined value of bark and sludge in proportion to their flow rate, 2.2 and 2.0 mg/kg. Therefore, the results of Lab3 were chosen for use in further studies.

The contents of Pb in certified reference material determined in Lab1 and Lab3 were both below the certified values. The contents of Pb in the bark and in fuel mixture were analysed as consistently higher in Lab1 compared to Lab3. The analysis results of Lab3 in tests U4 and U5, 1.2 mg/kg and 1.3 mg/kg, were closer to the combined value of bark and sludge in proportion to their flow rate, 1.2 and 1.0 mg/kg. Therefore, the results of Lab3 were chosen for further studies.

Plant RB

The contents of As, Cd, Cr, Mn, Ni and Pb in all the peat samples from plant RB were analysed in three laboratories (i.e. Lab1, Lab2, Lab3). The content of Hg was analysed only in Lab2. There were no significant differences in the analysis results, so the average values of each test were chosen for use in the mass balance calculations. The contents of As, Cd, Cr, Mn, Ni and Pb in peat in tests R3 and R4 were also analysed in Lab4, which used a totally different method for the digestion and analysis (see Appendix 1). The analysis results of tests R3 and R4 given in Table A2.2 show that the results of the method used in Lab4 matched well the results from the other laboratories. As an exception, the content of Mn in peat in test R3 was analysed slightly higher (i.e. 65 mg/kg), compared to the average of the other laboratories (i.e.59 mg/kg). The analysis results of Lab4 were, however, excluded from the average calculations.

Table A2.2. The trace element contents in the parallel peat samples of plant RB (i.e. tests R3 and R4) (mg/kg).

		Lab1	**Lab2**	**Lab3**	**Lab4**	**Mba**[1]
As						
	R3	13.0	15	18	12.8	15
	R4	10.8	14	15	10.8	13
Cd						
	R3	0.18	0.22	0.22	0.22	0.21
	R4	0.20	0.30	0.24	0.24	0.25
Cr						
	R3	8.6	10	8.3	8.7	9.0
	R4	9.9	11	9.4	10.4	10
Mn						
	R3	62.2	62	54	65	59
	R4	42.7	48	35	42	42
Ni						
	R3	4.5	3.6	3.8	4.0	4.0
	R4	5.8	5.0	5.0	5.5	5.3
Pb						
	R3	3.0	3.6	2.5	3.2	3.0
	R4	2.2	3.1	1.8	2.2	2.4

[1] the value used in the mass balance calculations

Plant TB

The contents of As, Cd, Cr, Mn, Mo, Ni and Pb in the fuel samples from plant TB were analysed in two laboratories (Lab1 and Lab2). The content of Hg was analysed only in Lab2.

The content of Hg in peat was determined as 0.03–0.04 mg/kg in tests T1–T3 and 0.05–0.07 mg/kg in tests T4–T6. The content of Hg in wood chips was determined as 0.01–0.02 mg/kg. The content of Hg in the fuel mixture was determined below the detection limit (i.e. 0.05 mg/kg), so the analysis results of both fuel fractions were combined in proportion to their flow rate and used as the content of Hg in the fuel mixture in the mass balance calculations.

The contents of Cd in peat and wood chips were analysed as very close to each other, and the contents of Cd in all the fuel samples analysed in Lab1 and Lab2 were quite equal (0.08–0.10 mg/kg). The contents of Pb in peat (i.e. 2.7–3.4 mg/kg) analysed in Lab1 and Lab2 were also rather equal. The content of Pb in wood chips was analysed as 0.5 mg/kg or less. The results of Lab1 were chosen for use in the mass balance calculations.

Table A2.3 shows significant differences in the contents of As, Cr, Mn, Mo and Ni analysed in two laboratories (i.e. Lab1 and Lab2). No relevant arguments were found from the quality control checks of the analysis to eliminate the results. Therefore, the element contents analysed in the fuel mixture samples were compared to the combined values of the individual contents in peat and wood chips in proportion to their flow rate. The mass balance was calculated first with the values determined in one laboratory (Lab1), and when ever the ratio between the outcoming and ingoing flow was not within the criterion limit of 0.7–1.3, the mass balance was calculated again with the analysis results determined in another laboratory.

Table A2.3. The trace element contents in the parallel fuel samples of plant TB (i.e. tests T1–T3 and T5–T6) (mg/kg).

	As			Cr			Mn		
	Lab1	Lab2	Mba(1	Lab1	Lab 2	Mba	Lab 1	Lab2	Mba
Peat									
T1	1.4	2.7	1.4	7.9	7.7	7.9	111	96	111
T2	1.4	2.5	1.4	9.6	9.9	9.6	99	98	99
T3	1.5	2.7	1.5	9.5	9.9	9.5	100	94	100
T5	0.72	2.35		9.3	8.6		124	114	
T6	0.99	2.16		9.0	8.6		124	117	
Wood chips									
T5	< 0.25	< 1.1		< 0.5	< 0.2		119	128	
T6	< 0.25	< 1.1		< 0.5	< 0.2		102	108	
Mixture (peat+wood)									
T5	0.6	1.6	1.6	5.4	4.3	5.4	115	112	115
T6	0.6	1.8	1.8	5.6	4.4	5.6	125	122	122

	Mo			Ni		
	Lab1	Lab2	Mba	Lab1	Lab2	Mba
Peat						
T1	0.55	< 1.1	0.55	3.8	5.1	3.8
T2	0.59	< 1.1	0.59	4.2	5.8	4.2
T3	0.68	< 1.1	0.68	4.3	5.9	4.3
T5	0.79	< 1.1		4.5	5.7	
T6	0.66	< 1.1		4.1	5.4	
Wood chips						
T5	< 0.5	< 1.1		< 0.5	< 0.5	
T6	< 0.5	< 1.1		< 0.5	< 0.5	
Mixture (peat+wood)						
T5	< 0.5	< 1.1	0.5	2.6	3.0	3.0
T6	< 0.5	< 1.1	0.5	2.6	3.2	3.2

[1] the value used in the mass balance calculations

The content of As in fuel analysed in Lab1 was consistently lower than the analysis results from Lab2. No reason was found from the quality control checks to eliminate the results of Lab1, so the results for As from Lab1 were chosen for further calculations during peat-combustion. The analytical problems of As were seen in the results of tests T4 and T5. The analysis result for peat in Lab1 was 1.4–1.5 mg/kg in tests T1–T3, and 0.7–1.0 mg/kg in tests T4–T6. The analysis results from Lab2 were much higher, at 2.5–2.7 mg/kg, and 2.2–2.8 mg/kg, respectively. The content of As in wood chips was determined below the detection limit, which was 0.3 mg/kg in Lab1, and 1.1 mg/kg in Lab2. The contents of As in the fuel mixtures were analysed as 0.6 mg/kg in Lab1. These values were very close to the combined value of peat and wood chips calculated in proportion to their mass fractions, i.e. 0.5 and 0.65 mg/kg. The contents of As in the fuel mixtures were analysed as 1.6 and 1.8 mg/kg in Lab2. These values were also very close to the combined value of peat and wood chips in proportion to their mass fractions, i.e. 1.6 and 1.5 mg/kg. This same degree of difference was also seen in the analysis results of peat.

First the contents of As determined in Lab1 were selected for further calculations. When the mass balances were calculated, the ratios between the outcoming and ingoing flows were 2.23 and 2.13 in tests T5 and T6, respectively. When the content of As in fuel determined in Lab2 was chosen, the ratio was much more acceptable (0.83 and 0.71). This means that Lab1 determined the contents of As in the fuel mixture, in peat and in wood chips at too low a level in tests T4–T6. The contents of As determined in Lab2 were chosen for further calculations during co-combustion.

The contents of Cr in the peat samples analysed in Lab1 and Lab2 were very equal in tests T1–T3. The contents of Cr in the fuel mixture, 5.4 and 5.6 mg/kg, were analysed higher in Lab1, whose values were closer to the combined value of peat and wood chips in proportion to their flow rate (6.7 and 6.3 mg/kg). The combined values based on the analysis results from Lab2 were also close to these (6.1 and 6.0 mg/kg). Therefore, the contents of Cr determined in Lab1 instead of Lab2 were selected for further calculations in all tests except for test T4, where the result is absent.

The contents of Mn in the peat samples analysed in Lab1 and Lab2 were very equal in tests T1–T3. The results from Lab1 were chosen for further calculations in tests T1–T3. The content of Mn in the fuel mixture was 115 mg/kg in test T5 analysed in Lab1, which is closer to the combined values of peat and wood chips in proportion to their flow rate analysed in both laboratories (123 and 118 mg/kg). The content of Mn in the fuel mixture was 122 mg/kg in test T6 analysed in Lab2, which is closer to the combined values of peat and wood chips in proportion to their flow rate analysed in both laboratories (118 and 114 mg/kg). There was no result for the fuel mixture from Lab1 for test T4. With these arguments, the contents of Mn in the fuel mixture determined in Lab2 were chosen for further calculations in tests T4 and T6, and the result of Lab1 was chosen for test T5.

The contents of Mo in the peat, wood chips and fuel mixture were determined below the detection limit (1.1 mg/kg) in Lab2. The contents of Mo in peat were analysed as 0.6–0.8 mg/kg in Lab1, which were used for the mass balance calculations. The content of Mo in the fuel mixture was determined below the detection limit (0.5 mg/kg) in Lab1. For the mass balance studies, the value was taken to be 0.5 mg/kg, which is based on the combined analysis values of peat and wood chips in proportion to their flow rate.

The contents of Ni in the peat analysed in Lab1 are consistently lower than the results from Lab2. The main argument for choosing the analysis results from Lab1 for the mass balance studies was the comparability of tests T1–T3 during pure peat-combustion. The contents of Ni in the fuel mixture analysed by Lab2 were selected for further calculations, because they were closer to the combined values of peat and wood chips in proportion to their flow rate analysed in both laboratories.

Plant VB

The contents of As, Cd, Cr, Mn, Mo, Ni and Pb in the fuel samples of plant VB were analysed only in Lab1. The content of Hg in the fuel was analysed in Lab2. Because there was no relevant fuel mixture sample available, the contents of trace elements in the peat and sawdust were determined individually, and a combined value was calculated in proportion to their flow rate. In addition to common quality control checks (determination of method blanks, etc.), the samples of fuel mixtures collected one week before (Vc1) and after (Vc2) the measurement campaigns were analysed in Lab1 as well. The results of the Vc-samples, which contained mainly peat and some sawdust, bark and cutter chips, in proportion to their supply flow rate, are shown in Table A2.4. These values could be only be utilised only as a rough guide. It must be remembered that the fuel supplied in tests V3 and V4 was mainly peat and some sawdust only. The contents of Cd, Hg, Mo and Ni in tests V3–V4 were close to the contents in the Vc-samples. The contents of As, Cr, Mn and Pb in the fuel were lower in tests V3–V4 than in the Vc-samples. No argument was found to eliminate any analysis results obtained in tests V1–V4.

Table A2.4. The trace element contents in the fuel samples of plant VB, i.e. tests Vc1 and Vc2, which were sampled a week before and a week after the measurement campaign (mg/kg).

	Vc1	**Vc2**
As	1.7	1.6
Cd	0.11	0.12
Cr	3.9	3.4
Hg	0.05	0.06
Mn	64	57
Mo	0.46	0.36
Ni	3.4	2.8
Pb	4.0	5.2

Appendix 3. The procedure to weed the element contents analysed in the ash samples at the bark- and peat-fired power plants

The trace element contents analysed in the ash samples of plants UB, RB, TB and VB are shown in Appendix 9. The procedure to weed the element contents determined in the parallel ash samples is presented in detail in this appendix.

Plant UB

The contents of As, Cd, Ni and Pb in the bottom ash and the PFA samples in tests U1–U2 and U4–U5 were analysed in Lab1 and Lab3. The contents of Cr and Mn were also analysed in Lab3, and the content of Hg was analysed in Lab2. In addition to common quality control checks (determination of method blanks, etc.), commercial reference materials were added to the digestion batch.

The content of Hg in the reference material (i.e. NBS 1633a, NIST: fly ash from coal burning) was analysed in Lab2 as well within the limits of the certified value. The content of Hg in bottom ash was determined below the detection limit, i.e. 0.04 mg/kg. The content of Hg in the PFA was 0.13–0.18 mg/kg during bark combustion and 0.15–0.23 mg/kg during co-combustion of bark and sludge.

The contents of Cr and Mn in the reference material (i.e. NBS 1633a, NIST) were analysed in Lab3 as well within the limits of the certified value. The content of Cr in bottom ash was 34–37 mg/kg during bark combustion and 35–41 mg/kg during co-combustion of bark and sludge. The content of Mn in bottom ash was 4410–4650 mg/kg during bark combustion and 4800–5600 mg/kg during co-combustion.

The contents of As, Cd, Ni and Pb in parallel ash samples and in commercial reference materials are shown in Table A3.1. The contents of Cd in the reference samples were analysed as well within the limits of the certified value in Lab3. The results of the reference materials indicated some difficulties associated with determining Pb in both laboratories, as well as As and Cd in Lab1, and Ni in Lab3.

Table A3.1. The trace element contents in the parallel bottom ash and PFA samples of plant UB (i.e. tests U1, U2, U4 and U5) and the results of the commercial reference samples (i.e. Lab1: NBS 1632b, NIST, bituminous coal; Lab3: NBS 1633a, NIST, fly ash from coal burning) (mg/kg).

	As			Cd		
	Lab1	**Lab3**	**Mba(1**	**Lab1**	**Lab3**	**Mba**
Bottom ash						
U1	1.4	2.1	2.1	0.28	0.32	0.32
U2	1.4	2.2	2.2	0.06	0.07	0.07
U4	1.1	1.5	1.5	0.06	0.11	0.11
U5	1.5	2.1	2.1	0.06	0.09	0.09
PFA						
U1	3.9	5.8	5.8	20	19	19
U2	3.2	4.9	4.9	18	18	18
U4	2.0	3.4	3.4	15	13	13
U5	2.3	3.9	3.9	15	16	16
Reference sample	2.8	134		0.066	0.91	
certified	3.72	145		0.0573	1.00	
	±0.09	±15		±0.0027	±0.15	

	Ni			Pb		
	Lab1	**Lab3**	**Mba**	**Lab1**	**Lab3**	**Mba**
Bottom ash						
U1	25	22	22	8.6	8.6	8.6
U2	19	20	20	5.7	7.3	7.3
U4	22	19	19	7.0	6.6	6.6
U5	21	19	19	6.5	7.1	7.1
PFA						
U1	62	51	51	64	47	47
U2	53	46	46	53	46	46
U4	78	60	60	44	31	31
U5	81	70	70	29	28	28
Reference sample	6.1	122		3.3	67.8	
certified	6.10	127		3.67	72.4	
	±0.27	±4		±0.26	±0.4	

[1] the value used in the mass balance calculations

Based on the data evaluation with the results of reference samples, the analysis results of <u>Lab3 were selected instead of Lab1 for further calculations of As, Cd, Ni and Pb</u>, with the following remarks.

The low recovery of As in the reference material was also seen in the results for the bottom ash and PFA determined by Lab1, which were consistently low compared to Lab 3. In spite of too high a recovery of Cd in the reference material, the contents of Cd in bottom ash were determined as consistently low by Lab1 compared to Lab3. The contents of Cd in the PFA determined by Lab1 and Lab3 were close to each other.

The content of Ni in the reference material was determined below the high certified value in Lab3. The contents of Ni in the bottom ash samples determined in these two laboratories were very close to each other. The content of Ni in the PFA was determined as consistently higher in Lab1 compared to Lab3. This indicates that the content of Ni in the PFA could be actually somewhat higher.

The contents of Pb in the reference material determined in Lab1 and Lab3 were both below the certified values. The content of Pb in bottom ash in test U1 was determined equal in both laboratories. Pb was determined higher in Lab3 in test U2 and U5 and some lower in test U4 compared to Lab1. The content of Pb in the PFA was determined consistently higher in Lab1 compared to Lab3, which indicates that the content of Pb in the PFA could be actually somewhat higher.

Plant RB

The contents of As, Cd, Cr, Mn, Ni and Pb in the bottom ash and PFA samples of plant RB were analysed in Lab1 and Lab3. The content of Hg was analysed only in Lab2.

The content of Hg in bottom ash was determined below the detection limit, i.e. 0.02 mg/kg. The content of Hg in the combined PFA sample was 0.38 mg/kg.

The contents of As, Cd, Cr, Mn, Ni and Pb analysed in the bottom ash and PFA are shown in Table A3.2. The results of the PFA sample analysed in Lab4 are also shown in Table A3.2. Lab4 used a totally different method for the digestion and analysis (see Appendix 1).

The results from the method used in Lab4 matched well the results from the other laboratories. As an exception, the content of Mn in peat in test R3 was analysed as somewhat higher (i.e. 65 mg/kg) compared to the average of the other laboratories (i.e.59 mg/kg). The analysis results of Lab4 were, however, excluded from the average calculations.

The averages of the analysis results from Lab1 and Lab3 were chosen for the mass balance calculations with following remarks. The contents of As, Mn, Ni and Pb in bottom ash were determined as consistently low in Lab1 compared to Lab3, as well as most of the Cd contents. The contents of Cr in bottom ash determined in these two laboratories were very close to each other.

Table A3.2. The trace element contents in the parallel bottom ash (i.e. BA) and PFA samples of plant RB (i.e. tests R1– R5) (mg/kg).

	As				Cd				Cr			
	Lab1	**Lab3**	**Lab4**	**Mba[1]**	**Lab1**	**Lab3**	**Lab4**	**Mba**	**Lab1**	**Lab3**	**Lab4**	**Mba**
BA												
R1	9.6	12		10.8	0.17	0.16		0.17	32.8	33		32.9
R2	14.8	17		15.9	0.21	0.26		0.24	31.2	31		31.1
R3	15.8	18		16.9	0.18	0.25		0.22	30.7	32		31.4
R4	11.1	14		12.6	0.17	0.20		0.19	21.7	23		22.4
R5	10.1	12		11.1	0.11	0.15		0.13	22.0	22		22.0
PFA												
R1–R5	151	124	172	138	2.1	2.4	2.5	2.3	96.7	100	101	98.4

	Mn				Ni				Pb			
	Lab1	**Lab3**	**Lab4**	**Mba**	**Lab1**	**Lab3**	**Lab4**	**Mba**	**Lab1**	**Lab3**	**Lab4**	**Mba**
BA												
R1	292	300		296	15.4	18		16.7	16.4	21		18.7
R2	294	320		307	16.1	19		17.6	11.9	18		15.0
R3	326	340		333	17.2	19		18.1	15.1	22		18.6
R4	226	280		253	12.3	16		14.2	13.9	23		18.5
R5	211	250		231	13.5	18		15.8	14.5	23		18.8
PFA												
R1–R5	585	610	630	598	53	61	56	57	32	35	35	34

[1] the value used in the mass balance calculations

The content of As in the PFA of plant RB was analysed in Lab3 below the contents determined in Lab1 and Lab4. Lab3 and Lab4 determined very equal contents of Cd, Cr and Pb in PFA, which were somewhat high compared to the contents determined in Lab1. The content of Mn determined in Lab3 is in between the analysis results from Lab1 and Lab4. The content of Ni determined in Lab3 is a little higher than the contents determined in Lab1 and Lab4.

Plant TB

In the case of plant TB, the contents of As, Cd, Cr, Mn, Mo, Ni and Pb in all the bottom ash samples and the PFA samples from three ESP hoppers were analysed in Lab3. The samples from tests T2–T3 and T5–T6 were digested and the trace elements were analysed in Lab1as well. The content of Hg was determined only in Lab2.

The content of Hg in bottom ash was determined below the detection limit, i.e. 0.07 mg/kg. The content of Mo in bottom ash was also determined below the detection limit, i.e. 0.5 mg/kg in Lab1 and 1.0 mg/kg in Lab3. The other element contents of the parallel bottom ash samples are shown in Table A3.3. The analysis results of Lab3 were selected with the following remarks for further calculations of As, Cd, Cr, Mn, Ni and Pb.

The contents of Cd and Ni in bottom ash determined in two laboratories were very close to each other. The content of As in bottom ash was determined as consistently lower in Lab1 compared to Lab3. (The same consistent difference was also seen in plants UB and RB). The contents of Cr in bottom ash determined in Lab1 were extremely high compared to the results of Lab3, and compared to the results of plants RB or VB. The contents of Mn and Pb determined in Lab1 were also higher. In the case of plant RB, the contents of Mn and Pb determined in Lab1 were low compared to the results of Lab3. This indicates that the true contents of Mn and Pb in the bottom ash samples of plant TB are approximately the values determined in Lab3. The element contents in reality could even be somewhat higher.

The contents of the trace elements in the PFA samples from three ESP hoppers were analysed in Lab1 and Lab3. The contents shown in Table A3.4 came up to expectations. The values are lowest in the first hopper, i.e. ESP1, which removes the coarse particulate fraction from the flue gases, and the contents are highest in the third hopper, i.e. ESP3, which removes the fine particulate fraction. Based on the data evaluation, the analysis results of Lab3 were selected for further calculations of As, Cd, Cr, Mn, Mo, Ni and Pb with the following remarks.

The contents of As and Cd in ESP1 and in ESP2 determined in Lab1 were very equal with the contents determined in Lab3. The contents of As in ESP3 were determined higher in Lab1 than in Lab3. The contents of Cd in ESP3 were determined in Lab 1 low compared to Lab3.

The contents of Cr in ESP2 determined in Lab1 and Lab3 were very equal, as well as in ESP1 with the exception of test T3. The contents of Cr in ESP3 were determined in Lab1 equally (test T3) or somewhat higher (T2, T5, T6) compared to Lab3. The contents of Mn and Pb in the ESP samples were determined as higher in Lab1 compared to Lab3. The contents of Mo and Ni in the ESP samples were determined as lower in Lab1 compared to Lab3. This means that the contents of Mn and Pb in the PFA samples could be in reality somewhat higher than the values determined in Lab3. On the other hand, the true contents of Mo and Ni in the PFA samples could be some lower than the values determined in Lab3.

The trace element contents in the PFA for the mass balance studies were calculated based on the flow rate ratio of each PFA stream (80% ESP1, 15% ESP2, and 5 % ESP3). These values are shown in Appendix 9.

Table A3.3. The trace element contents in the parallel bottom ash samples of plant TB (i.e. tests T2,T3,T5 and T6) (mg/kg).

Test ID	**As**			**Cd**			**Cr**		
	Lab1	**Lab3**	**Mba**[1]	**Lab1**	**Lab3**	**Mba**	**Lab1**	**Lab3**	**Mba**
T2	6.3	6.6	6.6	0.30	0.27	0.27	82	45	45
T3	5.4	5.9	5.9	0.33	0.31	0.31	94	60	60
T5	6.0	6.9	6.9	0.40	0.39	0.39	76	45	45
T6	5.4	6.1	6.1	0.38	0.38	0.38	80	55	55

Test ID	**Mn**			**Ni**			**Pb**		
	Lab1	**Lab3**	**Mba**	**Lab1**	**Lab3**	**Mba**	**Lab1**	**Lab3**	**Mba**
T2	628	558	558	21	20	20	19	13	13
T3	627	600	600	22	20	20	17	13	13
T5	668	641	641	20	20	20	19	17	17
T6	816	760	760	24	23	23	19	13	13

[1] the value used in the mass balance calculations

Table A3.4. Trace element contents in the PFA samples from the first three ESP hoppers (i.e. ESP1, ESP2, ESP3) at plant TB. (mg/kg).
Note: PFA = 0.80 x PFA(ESP1) + 0.15 x PFA(ESP2) + 0.05 x PFA(ESP3).

