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Occupational hygiene measurements at power plant sites

Sustainable Bioenergy
Solutions for Tomorrow

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Key words: Occupational hygiene, bioenergy, biological exposure, ash

Summary

The aim of the research was to clarify health and safety issues in the context of bioenergy supply chains. The main focus was on safety issues at biomass-fuelled power plant sites but also some health aspects were considered. Particularly the aim was to analyse the exposure of employees to the different emissions of fuels and their ashes.

Experimental measurements were carried out in the autumn and in the winter at three biomass and SRF fuelled power plants. First a technical survey on biomass operations at the selected power plants was performed to collect background information by interviews and observations. Fuel and ash sampling points were defined and recommendations for experimental measurement points were stated. Then, exposure measurements were carried out at the power plants. Exposure of employees to biological and chemical agents was studied during their normal duties. Air samples were collected from breathing zones and stationary sampling points. Material samples were collected from fuels, bottom ash and fly ash.

The model of sequential technical surveys and occupational hygiene measurements at selected power plant sites worked well. The main occupational exposure associated health risks for workers were found to be bacteria and fungi, which are easily spread to the air during the operations at biomass fired power plants. The measured exposure levels on endotoxin, actinobacteria and fungi were high especially in fuel reception. In addition, workers are exposed to mechanical irritation caused by organic dust, chemical irritation caused by VOCs and components of diesel exhausts. Truck drivers and power plant workers can also be exposed to ash during loading, especially in closed loading stations. It also seems that some heavy metals are enriched in respirable fly ash particle fraction. Only low spreading of contaminants to the environment was noticed during the measurements. Based on the results of experimental measurements, best practices were suggested for the power plants.

The key issue in preventing exposure associated respiratory impairment of workers at the biomass fuelled power plant sites is to improve the quality of fuels. The whole biomass supply chains has the main influence on the fuel quality. Microbial growth and microbial contamination in fuels can be prevented by strict control of temperature, moisture content and storage time. The better microbial quality ensures also higher energy content of solid biofuel. As a preventive technical measure, isolation of the spaces e.g. by closing doors in fuel reception halls and use of hoods around the crushers and screens, reduces spreading of bioaerosols and other agents to the surroundings. Control rooms for supervision of unloading of fuel trucks, automated fuel sampling and automatic cleaning systems for fuel trucks are favourable solutions to reduce the exposure of truck drivers.

All valuable preventive technical measures should be taken on use at biomass fired power plants to keep the occupational exposure as low as possible. If workers are still exposed to harmful substances after technical preventive measures, personal protective equipment has to be used and the workers have to be trained in its appropriate use.

Helsinki, November 2014

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Abbreviations

A1	Power plant A, first measurement round
A2	Power plant A, second measurement round
B1	Power plant B, first measurement round
B2	Power plant B, second measurement round
BA	Bottom ash
BFB	Bubbling fluidised bed
C1	Power plant C, first measurement round
C2	Power plant C, second measurement round
cfu	Colony forming unit
CHP	Combined heat and power
COPD	Chronic obstructive pulmonary disease
EDS	Energy dispersive X-ray spectroscopy
ESP	Electrostatic precipitator
EU	Endotoxin units
FA	Fly ash
g	Gravity
GC/PID	Gas chromatography, photoionization detector
IC	Ion chromatography
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
LOEL	Lowest observed effect level
MVOCs	Volatile organic compounds produced by micro-organisms
OEL	Occupational exposure limit
PAH	Polycyclic aromatic hydrocarbon
RH	Relative humidity
SCR	Selective catalytic reduction

SEM-EDS	Scanning electron microscope with energy dispersive X-ray spectroscopy
SRF	Solid recovered fuel
TD-GC-MS	Gas chromatograph equipped with thermal desorption injection technique and mass selective detector
TIC	Carbonate carbon
TLV	Threshold limit value
TOC	Non-carbonate carbon
TVOC	Total volatile organic compounds
VOC	Volatile organic compound
XRD	X-ray diffraction

1 Introduction

In 2013, CLEEN Ltd and FIBIC Ltd, both part of the Strategic Centres for Science, Technology and Innovation´s (SHOK) network, launched a research programme called Sustainable Bioenergy Solutions for Tomorrow (BEST). The duration of the programme is four years, but so far the funding granted by the Finnish Funding Agency for Technology and Innovation covers the first two years.

One of the BEST programme´s research groups is the Health, Safety and Environment (HSE) group, which focuses on studying health and safety issues in the bioenergy supply chain. The group is led by Tampere University of Technology´s (TUT) Department of Electronics and Communications Engineering (Environmental Health Group), and its members include VTT Technical Research Centre of Finland (VTT), the Finnish Institute of Occupational Health (FIOH) and the University of Eastern Finland (UEF), as well as companies such as Valmet Power, Stora Enso, UPM, ANDRITZ and Fortum.

The HSE group´s primary aim is to study the biological exposures encountered at power plant sites and the health issues related to ash. Businesses are clearly paying more attention to health, safety and environment issues, and the group aims to meet these needs and provide new perspectives for the bioenergy sector.

First, a literature survey (Fagernäs et al. 2014) was performed to compile earlier studies on the health issues in the bioenergy supply chain area to serve as a background for the research work. Based on the review, it was found that the occupational hazards of modern energy production that utilises renewable biomass have not been well studied. More surveys and measurements need to be carried out to assess the health and safety hazards. With increased biomass use and combustion, it will be important to assess the public health effects and give recommendations for future scenarios.