Test ID	**As**			**Cd**			**Cr**			**Hg**	
	Lab1	**Lab3**	**Mba(1**	**Lab1**	**Lab3**	**Mba**	**Lab1**	**Lab3**	**Mba**	**Lab2**	**Mba**
ESP1											
T1	m	15	15	m	0.61	0.61	m	81	81	0.04	0.04
T2	19	19	19	0.96	1.0	1.0	120	122	122	0.06	0.06
T3	16	14	14	0.76	0.71	0.71	106	93	93	0.04	0.04
T4	m	17	17	m	1.1	1.1	m	107	107	0.13	0.13
T5	14	13	13	1.1	0.97	0.97	104	101	101	0.08	0.08
T6	15	14	14	1.2	1.2	1.2	106	102	102	0.12	0.12
ESP2											
T1	m	25	25	m	1.3	1.3	m	92	92	0.38	0.38
T2	33	31	31	1.9	1.9	1.9	151	149	149	0.59	0.59
T3	30	30	30	1.7	1.6	1.6	143	146	146	0.45	0.45
T4	m	25	25	m	1.7	1.7	m	118	118	0.52	0.52
T5	22	20	20	1.7	1.6	1.6	125	124	124	0.47	0.47
T6	19	18	18	1.6	1.6	1.6	114	115	115	0.45	0.45
ESP3											
T1	m	49	49	m	2.8	2.8	m	107	107	1.5	1.5
T2	64	48	48	2.3	2.6	2.6	154	141	141	2.1	2.1
T3	60	43	43	2.2	2.7	2.7	168	168	168	1.6	1.6
T4	m	47	47	m	2.6	2.6	m	153	153	1.2	1.2
T5	53	43	43	2.3	2.8	2.8	163	151	151	1.7	1.7
T6	49	40	40	2.4	2.9	2.9	161	154	154	1.4	1.4

m: missing, not analysed

Table A3.4. Continued

Test ID	Mn			Mo			Ni			Pb		
	Lab1	Lab3	Mba	Lab1	Lab3	Mba	Lab1	Lab3	Mba	Lab1	Lab3	Mba
ESP1												
T1	m	1140	1140	m	3.7	3.7	m	38	38	m	27	27
T2	1290	1249	1249	4.8	4.5	4.5	42	53	53	42	34	34
T3	1120	954	954	3.1	3.3	3.3	36	41	41	34	25	25
T4	m	1541	1541	m	4.9	4.9	m	49	49	m	34	34
T5	1610	1440	1440	3.4	4.5	4.5	39	52	52	41	32	32
T6	1750	1603	1603	3.3	4.5	4.5	40	54	54	51	41	41
ESP2												
T1	m	1352	1352	m	5.2	5.2	m	44	44	m	40	40
T2	1690	1547	1547	6.1	7.9	7.9	60	66	66	61	44	44
T3	1540	1463	1463	3.8	7.7	7.7	53	61	61	54	41	41
T4	m	1685	1685	m	6.1	6.1	m	49	49	m	40	40
T5	2060	1927	1927	4.2	6.7	6.7	52	55	55	57	45	45
T6	1940	1821	1821	4.0	5.7	5.7	47	51	51	54	44	44
ESP3												
T1	m	2182	2182	m	8.7	8.7	m	70	70	m	53	53
T2	2520	2373	2373	7.5	9.9	9.9	74	84	84	68	55	55
T3	2330	2289	2289	7.6	9.7	9.7	78	90	90	70	61	61
T4	m	2258	2258	m	9.4	9.4	m	81	81	m	53	53
T5	2610	2519	2519	7.6	9.1	9.1	72	68	68	74	63	63
T6	2780	2669	2669	7.1	13	13	76	80	80	72	66	66

m: missing, not analysed

Plant VB

The contents of As, Cd, Cr, Mn, Mo, Ni and Pb in the bottom ash samples from plant VB were analysed in Lab1. The content of Hg was analysed in Lab2. The results are shown in Appendix 9. The contents of As and Cd were low compared to plants RB or TB. All the other contents were close to the contents determined in plants RB and TB.

Ash samples collected from the economiser and from four ESP hoppers at plant VB were combined before sample pre-treatment in ratio to their flow rate (i.e. 0.7 % PFA(ECO), 66.7 % PFA(ESP1), 28.9 % PFA(ESP2), 3.5 % PFA(ESP3) and 0.2 % PFA(ESP4)). The combined sample was recorded as the PFA sample.

The content of Hg in the PFA was analysed in Lab2, giving the content of 0.18 mg/kg during peat combustion and 0.13 and 0.15 mg/kg during co-combustion of peat and saw dust.

The contents of As, Cd, Cr, Mn, Mo, Ni and Pb in PFA samples were analysed in Lab1. In addition to common quality control checks, the sample of test V3 was digested and analysed in Lab3 to check the content level. The analysis results given in Table A3.5 show that the contents of As, Mo and Ni in PFA determined in Lab1 were low compared to the contents determined in Lab3. The contents of Cd and Pb were determined as quite equal in both laboratories. The content of Cr and Mn were determined higher in Lab1 than in Lab3. The content of Hg was determined in Lab3 as 0.10 mg/kg, which is lower than in Lab2.

Table A3.5. Trace element contents in the parallel PFA samples at plant VB (i.e. test V3) (mg/kg).

	Lab1	**Lab3**	**Mba**(1
As	19	25	19
Cd	1.7	1.9	1.7
Cr	92	85	92
Mn	1340	1200	1340
Mo	5.1	8.2	5.1
Ni	69	87	69
Pb	55	57	55

[1] the value used in the mass balance calculations

In addition, the samples from the first two ESP hoppers in tests V2 and V3 were digested and analysed separately in Lab1 to control the content level. The results are shown in Table A3.6. The element contents were lower in the first ESP hopper during both tests, as expected. The first hopper removes the coarse particulate fraction of flue gases. All the element contents were lower in both hoppers during co-combustion (V3), except for Mn, which is in accordance with the element contents in the fuel supplied.

The contents in the PFA determined in Lab1 and Lab3 fit well in between the contents of the PFA(ESP1) and PFA(ESP2), all with one exception. The Mo content of the PFA in test V3 was determined in Lab3 as 8.2 mg/kg, which is high compared to the contents of ESP1 and ESP2. Further examinations were carried out. Lab1 and Lab3 digested the sample of test V3 according to their own method and the solution was analysed in both laboratories. The content of Mo in the PFA digested in Lab1 was analysed as 5.1 mg/kg in Lab1, which is quite equal to the analysis result of Lab3, i.e. 5.0 mg/kg. The content of Mo in the PFA digested in Lab3 was analysed as higher, both in Lab1 (9.2–9.6 mg/kg) and Lab3 (8.2 mg/kg). As a conclusion, the digestion method of Lab1 was less effective for Mo than the method used in Lab3. This means that the contents of Mo in the PFA given in Appendix 9 can in reality be somewhat higher in tests V1–V4. The further examinations also confirmed that the samples had been combined in the correct ratio compared to the actual case.

Table A3.6. Trace element contents in the PFA samples and the samples from the first two ESP hoppers (i.e. ESP1, ESP2) at plant VB (i.e. tests V2 and V3).

Test ID	**As**		**Cd**		**Cr**	
	ESP1	**ESP2**	**ESP1**	**ESP2**	**ESP1**	**ESP2**
V2	25	40	1.5	2.5	105	124
V3	14	26	1.2	2.2	80	113

Test ID	**Mn**		**Mo**		**Ni**		**Pb**	
	ESP1	**ESP2**	**ESP1**	**ESP2**	**ESP1**	**ESP2**	**ESP1**	**ESP2**
V2	1040	1290	6.2	9.7	81	102	61	91
V3	1130	1660	4.0	7.6	57	87	44	72

Appendix 4. The procedure for handling the blank samples of the particulate and gaseous fractions in the flue gases of plants UB and TB

The trace element concentrations in the particulate and gaseous fractions of flue gases are shown in Appendix 9. Some of the pre-handled filters stored in laboratory during the measurement campaign were used as laboratory blank filters. Some of the pre-handled filters taken to the measurement place and mounted in the sampling line and in the sampling point in the stack were used as field blank samples. The blank filters were digested and analysed with the real samples. The field blank samples were also made for the absorption solutions and rinsing solutions of the sampling probe. The solution blanks were made of 50–75 ml of the absorption solution, which was prepared for the measurement campaigns. Each of the solutions was analysed with the real samples. When the element contents in the blank samples were analysed repeatable over the detection limit, the element content was by first deducted from the values analysed in the real samples before further calculations.

In plants UB, TB and VB, the filters were digested with 3 M HNO_3 + 3 M HCl and analysed in Lab2. The solution enabled the analysis of all the element contents, including mercury, of each sample. However, it must be kept in mind that some of the true contents can be higher. This is seen in Table A4.1 in the case of plant TB, where in addition to the field blank filters as a quality assurance method, the commercial reference ash from coal burning was added to the filter and digested with the real samples. All the element contents of the reference material were determined as much too low, recovering only 30–90 % of the certified values. The incomplete dissolution resulting from the digestion of coal fly ash materials with quartz fibre filters using a mixture of HNO_3 and HCl was experimentally studied in the pre-tests of plant SB and published by Laitinen *et al.* (1996). The method used for the coal-fired power plants and for plant RB was not possible to use in plants UB, TB and VB.

The trace element contents determined in the filter samples in the flue gases of plants UB and VB are shown in Table A4.2 and A4.3, respectively. In plant UB, the field blank filters were coded as U01–U03. The field blank filter samples were significantly low compared to the real samples in the case of Cd, Mn and

Pb. The contents of As and Hg in all the samples were close to the detection limit and below. In the case of Cr, the value of 1.9 μg/sample can be seen in the blank test U03, which is even higher than the content in test U6. In the case of Ni, the contents in the blank tests were close to the real tests. This indicates the difficulties concerning the filter material (quartz fibre), and the digesting and analysis of Cr and Ni.

The particulate concentrations were calculated by first deducting the average of the blank tests (i.e. meanU0) from the analysis values in the samples and dividing with the sample flow through the filter. The high contents of Cr, Mn and Ni in test U1 stem from the problems in the ESP, which was noticed in the control room of the plant about 2 hours after starting the sampling period. The results of test U1 were eliminated from further calculations.

The field blank filter samples of plant TB, coded as T01–T04, were significantly low compared to the real samples in the cases of As, Cd, Cr, Hg, Mn, Ni and Pb. The contents of Cr in the field blank filters were over the detection limit: the mean value was deducted from the analysis results of the real samples. The contents of Mo in field blank filters were below the detection limit in three of four samples. Therefore, the contents of Mo in the real samples were not transformed.

The absorption solution samples of plants UB and TB were also analysed in Lab2. In plant UB, the contents of As, Hg and Pb in the field blank solution samples were below the detection limit. The contents of Cd and Mn in the field blank solutions of the first absorption bottles were between the content in the blank acids and the real samples. The value of the field blank solution was deducted from the analysis results of the real sample solutions in the first bottles before further calculations. The contents of Ni and Cr in the field blanks were also deducted from the analysis results of the samples.

In plant TB, the contents of As, Cd, Hg, Mn, Mo, Ni and Pb in the field blank samples were below the detection limit. The contents of Cr in the field blank solutions of both absorption bottles were between the content in the blank acids and the real samples, which was deducted from the results of the analysis of the sample solutions in the first bottles.

Table A4.1. Trace element contents in the quartz fibre thimble filters (i.e. T01 and T02) spiked with commercial reference ash from coal burning (NIST NBS 1633a) (µg/g).

	T01	T02	Certified content in ash
As	122	103	145±15
Cd	0.57	0.59	1.00±0.15
Cr	71	62	196±6
Hg	< 0.8	< 0.8	0.16±0.01
Mn	86	80	179±8
Mo	27	27	(29)
Ni	61	52	127±4
Pb	40	37	72.4±0.4

Table A4.2. Trace element contents in flue gas particles collected on the quartz fibre thimble filter from plant UB (µg/filter) a) before and b) after deducting the values of the blanks (i.e. Mean U0).

a)

Test ID	Sample flow Nm³	As	Cd	Cr	Hg	Mn	Ni	Pb
U1	2.460	1.80	7.1	16.5	0.12	4600	14.40	8.5
U2	2.451	< 0.5	1.4	3.2	< 0.1	300	5.50	5.4
U3	2.508	< 0.5	1.2	12.4	< 0.1	300	17.50	7.4
U4	2.566	0.62	1.8	2.2	< 0.1	320	6.20	4.3
U5	2.541	0.60	1.8	2.5	< 0.1	460	4.90	6.0
U6	2.530	< 0.5	1.4	1.6	< 0.1	320	4.2	3.8
U01	0	< 0.5	0.49	0.48	< 0.1	0.43	3.20	0.69
U02	0	< 0.5	0.29	0.71	< 0.1	1.30	1.30	0.64
U03	0	< 0.5	0.59	1.90	< 0.1	0.39	3.30	0.76
MeanU0		**0**	**0.46**	**1.03**	**0**	**0.71**	**2.60**	**0.70**

b)

Test ID	Sample flow Nm³	As	Cd	Cr	Hg	Mn	Ni	Pb
U1	2.460	1.8	6.6	15.5	0.12	4599	11.8	7.8
U2	2.451	< 0.5	0.9	2.2	< 0.1	299	2.9	4.7
U3	2.508	< 0.5	0.7	11.4	< 0.1	299	14.9	6.7
U4	2.566	0.62	1.3	1.2	< 0.1	319	3.6	3.6
U5	2.541	0.60	1.3	1.5	< 0.1	459	2.3	5.3
U6	2.530	< 0.5	0.9	0.6	< 0.1	319	1.6	3.1

Table A4.3. Trace element contents in flue gas particles collected on the quartz fibre thimble filter from plant TB (µg/filter) a) before and b) after deducting the values of the blanks (i.e. Mean T0).

a)

Test ID	Sample flow Nm^3	As	Cd	Cr	Hg	Mn	Mo	Ni	Pb
T1	3.590	6.10	0.3	14.0	3.40	212	2.1	8.30	7.2
T2	3.426	4.20	0.2	15.0	0.92	140	2.7	6.70	5.1
T3	3.412	4.40	0.2	21.0	0.58	131	1.4	5.50	4.5
T4	3.390	4.20	0.3	12.0	1.20	189	1.2	7.00	5.5
T5	3.406	3.60	0.2	9.8	1.50	181	1.1	8.40	6.2
T6	3.523	3.50	0.28	10.0	0.93	222	1.1	7.20	6.1
T01	0	<1	<0.02	0.60	<0.2	<0.5	<0.5	<2	<1
T02	0	<1	<0.02	3.5	<0.2	<0.5	1.6	<2	<1
T03	0	<1	<0.02	1.9	<0.2	<0.5	<0.5	<8	<1
T04	0	<1	<0.02	2.3	<0.2	<0.5	<0.5	<2	<1
MeanT0		**0**	**0**	**2.08**	**0**	**0**	**0**	**0**	**0**

b)

Test ID	Sample flow Nm^3	As	Cd	Cr	Hg	Mn	Mo	Ni	Pb
T1	3.590	6.10	0.3	11.9	3.40	212	2.1	8.30	7.2
T2	3.426	4.20	0.2	12.9	0.92	140	2.7	6.70	5.1
T3	3.412	4.40	0.2	18.9	0.58	131	1.4	5.50	4.5
T4	3.390	4.20	0.3	9.9	1.20	189	1.2	7.00	5.5
T5	3.406	3.60	0.2	7.7	1.50	181	1.1	8.40	6.2
T6	3.523	3.50	0.28	7.9	0.93	222	1.1	7.20	6.1

Appendix 5. Comments on the trace element contents determined in the flue gases of plant RB with method MV and ME

The trace element concentrations in the flue gases of plant RB were measured with two different methods in parallel. The first sampling method was the one developed by VTT and IVO for the mass balance studies (see closer section 5.1.2), which has been used in all the measurement campaigns of this thesis. The quartz fibre thimble filters were digested in Lab2 by refluxing with nitric acid and hydrochloric acid for mercury analysis. Mercury was analysed using the cold vapour atomic absorption method (CVAAS) in Lab2. For the other trace element analysis, another series of quartz fibre thimble filters were digested in Lab5 with nitric acid, hydrochloric acid and hydrofluoric acid under microwave heating with boric acid addition. The contents of As, Cd, Cr, Mn, Ni and Pb were analysed using graphite furnace atomic absorption spectrometry (GFAAS). The gaseous elements were analysed in Lab2 from the probe rinsing samples and from the absorption solution samples. The absorbing solution for Hg was 4 w-% $K_2Cr_2O_7$/20 w-% HNO_3 and for other elements 38 w-% HNO_3. The results of this method in the case of plant RB are shown in Table A5.1 with the identifying codes of MV.

The second method used in plant RB was according to the EPA Method 29 with specific sampling, digestion and analysis methods. A flue gas sample was withdrawn isokinetically from the stack. The particulate fractions were collected in the probe and on a heated quartz fibre thimble filter. The gaseous fraction was then collected in an aqueous acidic solution of hydrogen peroxide, i.e. 5 v-% HNO_3/10 v-% H_2O_2, (analysed for all metals including Hg) and an aqueous acidic solution of potassium permanganate, i.e. 4 v-% $KMnO_4$/10 v-% H_2SO_4, (analysed only for Hg). The recovered samples were digested, and appropriate fractions were analysed for Hg by cold vapour atomic absorption spectroscopy (CVAAS), and for other elements by atomic absorption spectroscopy (AAS). The results of this method are shown in Table A5.1 with the identifying codes of ME.

The trace element concentrations in the particulate fractions of tests R1–R5 had significant differences based on the methods used. The detection limits of As, Cr and Mn for method ME were higher than the concentrations detected for method MV. The concentrations of Cd were determined as consistently higher with method ME. The concentrations of Hg and Pb were determined as consistently lower with method ME. The detection limits of both methods were too high for the low concentrations of Ni.

The trace element concentrations in the gaseous fractions of tests R1–R5 sampled with methods MV and ME also revealed significant differences. The detection limits of both methods were too high for the low concentrations of As. The concentrations of Cd with method ME were determined below the detection limit, which was lower than the detected values for method MV. The concentrations of Cr were determined higher with method ME in tests R2, R3 and R5. They were determined lower in test R1 and R4 compared to method MV. The concentrations of Hg were determined very equal with two methods in tests R4 and R5, but showed significant differences in tests R1–R3. The detection limit of method MV was high compared to the low concentrations of Mn determined with method ME. The concentrations of Ni were determined consistently higher with method ME in tests R2–R5. However, it was somewhat lower in test R1. The detection limit of method MV was higher than the low concentrations of Pb determined with method ME.

The total trace element concentrations in the flue gases are also shown in Table A5.1. There are significant differences in each test between the methods, especially in tests R3 and R4. The mean total concentration of As determined with method MV was 31 $\mu g/m^3$. This fits well with the approximated mean (all tests were below the detection limit) concentration determined with ME. The mean concentrations of Cd and Hg determined with methods ME and MV were very close to each other, too. There were remarkable differences in tests R3 and R4 in the case of Cd, and in tests R1–R3 in the case of Hg. The total concentration of Cr was determined below the high detection limit with method ME. The noticeable concentrations were far below the concentrations determined with method MV. The total concentrations of Mn were determined below the detection limit for both methods, except in test R4. The noticeable concentrations were significantly lower in method ME. The total concentrations of Ni were determined below the detection limit with both methods. The total concentrations of Pb were determined below the detection limit with method MV for all the tests. The noticeable concentrations of Pb determined with method MV were close to the values that were determined with method ME in tests R1–R3. As a conclusion, the significant differences between the two methods were found in determining the particulate fraction of Cd, Hg and Pb as well as in the gaseous fraction of Cd, Cr, Hg and Ni.

For the mass balance calculations the results of method MV were chosen, for the following reasons. The detection limit of method ME was high for particulate

As, Cr, Mn and Ni compared to the concentrations detected with method MV. The digestion and analysis method of MV was successfully verified experimentally with reference fly ash samples from coal burning in the pre-tests of the coal-fired power plant (Laitinen *et al.*, 1996).

Table A5.1. The trace element concentrations in the flue gases from plant RB (i.e. tests R1–R5) determined with methods ME and MV (µg/Nm^3, dry gas).