Second, in 2013-2014 occupational hygiene measurements were carried out at biomass and solid recovered fuel (SRF) power plant sites. This report presents the experimental measurements, analysis of the results and suggestions for best practices at the power plants.

2 Goal and execution of the research

The aim of the work was to clarify health and safety issues in the context of bioenergy supply chains. The main focus was on safety issues at biomass-fuelled power plant sites but also some health aspects were considered. Particularly the aim was to analyse the exposure to the different emissions of fuels and their ashes.

The research was performed according to the execution presented in Figure 1. First, a literature review on earlier studies on the health issues in the bioenergy supply chain was carried out and needs for experimental measurements were defined. Experimental measurements were carried out at different seasons (autumn, winter) at three biomass and SRF fuelled power plants located in separate parts of Finland.

The measurements included first a technical survey on biomass operations at the selected power plants. The study included collection of background information by interviews and observations about the power plant, fuels used and their delivery chains, working habits, work safety and health issues. Fuel and ash sampling points were defined and recommendations for experimental measurement points were stated. Then, exposure measurements were carried out at the power plants. Exposure of employees to biological and chemical agents was studied during their normal duties. Air samples were collected from breathing zones and stationary sampling points. Material samples were collected from fuels, bottom ash and fly ash. Based on the review and the results of experimental measurements, best practices were suggested for the power plants.

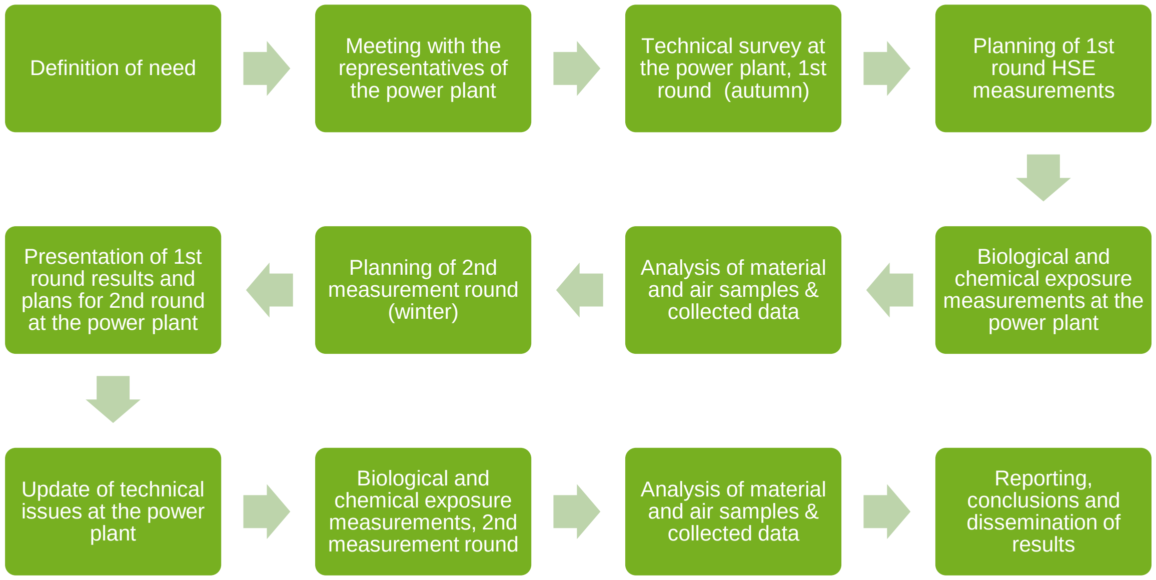

Figure 1. Schema of the execution of the research.

3 Biomass operations at selected power plants

3.1 Descriptions of the power plants

Three combined heat and power (CHP) plants were selected for case studies of occupational hygiene measurements. Selection was mainly based on variety of fuels, but other factors like the age of the plant were issues of the substance. Background information about the power plants is presented in Table 1.

Table 1. Basic information about the CHP plants of the case studies.

Power plant	**A**	**B**	**C**
Boiler type	BFB	BFB	BFB
Power (appr.)	75 MW_{fuel}	200 MW_{fuel}	170 MW_{fuel}
Age of the plant	New	~10 years	Old
Fuels used	Wood fuels 100% e.g. forest chips, used wood, whole-tree chips, stemwood chips, wood processing industry residues	Wood fuels 50% e.g. forest chips, stumps, forest residues, sawdust Bark 20% Milled peat 25% Waste water sludge 5%	Bark + waste water sludge 50% Solid recovered fuel (SRF) 50%
Additives used	Elemental sulphur	none	Elemental sulphur
Flue gas cleaning	Bag filter	Electrostatic precipitator (ESP)	ESP + Scrubber

3.2 Fuel reception

All the case power plants received at least one of the fuels by truck. All the fuels of power plant A were delivered as truckloads during the working days mainly. Rear-unloading full-trailer lorries (chain conveyor on the bottom of load space) or rear-tipping lorries arrive to the unloading through a plant’s weighing station. Examples of these two unloading ways are presented in Figures 2 and 3.

Figure 2. Rear-tipping of forest chips in a fuel receiving station of a power plant.

Figure 3. Rear-unloading of forest chips in a fuel receiving station of a power plant.

Forest residues and stumps were crushed at one plant and SRF was crushed in the other plant. Unloading of forest residues to the chipping line is illustrated in Figure 4.

Figure 4. Unloading of forest residues for the crushing. The driver is sitting in a tight cabin equipped with air-conditioning system during the unloading.

Fuel samples are taken at fuel receiving stations for moisture content and calorific value determinations. Sampling of fuels should be carried out by a standardised method, which means collection of several sub-samples from a load during unloading. Sampling was carried out manually by lorry drivers at each plant. At the power plant A there was an automatic sampling system, which was under initialisation.

Unloading of lorries produces lot of dust which is spread to the unloading station. Spreading of dust can be controlled by closed doors and side seals between the lorry and wall of the unloading station. Rear-unloading can be usually operated from a separate room with a window to the unloading room, which effectively reduces the dust exposure of a driver (Figure 5). Sometimes sampling of fuel is also possible through a small window from the same room (Figure 6). Usually the driver has to enter the unloading room several times during the unloading process. Duties that need the driver’s presence in the unloading room are sampling of fuel, cleaning and changing of the place of the lorry. During these duties attention has to be paid on appropriate prevention of workers’ exposure to hazards.

Figure 5. A driver can control rear-unloading from a separate room through a small window.

Figure 6. Sampling of fuel through a small window during unloading process.

3.3 Other noticeable process steps from HSE perspective

After receiving the fuels are screened, possible rejects crushed, and then conveyed to storage silos. There can be different lines for receiving, handling and storage of different fuel types. In the case of multifuel combustion, different fuel components can be fed to the same conveyer belt as layers before conveying to the boiler silo. Power plants B and C had also storage areas for bark from which the fuel was carried to combustion by long conveying belts.

There can be dusting of fuels during screening, crushing and shifting of fuels between the conveyors. Indoors the conveyors are usually open, but outside the building they are covered. Therefore fine dust, microbes and volatile gases typical for the fuels are always present in buildings where fuels are handled. The employees of the power plant take care of the process control, maintenance and cleaning the rooms. During these operations they are exposed to biological and chemical agents of fuels. Downstairs of fuel silos, covered conveyor belts and screening buildings were usually recognized as possible exposure places when asked from employees.

Paper mill waste water sludge is usually combusted in power plants on the same site. Sludge is at least mechanically dried and fed to the boiler together with other fuels. Wet sludge contains lot of microbes and can create at least an odour gas problem. Mixed sludge (dry matter content about 35w-%) from the own waste water treatment plant of the mill is transferred to power plant C as truckloads. The sludge is then thermally dried up to dry matter content of 80w-% by high-pressure steam and pneumatically conveyed to boiler.

Flue gas scrubber is used for heat recovery in the power plant C. Wastewater from the scrubber is treated by a lamella clarifier before discharge to waste water treatment plant. Wet sludge from clarifier is treated by a belt filter press. Operation and maintenance of these processes is carried out by the power plant staff.

Additives such as sulphur, china clay or ammonium sulphate are used to prevent fouling of the boiler heat transfer surfaces, to avoid corrosion caused by alkaline chlorides and to control air emissions. Additives influence on chemistry inside the boiler, and therefore have effect on ash quality also. Use of additives is increasing at biomass fuelled power plants and HSE issues during these new process stages should be carefully considered. Elemental sulphur was used as additive in the power plants A and C. Sulphur is delivered as granulated material to the power plant and dosing rate to the boiler is adjusted according to fuel, process and emission parameters.

3.4 Ash handling

Fly and bottom ashes are produced as by-products of energy production at the power plants. Ashes can be utilised or have to be landfilled depending on the environmental and technical properties of ashes, and the fuels used. Fly ashes from combustion of wood fuels and peat can be used as fertilizer products, if the requirements of the Finnish fertiliser legislation are fulfilled. Another option is the use of fly ashes in earth construction according to the notification procedure defined in the Finnish government decree on reuse of some waste materials in earth construction. An environmental permission is needed if the limit values of notification procedure are exceeded and also if solid recovered fuels are used. Landfilling of ashes is the last option if there are no possibilities for utilisation.

Usually two different ash fractions are collected in a combustion plant. In fluidised bed boilers the fly ash fraction is the largest, usually 80 - 90% of the total ash generated. Bottom ash fraction is collected from the bottom of a combustion chamber and it accounts from 10 to 20% of the total ash amount.

Fly ashes are separated from flue gases by an electrostatic precipitator or a bag filter and pneumatically conveyed to an ash silo. Fly ashes can be unloaded from ash silos as moistened or as dry depending on their way of delivery and end-use. The moistening of ash effectively diminishes dusting, but also accelerates the carbonisation reactions and hardens the ash. Ashes to be used as forest fertilizers are usually granulated and the moistening of ash is carried out during the treatment processes of an entrepreneur. For earth construction purposes the ashes are usually transferred to intermediate storage as moistened.

The fly ashes of the power plant A are used as fertilisers. Ashes are unloaded from the silo as dry and transferred to a fertiliser producer by a tank truck. The filling of the truck is done outdoors below the fly ash silo (Figure 7).

Figure 7. Loading of dry fly ash to a tank truck.

Fly ashes from power plants B and C were transferred to intermediate storage areas by lorries equipped with a container or a platform. Loading of the lorries was carried out indoors at power plant B and outdoors at power plant C (Figure 8).

Figure 8. Loading of moistened fly ash to trucks indoors and outdoors.