	As		Cd		Cr		Hg	
	ME	**MV**	**ME**	**MV**	**ME**	**MV**	**ME**	**MV**
R1								
Particulate	<20	9.3	0.3	0.1	< 20	1.8	0.1	0.3
Gaseous	< 5	< 1.3	< 0.05	0.35	2.3	3.6	1.7	0.73
Total	< 25	9.3	0.3	0.45	< 22	5.4	1.8	1.0
R2								
Particulate	<20	28.7	0.3	0.1	< 20	1.6	< 0.1	< 0.1
Gaseous	< 5	< 1.3	< 0.05	0.22	0.96	0.33	2.0	2.5
Total	< 25	29	0.3	0.32	< 21	1.9	2.0	2.5
R3								
Particulate	52.8	65.7	0.7	0.1	< 20	3.5	< 0.1	0.5
Gaseous	< 5	4.7	< 0.05	< 0.03	0.92	0.38	1.5	2.3
Total	< 58	70	0.7	0.1	< 21	3.9	1.5	2.8
R4								
Particulate	< 20	21.8	0.4	0.3	< 20	4.6	< 0.1	0.1
Gaseous	< 5	< 1.3	< 0.05	0.68	0.41	1.0	0.59	0.57
Total	< 25	22	0.4	0.98	< 21	5.6	0.59	0.67
R5								
Particulate	< 20	21.9	0.3	0.2	< 20	4.7	< 0.1	0.1
Gaseous	< 5	< 1.3	< 0.05	< 0.03	0.56	0.18	0.55	0.53
Total	< 25	22	0.3	0.2	< 21	4.9	0.55	0.63

	Mn		Ni		Pb	
	ME	**MV**	**ME**	**MV**	**ME**	**MV**
R1						
Particulate	< 40	20.5	< 300	< 30	4	5.2
Gaseous	1.4	< 20	2.8	3.3	0.3	< 3
Total	< 41	< 41	< 303	< 33	4.3	< 8
R2						
Particulate	< 40	17.9	< 300	< 30	4.3	4.9
Gaseous	0.45	< 20	1.9	0.36	0.4	< 3
Total	< 41	< 38	< 302	< 31	4.7	< 8
R3						
Particulate	< 40	43.2	< 300	< 30	8.9	12
Gaseous	0.72	< 20	1.1	< 0.4	0.35	< 2
Total	< 41	< 63	< 301	< 31	9.3	< 14
R4						
Particulate	41.5	56.0	< 300	< 30	5.1	17
Gaseous	0.44	< 20	1.1	< 0.4	< 0.7	< 3
Total	42	< 76	< 301	< 31	< 6	< 20
R5						
Particulate	< 40	50.7	< 300	< 30	4.4	15.4
Gaseous	1.1	< 20	1.2	< 0.5	< 0.7	< 3
Total	< 41	< 71	< 301	< 31	< 5	< 18

Appendix 6. The process parameters of each test for the coal-, bark- and peat-fired power plants

a) Plant HB, b) plant SB, c) plant MB, d) plant UB, e) plant RB, f) plant TB and g) plant VB

a) plant HB*: [a] on dry-weight basis, [b] in dry flue gas, [c] on dry-weight basis except water streams, [d] deviation: (maximum content − minimum content)/2.*

				Coal combustion					
Test ID		**H1**	**H2**	**H3**	**H4**	**H5**	**H6**	**Mean**	*Dev(d*
Main fuel	t/h(a	61.8	57.8	60.7	56.8	56.2	57.1	**58.4**	*2.8*
Fuel effect	MW	331	328	341	334	334	338	**334**	*6.5*
Gross load	MW	309	305	316	313	313	317	**312**	*6.0*
Fuel									
Moisture	m-%	15.9	14.3	14.3	13.7	14.0	14.4	**14.4**	*1.1*
LHV	MJ/kg(a	23.66	23.53	24.16	24.46	24.92	24.88	**24.27**	*0.70*
Ash	%(a	23.7	24.3	22.7	22.4	21.2	21.2	**22.6**	*1.6*
Volatiles	%(a	29.8	29.5	29.6	29.1	29.6	29.7	**29.6**	*0.4*
Sulphur	%(a	1.25	1.27	1.19	1.06	1.01	1.10	**1.15**	*0.13*
Flue gases upstream of FGD(b									
Flow rate	x10^3 Nm^3/h	498	497	467	512	486	510	**495**	*23*
Temperature	°C	143	144	144	142	140	142	**143**	*2*
Particles	mg/Nm^3	262	288	324	272	286	262	**282**	*31*
SO_2	ppm	978	836	847	706	703	715	**797**	*137*
NO_x	ppm	201	198	195	206	218	211	**205**	*11*
O_2	%	6.7	7.2	6.4	6.9	7.3	7.3	**7.0**	*0.5*
CO	ppm	646	450	1568	384	336	224	**601**	*672*
Flue gases downstream of FGD(b									
Flow rate	x10^3 Nm^3/h	498	497	467	512	486	510	**495**	*23*
Temperature	°C	88	86	86	86	87	86	**87**	*1.0*
Particles	mg/Nm^3	< 5	< 2	< 2	< 2	< 2	< 2	**< 2**	*n*
SO_2	ppm	107	99	100	99	82	82	**95**	*13*
NO_x	ppm	116	187	176	189	202	190	**177**	*43*
O_2	%	6.6	7.0	6.3	6.8	7.2	7.1	**6.8**	*0.5*
CO	ppm	600	660	1460	280	210	170	**563**	*645*
Other mass flows(c									
Lime	t/h	1.3	1.3	1.3	1.3	1.3	1.3	**1.3**	*0*
Sea water	m^3/h	12.4	12.4	12.4	12.4	12.4	12.4	**12.4**	*0*
Town water	m^3/h	5	5	5	5	5	5	**5**	*0*
Bottom ash	kg/h	1230	1210	1180	1100	1030	1040	**1132**	*100*
PFA	t/h	11.1	10.9	10.7	9.9	9.3	9.4	**10.2**	*0.9*
FGD coarse product	t/h	0.52	0.52	0.52	0.52	0.52	0.52	**0.52**	*0*
FGD end-product	t/h	4.68	4.68	4.68	4.68	4.68	4.68	**4.68**	*0*

b) Plant SB: *[a] on dry-weight basis, [b] in dry flue gas, [c] on dry-weight basis except water streams, [d] deviation: (maximum content − minimum content)/2.*

			Coal combustion						
Test ID		**S1**	**S2**	**S3**	**S4**	**S5**	**S6**	**Mean**	***Dev(d***
Main fuel	t/h(a	62.5	62.8	59.9	61.9	62.4	63.4	**62.2**	*1.8*
Fuel effect	MW	484	489	472	473	478	488	**481**	*9*
Gross load	MW	457	461	446	447	452	461	**454**	*8*
Fuel									
Moisture	m-%	8.9	8.8	8.8	8.8	8.9	8.7	**8.8**	*0.1*
LHV	MJ/kg(a	29.61	29.72	29.57	30.07	29.70	29.67	**29.72**	*0.25*
Ash	%(a	12.4	11.9	12.1	10.8	11.4	11.5	**11.7**	*0.8*
Volatiles	%(a	29.3	29.4	29.2	29.7	29.5	29.5	**29.4**	*0.3*
Sulphur	%(a	0.87	0.86	0.83	0.85	0.86	0.74	**0.84**	*0.07*
Flue gases upstream of FGD(b									
Flow rate	x10^3 Nm^3/h	630	641	619	619	626	626	**627**	*11*
Temperature	°C	132	136	131	130	129	132	**132**	*4*
Particles	mg/Nm^3	16.6	20.1	11.4	29.6	24.4	23.8	**21**	*9*
SO_2	ppm	524	503	503	546	545	549	**528**	*23*
NO_x	ppm	303	277	290	233	246	262	**269**	*35*
O_2	%	5.3	5.3	5.3	5.0	5.0	4.9	**5.1**	*0.2*
CO	ppm	78	71	88	87	82	79	**81**	*9*
Flue gases downstream of FGD(b									
Flow rate	x10^3 Nm^3/h	634	644	637	630	641	641	**638**	*7*
Temperature	°C	76	76	76	75	75	76	**76**	*1*
Particles	mg/Nm^3	< 5	< 5	< 5	< 5	< 5	< 5	**< 5**	*n*
SO_2	ppm	95	82	82	85	89	84	**86**	*7*
NO_x	ppm	280	288	283	m	254	m	**276**	*17*
O_2	%	5.5	5.8	5.6	5.3	5.4	5.4	**5.5**	*0.3*
Other mass flows(c									
Lime	t/h	1.0	1.1	1.0	1.1	1.1	1.1	**1.0**	*0.1*
Sea water	m^3/h	16.5	17.9	m	m	16	16.5	**16.7**	*0.9*
Bottom ash	kg/h	190	195	185	190	190	195	**191**	*5*
PFA	t/h	7.5	7.6	7.2	7.5	7.5	7.6	**7.5**	*0.2*
FGD product	t/h	1.92	2.04	1.95	2.02	2.10	2.04	**2.01**	*0.1*

c) Plant MB*: [a] on dry-weight basis, [b] in dry flue gas, [c] on dry-weight basis except water streams, [d] deviation: (maximum content– minimum content)/2.*

		Coal combustion				
Test ID		**M2**	**M3**	**M4**	**Mean**	*Dev(d*
Main fuel	t/h(a	154	152	153	**153**	*1*
Fuel effect	MW	1140	1126	1133	**1133**	*7*
Gross load	MW	590	583	587	**587**	*4*
Fuel						
Moisture	m-%	10.8	11.4	10.1	**10.8**	*0.7*
LHV	MJ/kg(a	29.60	28.85	29.36	**29.27**	*0.38*
Ash	%(a	11.20	13.85	12.19	**12.41**	*1.33*
Volatiles	%(a	30.01	28.56	29.79	**29.45**	*0.73*
Sulphur	%(a	0.62	0.73	0.70	**0.68**	*0.06*
Flue gases upstream of FGD(b						
Flow rate	x10^3 Nm^3/h	1 573	1 571	1 536	**1 560**	*19*
Temperature	°C	128	129	129	**128**	*0.5*
Particles	mg/Nm^3	8	9	15	**10**	*3.5*
Flue gases downstream of FGD(b						
Flow rate	x10^3 Nm^3/h	1 583	1 571	1 536	**1 563**	*24*
Temperature	°C	77	77	78	77	*0.5*
Particles	mg/Nm^3	7	6	3	**5**	*2*
Other mass flows(c						
Lime	t/h	4.8	5.7	5.9	**5.5**	*0.6*
Sea water	m^3/h	55.6	55.2	56.2	**55.7**	*0.5*
Town water	m^3/h	7.7	7.0	7.4	**7.4**	*0.4*
Bottom ash	kg/h	1720	2101	1861	**1894**	*191*
Ecoash	kg/h	516	630	558	**568**	*57*
PFA	t/h	15	18	16	**16**	*1.7*
Gypsum	t/h	8.0	9.5	9.6	**9.0**	*0.8*
Waste water	m^3/h	12.1	10.8	8.1	**10.3**	*2.0*
Filter cake	kg/h	157	162	151	**157**	*6*

***d) Plant UB**: m missing data, ^{a} on dry-weight basis, ^{b} in dry flue gas, ^{d} deviation: (maximum content− minimum content)/2.*

		Bark combustion					Bark and sludge co-combustion				
Test ID		**U1**	**U2**	**U3**	**Mean**	***Dev(d***	**U4**	**U5**	**U6**	**Mean**	***Dev***
Main fuel	t/h(a	15.0	15.5	15.3	**15.3**	*0.3*	12.0	12.8	12.3	**12.4**	*0.4*
Added fuel	t/h(a	0	0	0	**0**	*0*	0.9	0.9	0.9	**0.9**	*0*
Fuel effect	MW	99.2	103	100	**101**	*2*	86.7	104	93.5	**95**	*8.7*
Gross load	MW	67	70	68	**68**	*2*	59	71	64	**65**	*6*
Main fuel											
Moisture	m-%	44.3	45.4	44.8	**44.8**	*0.6*	49.5	42.0	m	**45.8**	*3.8*
LHV	MJ/kg(a	20.87	20.88	20.77	**20.84**	*0.05*	20.79	21.99	m	**21.39**	*0.60*
Ash	%(a	1.7	1.8	1.8	**1.8**	*0.1*	2.6	1.8	m	**2.2**	*0.4*
Volatiles	%(a	81.2	80.2	78.6	**80.0**	*1.3*	77.6	80.3	m	**79.0**	*1.4*
Sulphur	%(a	0.02	0.03	0.03	**0.03**	*0.01*	0.03	0.03	m	**0.03**	*0*
Added fuel											
Moisture	m-%						84.3	83.7	m	**84.0**	*0.3*
LHV	MJ/kg(a						18.49	18.67	m	**18.58**	*0.09*
Ash	%(a						14.2	14.7	m	**14.5**	*0.3*
Volatiles	%(a						69.6	69.2	m	**69.4**	*0.2*
Sulphur	%(a						1.08	1.20	m	**1.14**	*0.06*
Fuel mixture											
LHV	MJ/kg(a	20.87	20.88	20.77	**20.84**	*0.05*	19.63	21.24	20.34	**20.40**	*0.81*
Ash	%(a	1.7	1.8	1.8	**1.8**	*0.1*	3.7	2.7	3.8	**3.4**	*0.6*
Volatiles	%(a	81.2	80.2	78.6	**80.0**	*1.3*	77.7	79.5	76.5	**77.9**	*1.5*
Sulphur	%(a	0.02	0.03	0.03	**0.03**	*0.01*	0.07	0.09	0.08	**0.08**	*0.01*
Flue gases(b											
Flow rate	x10^3 Nm^3/h	151	148	151	**150**	*2*	155	148	130	**144**	*13*
Temperature	°C	180	177	174	**177**	*3*	173	182	178	**178**	*5*
Particles	mg/Nm^3	m	13	15	**14**	*1*	12	17	9	**13**	*4*
SO$_2$	ppm	2	1	5	**3**	*2*	6	9	5	**7**	*2*
NO$_x$	ppm	70	80	70	**73**	*5*	70	110	80	**87**	*20*
O$_2$	%	6.1	5.9	5.7	**5.9**	*0.2*	7.0	6.2	6.1	**6.4**	*0.5*
CO	ppm	230	300	390	**307**	*80*	90	180	200	**157**	*55*
Bottom ash	kg/h(a	105	121	95	**107**	*13*	89	106	212	**136**	*62*
Ecoash	kg/h(a	26	30	24	**27**	*3*	22	27	53	**34**	*16*
PFA	t/h(a	0.30	0.32	0.31	**0.31**	*0.01*	0.42	0.42	0.42	**0.42**	*0*
Sea-sand	kg/h(a	94	94	94	**94**	*0*	52	52	52	**52**	*0*

***e) Plant RB**: [a] on dry-weight basis, [b] in dry flue gas, [d] deviation: (maximum content − minimum content)/2.*

				Peat combustion				
Test ID		**R1**	**R2**	**R3**	**R4**	**R5**	**Mean**	***Dev(d***
Main fuel	t/h(a	43.8	44.9	46.4	52.7	52.8	**48.1**	*4.5*
Fuel effect	MW	248	255	263	298	296	**272**	*25*
Gross load	MW	191	202	191	219	190	**199**	*14.5*
Main fuel								
Moisture	m-%	50.4	48.5	45.8	43.7	46.6	**47.0**	*3.4*
LHV	MJ/kg(a	20.43	20.43	20.41	20.38	20.19	**20.37**	*0.12*
Ash	%(a	8.7	9.0	9.2	7.8	8.6	**8.7**	*0.7*
Volatiles	%(a	64.1	64.0	63.8	64.7	64.2	**64.2**	*0.5*
Sulphur	%(a	0.40	0.36	0.36	0.49	0.53	**0.43**	*0.09*
Flue gases(b								
Flow rate	x10^3 Nm^3/h	480	460	510	530	540	**504**	*40*
Temperature	°C	117	118	120	126	123	**121**	*5*
Particles	mg/Nm^3	17	22	58	71	69	**47**	*27*
SO_2	ppm	368	331	330	446	472	**389**	*71*
NO_x	ppm	190	179	188	206	202	**193**	*14*
O_2	%	6.3	6.3	6.2	6.1	6.3	**6.2**	*0.1*
Bottom ash	kg/h(a	147	151	157	262	263	**196**	*58*
PFA	t/h(a	3.66	3.76	3.89	5.41	5.43	**4.43**	*0.88*
Water	10^{-3} m^3/h	90	90	90	90	90	**90**	*0*
Sea-sand	kg/h(a	28	28	28	28	57	**34**	*15*

f) Plant TB *(sand flow was 0 kg/h in all the tests): m missing data,* ^{a} *on dry-weight basis,* ^{b} *in dry flue gas,* ^{d} *deviation: (maximum content–- minimum content)/2.*

		Peat combustion					Peat and wood-chips co-combustion				
Test ID		**T1**	**T2**	**T3**	**Mean**	***Dev(d***	**T4**	**T5**	**T6**	**Mean**	***Dev***
Main fuel	t/h(a	60.6	59.2	*59.5*	**59.8**	*0.7*	43.7	43.6	45.3	**44.2**	*0.8*
Added fuel	t/h(a	0	0	0	**0**	*0*	18.7	18.7	19.4	**18.9**	*0.4*
Fuel effect	MW	316	312	313	**313**	*2*	313	311	316	**313**	*3*
Gross load	MW	288	286	287	**287**	*1*	286	286	288	**287**	*1*
Main fuel											
Moisture	m-%	48.3	*46.5*	46.6	**47.1**	*0.9*	50.0	48.6	49.2	**49.3**	*0.7*
LHV	MJ/kg(a	21.06	21.1	21.05	**21.07**	*0.03*	m	21.59	21.24	**21.4**	*0.2*
Ash	%(a	6	5.9	6.4	**6.1**	*0.3*	m	6.0	5.9	**6.0**	*0.05*
Volatiles	%(a	*67.7*	*67.6*	*67.9*	**67.7**	*0.2*	m	68.4	68.7	**68.6**	*0.1*
Sulphur(1	%(a	0.22	0.23	0.22	**0.22**	*0.01*	m	0.22	0.21	**0.22**	*0.01*
Added fuel											
Moisture	m-%						53.4	53.1	55.0	**53.8**	*0.9*
LHV	MJ/kg(a						m	19.34	19.39	**19.37**	*0.03*
Ash	%(a						m	0.4	0.4	**0.4**	*0*
Volatiles	%(a						m	85.4	85.7	**85.6**	*0.1*
Sulphur	%(a						m	0.01	0.02	**0.015**	*0.005*
Fuel mixture											
LHV	MJ/kg(a	21.06	21.1	21.05	**21.07**	*0.03*	20.54	20.47	20.27	**20.43**	*0.14*
Ash	%(a	6.0	5.9	6.4	**6.1**	*0.3*	4.7	3.3	3.7	**3.9**	*0.7*
Volatiles	%(a	*67.7*	*67.6*	*67.9*	**67.7**	*0.2*	72.2	76.1	75.1	**74.5**	2.0
Sulphur	%(a	0.22	0.23	0.22	**0.22**	*0.01*	0.15	0.11	0.15	**0.14**	*0.02*
Flue gases(b											
Flow rate Nm^3/h	x10^3	445	428	475	**450**	*23*	363	400	442	**402**	*40*
Temperature	°C	141	139	140	**140**	*1*	140	140	142	**141**	*1*
Particles	mg/Nm^3	33	24	18	**25**	*8*	33	24	49	**35**	*13*
SO$_2$	ppm	174	191	181	**182**	9	169	162	174	**168**	6
NO$_x$	ppm	96	109	113	**106**	9	81	93	94	**89**	*7*
O$_2$	%	m	m	m	**3.5**	*m*	m	m	m	**2.8**	*m*
CO	ppm	m	m	m	**70**	*m*	m	m	m	**134**	*m*
Bottom ash	kg/h(a	*775*	*425*	*1048*	**749**	*312*	*543*	*195*	*532*	**423**	*174*
Ecoash	kg/h(a	234	245	214	**231**	*16*	245	263	256	**255**	9
PFA	t/h(a	4.46	4.66	4.06	**4.39**	*0.30*	4.66	4.99	4.86	**4.83**	*0.17*

***g) Plant VB:** (sand flow was 0 kg/h in all the tests) [a] on dry-weight basis, [b] in dry flue gas, [d] deviation: (maximum content − minimum content)/2.*

		Peat combustion				Peat and sawdust co-combustion			
Test ID		**V1**	**V2**	**Mean**	***Dev*[d]**	**V3**	**V4**	**Mean**	***Dev***
Main fuel	t/h[a]	64.1	64.4	**64.3**	*0.2*	49.4	49.5	**49.5**	*0.1*
Added fuel	t/h[a]	0	0	**0**	*0*	18.1	17.7	**17.9**	*0.2*
Fuel effect	MW	331	332	**332**	*0.5*	333	334	**334**	*0.5*
Gross load	MW	299	299	**299**	*0*	299	299	**299**	*0*
Main fuel									
Moisture	m-%	40.2	40.1	**40.2**	*0.1*	43.8	41.8	**42.8**	*1.0*
LHV	MJ/kg[a]	20.25	20.22	**20.24**	*0.02*	20.25	20.31	**20.28**	*0.03*
Ash	%[a]	3.8	4.3	**4.1**	*0.3*	3.6	3.3	**3.5**	*0.2*
Volatiles	%[a]	70.1	68.7	**69.4**	*0.7*	69.4	69.6	**69.5**	*0.1*
Sulphur	%[a]	0.14	0.14	**0.14**	*0*	0.14	0.14	**0.14**	*0*
Added fuel									
Moisture	m-%					55.8	56.8	**56.3**	*0.5*
LHV	MJ/kg[a]					19.30	19.19	**19.25**	*0.05*
Ash	%[a]					0.20	0.30	**0.25**	*0.05*
Volatiles	%[a]					86.7	85.8	**86.3**	*0.5*
Sulphur	%[a]					0.03	0.03	**0.03**	*0*
Fuel mixture									
LHV	MJ/kg[a]	20.25	20.22	**20.24**	*0.02*	19.99	20.02	**20.00**	*0*
Ash	%[a]	3.8	4.3	**4.1**	*0.3*	2.7	2.5	**2.6**	*0.1*
Volatiles	%[a]	70.1	68.7	**69.4**	*0.7*	74.1	73.7	**73.9**	*0.2*
Sulphur	%[a]	0.14	0.14	**0.14**	*0*	0.11	0.11	**0.11**	*0*
Flue gases[b]									
Flow rate	x10^3 Nm^3/h	456	476	**466**	*9.7*	480	465	**473**	*7.7*
Temperature	°C	135	135	**135**	*0*	135	135	**135**	*0*
Particles	mg/Nm^3	5.3	5.5	**5.4**	*0.1*	5.2	6.0	**5.6**	*0.4*
SO_2	ppm	118	125	**122**	*4*	93	96	**94**	*1.4*
NO_x	ppm	115	100	**107**	*7*	99	100	**100**	*0.4*
O_2	%	6.4	6.3	**6.4**	*0.1*	6.3	6.4	**6.4**	*0.1*
CO	ppm	3.0	6.0	**4.5**	*1.5*	4.0	4.0	**4.0**	*0*
Bottom ash	kg/h[a]	870	870	**870**	*0*	460	460	**460**	*0*
PFA	t/h[a]	1.76	1.76	**1.76**	*0*	2.07	2.07	**2.07**	*0*

Appendix 7. The trace element contents in the mass streams of the coal-fired power plants

Plant HB	**Content**	**As**		**Be**		**Cd**		**Cr**		**Hg**		**Mn**		**Ni**		**Pb**		**Tl**		**Zn**	
		Mean(	***Dev(***	**Mean**	***Dev***	**Mean**	***Dev***	**Mean**	***Dev***	**Mean**	***Dev***	**Mean**	***Dev***	**Mean**	***Dev***	**Mean**	***Dev***	**Mean**	***Dev***	**Mean**	***Dev***
Coal	mg/kg(a	6.3	*1.0*	3.0	*0.5*	0.23	*0.03*	39	*1*	0.15	*0.06*	190	*15*	26	*3*	33	*8*	0.93	*0.41*	69	*13*
Lime	mg/kg(a	1.0	*0.4*	< 0.4	*n*	0.12	*0.05*	6.1	*0.4*	0.03	*0.02*	190	*5*	3.8	*2.1*	2.1	*0.3*	0.28	*0.04*	9.8	*2.3*
Sea water	µg/l	< 5	*n*	< 5	*n*	< 0.5	*n*	3.5	*4.3*	< 0.1	*n*	25	*6*	3.4	*3.9*	< 5	*n*	< 6	*n*	< 0.01	*n*
Town water	µg/l	< 5	*n*	< 5	*n*	< 0.2	*n*	< 2	*n*	< 0.1	*n*	3.0	*0.7*	< 2	*n*	< 5	*n*	< 5	*n*	< 0.01	*n*
Bottom ash	mg/kg(a	5.2	*1.1*	11	*1*	0.14	*0.06*	1050	*470*	0.26	*0.18*	940	*60*	800	*180*	53	*9*	0.85	*0.21*	120	*5*
PFA	mg/kg(a	32	*3*	14	*2*	1.1	*0.2*	150	*15*	0.38	*0.06*	790	*20*	70	*6*	190	*20*	4.8	*0.8*	330	*55*
Flue gas upstream of FGD(b																					
Particulate	µg/Nm^3	46	*21*	3.5	*1.7*	1.1	*0.6*	66	*38*	0.19	*0.13*	270	*170*	33	*23*	170	*110*	< 16	*n*	280	*130*
Gaseous	µg/Nm^3	< 1.7	*n*	< 0.8	*n*	0.09	*0.08*	< 2.3	*n*	2.3	*1.1*	< 0.2	*n*	< 1.2	*n*	< 1.8	*n*	< 1.7	*n*	11	*5*
FGD coarse product	mg/kg(a	3.8	*0.5*	0.65	*0.15*	0.18	*0.05*	5.9	*1.1*	0.13	*0.08*	110	*5*	7.0	*2.0*	13	*3*	0.55	*0.16*	29	*7*
FGD	mg/kg(a	5.6	*2.4*	0.63	*0.05*	0.20	*0.02*	5.8	*3.2*	0.18	*0.07*	110	*5*	6.5	*1.0*	17	*3*	0.73	*0.05*	35	*3*
Flue gas downstream of																					
Particulate	µg/Nm^3	< 0.13	*n*	< 0.04	*n*	< 0.01	*n*	0.11	*0.14*	0.002	*0.001*	0.40	*0.26*	< 0.02	*n*	0.03	*0.04*	< 0.08	*n*	0.7	*0.8*
Gaseous	µg/Nm^3	< 1.9	*n*	< 0.9	*n*	0.07	*0.03*	< 2.5	*n*	0.11	*0.02*	0.20	*0.10*	< 1.2	*n*	< 2.2	*n*	< 1.9	*n*	52	*29*

[a] on dry-weight basis
[b] in dry flue gas, NTP
[c] mean of tests H1–H6
[d] deviation: [(maximum of tests H1–H6) – (minimum of tests H1–H6)] /2
n: not possible to calculate the deviation

Plant SB	**Conte**	**As**		**Be**		**Cd**		**Co**		**Cr**		**Cu**		**Hg**		**Mn**		**Ni**		**Pb**		**Se**		**Tl**	
		Mean	***Dev(***	**Mean**	***Dev***	**Mea**	***De***	**Mea**	**Dev**	**Mea**	***Dev***	**Mea**	***De***	**Mea**	***Dev***	**Mea**	***Dev***	**Mea**	***Dev***	**Mea**	***Dev***	**Mea**	***Dev***	**Mea**	***Dev***
Coal	mg/k	4.1	*0.1*	1.3	*0.2*	0.18	*0.0*	8.8	*1.7*	29	*4*	23	*2*	0.08	*0.02*	92	*12*	31	*3*	18	*1*	0.9	*0.2*	< 0.5	*n*
Lime	mg/k	2.7	*0.1*	< 0.1	*n*	0.09	*0.0*	1.6	*0.3*	9.5	*1.2*	15	*0.5*	<	*n*	170	*0*	5.5	*0.7*	2.4	*0.2*	< 20	*n*	0.80	*0.13*
Sea water	µg/l	< 4	*n*	0.08	*0.03*	0.17	*0.0*	< 0.8	*n*	0.53	*0.10*	1.7	*0.8*	< 1	*n*	7.1	*1.3*	< 0.7	*n*	4.5	*0.5*	2.1	*0.7*	1.8	*0.7*
Bottom	mg/k	< 10	*n*	9.2	*0.6*	0.17	*0.0*	53	*10*	820	*600*	130	*10*	<	*n*	890	*100*	790	*530*	41	*2*	< 2	*n*	0.61	*0.13*
PFA	mg/k	39	*2*	13	*1*	1.5	*0.6*	70	*7*	200	*16*	180	*2*	0.31	*0.05*	820	*50*	250	*10*	174	*17*	5.6	*1.3*	3.1	*0.3*
Flue gas upstream of FGD(b																									
Particulat	µg/N	3.5	*0.6*	0.36	*0.10*	0.15	*0.0*	2.8	*0.3*	9.0	*1.3*	8.6	*2.8*	0.07	*0.01*	15	*4*	8.7	*2.0*	11	*2*	3.3	*1.1*	0.53	*0.16*
Gaseous	µg/N	1.6	*0.2*	0.49	*0.03*	0.42	*0.4*	0.89	*0.13*	2.4	*1.3*	3.4	*0.7*	4.1	*0.4*	64	*44*	1.5	*0.1*	1.5	*0.7*	13	*0.1*	2.2	*1.0*
FGD	mg/k	2.5	*0.3*	< 0.1	*n*	0.09	*0.0*	1.5	*0.1*	6.7	*1.0*	11	*1*	0.18	*0.07*	83	*5*	2.8	*1.5*	3.8	*0.4*	< 20	*n*	0.35	*0.10*
Flue gas downstream of FGD(b																									
Particulat	µg/N	0.08	*0.04*	<	*n*	0.005	*0*	<	*n*	0.68	*0.14*	1.6	*0.7*	0.08	*n*	4.9	2.6	1.2	*0.7*	0.03	*0.02*	<	*n*	<	*n*
Gaseous	µg/N	< 2.5	*n*	< 1	*n*	0.53	*0.3*	< 2.2	*n*	6.3	*0.6*	11	*5*	1.8	*0.2*	6.7	*0.6*	2.4	*0.5*	3.3	*0.5*	< 9	*n*	< 2.3	*n*

[a] on dry-weight basis

[b] in dry flue gas, NTP

[c] mean of the tests S1,S2,S5,S6

[d] deviation: [(maximum of tests S1,S2,S5,S6) – (minimum of tests S1,S2,S5,S6)] /2

n: not possible to calculate the deviation

Plant MB	Conten	As		Be		Cd		Co		Cr		Cu		Hg	
		Mean(c	*Dev(*	Mea	*Dev*	Mean	*Dev*	Mea	*Dev*	Mea	*Dev*	Mea	*Dev*	Mean	*Dev*
Coal	mg/kg(	5.9	*3.2*	1.8	*0*	0.15	*0.06*	8.4	*0.4*	120	*33*	21	*1*	0.15	*0.04*
Lime	mg/kg(	1.0	*0.2*	< 1	*n*	0.06	*0.01*	< 0.5	*n*	3.3	*0.2*	1.4	*0.1*	0.045	*0.022*
Sea water	µg/l	< 10	*n*	< 2	*n*	0.28	*0.03*	m	*m*	1.2	*0.2*	m	*m*	< 0.12	*n*
Town water	µg/l	< 2	*n*	< 2	*n*	< 0.1	*n*	m	*m*	0.23	*0.15*	m	*m*	< 0.12	*n*
Bottom ash	mg/kg(	8.8	*0.6*	12	*1*	0.16	*0.00*	79	*18*	4200	*1800*	200	*39*	0.010	*0.002*
Ecoash	mg/kg(	13	*2*	13	*1*	0.35	*0.08*	48	*6*	190	*16*	120	*10*	0.020	*0.005*
PFA	mg/kg(	34	*1*	17	*1*	0.88	*0.05*	68	*16*	220	*3*	180	*5*	0.68	*0.07*
Flue gas upstream of FGD(b															
Particulate	µg/Nm³	3.1	*0.3*	0.41	*0.06*	0.10	*0.02*	m	*m*	3.1	*0.7*	m	*m*	0.006	*0.004*
Gaseous	µg/Nm³	< 3	*n*	< 6	*n*	0.62	*0.31*	m	*m*	2.2	*0.9*	m	*m*	1.5	*0.6*
Gypsum	mg/kg(	0.82	*0.09*	< 1	*0.00*	< 0.05	*n*	< 0.5	*n*	2.2	*0.2*	1.4	*0.4*	0.12	*0.02*
Waste water	µg/l	24	*2*	17	*2*	3.6	*0.8*	m	*m*	2.8	*1.6*	m	*m*	< 0.12	*n*
Filter cake	mg/kg(	18	*2*	3.1	*1.7*	1.3	*0.1*	19	*1*	53	*2*	36	*2*	0.59	*0.02*
Flue gas downstream of FGD(b															
Particulate	µg/Nm³	1.6	*0.8*	0.13	*0.04*	0.04	*0.02*	m	*m*	12	*11*	m	*m*	0.010	*0.001*
Gaseous	µg/Nm³	< 2	*n*	< 3	*n*	0.19	*0.12*	m	*m*	0.87	*0.23*	m	*m*	0.74	*0.15*

[a] on dry-weight basis

[b] in dry flue gas, NTP

[c] mean of the tests M2,M3,M4

[d] deviation: [(maximum of tests M2,M3,M4) – (minimum of tests M2,M3,M4)]/2

n: not possible to calculate the deviation

m: missing, not analysed

Plant MB (continued)	Conten	Mn		Ni		Pb		Se		Tl	
		Mea	***Dev***	**Mea**	***Dev***	**Mea**	***Dev***	**Mea**	***Dev***	**Mea**	***Dev***
Coal	mg/kg(	110	*10*	58	*13*	19	*3*	1.1	*0.2*	< 2	*n*
Lime	mg/kg(	120	*5*	2.6	*0.1*	1.6	*0.1*	< 2	*n*	0.63	*0.05*
Sea water	µg/l	8.8	*4.1*	< 2.5	*n*	< 10	*n*	< 100	*n*	m	*m*
Town water	µg/l	19	*3*	< 1	*n*	< 0.5	*n*	< 10	*n*	m	*m*
Bottom ash	mg/kg(	1100	*140*	2200	*890*	54	*1*	< 2	*n*	< 1	*n*
Ecoash	mg/kg(	880	26	120	*8*	55	9	< 2	*n*	< 2	*n*
PFA	mg/kg(	910	*50*	170	*7*	140	2	8.9	*0.4*	3.6	*0.8*
Flue gas upstream of FGD(b											
Particulate	µg/Nm^3	26	2	6.0	*1.1*	7.3	*0.8*	2.3	*0.1*	m	*m*
Gaseous	µg/Nm^3	2.5	*1.7*	< 2	*n*	3.8	*1.5*	< 170	*n*	m	*m*
Gypsum	mg/kg(	13	*3*	2.0	*0.3*	1.1	*0.1*	3.5	*1.1*	< 2	*n*
Waste water	µg/l	5000	*7500*	19	22	< 50	*n*	< 500	*n*	m	*m*
Filter cake	mg/kg(	4500	*150*	54	*1*	53	*4*	120	*4*	2.4	*0.4*
Flue gas downstream of FGD(b											
Particulate	µg/Nm^3	7.6	*3.8*	6.1	*5.2*	2.1	*1.1*	2.8	*1.9*	m	*m*
Gaseous	µg/Nm^3	0.64	*0.48*	< 2	*n*	2.1	*0.1*	< 90	*n*	m	*m*

[a] on dry-weight basis

[b] in dry flue gas, NTP

[c] mean of the tests M2,M3,M4

[d] deviation: [(maximum of tests M2,M3,M4) – (minimum of tests M2,M3,M4)]/2

n: not possible to calculate the deviation

m: missing, not analysed

Appendix 8. Comments on the trace element contents in the coal-fired power plants

The trace element contents in different streams of the coal-fired power plants were examined in the two following ways:

i) the trace element content in each solid mass stream was divided by the trace element content in the fuel

ii) the relative enrichment factor of each element in the solid material was calculated according to the formula (3.1)

The results are shown and discussed in detail in this appendix.

The mean contents of trace elements in the lime samples are shown in Appendix 7 and in Table A8.1. The ratio between the content in lime and in coal is shown in italics. The contents of As, Be, Cd, Cr, Hg, Ni and Pb in the lime samples were low compared to the contents in the coal samples. This was also the case for Co and Cu at plants SB and MB, and for Zn at plant HB. The contents of Mn in the lime and coal were approximately equal at plants HB and MB. At plant SB, the lime was richer than the coal in Mn and Tl. In the case of plants HB and MB, the coal was richer than the lime in Tl. For Se, the low content combined with the high detection limit of the analysis did not make this kind of comparison possible.

The mean concentrations of trace elements in the seawater and tap water samples at plants HB, SB and MB are shown in Appendix 7. Water from the sea beside the plant was mechanically filtered and conducted to the bottom ash quenching basin and to slurry production for the FGD. Plants HB and MB also used water supplied from the municipal water utility. The concentrations of As, Be, Cd, Cr, Hg, Ni, Pb and Tl were very low, of course. The concentrations of Co, Cu and Se were also low at plant SB, as well as Zn at plant HB. The detection limit of Se was very high (100 mg/m^3) at plant MB. The concentrations of Mn were 6–30 mg/m^3, which was utilised to control the magnitudes of the mass flows in the mass balance calculations.

Table A8.1. The mean contents of trace elements in the lime samples at plants HB, SB and MB (mg/kg in dry lime). The ratio of the element content in lime to the content in coal is shown in italics.

Plant	**As**		**Be**		**Cd**		**Cr**		**Hg**	
HB	1.0	*0.2*	<0.4	*<0.1*	0.12	*0.5*	6.1	*0.2*	0.03[2]	*≤0.2*
SB	2.7	*0.7*	<0.1	*<0.1*	0.09	*0.5*	10	*0.3*	<0.01	*<0.15*
MB	1.0	*0.2*	<1	*<0.6*	0.06	*0.4*	3.3	*0.03*[1]	0.05	*0.3*

Plant	**Mn**		**Ni**		**Pb**		**Tl**	
HB	190	*1.0*	3.8	*0.1*	2.1	*0.1*	0.3	*0.3*
SB	170	*1.9*	5.5	*0.2*	2.4	*0.1*	0.8	*1.6*
MB	120	*1.0*	2.6	*0.05*[1]	1.6	*0.1*	0.6	*0.3*

[1] Exceptionally high Cr and Ni contents in fuel

[2] Hg content in lime in tests H3–H6 below 0.01 mg/kg

The mean values of trace elements in the bottom ash samples at plants HB, SB and MB are shown in Appendix 7 and in Table A8.2. The mean values expressed and compared to those for coal, as well as the mean values of the relative enrichment factors are also shown in Table A8.2. The contents of As and Cd were of the same level in the bottom ash and coal samples at all the plants. The contents of Tl were also similar at plant HB. These trace elements had the lowest enrichment factors, i.e. 0.1–0.2 as well. At all the plants, the content of Pb in the bottom ash was about twice as high as that for coal. The relative enrichment factor was 0.4. The content of Zn, analysed only at plant HB, was at the same level. The contents of Be and Mn were 4–10 times higher in all the bottom ash samples than in the coal samples, as well as Co and Cu at plants SB and MB. Their relative enrichment factors were 0.7–1.2. The contents of Cr and Ni were much higher in the bottom ash samples than in the coal samples, with enrichment factors of 3–7. The content of Hg in bottom ash was 0.26 mg/kg at plant HB, which was much higher at plants SB and MB. The enrichment factor was 0.4, which is high compared to 0.01 in the case of plant MB. Hg was the trace element that obviously had different values at the different plants. The high detection limits of Se and Tl at plants SB and MB did not make this kind of comparison possible.

The trace element values in the ash coming from the economiser at plant MB (see Table A8.2) were quite equal to the bottom ash samples for As, Be, Mn and

Pb, as well as for Se and Tl. The ecoash had a higher content and enrichment of Cd and Hg, and lower contents and enrichments of Cr and Ni compared to the bottom ash.

Table A8.2. The mean contents of trace elements in the bottom ash samples at plants HB, SB and MB (mg/kg in dry basis). The ratio of the element content in bottom ash to the content in coal is shown in brackets. The relative enrichment factor is shown in italics. The bottom row shows the corresponding values for the ash samples from the economiser (i.e. ecoash) at plant MB.

Plant	**As**		**Be**		**Cd**		**Cr**	
HB	5.2 (0.8)	*0.2*	11 (3.5)	*0.8*	0.14 (0.6)	*0.13*	1050 (27)	*6.0*
SB	<10 n	*n*	9.2 (6.9)	*0.8*	0.17 (0.9)	*0.12*	820 (29)	*3.4*
MB	8.8 (1.5)	*0.2*	12 (6.5)	*0.8*	0.16 (1.1)	*0.16*	4200 (36)	*4.9*
MB ecoash	13 (2.1)	*0.3*	13 (7.2)	*0.9*	0.35 (2.4)	*0.4*	190 (1.6)	*0.2*

Plant	**Hg**		**Mn**		**Ni**		**Pb**	
HB	0.26 (1.8)	*0.4*	940 (4.9)	*1.1*	800 (30)	*6.9*	53 (1.6)	*0.4*
SB	<0.01 n	*n*	890 (9.7)	*1.1*	790 (26)	*3.1*	41 (2.2)	*0.3*
MB	0.01 (0.07)	*0.01*	1100[1] (9.4)	*1.2*	2200[2] (38)	*4.9*	54 (2.9)	*0.4*
MB ecoash	0.02 (0.14)	*0.02*	880 (7.7)	*1.0*	120 (2.1)	*0.3*	55 (2.9)	*0.4*

[1] Mn content in test M2 high (1 200 mg/kg)

[2] Ni content in test M2 high (3 000 mg/kg) and in test M4 low (1 300 mg/kg)

n: not possible to calculate

The mean contents of trace elements in the pulverised ash samples from the ESP (i.e. PFA) at plants HB, SB and MB are shown in Appendix 7 and in Table A8.3. The mean values expressed and compared to those for coal, as well as the mean values of the relative enrichment factors are also shown in Table A8.3. The contents of As, Be, Cd and Pb in the PFA were 4–10 times higher than in the coal at all the plants. This was also the case for Co, Cu and Se at plants SB and MB, and for Tl and Zn at plant HB. Their relative enrichment factors were about 1, which is high compared to the bottom ash. The relative enrichment factor of Mn is 1.0 in both the bottom ash and the PFA.

The PFA was richer than bottom ash Co and Cu at plant SB. The PFA was not as rich as bottom ash in Co and Cu at plant MB. The PFA was richer than bottom ash in Se at both plants (not analysed at plant HB). The relative enrichment factor of Zn analysed only at plant HB was also much higher in PFA than in bottom ash. The contents of Cr in PFA at plant MB, Ni at plant HB and MB were 2–3 times higher than for coal, but much less than in the bottom ash. All the relative enrichment factors for Cr and Ni were much lower for PFA than for bottom ash. The content of Hg was lowest at all the plants, representing the relative enrichment factor of 0.5–0.6, which is high compared to the content in bottom ash.

Table A8.3. The mean contents of trace elements in pulverised ash samples from the ESP (i.e. PFA) at plants HB, SB and MB (mg/kg in dry basis). The ratio of the element content in PFA to the content in coal is shown in brackets. The relative enrichment factor is shown in italics.

Plant	**As**		**Be**		**Cd**		**Cr**	
HB	32	*1.2*	14	*1.1*	1.1	*1.1*	150	*0.9*
	(5.1)		(4.7)		(4.7)		(3.8)	
SB	39	*1.1*	13	*1.1*	1.5	*1.0*	200	*0.8*
	(9.5)		(9.6)		(8.7)		(7.0)	
MB	34	*0.9*	17	*1.1*	0.9	*0.8*	220	*0.3*
	(5.7)		(9.2)		(6.0)		(1.9)	

Plant	**Hg**		**Mn**		**Ni**		**Pb**	
HB	0.4	*0.6*	790	*0.9*	71	*0.6*	190	*1.3*
	(2.6)		(4.2)		(2.7)		(5.6)	
SB	0.3	*0.5*	820(1	*1.1*	250	*0.9*	170	*1.1*
	(3.9)		(8.9)		(8.0)		(9.5)	
MB	0.7	*0.6*	910(1	*1.0*	170	*0.4*	140	*1.0*
	(4.6)		(8.0)		(3.0)		(7.6)	

[1] Mn content in test S1 low (750 mg/kg) and in test M1 high (960 mg/kg)

The mean concentrations of trace elements in the gaseous and particulate fractions in flue gases after the ESP, i.e. upstream of the FGD at plants HB, SB and MB are shown in Appendix 7 and in Table A8.4. The relative enrichment factors have been calculated for the particles collected on the sampling filter; the values are also shown in Table A8.4. The relative enrichment factors of particles were high (i.e. 4–11) for As, Cd and Pb at all the plants, as well as in the case of Se at plant SB. The enrichment of Se in the flue gas particles was extremely high (i.e. 27) at plant MB. The enrichment of Be, Mn and Ni was 1.0 or somewhat over at all the plants, as well as Co and Cu at plant SB, and Zn at plant HB. The enrichment of Cr and Hg was below 1.0 at plant MB, and over 1.0 at plants HB and SB.

Table A8.4. The mean concentrations of trace elements in the gaseous (i.e. Fg) and in the particulate (i.e. Fp) fractions of the flue gases after the ESP, i.e. upstream of the FGD at plants HB, SB and MB ($\mu g/Nm^3$, dry gas). The relative enrichment factors for the particulate fraction are shown in italics.

Plant	**As**		**Be**		**Cd**		**Cr**	
	Fg	**Fp**	**Fg**	**Fp**	**Fg**	**Fp**	**Fg**	**Fp**
HB	<1.7	46	<0.8	3.5	0.1	1.1	<2.3	66
		7.1		*1.0*		*4.0*		*1.3*
SB	1.6	3.5	0.5	0.4	0.4	0.15	2.4	9.0
		4.4		*1.6*		*4.6*		*2.6*
MB	<3	3.1	<6	0.4	0.6	0.1	2.2	3.1
		9.7		*2.7*		*11*		*0.4*

Plant	**Hg**		**Mn**		**Ni**		**Pb**	
	Fg	**Fp**	**Fg**	**Fp**	**Fg**	**Fp**	**Fg**	**Fp**
HB	2.3	0.2	<0.2	270	<1.2	25	<1.8	170
		1.1		*1.2*		*2.4*		*4.3*
SB	4.1	0.07	64	15	1.5	8.7	1.5	11
		6.1		*1.1*		*1.8*		*3.8*
MB	1.5	0.01	2.5	26	<2	6.0	3.8	7.3
		0.5		*2.9*		*1.4*		*5.0*

The mean concentrations of trace elements in the gaseous and particulate fractions in flue gases in the stack at plants HB, SB and MB are shown in Appendix 7 and in Table A8.5. The relative enrichment factors have been calculated for the particles collected on the sampling filter; these values are also shown in Table A8.5. All the trace element concentrations were low. The relative enrichment factors were low for most of the trace elements with the exception of Hg at plant SB, and As and Se at plant MB. The enrichments of trace elements in the particles in the flue gases of plant MB were typically higher than at plants HB and SB.

Table A8.5. The mean concentrations of trace elements in the gaseous (i.e.Fg) and particulate (i.e.Fp) fractions of flue gases in the stack at plants HB, SB and MB (µg/Nm^3, dry gas). The enrichment factors for the particulate fractions are shown in italics.