Bottom ashes were collected to a container, which was emptied when necessary in all the case power plants (Figure 9). Bottom ashes are typically utilised in earth construction applications if their technical and environmental properties fulfil the requirements set for the use.

Figure 9. Container for bottom ash.

3.5 Present protective measures at selected power plants

Drivers of fuel lorries were advised to use a crash helmet, goggles, protective shoes and clothes while working at the fuel receiving station at the power plant B (Figure 10). Same requirements were given to all drivers working in the mill area. In addition, hearing protectors have to be used in process premises and chemical-specific protection in the case of chemical transportations. It was also suggested to use FFP3 class respirators while working at the fuel receiving station. Observations revealed that basic requirements were followed quite well by the drivers, but respirators were used quite seldom.

Figure 10. Requirements for personal protection at a fuel receiving station at a power plant. A Crash helmet, goggles, protective shoes and clothes has to be used.

Regular cleaning is a good way to prevent spreading of dust or microbial growth. Some of the power plants had weekly procedures for the cleaning. Different parts of the process were cleaned during certain weekdays by the power plant staff. Cleaning by washing was a general way to clean the process premises, but also shovelling and brushing were used. The use of pressurised air is not allowed in cleaning, but vacuum cleaners can be used. At the plant B the excess heat was used to warm the conveyors, which enables the washing with water also during the winter time.

Drivers of fuel trucks were responsible for the cleaning of possible mess after unloading at all the power plants. Some of the drivers did their duties carefully, but some were more careless in the cleaning work. Typical situation was that a layer of biomass fuels was seen in the floor of fuel receiving station or in the front of a rear-tipping place. These fuels are easily spread to the surroundings of the power plant site by the truck wheels or windblown. The spreading of dust to the power plant area or to the vicinity of the plant was also prevented by the doors and side seals of the fuel receiving stations. It was guided to close the doors after unloading and also during unloading if possible. In practice the doors were noticed to open quite often. At the new power plant A, the opening and closing of doors was partly automated, which was noticed to be a good practise.

The power plant staff is usually taking care of the moisture content determination of the fuel samples taken during the unloading. Therefore they have to mix and divide the fuel sample to suitable sub-samples, and weigh them before and after the drying in an oven. These operations can be performed at fuel receiving stations or in a separate laboratory room. It was noticed that during these operations the importance of respirators use is not recognized.

Remarkable odour was present in the vicinity of bark-sludge conveyor at the power plant B. There is no need to work in the conveying room regularly, but conveyors have to be inspected and cleaned after a certain period. Respirators or fan-assisted respirators were told to be used during these operations.

Crushing and sieving are typical process steps in handling of SRF at the power plant site. Crushers and sieves need regular maintenance and cleaning, which is performed by power plant staff. SRF can contain biological agents or chemical substances that can be harmful for health and therefore attention must be paid on proper protection. Hepatitis vaccination was recommended for employees working in the SRF crusher area in addition to normal personal protection to be used in process premises. FFP3 type respirators together with protective clothing, gloves, goggles, protective cap and shoes were used during the cleaning work of SRF sieve.

4 Materials and methods

4.1 Materials

Fuel samples were collected from fuel reception sites, different process stages and from conveyors before the boiler if possible. Collected fuel samples are summarised to Table 2. The sampling of ashes was performed according to Table 3. The collected air samples and measurements with direct reading instruments are summarised in Table 4.

Table 2. Number of fuel samples collected for microbial analysis from the power plants during the measurement rounds.

Fuel	Number of samples
Wood chips	6
Hog fuel from stumps	1
Bark	3
Sawdust	1
Thermally dried sludge	1
Mixture	5
Peat	3
Solid recovered fuel (SRF)	3

Table 3. Sampling points of ash samples.

Sample	Sampling point	Sampler
FA A1 & A2	From fly ash silo while loading an ash truck	Power plant staff
FA B1 & B2	From top of the fly ash silo with the method developed by the power plant. Ash sample was combined from sub-samples taken during five consecutive days	Power plant staff
FA C1 & C2	From fly ash silo while loading an ash truck	VTT
All BA samples	From bottom ash container of a power plant	FIOH or VTT

Table 4. Number of air samples and measurements with direct reading instruments at the power plants.

Place/operation	Samples				Measurements	
	Microbes	Endotoxin	Inhalable organic/ inorganic dust	Other	Particles	Gases
Fuel reception	11	17	17	6	13	22
Processing of solid biofuels	16	18	13	26	9	21
Ash loading			5	1	3	4
Control room	5	5	4	3	2	
Environmental air	11	8				

4.2 Accreditation of FIOH

The Client Services of the Finnish Institute of Occupational Health, T013, is an accredited test laboratory (FINAS accreditation services EN ISO/IEC 17025), which specializes in chemical exposures and aerosol specification in work environments/indoor air. The collection and analysis method of endotoxin, inhalable dust, respirable crystalline silica and volatile organic compounds, used in this study falls under the purview of accreditation. Also analysis of inorganic acids and sodium hydroxide are included in the purview of accreditation.

4.3 Calibration of sampling pumps

For sampling of specimens used pumps (Gilian 5000 flow rate from 800 ml to 5000 ml and Gilian LFS-113DC from 1 to 350 ml/min, Sensidyne) were calibrated before sampling with pump calibrator (Drycal Defender 510, Bios International) using in house protocol TY-TY-001 of Finnish Institute of Occupational Health (FIOH).