Plant	**As**		**Be**		**Cd**		**Cr**	
	Fg	**Fp**	**Fg**	**Fp**	**Fg**	**Fp**	**Fg**	**Fp**
HB	<1.9	<0.13	<0.9	<0.04	0.07	0.01(1	<2.5	0.1
		n.		*n*		*2.2*		*0.4*
SB	<2.5	0.08	<1.0	<0.003	0.5	0.005	6.3	0.7
		1.1		*n*		*1.3*		*0.7*
MB	<2	1.6	<3	0.13	0.2	0.04	0.9	12
		10.4		*2.1*		*9.6*		*2.6*

Plant	**Hg**		**Mn**		**Ni**		**Pb**	
	Fg	**Fp**	**Fg**	**Fp**	**Fg**	**Fp**	**Fg**	**Fp**
HB	0.1	0.002	0.2	0.4	<1.2	<0.02	<2.2	0.03
		0.3		*0.2*		*n*		*0.09*
SB	1.8	0.08	6.7	4.9	2.4	1.2	3.3	0.03
		19		*1.5*		*1.1*		*0.05*
MB	0.7	0.01	0.6	7.6	<2	6.1	2.1	2.1
		1.2		*1.8*		*2.6*		*3.0*

[1] only one value. The other five were below 0.01 µg/Nm^3

n: not possible to calculate

The mean contents of trace elements in the FGD production samples at plants HB, SB and MB are shown in Appendix 7 and in Table A8.6. The relative enrichment factors have also been calculated and expressed in Table A8.6. It can be seen that there were no big differences in the results between the coarse fractions (i.e. Cpro) and the fractions removed by the fabric filter (i.e. Pro) at plant HB. The relative enrichment factors were 0.1–0.2 for As, Cd, Mn, Pb, Tl and Zn at plant HB. The corresponding value was over 0.2 for Hg and below 0.1 for Be, Cr and Ni. The contents of As, Be, Cd, Cr, Hg, Mn, Ni and Pb in the particulate fraction of flue gases upstream of the FGD were higher at plant HB than at plant SB. The trace element concentrations in the gaseous fraction were quite equal in both plants. The contents of As, Cd, Hg and Mn in lime supplied to the FGD at plant HB were also high compared to plant SB. These differences were also seen in the trace element contents in the FGD products. The contents of As, Be, Cd, Mn, Ni and Pb in the FGD products of plant HB were higher than in plant SB. The content of Tl in the FGD products of plant HB was also higher than at plant SB. (The Tl concentrations in flue gases upstream of the FGD were determined below the detection limits.) The contents of Hg in FGD products were very equal in both plants.

Table A8.6. The mean contents of trace elements in FGD production samples at plants HB and SB as well as in gypsum (i.e. Gy) and filter cake (i.e. Fc) samples from plant MB (mg/kg in dry basis). The coarse fraction (i.e. Cpro) and the fraction removed by the fabric filter (i.e.Pro) at plant HB are shown separately. The relative enrichment factor is shown in italics.

Plant	As		Be		Cd		Cr		Hg	
HB Cpro	3.8	*0.14*	0.7[1]	*0.04*	0.2	*0.18*	5.9	*0.03*	0.13	*0.24*
HB Pro	5.6	*0.20*	0.6	*0.05*	0.2	*0.20*	5.8	*0.03*	0.18	*0.30*
SB Pro	2.5	*0.07*	<0.1	*0.01*	0.1	*0.07*	6.7	*0.03*	0.18	*0.28*
MB Gy	0.82	*0.02*	< 1	*n*	<0.05	*n*	2.2	*0.002*	0.12	*0.1*
MB Fc	18	*0.5*	3.1	*0.2*	1.3	*1.2*	53	*0.06*	0.59	*0.5*

Plant	Mn		Ni		Pb		Tl	
HB Cpro	110	*0.13*	7.0	*0.06*	13	*0.09*	0.6	*0.14*
HB Pro	110	*0.12*	6.5	*0.06*	17	*0.12*	0.7	*0.19*
SB Pro	83	*0.11*	2.8	*0.01*	3.8	*0.02*	0.4	*n*
MB Gy	13	*0.01*	2.0	*0.12*	1.1	*0.01*	< 2	*n*
MB Fc	4450	*4.9*	54	*0.01*	53	*0.4*	2.4	*n*

[1] Be content in the tests H1–H4: <0.4 mg/kg
n: not possible to calculate

The mean contents of trace elements in gypsum, filter cake and wastewater samples at plant MB are shown in Appendix 7. The contents in gypsum and filter cake are shown in Table A8.6. The relative enrichment factors have been calculated and are shown in Table A8.6, as well. The contents of all the elements in gypsum were low compared to the FGD products at plants HB and SB. The enrichments were very low. The contents of As and Pb were low and the contents of Cu, Mn, Ni and Se were a little high compared to the contents determined by Meij (1989). The contents of all the elements were high in the filter cake samples, as expected. The contents of Cd, Cr, Mn, Ni and Se were higher and the content of Hg in the filter cake sample was lower in plant MB than the contents determined by Meij (1989). The relative enrichment factors in filter cake were higher than in for PFA in the case of Cd, Mn and Se. The contents of As, Be, Cd, Ni and Pb were determined high compared to the contents in seawater and tap water at plant MB. The contents of Be, Cd, Ni and Pb in waste water were low compared to the contents reported by Meij (1989). Meij (1989) has reported the content of Mn in wastewater as high as 7600 mg/m^3.

Appendix 9. The trace element contents in the mass streams of the bark- and peat-fired power plants

a) plant UB, b) plant RB, c) plant TB and d) plant VB

***a) Plant UB**: [a] tests U1, U2, U3; [b] tests U4, U5, U6; [c] on dry-weight basis; [d] in dry flue gas, NTP; [e] deviation: (maximum−minimum)/2;n: not possible to calculate the deviation.*

Plant UB		**As**		**Cd**		**Cr**		**Hg**		**Mn**		**Ni**		**Pb**	
Bark combustion(a		***Mea***	***Dev(***	***Mea***	***Dev***	***Mea***	***Dev***	***Mean***	***Dev***	***Mea***	***Dev***	***Mea***	***Dev***	***Mea***	***Dev***
Fuel	mg/kg(	< 0.1	*n*	0.37	*0.03*	0.80	*0.11*	0.02	*0*	430	*15*	0.57	*0.06*	0.80	*0.09*
Bottom ash	mg/kg(	2.0	*0.2*	0.17	*0.12*	35	*2*	< 0.04	*n*	4500	*120*	20	*2*	7.5	*1.0*
Ecoash	mg/kg(	1.4	*0.2*	2.3	*0.2*	30	*4*	< 0.04	*n*	5000	*580*	22	*3*	11	*2*
PFA	mg/kg(	5.0	*0.8*	18	*2*	50	*7*	0.16	*0.03*	18700	*850*	45	*6*	45	*3*
Flue gas(d															
Particulate	µg/Nm³	< 0.2	*n*	0.34	*0.04*	2.7	*1.8*	< 0.04	*n*	120	*2*	3.6	*2.4*	2.3	*0.4*
Gaseous	µg/Nm³	< 1.1	*n*	0.05	*0.02*	0.53	*0.09*	0.92	*0.06*	1.3	*n*	0.37	*0.03*	0.77	*0.18*

Plant UB		**As**		**Cd**		**Cr**		**Hg**		**Mn**		**Ni**		**Pb**	
Bark and sludge co-		***Mea***	***Dev***	***Mea***	***Dev***	***Mea***	***Dev***	***Mean***	***Dev***	***Mea***	***Dev***	***Mea***	***Dev***	***Mea***	***Dev***
Fuel	mg/kg(	0.12	*0.05*	0.67	*0.16*	3.2	*0*	0.03	*0.01*	710	*110*	2.3	*0.3*	1.3	*0.1*
Bottom ash	mg/kg(	1.9	*0.3*	0.10	*0.01*	38	*3*	< 0.04	*n*	5100	*400*	20	*1*	6.5	*0.7*
Ecoash	mg/kg(	1.7	*0.4*	1.8	*0.2*	80	*6*	< 0.04	*n*	14000	*2950*	71	*13*	6.9	*1.3*
PFA	mg/kg(	3.7	*0.3*	15	*2*	69	*6*	0.18	*0.04*	21000	*2500*	64	*5*	30	*2*
Flue gas(d															
Particulate	µg/Nm³	0.23	*0.02*	0.47	*0.08*	0.42	*0.18*	< 0.04	*n*	140	*29*	0.98	*0.39*	1.6	*0.4*
Gaseous	µg/Nm³	< 0.9	*n*	0.03	*0.01*	0.86	*0.54*	1.5	*0.8*	4.3	*2.6*	0.28	*0.13*	0.56	*0.18*

***b) Plant RB**: [a] tests R1–R5; [b] on dry-weight basis; [c] in dry flue gas, NTP; [d] deviation: [(maximum content of tests R1–R5) − (minimum content of tests R1–R5)]/2;n: not possible to calculate the deviation; m: missing, not analysed.*

Plant RB		**As**		**Cd**		**Cr**		**Hg**		**Mn**		**Ni**		**Pb**	
Peat		**Mea**	***Dev(***	**Mea**	***Dev***	**Mea**	***Dev***	**Mean**	***Dev***	**Mea**	***Dev***	**Mea**	***Dev***	**Mea**	***Dev***
Fuel	mg/kg(	14	*1*	0.22	*0.03*	9.9	*0.9*	0.030	*0.004*	51	*9*	4.7	*1.0*	2.7	*0.6*
Sand	mg/kg(	1.1	*n*	0.04	*n*	6.7	*n*	< 0.05	*n*	159	*n*	5.0	*n*	7.1	*n*
Water	µg/l	< 1	*n*	< 0.1	*n*	0.5	*0.2*	< 0.2	*n*	0.15	*0.02*	0.80	*0.20*	0.40	*0.10*
Bottom ash	mg/kg(	13	*3*	0.19	*0.06*	28	*5*	< 0.02	*n*	280	*51*	17	*2*	18	*2*
PFA	mg/kg(	140	*n*	2.3	*m*	98	*n*	0.38	*n*	600	*n*	57	*n*	34	*n*
Flue gas(c															
Particulate	µg/Nm	29	*28*	0.16	*0.10*	3.2	*1.6*	0.22	*0.20*	38	*19*	< 30	*n*	11	*6*
Gaseous	µg/Nm	1.5	*n*	0.26	*0.33*	1.1	*1.7*	1.3	*1.0*	< 20	*n*	0.90	*1.5*	< 3	*n*

c) Plant TB*: [a] tests T1, T2, T3; [b] tests T4, T5, T6; [c] on dry-weight basis; [d] in dry flue gas, NTP; [e] deviation: (maximum content - minimum content)/2;n: not possible to calculate the deviation.*

Plant TB		**As**		**Cd**		**Cr**		**Hg**		**Mn**		**Mo**		**Ni**		**Pb**	
Peat combustion(a		**Mea**	***Dev(***	**Mean**	***Dev***	**Mea**	***Dev***	**Mean**	***Dev***	**Mea**	***Dev***	**Mea**	***Dev***	**Mea**	***Dev***	**Mea**	***Dev***
Fuel	mg/kg(	1.4	*0.1*	0.10	*0*	9.0	*0.9*	0.03	*0.01*	100	*6*	0.61	*0.07*	4.1	*0.3*	2.9	*0*
Bottom ash	mg/kg(	7.3	*1.7*	0.26	*0.06*	49	*9*	< 0.07	*n*	610	*49*	< 1	*n*	20	*1*	13	*1*
Ecoash	mg/kg(	7.3	*1.4*	0.33	*0.06*	68	*5*	< 0.07	*n*	790	*56*	1.2	*0.2*	27	*2*	15	*1*
PFA	mg/kg(	19	*2*	1.0	*0.2*	110	*22*	0.20	*0.04*	1200	*130*	4.6	*0.6*	48	*8*	32	*4*
Flue gas(d																	
Particulate	µg/Nm³	1.4	*0.3*	0.07	*0.01*	4.2	*1.1*	0.46	*0.39*	46	*10*	0.59	*0.19*	2.0	*0.4*	1.6	*0.3*
Gaseous	µg/Nm³	< 3	*n*	0.17	*n*	0.75	*0.39*	1.4	*0.6*	0.84	*0.07*	< 2.9	*n*	< 3		< 3	*n*

Plant TB		**As**		**Cd**		**Cr**		**Hg**		**Mn**		**Mo**		**Ni**		**Pb**	
Peat and wood chips co-		**Mea**	***Dev***	**Mean**	***Dev***	**Mea**	***Dev***	**Mean**	***Dev***	**Mea**	***Dev***	**Mea**	***Dev***	**Mea**	***Dev***	**Mea**	***Dev***
Fuel	mg/kg(	1.8	*0.2*	0.09	*0.01*	5.5	*0.1*	0.04	*0*	120	*4*	0.50	*0*	3.4	*0.5*	1.9	*0.4*
Bottom ash	mg/kg(	6.7	*0.6*	0.39	*0.01*	50	*5*	< 0.07	*n*	670	*76*	< 1	*n*	22	*2*	14	*2*
Ecoash	mg/kg(	7.5	*2.9*	0.47	*0.09*	71	*8*	< 0.07	*n*	950	*68*	1.9	*1.3*	32	*5*	18	*3*
PFA	mg/kg(	17	*2*	1.3	*0.1*	110	*2*	0.23	*0.01*	1600	*61*	5.2	*0.1*	53	*3*	38	*4*
Flue gas(d																	
Particulate	µg/Nm³	1.1	*0.1*	0.07	*0.01*	2.5	*0.3*	0.35	*0.09*	57	*5*	0.33	*0.02*	2.2	*0.2*	1.7	*0.1*
Gaseous	µg/Nm³	< 3.3	*n*	< 0.16	*n*	1.3	*0.5*	2.4	*1.2*	1.4	*0.9*	< 3.1	*n*	< 3.3	*n*	< 3.7	*n*

***d) Plant VB**: ^{a} tests V1, T2; ^{b} tests V3, V4; ^{c} on dry-weight basis; ^{d} in dry flue gas, NTP; ^{e} deviation: (maximum content - minimum content)/2; n: not possible to calculate the deviation.*

Plant VB		**As**		**Cd**		**Cr**		**Hg**		**Mn**		**Mo**		**Ni**		**Pb**	
Peat combustion(a		**Mea**	***Dev(***	**Mean**	***Dev***	**Mea**	***Dev***	**Mean**	***Dev***	**Mean**	***Dev***	**Mea**	***Dev***	**Mea**	***Dev***	**Mea**	***Dev***
Fuel	mg/kg(	0.90	*0.04*	0.08	0	4.1	0.2	0.04	0	35	4	< 0.5	n	3.5	0.2	2.9	0.3
Bottom ash	mg/kg(	< 1	*n*	0.05	0.01	30	2	< 0.06	n	250	5	< 0.5	n	21	1	15	1
PFA	mg/kg(	31	*0*	2.1	0.1	100	8	0.18	0	1100	55	6.7	0.1	84	6	90	14
Flue gas(d																	
Particulate	µg/Nm³	0.93	*0.05*	0.06	0.01	0.97	0.02	< 0.02	n	13	1	0.15	0	1.2	0	1.8	0.3
Gaseous	µg/Nm³	< 1.6	*n*	< 0.32	n	5.6	1.2	2.8	0.1	< 0.92	n	< 1.9	n	< 1.9	n	< 1.4	n

Plant VB		**As**		**Cd**		**Cr**		**Hg**		**Mn**		**Mo**		**Ni**		**Pb**	
Peat and saw dust co-		**Mea**	***Dev***	**Mean**	***Dev***	**Mea**	***Dev***	**Mean**	***Dev***	**Mean**	***Dev***	**Mea**	***Dev***	**Mea**	***Dev***	**Mea**	***Dev***
Fuel	mg/kg(	0.66	*0*	0.09	*0.01*	2.9	*0.1*	0.05	*0.01*	47	*1*	< 0.5	*n*	2.7	*0*	1.6	0
Bottom ash	mg/kg(	< 1	*n*	0.06	*0*	30	2	< 0.06	*n*	310	*15*	< 0.5	*n*	20	*1*	15	1
PFA	mg/kg(	21	*2*	1.8	*0.1*	97	*5*	0.14	*0.01*	1400	*85*	5.5	*0.4*	74	*5*	59	4
Flue gas(d																	
Particulate	µg/Nm³	0.82	*0.05*	0.06	*0.01*	1.1	*0.1*	< 0.02	*n*	19	*2*	0.17	*0.02*	1.5	*0.3*	1.3	0
Gaseous	µg/Nm³	< 1.9	*n*	< 0.37	*n*	0.40	*0.09*	2.3	*0*	< 0.73	*n*	< 2.2	*n*	< 2.2	*n*	< 1.6	n

Appendix 10. Comments on the trace element contents in the bark- and peat-fired power plants

The trace element contents in different solid streams of the bark- and peat-fired power plants were examined in the two following ways:

i) the trace element content in each solid mass stream was divided by the trace element content in the fuel

ii) the relative enrichment factor of each element in the solid material was calculated according to the formula (3.1)

The results are shown and discussed in detail in this appendix.

The trace elements in sea-sand were analysed only at plant RB. The element contents analysed are shown in Appendix 9 and in Table A10.1. The content of Hg was analysed below the detection limit (i.e. 0.05 mg/kg). The contents of As and Cd in the sand were low compared to the contents in the peat. The contents of Mn and Pb in the sand were twice as high as the content in the peat. The contents of Cr and Ni were almost equal in the sand and peat.

Table A10.1. The contents of trace elements in the sea-sand sample from plant RB (mg/kg in dry basis). The ratio of the element content in sea-sand to the content in peat is shown in italics in the bottom row.

	As	**Cd**	**Cr**	**Mn**	**Ni**	**Pb**
Lab1	0.83	0.034	7.6	98	3.9	5.9
Lab3	1.3	0.035	5.8	220	6.0	8.3
Mean	**1.1**	**0.035**	**6.7**	**159**	**5.0**	**7.1**
Sdev	0.3	0.001	1.3	86	1.5	1.7
Massb(1	**1.1**	**0.035**	**6.7**	**159**	**5.0**	**7.1**
sand/peat	*0.07*	*0.16*	*0.68*	*3.12*	*1.05*	*2.63*

[1] the value used in mass balance calculations

Plant RB used some mechanically sieved water from the lake beside the plant for the bottom ash quenching basin. The element concentrations, given in Appendix 9, were low and below the detection limit for As (i.e. 1.0 mg/m^3), Cd (i.e. 0.1 mg/m^3) and Hg (i.e. 0.2 mg/m^3). The mean concentration of Cr in the water was 0.5 mg/m^3, Ni 0.8 mg/m^3, Pb 0.4 mg/m^3 and Mn 150 mg/m^3. The contents were equal or less compared to the contents determined in the seawater and the tap water samples from the coal-fired power plants for all the trace elements, except for Mn and Ni.

The mean values of trace elements in the bottom ash samples at plants UB, RB, TB and VB are shown in Appendix 9 and in Table A10.2. The mean values expressed and compared to those for fuel supplied, as well as the mean values of the relative enrichment factors are also shown in Table A10.2. The corresponding values for the ash coming from the economiser (i.e. ecoash) at plants UB and TB are shown in Appendix 9 and in Table A10.3.

The contents of As and Cd were of the same level in the bottom ash and peat samples at plant RB. The contents of As and Cd in the bottom ash were lower compared to their content in the fuel at plant VB, as well as for Cd at plant UB. The content of Hg in the bottom ash was also low compared to it's content in the fuel at all the plants. The relative enrichment factors of the trace elements in these cases were low, less than 0.1. The relative enrichment of Mo in the bottom ash at plant TB was also low. The comparison was not possible in the case of Mo at plant VB because of the low concentration with a high detection limit in the fuel. All the other trace elements were analysed significantly higher in the bottom ash compared to the fuel. The relative enrichment factor of Cr was 0.8 and of Ni was 0.6 at plant UB during bark-combustion. The bottom ash at plant RB was also as rich. All the other enrichment factors were below 0.6 for each trace element at all the plants.

The ash samples from the economiser showed quite equal contents of trace elements in the bottom ash at plants UB and TB for As, Hg and Pb. The ecoash was richer than bottom ash in the case of Cd at both plants. The contents of Cr and Mn in the ecoash were high compared to the bottom ash at plant UB during co-combustion and at plant TB during peat- and co-combustion. The contents of Mo (analysed only at plant TB) and of Ni in the ecoash were also higher than the contents in the bottom ash.

Table A10.2. The mean contents of trace elements in bottom ash samples at plants UB, RB, TB and VB (mg/kg in dry basis). The ratio of the element content in bottom ash to the content in fuel is shown in brackets. The relative enrichment factor is shown in italics.

Plant	Tests	As		Cd		Cr		Hg	
UB	**U13**	2.0	*n*	0.17	*0.008*	35	*0.8*	<0.04	*<0.04*
		(n.c.)		(0.5)		(44)		(<2)	
	U46	1.9	*0.3*(1	0.10	*0.005*	38	*0.4*	<0.04	*<0.05*
		(7.5)(1		(0.2)		(12)		(<1.5)	
RB	**R16**	13	*0.08*	0.19	*0.08*	28	*0.3*	<0.02	*<0.06*
		(0.9)		(0.9)		(2.8)		(<0.7)	
TB	**T13**	7.3	*0.31*	0.26	*0.16*	49	*0.3*	<0.07	*<0.13*
		(5.1)		(2.6)		(5.5)		(<2)	
	T46	6.7	*0.15*	0.39	*0.16*	50	*0.4*	<0.07	*<0.07*
		(3.8)		(4.2)		(9.0)		(<2)	
VB	**V12**	<1	*<0.05*	0.05	*0.02*	30	*0.3*	<0.06	*<0.06*
		(<1.1)		(0.6)		(7.2)		(<1.5)	
	V34	<1	*<0.04*	0.06	*0.02*	30	*0.2*	<0.06	*<0.03*
		(<1.5)		(0.7)		(11)		(<1.3)	

Plant	Tests	Mn		Mo		Ni		Pb	
UB	**U13**	4500	*0.18*	m	*m*	20	*0.6*	7.5	*0.2*
		(10)				(35)		(9.5)	
	U46	5100	*0.24*	m	*m*	20	*0.3*	6.5	*0.2*
		(7.1)				(8.9)		(5.1)	
RB	**R16**	280	*0.5*	m	*m*	17	*0.3*	18	*0.6*
		(5.6)				(3.5)		(6.5)	
TB	**T13**	610	*0.4*	<1.0	*<0.1*	20	*0.3*	13	*0.3*
		(5.9)		(<2)		(5.0)		(4.4)	
	T46	670	*0.2*	<1.0	*<0.1*	22	*0.3*	14	*0.3*
		(5.6)		(<2)		(6.4)		(7.4)	
VB	**V12**	250	*0.3*	<0.5	*n*	21	*0.2*	15	*0.2*
		(7.0)		(n)		(5.9)		(5.2)	
	V34	310	*0.2*	<0.5	*n*	20	*0.2*	15	*0.2*
		(6.4)		(n)		(7.4)		(9.0)	

[1] As content in fuel analysed was above the detection limit only in test U4

m: missing, not analysed

n: not possible to calculate

Table A10.3. The mean contents of trace elements for the ash samples from the economiser (i.e. ecoash) at plants UB and TB (mg/kg in dry basis). The ratio of the element content in ecoash to the content in fuel is shown in brackets. The relative enrichment factor is shown in italics.

Plant	**Tests**	**As**		**Cd**		**Cr**		**Hg**	
UB	**U13**	1.4	*n*	2.3	*0.1*	30	*0.7*	<0.04	*<0.04*
		(n)		(6.1)		(37)		(<2)	
	U46	1.7	*0.3*(1	1.8	*0.1*	80	*0.9*	<0.04	*<0.05*
		(7.0)(1		(2.6)		(25)		(<2)	
TB	**T13**	7.3	*0.3*	0.33	*0.2*	70	*0.5*	<0.07	*<0.1*
		(5.1)		(3.3)		(7.6)		(<2)	
	T46	7.5	*0.2*	0.47	*0.2*	70	*0.5*	<0.07	*<0.1*
		(4.2)		(5.1)		(13)		(<2)	

Plant	**Tests**	**Mn**		**Mo**		**Ni**		**Pb**	
UB	**U13**	5000	*0.2*	m	*m*	22	*0.7*	11	*0.2*
		(12)				(39)		(14)	
	U46	14000	*0.7*	m	*m*	71	*1.1*	6.9	*0.2*
		(19)				(31)		(5.4)	
TB	**T13**	790	*0.5*	1.2	*0.12*	27	*0.4*	15	*0.3*
		(7.6)		(2.0)		(6.7)		(5.2)	
	T46	950	*0.3*	1.9	*0.15*	32	*0.4*	18	*0.4*
		(8.0)		(3.7)		(9.4)		(9.3)	

[1] As content in fuel analysed was above the detection limit only in test U4

m: missing, not analysed

n: not possible to calculate

Table A10.4. The mean contents of trace elements in pulverised ash samples from the ESP (i.e. PFA) at plants UB, RB, TB and VB (mg/kg in dry basis). The ratio of the element content in PFA to the content in fuel is shown in brackets. The relative enrichment factor is shown in italics.

Plant	Tests	As		Cd		Cr		Hg	
UB	**U13**	5.0	*n*	18	*0.8*	50	*1.1*	0.16	*0.14*
		(n)		(48)		(63)		(7.8)	
	U46	3.7	*0.6*(1	15	*0.8*	69	*0.7*	0.18	*0.2*
		(17)(1		(22)		(22)		(6.8)	
RB	**R16**	138	*0.8*	2.3	*0.9*	98	*0.9*	0.38	*1.1*
		(9.6)		(11)		(10)		(13)	
TB	**T13**	19	*0.8*	1.0	*0.6*	105	*0.7*	0.20	*0.4*
		(14)		(9.9)		(12)		(6.0)	
	T46	17	*0.4*	1.3	*0.5*	108	*0.8*	0.23	*0.2*
		(9.7)		(14)		(20)		(6.0)	
VB	**V12**	31	*1.4*	2.1	*1.1*	103	*1.0*	0.18	*0.2*
		(35)		(26)		(25)		(4.5)	
	V34	21	*0.8*	1.8	*0.6*	97	*0.9*	0.14	*0.1*
		(31)		(21)		(34)		(3.1)	

Plant	Tests	Mn		Mo		Ni		Pb	
UB	**U13**	18700	*0.8*	m	*m*	45	*1.4*	45	*1.0*
		(43)				(79)		(57)	
	U46	20900	*1.0*	m	*m*	64	*1.0*	30	*0.8*
		(29)				(28)		(24)	
RB	**R16**	600	*1.0*	m	*m*	57	*1.1*	34	*1.1*
		(12)				(12)		(12)	
TB	**T13**	1220	*0.7*	4.6	*0.5*	48	*0.7*	32	*0.7*
		(12)		(7.6)		(12)		(11)	
	T46	1620	*0.5*	5.2	*0.4*	53	*0.6*	38	*0.8*
		(14)		(10)		(16)		(20)	
VB	**V12**	1110	*1.3*	6.7	*n.*	84	*1.0*	90	*1.3*
		(32)		(n)		(24)		(31)	
	V34	1430	*0.8*	5.5	*n.*	74	*0.7*	59	*1.0*
		(30)		(n)		(27)		(36)	

[1] As content in fuel analysed was above the detection limit only in test U4
m: missing, not analysed
n: not possible to calculate

The mean contents of trace elements in the pulverised ash samples from the ESP (i.e. PFA) at plants UB, RB, TB and VB are shown in Appendix 9 and in Table A10.4. The mean values expressed and compared and to those for the fuel supplied, as well as the mean values of the relative enrichment factors are also shown in Table A10.4. All the trace elements were analysed in the PFA significantly higher compared to the fuel, and the relative enrichment factors of the trace elements were determined high for the PFA compared to the bottom ash or ecoash. Most of the relative enrichment factors in the PFA were close to 1.0. The lowest RE values were in the case of Hg at plants UB, TB and VB .The highest RE values (1.3–1.4) were found for Ni at plant UB during bark combustion and for As, Mn and Pb at plant VB during peat-combustion. Plant TB did not have as high enrichments of As, Cd, Hg, Mn and Pb in the PFA as the other peat-fired or the coal-fired power plants.

The mean concentrations of trace elements in the gaseous and particulate fractions in the flue gases after the ESP (i.e. in the stack) at plants UB, RB, TB and VB are shown in Appendix 9 and in Table A10.5. The relative enrichment factors for trace elements in the particles collected on the sampling filter are also expressed in Table A10.5. All the trace element concentrations were low.

The detection limit of As of the gaseous fraction of As was higher than the small concentrations measured in the particulate fraction at plants UB, TB and VB. Plant RB had a high As concentration in the flue gases (which results from the high content of As in the peat). Cd, Mn, Ni and Pb were found mainly in the particulate fraction at plant UB. Hg was mainly present in the gaseous form. The concentrations of Cr and Ni in the particulate fraction were remarkable high in test U3, as well as the relative enrichment factors. The relative enrichment of Cr and Ni in the flue gas particles was even higher than in the PFA. The test U3 was most probably contaminated during the sampling or analysis procedure and the result was weeded out. As a conclusion, it can be said that Cr and Ni are present both in the particulate and gaseous fractions at plant UB. The emissions of Cd, Hg and Mn appeared to be at a higher level and the emissions of Ni and Pb at a lower level during co-combustion of bark and sludge with pure bark combustion. The relative enrichment factors of As, Hg and Mn in flue gas particles at plant UB were lower than those for peat-fired power plants during pure peat combustion. The enrichments of the other trace elements in the flue gas particles were approximately at the same level.

The detection limits of Cd in the gaseous fraction were higher than the small concentrations measured in the particulate fractions at plants TB and VB. A small amount of Cd was found in both fractions at plant RB and at plant TB during peat combustion. Cr occurred both in the gaseous and particulate form at all the peat-fired power plants. Hg was mainly present in the gaseous form. The concentrations became higher during co-combustion at plant TB, and decreased at plant VB. Mn occurred mainly in the particulate fraction at all these peat-fired power plants. Mo, Ni and Pb were found in the particulate fractions at plants TB and VB, where the detection limits of the gaseous fractions were too high to consider dividing. The detection limit of Ni in the particulate fraction was high compared to the low concentration measured in the gaseous fraction at plant RB.

The particulate fractions of the flue gases of the coal-fired power plants were not as rich in As and Hg as the peat-fired power plants. The enrichment was found to be higher for Cd and Pb in the particulate fraction of the flue gases in the coal-fired power plants than in the peat-fired power plants.

The summary of the results based on the relative enrichment factors is shown in Table 6.5 for the bark- and peat-fired power plants. The relative enrichment factors determined for plants UB, RB, TB and VB follow, in principle, the classification reported by Meij (1997) for Dutch coal-fired power plants equipped with ESPs.

None of the trace elements under study fell into class I because the bottom ash had enrichment factors below 0.8 for all the elements. As fell into class IIb at plant UB during the co-combustion because of the lower RE of As in the particulate fraction in the flue gases compared to the other plants, which fell into class IIa.

Cd was classified in class IIc at plants UB, RB and TB. The bottom ash was very poor in Cd at plant UB, but some Cd could be found in the particulate fractions of flue gases, as was also the case for plants RB and TB. The flue gas particles at plant VB were richer in Cd, although the concentrations were low. The Cd results at plant VB fell into classes IIa and IIb.

The RE of Cr in PFA was approximately 1.0 and in particulate fractions of flue gases 0.4–2. These led that Cr was falling to the class IIc in all the cases.

The RE of Hg in the bottom ash samples was much below 1, as was the RE in the PFA at plants UB, TB and VB. The flue gas particles were very poor in Hg at plants UB and VB, which led to class III. A part of the Hg was enriched in the flue gas particles at plants RB and TB. The RE of Hg in the PFA was also high (i.e. 1.1) at plant RB, which put Hg into class IIa or III.

Table A10.5. The mean concentrations of trace elements in gaseous (i.e. Fg) and particulate (i.e. Fp) fractions of flue gases in the stack (so called fly ash) at plants UB, RB, TB and VB (µg/Nm^3, in dry gas). The relative enrichment factors for particulate fractions are shown in italics.

Plant	**Tests**	**As**		**Cd**		**Cr**		**Hg**	
		Fg	**Fp**	**Fg**	**Fp**	**Fg**	**Fp**	**Fg**	**Fp**
UB	**U13**	<1	<0.2	0.05	0.3	0.5	0.9[3]	0.9	<0.04
			n		*1.2*		*1.4*		*<3*
	U46	<1	0.2	0.03	0.5	0.9	0.4	1.5	<0.04
			3.7[1]		*1.9*		*0.4*		*<4*
RB	**R16**	<1[2]	29	0.3	0.2	1.1	3.2	1.3	0.2
			9.0		*1.3*		*0.6*		*13*
TB	**T13**	<3	1.4	0.2	0.07	0.8	4.2	1.4	0.5
			130		*1.6*		*1.1*		*34*
	T46	<3	1.1	<0.2	0.07	1.3	2.5	2.4	0.4
			72		*0.9*		*0.5*		*10*
VB	**V12**	<2	0.9	<0.3	0.06	5.6	1.0	2.8	<0.02
			74		*5.2*		*1.8*		*<4*
	V34	<2	0.8	<0.4	0.06	0.4	1.1	2.3	<0.02
			75		*3.0*		*1.7*		*<2*

Plant	**Tests**	**Mn**		**Mo**		**Ni**		**Pb**	
		Fg	**Fp**	**Fg**	**Fp**	**Fg**	**Fp**	**Fg**	**Fp**
UB	**U13**	1.3	120	m	m	0.4	1.2[3]	0.8	2.3
			0.4				*2.8*		*3.6*
	U46	4.3	140	m	m	0.3	1.0	0.6	1.6
			0.5				*1.2*		*3.3*
RB	**R16**	<20	38	m	m	1[4]	<30	<3	11
			1.4				*<12*		*7.3*
TB	**T13**	0.8	46	<3	0.6	<3	2.0	<3	1.6
			1.1		*2.4*		*1.2*		*1.4*
	T46	1.4	57	<3	0.3	<3	2.2	<4	1.7
			0.5		*0.7*		*0.7*		*1.0*
VB	**V12**	<1	13	<2	0.2	<2	1.2	<2	1.8
			2.8		*n*		*2.6*		*4.7*
	V34	<1	19	<2	0.2	<2	1.5	<2	1.3
			1.8		*n*		*2.6*		*3.8*

[1] As content in fuel analysed was above the detection limit only in test U4

[2] As 4,7 µg/Nm^3 in test R3

[3] Cr and Ni in test U3 weeded out

[4] Ni 3,3 µg/Nm^3 in test R1, 0,4 µg/Nm^3 in test R2, < 0,5µg/Nm^3 in tests R3–R5

m: missing, not analysed

n: not possible to calculate

Mn at plant VB fell into class IIb during peat-combustion because of the rich flue gas particles. Mn was in class IIc in all other cases.

Mo at plant TB fell into class IIb during peat-combustion and into class IIc during co-combustion. The differences came from the enrichment of Mo in the flue gas particles, which was not as high as reported by Mej (1997). The detection limit of the gaseous fraction was too high to draw conclusions, if the particulate fraction was the dominant Mo flow in the flue gases.

The REs of Ni in the bottom ash and in the PFA led to Ni falling into classes IIb–IIc at plants TB and VB, depending on the relative enrichment of Ni in the flue gas particles. This was also the case for plant UB, when the test U3 was excluded from the calculations. The high detection limit of Ni in the flue gas particles provided no possibilities for closer classification at plant RB.

The REs of Pb in the bottom ash and in the PFA led to Pb falling in classes IIa–IIc at the peat-fired power plants and at plant UB, depending on the relative enrichment of Pb in the flue gas particles.

The flue gas particles were richest in Pb at plants RB and VB during peat-combustion, which placed Pb in class IIa. The lesser enrichment of Pb in the particulate fraction led plants UB and VB during co-combustion to fall into class IIb.

In the case of Hg, Mn and Mo, the bark-fired and peat-fired power plants differed from the classes of the coal-fired power plants HB, SB and MB.

Appendix 11. The total ingoing and outcoming flows and the closure of the mass balance at the coal-fired power plants

a) Plant HB, b) plant SB and c) plant MB

a) Plant HB: *[a] not included in Mba, when Out/In is not 0.7–1.3; Mba: mean value of the tests.*

Plant HB	**As**			**Be**			**Cd**			**Cr**			**Hg**		
Test ID	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In
H1	287	365	1.27	187	196	1.05	12	12	1.05	2034	2433	1.20	8.4(a	4.7(a	0.57
H2	254(a	413(a	1.62	159	168	1.06	11(a	15(a	1.39	1940	2528	1.30	9.4(a	5.8(a	0.62
H3	366	355	0.97	161	165	1.02	14	14	1.03	2089	2465	1.18	10.9(a	5.6(a	0.52
H4	330	331	1.00	137	143	1.04	12	12	1.02	1919(a	2656(a	1.38	5.4	5.5	1.01
H5	325	344	1.06	126	143	1.14	10	11	1.06	1941(a	3080(a	1.59	4.8	4.5	0.93
H6	323	336	1.04	132	146	1.10	12	10	0.84	1866(a	3137(a	1.68	4.9	4.4	0.91
Mba	326	346	1.07	150	160	1.06	12	12	1.00	2021	2475	1.22	5.0	4.8	0.95

Plant HB	**Mn**			**Ni**			**Pb**			**Tl**			**Zn**		
Test ID	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In
H1	10100	10100	1.00	1300(a	1710(a	1.31	2290	2480	1.08	78	67	0.85	3490	4460	1.28
H2	10700	10400	0.97	1490	1590	1.07	1640(a	2450(a	1.49	35(a	64(a	1.84	3580	4610	1.29
H3	10700	10200	0.95	1300	1570	1.21	1770	2060	1.16	47	57	1.23	4390	4330	0.99
H4	9070	9070	1.00	1380	1530	1.11	1430	1820	1.28	45	49	1.09	3250	3100	0.95
H5	8950	9040	1.01	1160(a	1760(a	1.51	1450	1730	1.19	39	43	1.10	2860	2930	1.02
H6	9050	9130	1.01	1230(a	1760(a	1.43	1420	1760	1.24	37	43	1.15	3140	3060	0.97
Mba	9750	9660	0.99	1390	1570	1.13	1670	1970	1.18	49	52	1.05	3450	3750	1.09

b) Plant SB*: [a] not included in Mba, when Out/In is not 0.7–1.3; Mba: mean value of the tests; n: not possible to calculate.*

Plant SB	**As**			**Be**			**Cd**			**Co**			**Cr**			**Cu**		
Test ID	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In
S1	248	314	1.27	65	89	1.36	7.6	7.8	1.03	577	493	0.85	1780	n	n	1442	1422	0.99
S2	241	288	1.19	81	95	1.17	7.6	8.4	1.10	546	604	1.11	1680	1700	1.01	1371	1440	1.05
S5	232	288	1.24	72(a	102(a	1.43	11(a	14(a	1.32	519	576	1.11	1370	1570	1.15	1267	n	n
S6	240	310	1.29	88	104	1.19	15	17	1.17	392	506	1.29	1820	1740	0.96	1366	n	n
Mba	240	300	1.25	78	96	1.23	10	11	1.12	508	545	1.07	1670	1670	1.00	1361	1431	1.05

Plant SB	**Hg**			**Mn**			**Ni**			**Pb**			**Se**			**Tl**		
Test ID	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In
S1	5.5(a	3.8(a	0.69	5640	5930	1.05	1960	1890	0.96	998	1210	1.21	< 55	< 73	n	< 29	23	n
S2	5.1	4.0	0.79	4620(a	6550(a	1.42	1800	2050	1.14	1060	1230	1.16	< 79	< 74	n	< 30	23	n
S5	4.2	3.4	0.80	5700	6670	1.17	1730	1990	1.15	1040(a	1410(a	1.36	< 79	< 90	n	< 30	26	n
S6	3.8	4.4	1.16	6030	6840	1.13	1640	2110	1.28	1180	1490	1.27	< 80	< 94	n	< 30	27	n
Mba	4.4	3.9	0.90	5790	6480	1.12	1780	2010	1.13	1080	1310	1.22	< 80	< 90	n	< 30	25	n

*c) **Plant MB**: [a] not included in Mba, when Out/In is not 0.7–1.3; [b] the gaseous flue gas fraction excluded; Mba: mean value of the tests; n: not possible to calculate.*

Plant MB	**As**			**Be**			**Cd**			**Co**			**Cr**			**Cu**		
Test ID	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In
M2	581	559	0.96	276	291	1.05	17	15	0.90	1250	> 1500	n	13200	13500	1.02	3020	> 3300	n
M3	1530(a	>	n	273(a	> 330(a	n	35(a	> 18(a	n	1340	> 1200	n	23100(	>	n	3300	> 3800	n
M4	618	560	0.91	275	287	1.04	17	14	0.85	1290	> 1100	n	16900(	7880(a	0.47	3350	> 3400	n
Mba	599	560	0.93	276	289	1.05	17	15	0.88	1290	> 1300	n	13200	13500	1.02	3220	> 3500	n

Plant MB	**Hg**			**Mn**			**Ni**			**Pb**			**Se**			**Tl**		
Test ID	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In
M2	20(a	13(a	0.65	16300	17800	1.09	7460	7850	1.05	2830	2320	0.82	194	180(b	0.93	< 310	n	n
M3	29(a	13(a	0.46	19000(	> 19900	n	11200(	> 8000	n	3330(a	> 2800	n	177(a	> 220(b	n	< 307	n	n
M4	19	14	0.74	18800	17200	0.91	8030(a	5360(a	0.67	2540	2440	0.96	119(a	199(ab	1.67	< 309	n	n
Mba	19	14	0.74	17500	17500	1.00	7460	7850	1.05	2690	2380	0.89	194	180(b	0.93	n	n	n

Appendix 12. The total ingoing and outcoming flows and the closure of the mass balance at the bark- and peat-fired power plants

a) Plant UB, b) plant RB, c) plant TB and d) plant VB

a) Plant UB	**As**			**Cd**			**Cr**			**Hg**		
Test ID	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In
Bark combustion												
U1	< 1.5	2.0	n	6.2	5.8	0.94	14(a	22(a	1.58	0.30(a	n	n
U2	< 1.5	1.8	n	5.4	5.8	1.07	14(a	21(a	1.50	0.31	0.18	0.57
U3	n	1.5	n	5.4	5.1	0.95	11(a	18(a	1.62	0.31	0.19	0.62
Mba	< 1.5	1.8	n	5.6	5.6	0.99	n	n	n	0.31	0.19	0.61
Bark and sludge co-combustion												
U4	2.6	1.6	0.63	6.8	5.6	0.82	42	34	0.81	0.26	0.27	1.03
U5	< 1.4	2.0	n	11.5(a	6.9(a	0.60	44	38	0.86	0.41(a	0.20(a	0.49
U6	n	2.1	n	8.4	6.9	0.82	42	40	0.93	0.40	0.39	0.98
Mba	2.6	1.6	0.63	7.6	6.3	0.82	43	37	0.87	0.33	0.33	1.00

Plant UB	**Mn**			**Ni**			**Pb**		
Test ID	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In
Bark combustion									
U1	6770	6400	0.95	9.9(a	18(a	1.83	13	15	1.17
U2	6670	6240	0.94	9.4(a	17(a	1.88	11(a	16(a	1.41
U3	6450	6530	1.01	8.3(a	14(a	1.75	14	14	1.03
Mba	6630	6390	0.96	n	n	n	14	15	1.10
Bark and sludge co-combustion									
U4	7500	8520	1.14	30	29	0.95	16	14	0.89
U5	11000	11000	1.00	35	34	0.98	18	13	0.72
U6	10000	10500	1.04	27	34	1.29	18	15	0.86
Mba	9510	10000	1.05	30	32	1.06	17	14	0.82

[a] not included in Mba, when Out/In is not 0.7–1.3, Mba: mean value of the tests; n: not possible to calculate

b) Plant RB		**As**			**Cd**			**Cr**			**Hg**	
Test ID	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In
Peat combustion												
R1	586	617	1.05	10	10	1.08	447	443	0.99	1.3(a	2.2(a	1.72
R2	678	627	0.92	8.5	10	1.22	422	441	1.05	1.2(a	2.8(a	2.43
R3	710	649	0.91	10	10	1.05	418	443	1.06	1.5(a	3.1(a	2.02
R4	701	626	0.89	13	11	0.82	532	445	0.83	1.6	2.0	1.25
R5	798	626	0.78	12	10	0.85	566	444	0.79	1.7	2.0	1.16
Mba	695	628	0.90	11	10	0.98	477	443	0.93	1.7	2.0	1.20

Plant RB		**Mn**			**Ni**			**Pb**	
Test ID	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In
Peat combustion									
R1	2230	2700	1.21	193(a	256(a	1.33	145	156	1.08
R2	2670	2700	1.01	175(a	255(a	1.46	126	155	1.23
R3	2760	2720	0.99	186(a	255(a	1.37	139	160	1.14
R4	2210	2740	1.24	279	256	0.92	127	164	1.30
R5	2190	2740	1.25	312	257	0.82	116(a	164(a	1.41
Mba	2410	2720	1.13	296	256	0.87	134	159	1.18

[a] not included in Mba, when Out/In is not 0.7–1.3

Mba: mean value of the tests

c) Plant TB	As			Cd			Cr			Hg		
	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In
Peat combustion												
T1	85	90	1.06	6.1(a	4.0(a	0.66	479	424	0.89	1.8	1.5	0.85
T2	83	110	1.30	5.9	5.9	1.00	568	630	1.11	1.8	1.8	1.02
T3	89	81	0.91	6.0	4.2	0.71	565	506	0.90	2.4	1.8	0.75
Mba	86	93	1.09	6.0	5.1	0.86	537	520	0.97	2.0	1.7	0.86
Peat and wood chips co-combustion												
T4	121	100	0.83	5.6	6.3	1.13	349(a	564(a	1.62	2.2	1.7	0.80
T5	100	83	0.83	5.6	6.0	1.07	336(a	561(a	1.67	2.5	2.8	1.12
T6	116	83	0.71	6.5	6.9	1.07	362(a	568(a	1.57	2.6	2.2	0.84
Mba	112	89	0.79	5.9	6.4	1.09	n	n	n	2.4	2.2	0.92

Plant TB	Mn			Mo			Ni			Pb		
	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In
Peat combustion												
T1	6720	6180	0.92	33(a	19(a	0.58	230	207	0.90	176	147	0.84
T2	5860	6740	1.15	35	25	0.73	248	282	1.13	172	182	1.06
T3	5950	5250	0.88	40(a	18(a	0.44	256	214	0.84	173	135	0.78
Mba	6180	6060	0.98	35	25	0.73	245	234	0.96	173	155	0.89
Peat and wood chips co-combustion												
T4	7570	8040	1.06	n	26	n	248	254	1.03	127	180	1.42
T5	7170	8200	1.14	31	26	0.83	187(a	276(a	1.48	93	188	2.01
T6	7890	8870	1.12	32	25	0.78	207(a	289(a	1.39	149	221	1.48
Mba	7540	8370	1.11	32	26	0.80	248	254	1.03	n	n	n

a not included in Mba, when Out/In is not 0.7–1.3. Mba: mean value of the tests, n: not possible to calculate

d) Plant VB	**As**			**Cd**			**Cr**			**Hg**		
Test ID	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In
Peat combustion												
V1	55	55	1.00	5.1	3.9	0.77	250	197	0.79	2.6	1.6	0.63
V2	60	55	0.92	5.1	3.6	0.70	277	222	0.80	2.6	1.6	0.63
Mba	57	55	0.96	5.1	3.8	0.73	263	209	0.79	2.6	1.6	0.63
Peat and saw dust co-combustion												
V3	44	40	0.89	6.1	3.6	0.59	198	204	1.03	3.5	1.4	0.39
V4	44	41	0.92	5.4	3.5	0.66	188	202	1.07	2.7	1.3	0.50
Mba	44	40	0.91	5.7	3.6	0.62	193	203	1.05	3.1	1.4	0.44

Plant VB	**Mn**			**Mo**			**Ni**			**Pb**		
Test ID	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In	In (g/h)	Out (g/h)	Out/In
Peat combustion												
V1	1990	2070	1.04	< 32	12	n	211	155	0.73	205	196	0.96
V2	2510	2260	0.90	< 32	12	n	232	175	0.76	167	147	0.88
Mba	2250	2160	0.96	< 32	12	n	222	165	0.75	186	171	0.92
Peat and saw dust co-combustion												
V3	3290	2920	0.89	< 34	11	n	184	152	0.83	109	121	1.11
V4	3100	2920	0.94	< 34	11	n	178	153	0.86	109	122	1.12
Mba	3200	2920	0.91	< 34	11	n	181	153	0.84	109	122	1.12

[a] not included in Mba, when Out/In is not 0.7–1.3
Mba: mean value of the tests
n: not possible to calculate

Appendix 13. PCA for the process parameters

The process parameters given in Appendix 6 were studied with principle component analysis (PCA) to find out

i) the main similarities/differences in the process parameters in the coal-fired power plants HB, SB and MB

ii) the main similarities/differences in the process parameters in the bark-fired power plant UB and in the peat-fired power plants RB, TB and VB

iii) the differences in the process parameters between each test in each plant.