4.4 Sampling of specimens

Workers' exposure to biological and chemical agents was measured from stationary sites 1.5 m above ground level from different departments of biomass-fired power plants (Figure 11, on the left side). The stationary sampling points were reserved for source identification and mapping out concentration levels in different working areas. To measure personal exposure during a working task, the employees' exposure was monitored from their breathing zone (Figure 11, on the right side). Sampling periods varied from 26 to 169 minutes in workers' breathing zone and from 38 to 433 minutes in stationary sites.

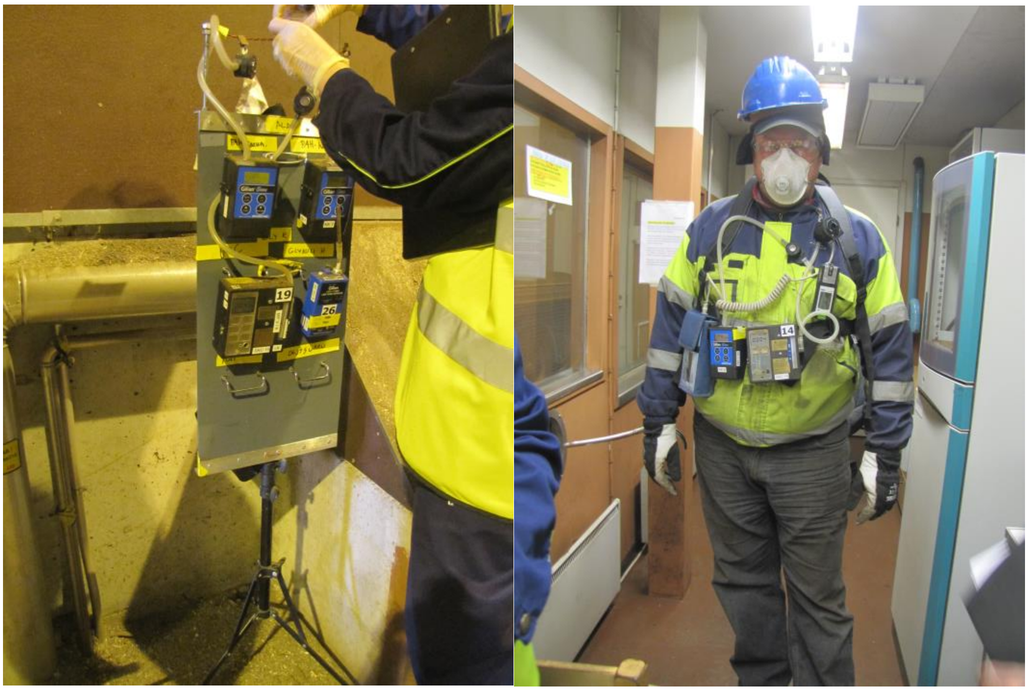

Figure 11.Stationary site sampling above 1.5 meter ground level during unloading (on the left) and truck drivers' exposure measurement from his breathing zone during unloading process of peat (on the right).

4.5 Biological exposure

4.5.1 Collection of microbial samples

Airborne viable bacteria and fungi were collected by open face cassette with polycarbonate filters (0.4 µm, Ø 37 mm, Whatman International Ltd., Kent, UK) at a flow rate of 2 litres/min in a sample pump. Material samples (1-3 litres) were taken direct from fuels into the plastic bags. All samples used for microbial cultivations and analysis of endotoxins were processed within 24 h of sampling.

4.5.2 Microbial cultivation

The viable bacteria and fungi of the samples were cultivated between 3 to 14 days on the following culture media at the temperatures specified. Mesophilic actinobacteria (*Streptomyces* spp.) and other bacteria were cultivated on tryptone yeast extract glucose –agar (+25 °C), mesophilic fungi on media with Rose Bengal (Hagem) and on Dichloran 18% glycerol –agar (+25 °C), thermotolerant fungi on Hagem –agar (+40 °C), and thermophilic actinobacteria on Half-strength nutrient –agar (+55 °C). After the incubation period, colonies were counted and those of actinobacteria and fungi were identified by microscopic examination of morphology. Concentrations of viable microorganisms are expressed in cfu/m^3 (colony forming units per cubic meter air for bioaerosols), and in cfu/g (colony forming units per gram for the biomass).

4.5.3 Measurement of endotoxins

All gram-negative bacteria in the biomass contain components called endotoxin as a part of their cell walls. Therefore, the detection method for endotoxins serves as a marker for the whole group of gram-negative bacteria, and indicates their presence in the sample. Inhalable endotoxins were collected by IOM Sampler (SKC Inc.) at a flow rate of 2 litres/min. The biologically active endotoxins in air samples were measured using a validated kinetic chromogenic *Limulus* amebocyte lysate (LAL) assay (Kinetic QCL, Lonza, Walkersville, MD, USA). The collected glass fiber filters (1.0 µm, Ø 25 mm, SKC) were extracted with 5 ml of non-pyrogenic water for 1 h, and then the extracts were centrifuged at 1120 x *g* for 15 min. The supernatants were diluted in 1:25 (vol/vol), and analysed in duplicate for the presence of endotoxin. All standard curves were made by reconstituting the endotoxin standard of *Escherichia coli* O55:B5 in non-pyrogenic water. The spiked samples were analysed to determine whether inhibition or enhancement was affecting the endotoxin assay. The results were expressed as EU/m^3 (Endotoxin Units per cubic meter air).