Coal-fired power plants

When the process parameters of plants HB, SB and MB given in Appendix 6 were loaded as the variables with the weights of 1/stdev for the PCA, the first principle component explained 60 % and the first two PCs explained 80 %. The bi-plot of scores and loadings with the first two PCs is shown in Figure A13.1. The tests of each plant form own groups. No significant differences were found between the tests at each plant. Plant MB has higher mass flows (i.e. Fuel, PFA, BA, lime, Fgu, Fgd, SW) and fuel effect than other plants. The moisture and ash content (i.e. Ash) in the coal is high and heat value of the coal (i.e LHV) is low at plant HB. The particle concentration in the flue gases upstream of the FGD (i.e. Partu) is highest at plant HB.

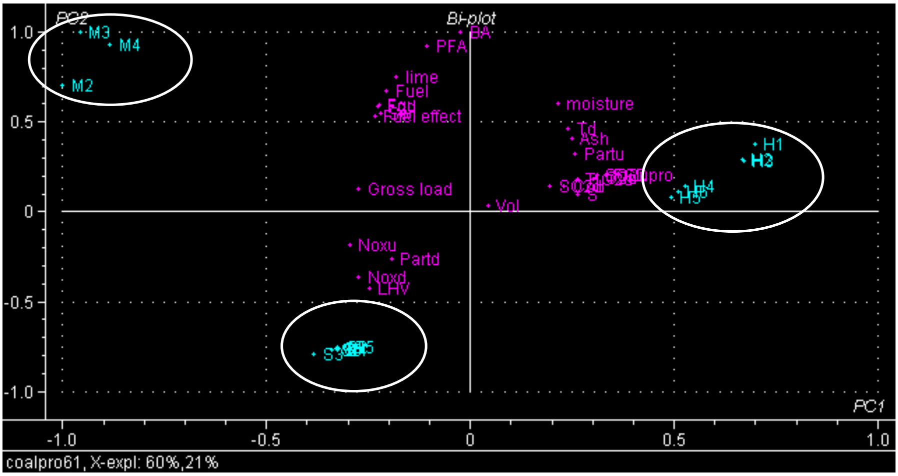

Figure A13.1. The bi-plot of scores and loadings with the first and the second principle components for the coal-fired power plants HB, SB and MB) using the process parameters given in Appendix 6 as the variables with weights of 1/stdev.

Fluidised bed plants

When the process parameters of plants UB, RB, TB and VB given in Appendix 6. were loaded as the variables with the weights of 1/stdev for the PCA, the first principle component explained 46 % and the first two PCs explained 69 %. The bi-plot of scores and loadings with the first two PCs is shown in Figure A.13.2. The objects (i.e. the tests) are distributed in three main groups. Tests U1–U6 constitute one group, tests R1–R5 another group and the tests T1–T6 and V1–V4 the third group. Besides the fuel effect and gross load the separation of plants TB and VB is most effected by their high flow rate of bottom ash (i.e. BA). Plant RB has the highest ash and sulphur content in fuel (i.e. Ash, Sulphur) as well as the highest SO_2, NOx and particle concentrations in the flue gases (i.e. Fp). The flow of PFA is lowest at plant UB. Plant UB has low SO_2 and NOx concentration and high CO concentration in the flue gases at high temperature (i.e FG Temp) compared to the other plants. The content of volatiles in the fuel (i.e. Volatiles) is also high in the tests of bark-fired power plant (i.e. U1–U6).

No changes in the bi-plot figure were found when the process parameters were loaded with weights of 1.0 as variables. The first PC explained 66 % and the first two PCs explained 87 %.

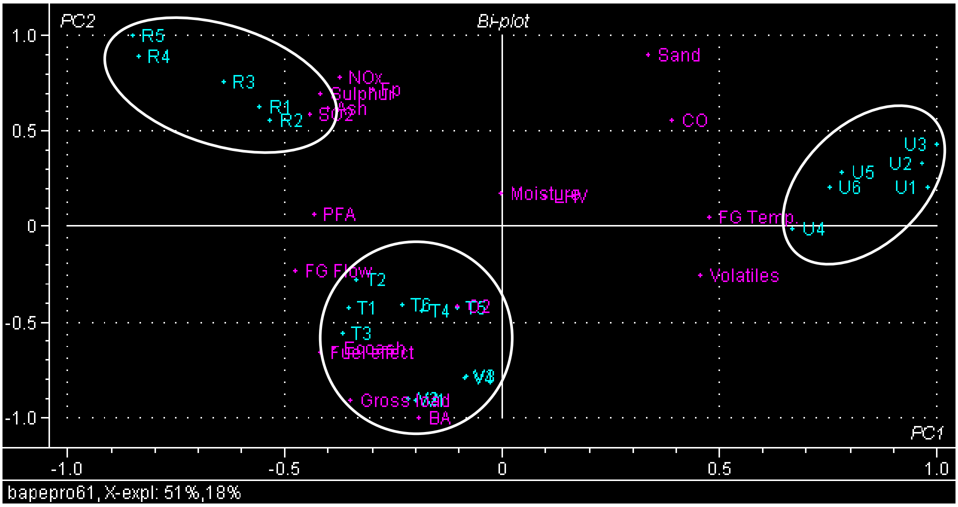

Figure A13.2. The bi-plot of scores and loadings with the first and the second principle components for the bark-fired power plant UB and the peat-fired power plants RB, TB and VB using the process parameters given in Appendix 6 as the variables with weights of 1/stdev.

When the process parameters of plant UB given in Appendix 6 were used as variables with the weights of 1/stdev, tests U1–U3 and U4–U6 formed two distinct groups. The tests of bark combustion (U1–U3) have the higher flow rate of sand supplied, the higher CO concentration in flue gases and the higher content of volatiles in fuel compared to the tests of co-combustion (U4–U6). The conclusion of the PCA is that the pure bark-combustion tests (U1–U3) were clearly distinct from the co-combustion tests (U4–U6). The repeatability of tests U1–U3 and U4–U6 is good if the random value of coarse ash (bottom ash and ecoash) flow and high NOx-concentration in the flue gases in test U5 are accepted.

In case of plant TB, the first two PCs showed their own specific groups in the bi-plot figure for pure peat-combustion tests (T1–T3) and for co-combustion tests (T4–T6), as seen in Figure A13.3. The locations of tests T1–T3 mainly resulted from the higher heat value, the higher content of ash and sulphur in fuel (i.e. LHV, Ash, Sulphur) compared to tests T4–T6. The concentrations of SO_2 and NOx in flue gases were higher during pure peat combustion (i.e. T1–T3). The content of volatiles in the fuel was higher and the flow rates of ecoash and PFA were higher during co-combustion (i.e. T4–T6) compared to pure peat combustion (i.e. tests T1–T3). The repeatability of tests T1–T3 and T4–T6 is rather good if the random value of bottom ash flow and high particle concentration in the flue gases in test T6 are accepted.

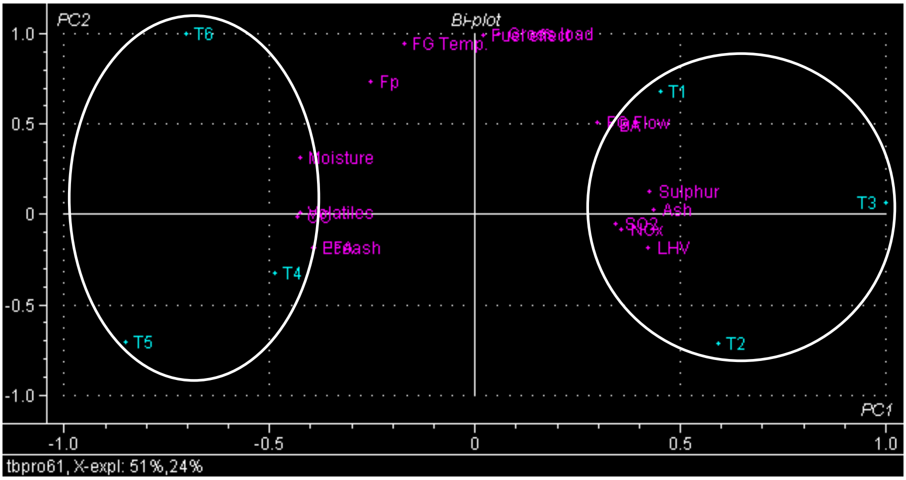

Figure A13.3. The bi-plot of scores and loadings with the first and the second PCs for plant TB using the process parameters given in Appendix 6 as the variables with weights of 1/stdev.

When the process parameters of plant TB given in Appendix 6 were used as variables with the weights of 1/stdev, tests V1–V2 and V3–V4 formed two distinct groups in the bi-plot of the first two PCs according to the pure peat-combustion and co-combustion with saw dust. The co-combustion tests (V3 and V4) have the higher fuel effect, the higher content of volatiles in the fuel and the higher flow rate of PFA compared to pure peat combustion. The repeatability of tests V1–V2 and V3–V4 is excellent.

The highest content of sulphur in fuel and SO_2-concentration in flue gases were found at plant RB, especially during tests R4 and R5. The repeatability of the tests R1–R5 was not good. This is seen in the bi-plot of the first two PCs in Figure A13.4, where the first PC explained 56 % and the first two PCs explained 73 %. Tests R1, R2 and R3 obviously differed from tests R4 and R5. The flow rate of flue gases (i.e. FG flow), particle concentration (i.e. Fp), NOx and SO_2 concentrations in flue gases as well as the flow rate of bottom ash and PFA (i.e.

BA, PFA) were higher in tests R4 and R5 than in tests R1 and R2. Test R3 was closer to tests R1 and R2, according to these parameters and according to the content of ash in the fuel and the low heat value of the fuel (i.e. Ash, LHV).

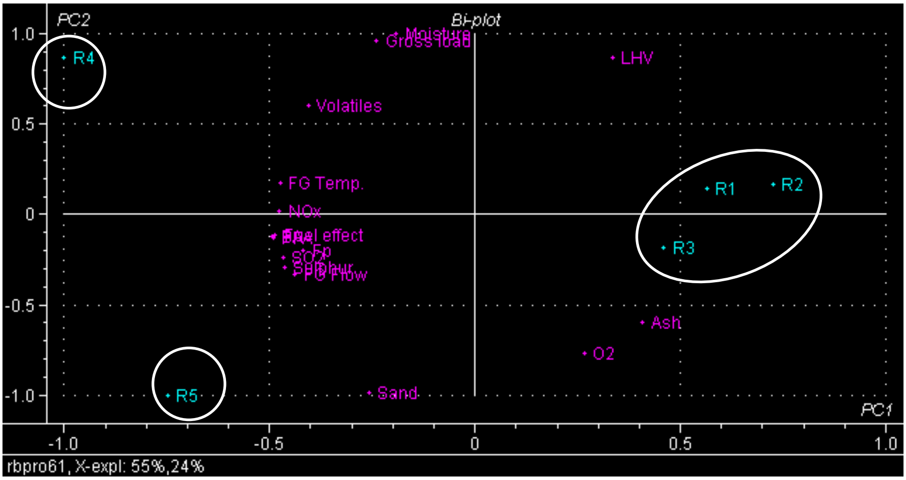

Figure A13.4. The bi-plot of scores and loadings with the first and the second PCs for plant RB using the process parameters given in Appendix 6 as the variables with the weights of 1/stdev.

When the PC analysis was performed for the process parameters in the case of the peat-fired power plants, it could clearly be seen (in Figure A13.5), that the tests of plant RB (i.e. R1–R5) formed their own group. Plant RB, which was equipped with a bubbling fluidised bed, had a lower fuel effect, lower gross load, cooler flue gases and a lower mass flow of the bottom ash than in plants TB and VB. The significant differences of tests R1–R5 compared to the other tests were high SO_2- and NOx-concentrations in the flue gases. Plants TB and VB were equipped with circulating fluidised beds, which produce a higher flow rate of bottom ash.

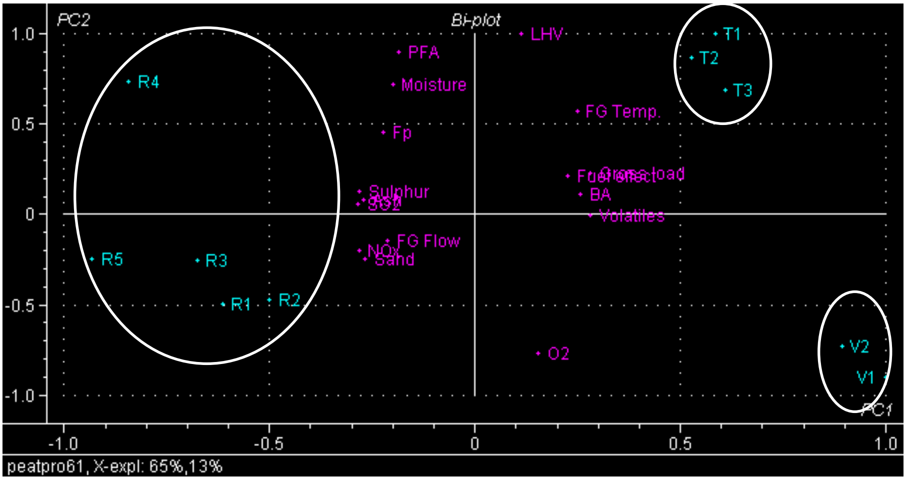

Figure A13.5. The bi-plot of scores and loadings with the first and the second PCs for the peat-fired power plants RB, TB and VB using the process parameters given in Appendix 6 as the samples with the weights of 1/stdev.

As a conclusion of the process parameters, it can be summarised that tests U1–U3, U4–U6, T1–T3, T4–T6, V1–V2 and V3–V4 have good repeatability. Tests R1–R3 and R4–R5 are better to study separately in the case of plant RB. The flow rate of bottom ash is significantly higher in the circulating fluidised bed plants (TB, VB) than in the bubbling fluidised plant (RB) during peat combustion. If the process parameters given in Appendix 6 are used as the arguments, plants UB, TB and VB demonstrate appropriate techniques for co-combustion. The energy contents in the different fuels were utilised effectively in all cases during pure bark or peat combustion, as well as during co-combustion of bark and sludge, or peat and wood chips/sawdust. The plants were operated with a high co-efficient of utilisation producing maximum gross load without any disturbances during the measurements. The higher ash content in the fuel was seen only in the increased stream of pulverised ash, not in particle concentration in flue gases in stack. From the environmental point of view, the concentration of SO_2 was decreased during the co-combustion of peat and wood chips or sawdust, because of the low content of sulphur in the wood. In the case of the bark-fired power plant, the higher content of sulphur in sludge did not increase the SO_2 concentration in flue gases even close to the requirement of the environmental authorities (i.e. 70 ppm; 1017/2002). The NOx concentrations in flue gases were also well below the requirements of the environmental authorities in all cases.

Appendix 14. PCA for the trace element contents

The Principle Component Analysis was carried out with the trace element contents of each test at the coal-fired power plants (HB, SB and MB), at the bark-fired power plant (UB) and at the peat-fired power plants (RB, TB and VB). The mean values of the trace element contents are shown in Appendix 7 and in Appendix 9. The contents of trace elements in fuel are shown in Tables 6.2 and 6.4.

The multivariate analysis was used to find out

i) the main differences in the fuel supplied at the coal-fired power plants

ii) the main differences in the fuel supplied at the peat-fired power plants

iii) the main similarities/differences in the outcoming trace element contents at the coal-fired power plants

iv) the main similarities/differences in the outcoming trace element contents at the bark- and peat-fired power plants

v) the significant variations in outcoming trace element contents in each plant

vi) the potential correlation between the trace element contents and the process parameters or combustion technique

vii) the main similarities/differences in the relative enrichment factors at coal-fired power plants

viii) the main similarities/differences in the relative enrichment factors at the bark- and peat-fired power plants.

Trace elements in coal supplied at plants HB, SB and MB

PCA was used to analyse the data set of the trace element contents in the coal supplied to obtain an overview of the different tests at plants HB, SB and MB. The first PC explained 28 % and first two PCs explained 55 % when the variables were weighted with 1/stdev. The first two PCs divide the data into three groups as seen in Figure A14.1. Tests H1–H6 formed the first group based on the higher contents of As, Be, Hg, Cd, Mn and Pb in the coal compared to the other tests. Tests S1–S4 differed from the tests M2–M4 according to the higher content of Co and Cu in the coal at plant HB. The specific location of tests M2–M4 was influenced by the exceptionally high contents of Cr and Ni and by the high detection limit for Tl.

Based on the results of the PC analysis, the coal supplied at plant HB differed from the coal supplied at plants SB and MB according to its somewhat high contents of Be, Cd, Mn and Pb. The contents of As and Hg were higher in the coal supplied at plants HB and MB than at plant SB.

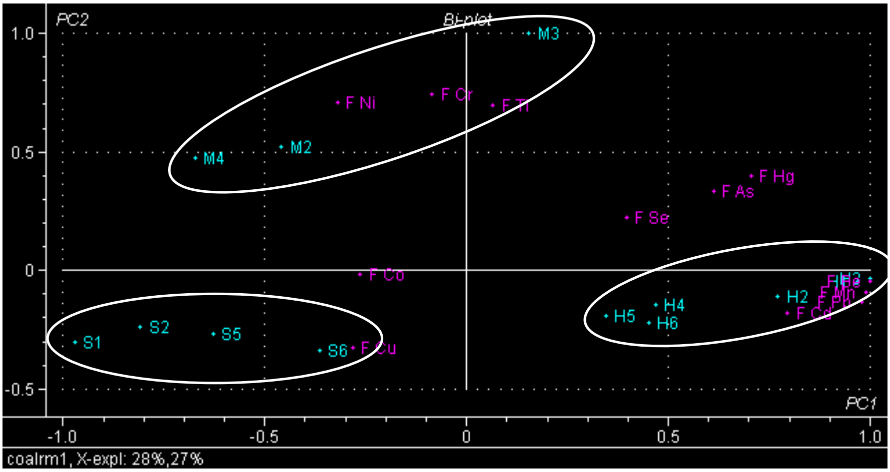

Figure A14.1. The bi-plot of scores and loadings with the first and the second PCs for plants HB, SB and MB using the trace element contents in the coal as the variables with weights of 1/stdev. (The content of Zn analysed only at plant was excluded from the variables.)

Trace elements in the fuel supplied at plants UB, RB, TB and VB

PCA was used to analyse the data set of the trace element contents in the fuel mixture supplied and to obtain an overview of the different tests at plants UB, RB, TB and VB. The first PC explained 57 % and first two PCs explained 78 % when the variables were weighted with 1/stdev. The first two PCs divide the data into several groups, as seen in Figure A14.2. Tests R1–R5 form the first group based on the higher contents of As, Cr and Ni in fuel (i.e. peat) and on the lower content of Hg in fuel compared to the tests of the other peat-fired power plants (i.e. T1–T6, V1–V4). (The content of Mo was not analysed in the tests U1–U6 and R1–R5.) Tests T1–T6 and V1–V4 form the second group with a distinct location for test T3. The specific location of test T3 is influenced by the highest content of Mo. This second group is formed mainly according to the higher content of Hg in the fuel compared to tests U1–U6 and R1–R5. The co-combustion tests T4–T6 have a specific location compared to the peat-combustion tests T1–T3 according to their higher content of As and Mn in the fuel, and according to their lower content of Cr, Mo, Ni and Pb in the fuel. Test T4 differs from the other co-combustion tests mainly because of the higher content of As and Ni in the fuel. The locations of the co-combustion tests V3–V4 differ from the peat-combustion tests V1–V2 based on their lower content of As, Cr, Ni and Pb, and according to their higher content of Mn in fuel.

Tests U1–U6 form the third group based on their high content of Cd and Mn in the fuel. The co-combustion tests U4–U6 differ from the bark-combustion tests according to their higher content of Cd and Mn in the fuel mixture of bark and sludge.

As a conclusion, it can be said that the peat supplied at plants RB, TB and VB differed from each other according to the contents of As, Cd, Cr, Hg and Mn. The contents of Ni and Pb in the peat were close to each other. The mixture of peat and wood chips differed from peat supplied at plant TB in the contents of As, Cr, Mn, Mo, Ni and Pb. The contents of Cd and Hg in the fuel mixture were close to the level in peat at plant TB. The mixture of peat and sawdust differed from peat supplied at plant VB in the contents of As, Cr, Mn, Ni and Pb. The contents of Cd and Hg in the fuel mixture were close to the contents in peat at plant VB. The bark and the mixture of bark and sludge supplied at plant UB showed a significant difference in contents of As, Cd and Mn compared to the fuels supplied at plants RB, TB and VB. The mixture of bark and sludge had higher contents of Cd, Cr, Mn, Ni and Pb than pure bark. The content of Hg in the bark was almost equal to the content in the mixture of bark and sludge.