4.5.4 Occupational limit values for biological agents

In the wood-processing industry, dose-response relationships have been found between personal exposure to fungi and bacteria, and work-related symptoms (Alwis et al. 1999). Bacterial and fungal components in biomass are also associated with diseases, ranging from toxic pneumonitis symptoms to severe chronic lung diseases as asthma, chronic obstructive pulmonary disease (COPD) and allergic alveolitis (van Assendelft et al. 1985, Lacey and Crook 1988, Rask-Andersen 1989, Halpin et al. 1994, Cormier et al. 1998)

A Dutch study group has suggested before that fungal and bacterial concentrations >10^4 cfu/m^3 should be considered a threat to workers' health (Heida et al., 1995). For single fungal species as thermotolerant *Aspergillus fumigatus*, have suggested a threshold limit value (TLV) of 500 cfu/m^3. Mycotoxin-producing and pathogenic species have to be detected specifically, because of their higher toxicity (Eduard 2009). In epidemiological studies of highly exposed working populations' lung function decline, respiratory symptoms and airway inflammation began to appear at exposure levels of 10^5 spores/m^3. Spores are often regarded as the most prevalent fungal particles that are airborne. Spore sizes of fungi range typically from 2 to 10 µm among species and vary even among spores from the same species. The actinobacteria are gram-positive bacteria, which spores are smaller than fungal spores, typically 0.5–1.5 µm. Thus, human challenge and epidemiological studies support a lowest observed effect level (LOEL) of approximately 10^5 spores/m^3 for diverse fungal species in nonsensitized populations. Individuals with asthma and sensitized to fungal allergens are more sensitive than working populations in general. The available evidence suggests a safety factor of 10 (Eduard 2009). In addition, it has to remember that spores-unit includes total microbes (dead and viable) while as cfu-unit is only for cultivable (viable) microbes.

All gram-negative bacteria in biomass include endotoxin, which is a fragment of their cell walls. Endotoxin may be included in small particles below 1 µm, which are present in the air at solid biofuel plants (Madsen et al. 2009). Endotoxins are pulmonary immunotoxicants. They can cause acute systemic and respiratory symptoms (dry cough, shortness of breath, fever, shivering and joint pain) and acute changes in lung function. The chronic effect of endotoxin can be an accelerated decline in lung function and increased bronchial reactivity, which can lead to COPD. The Nordic and Dutch Expert Group (2011) has concluded that adverse health effects are expected after chronic occupational exposure at approximately 90 EU/m^3.

In the Danish study, working on a solid biofuel heating or power plant did not pose any considerable additional risk for airway diseases compared with working in conventional plants, but the level of micro-organisms seemed to have an impact on the occurrence of respiratory symptoms (Schlünssen et al. 2011). A trend for increasing work-related nose and asthma symptoms with increasing endotoxin exposure was seen for the most exposed group. However, occupational exposure levels were low in their study: median (range) average personal exposures in solid biofuel plants were 0.05 (0 to 0.33) mg/m^3 for total dust and 3.5 (0 to 294) EU/m^3 for endotoxin. At those plants woodchips contained 40–50% water and were delivered directly to the storage room without any manual handling before use.

4.6 Exposure to particular, vaporous and gaseous agents

4.6.1 Spectrum of collected specimens

Biomass-fired power plant operators' and truck drivers' exposure to inhalable dust, respirable crystalline silica, volatile organic compounds (VOCs), components of diesel exhausts (nitric oxide, nitrogen dioxide, carbon monoxide), sixteen polycyclic aromatic hydrocarbons (PAHs), reduced sulphur compounds (hydrogen sulphide, methyl mercaptan, dimethyl sulphide and dimethyl disulphide), inorganic acids (sulphuric, hydrofluoric and hydrochloric acids), ammonia and sodium hydroxide were measured. Also levels of oxygen and carbon dioxide were measured in the processing of solid biofuels.

4.6.2 Sampling and analysis methods of specimens

The inhalable dust was collected in Millipore-filter (25 mm AAWP, pore size 0.8 µm, Merck Millipore) by using an IOM sampler (SKC) at a calibrated flow rate of 2.0 L/min according to in house method TY-TY-003. Respirable crystalline silica was sampled in Millipore-filter (37 mm AAWP, pore size 0.8 µm, Merck Millipore) by using GS-3 cyclone (SKC) at a calibrated flow rate of 2.75 L/min. After the sample collection, filters were first gravimetrically analysed and further crystalline silica analysis of the respirable dust samples was done by FT-IR technique (NIOSH 7602, 1994) using in house method AR1204-TY-025. Inhalable dust was also measured with direct reading instrument SPLIT 2 (SKC). The results of direct reading instruments were corrected gravimetrically.

Volatile organic compounds (VOCs) were collected in Tenax TA adsorption tubes (SKC) at a calibrated flow rate of 0.1 L/min using in house protocol TY-TY-004. Samples were analysed using gas chromatograph equipped with the thermal desorption injection technique and mass selective detector (TD-GC-MS) (SFS-EN ISO 16017-1, 2000) using in house method AR1204-TY-031.

X-am 5600, X-am 7000 and PAC 7000 (Dräger) direct reading instruments were used to measure concentrations of *carbon monoxide, carbon dioxide, nitric oxide, nitrogen dioxide, ammonia and hydrogen sulphide.* Measured data was recorded on data loggers and the recorded values represented the average values of sampling intervals from 10 seconds to 1 minute. The gas monitor sensors for carbon monoxide, carbon dioxide, nitric oxide and nitrogen dioxide were calibrated using calibrating gases (AGA) with known concentrations. Other sensor was calibrated in service provided by the manufacture of the instrument.