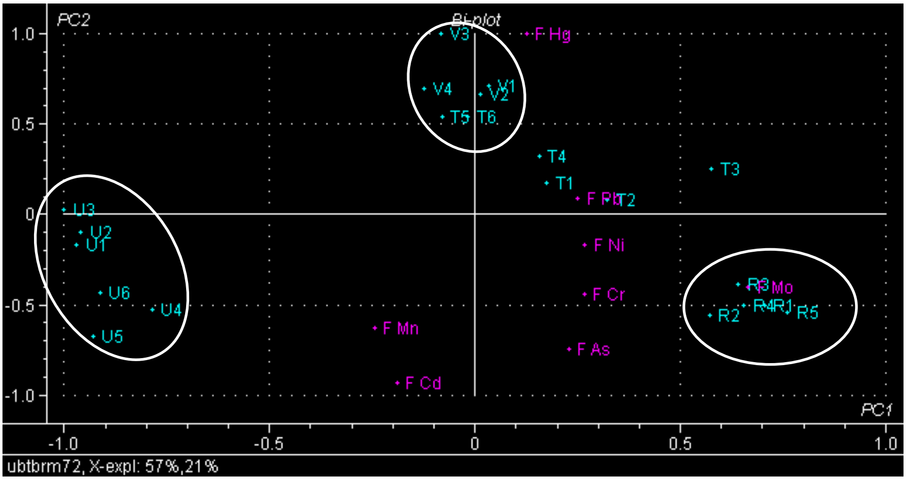

Figure 14.2. The bi-plot of scores and loadings with the first and the second PCs for plants UB, RB, TB and VB using the trace element contents in the fuel as the variables with weights of 1/stdev.

The outcoming trace element contents at plants HB, SB and MB

The principle components of the outcoming trace element contents from plant HB, SB and MB were analysed using the data from the ratio of trace element contents in the samples to their contents in the coal supplied. The data excluded the contents of Zn and all trace element contents in the ecoash, which were analysed only at plant MB. The contents in the FGD solid streams (i.e. FGD products, gypsum) and waste water were also excluded, because they were not available inform of all the plants. The bi-plot of the first two PCs is shown in Figure A14.3. The first PC explained 29 % and two first PCs explained 39 %, which means a weak correlation. The ratio between the trace element contents in the particulate fraction upstream of the FGD to their content in the coal is high for tests H1–H6. The ratio of Cr and Ni contents in the PFA to that in the coal are high in the tests of plant SB. Test M2 has higher ratio between the trace element content in the stack flue gas particles and that in coal than tests M3 and M4.

The PCA for relative enrichment factors did not express any additional consistent information about the tests or the plants.

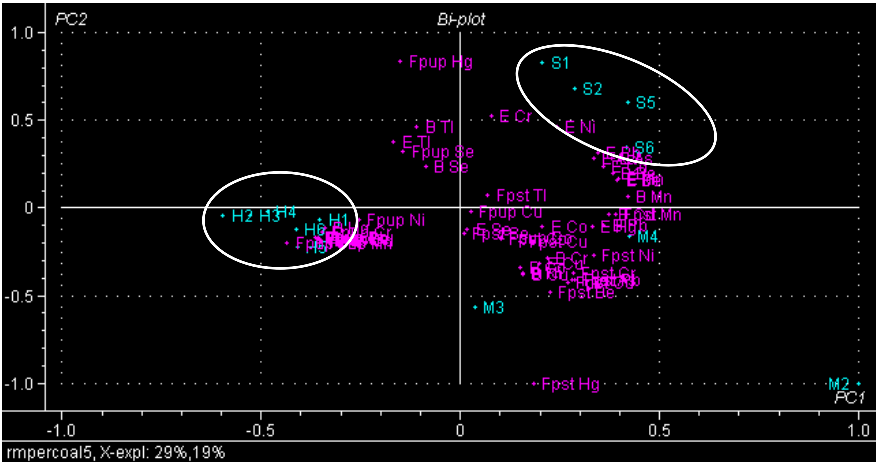

Figure A14.3. The bi-plot of scores and loadings with the first and the second PCs for plants HB, SB and MB using the ratio between the outcoming trace element contents and the content in coal as the variables with weights of 1/stdev.

The outcoming trace element contents at plants UB, RB, TB and VB

The principle components of the outcoming trace element contents from plants UB, RB, TB and VB were analysed using data from the ratio of trace element contents in the samples to their contents in the fuel supplied. The data excluded the contents of As and Mo in the gaseous fraction of the flue gases, Hg in the ecoash, and Hg and Mo in the bottom ash, which were analysed below the determination limit in all the tests. The bi-plot of the first two PCs is shown in Figure A14.4. The first PC explained 29 % and first two PCs explained 39 %, which means weak correlation. It can be seen that the ratios of As and Cd in the bottom ash and Hg in the gaseous and particulate fraction of the flue gases affect the specific location of tests T1–T6. The ratio of Cr and Hg in the gaseous fraction of the flue gases and As in the PFA affect the location of tests V1–V4. The ratio of As, Mn and Pb in the flue gas particles and Hg in the PFA affect the location of tests R1–R5. The first and the second PC had no significant effects on tests U4–U6. The group of the tests U1–U3 are located separately from the other tests mainly based on the ratio of Cd, Cr, Mn, Ni and Pb in PFA, and of Cr and Mn in the bottom ash.

In conclusion it can be seen that the high ratio of Cd in the bottom ash, and Hg in the gaseous fraction of the flue gases, and the low ratio of Pb in the flue gas particles compared to the contents in the fuel differed between tests T1–T6 and V1–V4, and tests R1–R5 and U1–U6. This difference arises according to the combustion technology. Tests U1–U6 and R1–R5 were carried in a bubbling fluidised bed, and tests T1–T6 and V1–V4 in a circulating fluidised bed. Tests U1–U3 with pure bark combustion differed from the other tests because of the high ratio of Cr, Ni and Pb in the bottom ash, ecoash, PFA and the flue gas particles. The ratio of Cd and Mn in the PFA was also high in tests U1–U3.

The PCA was also performed for the data of relative enrichment factors. The first PC explained 55 % and the first two PCs explained 88 %. The tests of each plant formed the groups based mainly on the trace element enrichments in the flue gas particles, as seen in Figure A14.5. The tests of plant RB differed from the other tests based on the higher RE of Pb in the flue gas particles. The second group was formed by tests V1–V4 based on the high RE of Cd in the flue gas particles. Tests T1–T6 formed a third distinct group because of their low RE of Ni and Pb in the flue gas particles. The tests did not differ according to the combustion technology as in the previous case.

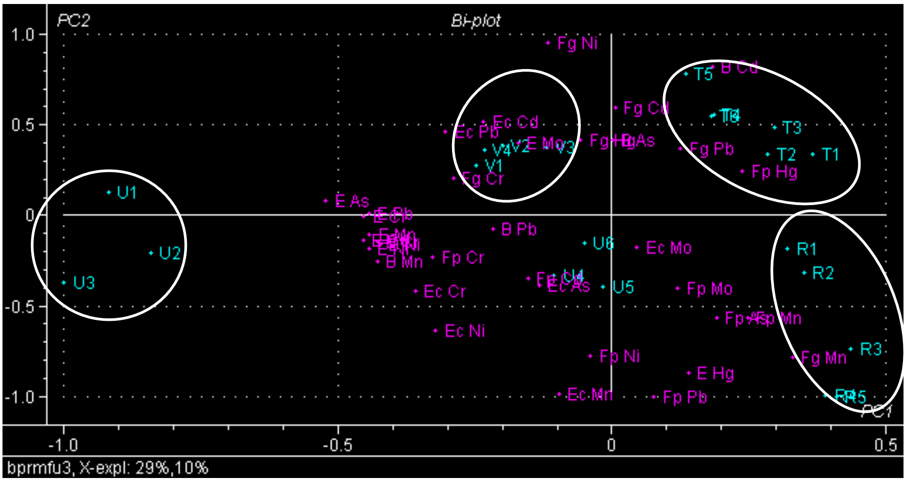

Figure A14.4. The bi-plot of scores and loadings with the first and the second PCs for plants UB, RB, TB and VB using the ratio between the outcoming trace element contents and the content in fuel as variables with weights of 1/stdev.

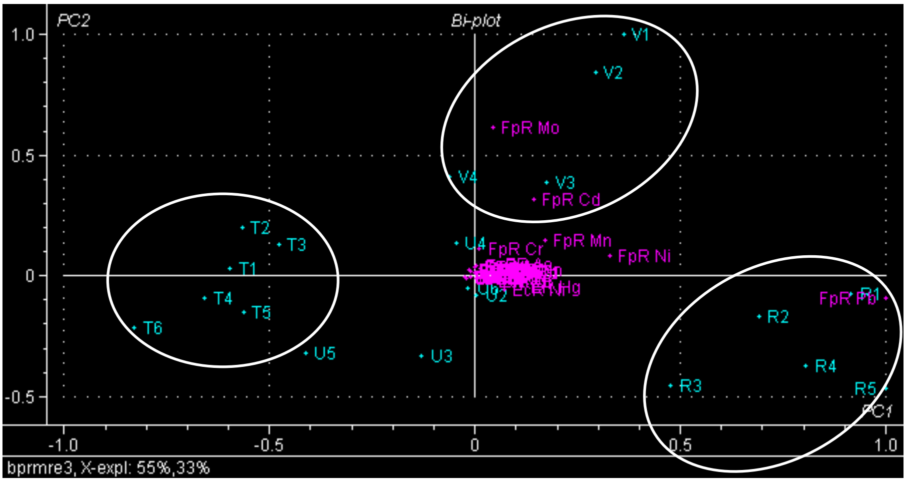

Figure A14.5. The bi-plot of scores and loadings with the first and the second PCs for plants UB, RB, TB and VB using the relative enrichment factors of trace elements as the variables with weights of 1.0.

Appendix 15. PLS for the trace element contents and the process parameters

PLS was carried out for the data of i) relative enrichment factors and ii) values of flue gas temperature, NOx, SO_2 and particle concentrations in the flue gases upstream of the FGD (i.e. downstream of the ESP) and contents of moisture, volatiles, sulphur and ash in the fuel. It can be seen from Figure A15.1 that the tests of the fluidised bed plants formed groups beside each other resulting from their higher content of volatiles and moisture in the fuel. The relative enrichment factors of As and Hg in the flue gas particles downstream of the ESP (FpRu As, FpRu Hg) are high, and the enrichments of Cr and Ni in the PFA (ER Cr, ER Ni) are high at plants UB, TB and VP compared to the coal-fired power plants.

The enrichment factors of As, Cd, Hg, Mn and Pb in the bottom ash (BR As, BR Cd, BR Hg, BR Mn, BR Pb) and in the PFA (ER As, ER Cd, ER Hg, ER Mn, ER Pb) are high at coal-fired power plants compared to the bark- and peat-fired power plants, especially at plant HB. Plant HB has high content of sulphur and ash in the fuel, as well as high SO_2 concentrations in the flue gases upstream of the FGD (i.e. downstream of the ESP).

The PLS was carried out for the data of the fluidised bed plants alone. The results are shown in Figure A15.2. The tests with higher content of ash and sulphur at plant RB differ from the other tests – the enrichment factors of Mn and Pb in the bottom ash (i.e. BR Mn, BR Pb) are high, as well as of Hg in all ashes (i.e. BR Hg, ER Hg, FpRu Hg). The concentrations of NO_x and SO_2 in flue gases are also higher at plant RB compared to the other fluidised bed plants. The contents of ash and sulphur in the fuel have weak negative correlation to the enrichment of Cr in the bottom ash (i.e. BR Cr) and of Ni in the PFA (i.e ER Ni).

The contents of ash and sulphur in the fuel correlate positively with the enrichment factors of Hg, Cd, Mn, Pb in the bottom ash and of Hg in the PFA both at the coal-fired power plants and at the fluidised bed plants. The correlation of ash and sulphur contents in the fuel is negative to the enrichment of Cr and Ni in the PFA in both cases.

PLS was used to detect any correlation between the contents of different trace elements in the case plants. The results of PLS did not reveal any further information for the concentrations of outcoming trace elements.

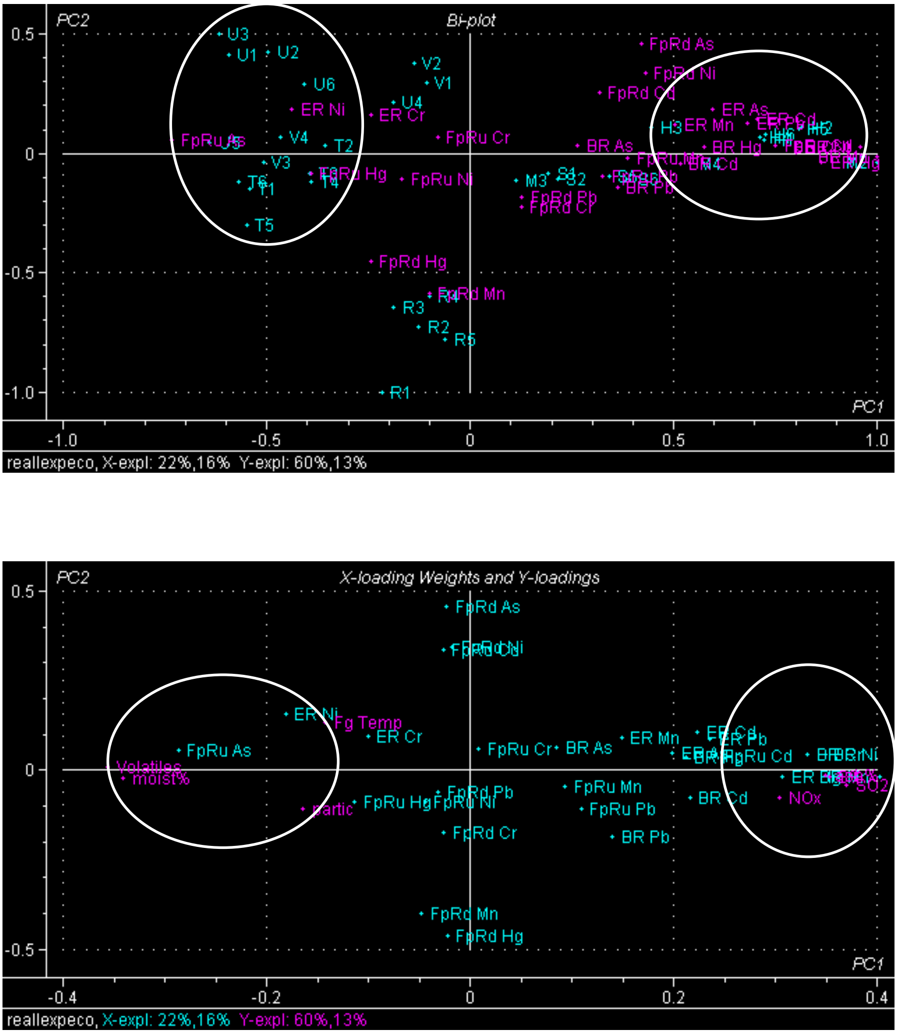

Figure A15.1. The results of PLS for all the case plants. Regression of i) the enrichment factors of trace elements and ii) the contents of moisture, volatiles, sulphur and ash in the fuel, flue gas temperature and NOx, SO_2 and particle concentration in flue gas downstream of the ESP.

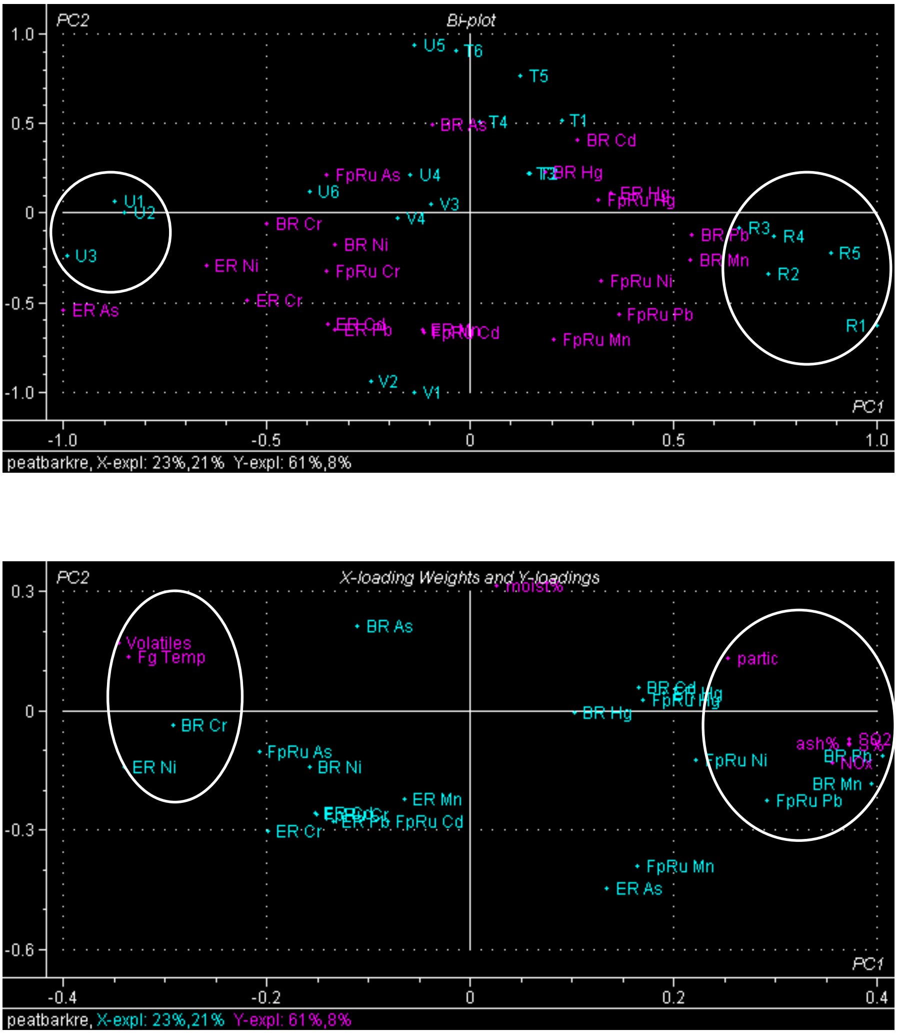

Figure A15.2. The results of PLS for the fluidised bed plants. Regression of i) the enrichment factors of trace elements and ii) the contents of moisture, volatiles, sulphur and ash in the fuel, flue gas temperature and NOx, SO_2 and particle concentration in flue gas downstream of the ESP (i.e. in the stack).

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Mass balance determination for trace elements at coal-, peat- and bark-fired power plants

Abstract

Determining the distribution of trace elements in a large-scale power plant is a challenge for both sampling and analysis. Besides the accuracy determination of the element content, the quantity flow rate of each stream of the plant is also a challenge because there are many streams without any flow recorders. This thesis describes a method to determine the steady-state mass balance of trace elements with highly satisfactory closures. When the method first developed for coal-fired power plants is applied to bark- and peat-fired power plants equipped with a fluidised bed, in order to attain a high closure of balance, some critical factors must be considered (running parallel tests, analysing parallel samples, sampling the main fuel and added fuel separately, including at least one element that is determined well above the detection limit in all the streams, waiting a long time to start sampling after the fuel supplying change etc.).

This thesis presents the results and evaluation of the mass balances for 14 trace elements (i.e. As, Be, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Tl, Se and Zn) determined in three coal-fired, three peat-fired power plants, and one bark-fired power plant in Finland. Each plant is equipped with specific low-NOx burning technology (i.e. low-NOx burners, staged over-fire air suppliers, selective catalytic NOx reduction or fluidised bed combustor) and an electrostatic precipitator. In addition, the coal-fired power plants were equipped with SO_2 control technology including a fabric filter or gypsum production unit. Some of the results pertain to the co-combustion of peat and bark with wooden waste material or sludge from the wastewater treatment plant.

The outcoming trace element flows of the power plants were low. Most of the trace elements exit the plant via the pulverised fly ash, removed by electrostatic precipitator, except for mercury. The collection efficiency of the electrostatic precipitators (ESP) was from 92 % to over 99 % for As, Be, Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn at the coal-fired power plants. In respect of the atmosphere though, the ESP is followed by a flue gas desulphurisation plant (FGD), which removes the majority of the penetrated trace elements. The collection efficiency of the ESPs were from 94 % to over 99 % for As, Cd, Cr, Mn, Mo, Ni and Pb at the fluidised bed plants. The mercury in the flue gases was removed effectively by a semi-dry flue gas desulphurisation plant in the coal-fired power plants, but it was released mainly in the vapour phase to the atmosphere in the other plants.

The results of multivariate data analysis showed that the plants operating at maximum load was able to run well repeatable. The low-NOx burning technique had no significant effects on the enrichments of the trace elements in the outcoming streams compared to those of the conventional burning technique reported in the literature. No significant differences were found in the relative enrichment of trace elements in the outcoming streams of the plants between the coal-fired power plants equipped with semi-dry and wet flue gas desulphurisation. The case fluidised bed plants demonstrate appropriate techniques for co-combustion. The co-combustion tests revealed differences between pure bark and peat combustion according to the differences in the contents of Cd, Cr, Ni and Pb in the outcoming streams of the plant and in the relative enrichment factors of these trace elements. In addition to the relative enrichment factor of trace elements, the ratio of trace element content in the ash samples to the content in the fuel was found to be useful for element characterisation. The peat-fired power plants equipped with bubbling and circulating fluidised beds showed differences in the ratio of Cd, Hg and Pb in the outcoming streams compared to the contents in the fuel.

Keywords
trace elements, emissions, steady-state mass balance, measuring methods, solid fuels, sampling, analysis, data processing, power plants, fluidized bed combustion, co-combustion

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Mass balance determination for trace elements at coal-, peat- and bark-fired power plants

Merja Tolvanen

Determining the distribution of trace elements in a large-scale power plant is a challenge for both sampling and analysis. The contents of each trace element in different streams can have variations of several magnitudes. In determining the quantity of all the ingoing and outcoming flows of each element, the low contents of the elements must also be determined. Besides the accuracy determination of the element content, the quantity flow rate of each stream of the plant is also a challenge because there are many streams without any flow recorders. This thesis describes a method to determine the steady-state mass balance of trace elements with highly satisfactory closures.

This thesis presents the results and evaluation of the mass balances for 14 trace elements (i.e. As, Be, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Tl, Se and Zn) determined in three coal-fired, three peat-fired power plants, and one bark-fired power plant in Finland. Each plant is equipped with specific low-NOx burning technology (i.e. low-NOx burners, staged over-fire air suppliers, selective catalytic NOx reduction or fluidised bed combustor) and an electrostatic precipitator. In addition, the coal-fired power plants were equipped with SO_2 control technology including a fabric filter or gypsum production unit. Some of the results pertain to the co-combustion of peat and bark with wooden waste material or sludge from the wastewater treatment plant. The results from each plant are analysed and presented as relative enrichment factors of trace elements and as the removal effects of particulate control devices. Not many reports on experimental tests for mass balance studies have been published, and especially not to such a large extent as reported in this thesis.

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