Vaporous PAHs were collected into adsorption tubes (Supelco Orbo 43, SKC) at a calibrated flow rate of 0.1 L/min. *The particulate PAHs* were collected in a glass fibre filter at a calibrated flow rate of 2.0 L/min. The analysis of both samples used the GC/MS technique (US EPA Method 610—Polycyclic aromatic hydrocarbons, 1982) according to the in house method TY-KEMIA-ANO-001.

Reduced sulphur compounds were collected to sample bags (Standard FlexFoil 263-20, SKC) using evacuating sampling chamber. Samples were analysed using GC/PID technique.

Inorganic acids was sampled into absorption liquid, (distilled water) at the calibrated flow rate 1 L/min. Samples were analysed with IC technique according to the in house protocol AR1204-TY-007.

Ammonia was collected to adsorption tubes (charcoal tubes, which were impregnated with sulphuric acid, SKC) at the calibrated flow rate 0.1 L/min. Samples were analysed with LC/UV-technique according to the in house method AR1204-TY-015. Ammonia was also measured with direct reading electrochemical cell (X-am 7000, Dräger), which was calibrated by manufacturer.

Sodium hydroxide was sampled on the Teflon filter (PFTE, Fluoro-pore, 37 mm) at the calibrated flow rate 2 L/min. Samples were analysed using IC-technique (NIOSH 7401) according to the in house method TY01-TY-008.

4.6.3 Occupational limit values for particular, vaporous and gaseous agents

In Table 5 occupational exposure limit values (OEL) for measured chemicals are shown. The measurement results obtained from at least two hours measurement period were compared to OEL_{8hours}-values. These values are the maximum average concentrations of a chemical in air to which workers can be exposed during a normal 8-hour working day and 40-hour week. On the other hand, obtained short terms measurement periods were compared to $OEL_{15\ minutes}$ –values, which are the maximum average concentrations to which workers can be exposed for a short period (usually 15 minutes). Finnish Ministry of Social Affairs and Health has established following list (Table 5) of OEL-values for measured chemicals (STM 2014). Exceeding of these values in the occupational measurements at the work place means instant requirement for the employer to improve working conditions with technical measures. If these actions are not capable to reduce exposure level under OEL-values, workers have to use personal protective equipment at the workplace.

The concentration of oxygen should not decrease below 18%, otherwise the workers may start to suffer lack of oxygen (STM 2014).

Finnish Institute of Occupational Health has established for TVOC (Total Volatile Organic Compounds) reference value, which should not be exceeded in good industrial environment. This recommended value is 3000 µg/m^3. For the high quality environments is established target value 300 µg/m^3 (Tuomi et al. 2012). Both these values are based on measurement data collected from different workplaces in occupational hygienic measurements during the last decade by FIOH.

Table 5. Occupational exposure limit values for measured agents.

Compound	OEL$_{8\ hours}$ ppm	OEL$_{8\ hours}$ mg/m^3	OEL$_{15\ min}$ ppm	OEL$_{15\ min}$ mg/m^3	Notice
Acetic acid	5	13	10	25	
Acetone	500	1 200	630	1 500	
Ammonia	20	14	50	36	
Benzo(a)pyrene		0.01			Skin
Benzoic alcohol	10	45			
Carbon dioxide	5 000	9 100			
Carbon monoxide	30	35	75	87	
Ethanol	1 000	1 900	1 300	2 500	
Hydrochloric acid			5	7.6	
Hydrofluoric acid	1.8	1.5	3	2.5	Skin
Hydrogen sulphide	5	7	10	14	
Inorganic dust		10			
Methyl mercaptan	0.5	1	1.5	3	
Naphthalene	1	5	2	10	
Nitric acid	0.5	1.3	1	2.6	
Nitric oxide	25	31			
Nitrogen dioxide	3	5.7	6	11	
Organic dust		5		10	
Pentane	500	1 500	630	1 900	
Propanol	200	500	250	620	
Respirable crystalline silica		0.05			Alveolic fraction
Sodium hydroxide				2	Ceiling value
Sulphuric acid		0.05		0.1	Thoracic fraction
Turpentine (terpenes)	25	140	50	280	Skin
Xylene	50	220	100	440	Skin

4.7 Ash analyses

4.7.1 Analysed samples

Both fly and bottom ash samples were used in analyses. Bottom ash samples were first sieved with 4 mm sieve to remove the biggest particles. This fraction was used in analyses, except for samples BA A1 and BA A2 were not analysed because the samples were entirely at the large particle size class. All fly and bottom ash samples were then sieved with 45 µm sieve (Retsch AS200 sieving machine with metal wire sieves) and still with 10 µm sieve (HK Technologies Ultrasonic sieving machine with stainless steel/nickel wire sieves). Fractions used in analyses are listed in Table 6.

Table 6. Samples collected from power plants (FA=fly ash, BA=bottom ash, number codes 1 and 2 describe different measurement rounds and letters A, B and C different power plants).

Date when collected	Fractions	Particle size	Analyses	Notes
29.10.2013	FA A1	Unsieved	ICP-MS, ICP-OES, XRD	
	FA A1 <10	< 10 µm	XRD	
23.10.2013	BA A1	< 4 mm	-	Not analysed
28.9.2013 29.9.2013 30.9.2013 1.10.2013 2.10.2013 3.10.2013	FA B1	Unsieved	ICP-MS, ICP-OES, XRD	Combined sample
	FA B1 <10	< 10 µm	XRD	
3.10.2013	BA B1	< 4 mm	ICP-MS, ICP-OES, XRD	
	BA B1 <10	< 10 µm	XRD	
31.10.2013	FA C1	Unsieved	ICP-MS, ICP-OES, XRD	
	FA C1 <10	< 10 µm	XRD	
19.11.2013	BA C1	< 4 mm	ICP-MS, ICP-OES, XRD	
	BA C1 <10	< 10 µm	XRD	
Exact date not known	FA A2	Unsieved	-	
	FA A2 <10	< 10 µm	ICP-MS, IC, XRD	
12.2.2014	BA A2	< 4 mm	-	Not analysed
26.3.2014	FA B2	Unsieved	-	
	FA B2 <10	< 10 µm	ICP-MS, IC, XRD	
26.3.2014	BA B2	< 4 mm	-	
	BA B2 <10	< 10 µm	ICP-MS, IC, XRD	
20.2.2014	FA C2	Unsieved	-	
	FA C2 <10	< 10 µm	ICP-MS, IC, XRD	
20.2.2014	BA C2	< 4 mm	-	
	BA C2 <10	< 10 µm	ICP-MS, IC, XRD	

4.7.2 Chemical composition (ICP-MS & ICP-OES)

Chemical composition of first round samples were analysed using unsieved samples (except for bottom ashes using < 4 mm fractions) with inductively coupled plasma optical emission spectrometry (ICP-OES) (Al, Ba, Ca, Fe, K, Mg, Na, P, Ti and Si) and with inductively coupled mass spectrometry (ICP-MS) (Ag, As, B, Be, Bi, Cd, Co, Cr, Cu, Li, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sr, Th, Tl, U, V and Zn). ICP-OES analyses were carried out according to EN ISO 11885 with Perkin Elmer Optima 2100 DV. Prior to analyses, sample melting was carried out according to DIN 51729-1/11 using lithium borate and HCl extraction. The detection limits were 1 µg/mg. ICP-MS analyses were carried out with Agilent Technologies 7700 according to standard EN ISO 17294-2. Prior to analyses, the samples were digested using microwaves according to EN 15297 using HNO_3 and HF. The detection limits were

0.0002 µg/mg (Be, Bi, Cd, Tl, Th and U), 0.001 µg/mg (Sb, B, Cr, Co, Cu, Mn, Rb, Se, Ag, V and Zn), 0.002 µg/mg (Pb, Mo and Sr), 0.005 µg/mg (Li) and 0.008 µg/mg (As). Total organic carbon (TOC, non-carbonate carbon) and total inorganic carbon (TIC, carbonate carbon) were analysed according to standard EN 13137. The detection limits were 1 µg/mg. Dry matter was analysed according to standard EN 14346. The detection limit was 0.1%.

Chemical composition of second round samples was analysed with the ICP-MS and with ion chromatography (IC) using < 10 µm fractions. Metals and other elements were analysed with ICP-MS as described previously. The absolute detection limits were 0.0005 µg (Be, B, V, Cr, Co, Ni, Cu, As, Se, Rb, Sr, Mo, Cd, Sb, Ba, Tl, Pb, Bi, Th and U), 0.002 µg (Li, Al, Ti, Mn, Zn and Ag), 0.007 µg (Fe), 0,02 µg (Mg and Ca), 0.1 µg (Na and K). Anions (Br^-, Cl^-, NO_3^-, SO_4^{2-}, F^-, PO_4^{3-}) were analysed with IC (Metrohm Compact 882 ICplus with column Metrosep a SUPP5-150/4.0) according to standard EN ISO 10304-1/2. The samples were prepared by eluting with NaOH and Na_2CO_3 in an ultrasonic treatment. The absolute detection limits were 0.1 µg (Br^-, Cl^-. NO_3^-, SO_4^{2-} and PO_4^{3-}) and 0.2 µg (F^-). The detection limits per sample mass are presented in Appendix 4.

Heavy metals studied are same metals as mentioned in directive on industrial emissions 2010/75/EU. In addition to them, Zn was included.

4.7.3 Chemical structure (XRD)

X-ray diffraction (XRD) was performed on a Bruker AXS D8 Advance (Cu Kα source, 40 kV, 40 mA) with a Lynx Eye 1D detector. The diffraction was measured between 2θ angles of 5 and 80° with step size of 0.02°. The crystalline compounds were identified using the PDF-4+ 2014 crystallography database. Both the unsieved and the < 10 µm fraction of the first round samples and the < 10 µm fractions of the second round samples were analysed.

4.7.4 Morphology (SEM-EDS)

Scanning electron microscope (SEM) with energy dispersive microscope (EDS) was used to study morphology and chemical composition of the ashes. One fly ash sample (FA B2 <10) and one bottom ash sample (BA B2 <10) was analysed. Samples were sprinkled to stub coated with carbon varnish.

4.8 Weather observations

Davis Vantage Pro weather stations were used to collect weather observation data. The weather stations were equipped with anemometer, temperature and humidity sensors, rain collector and solar radiation sensor. Wind speed and direction, relative humidity and temperature were the most important parameters to be followed and recorded in this research. Weather data was collected by a data logger and downloaded after the measurements.

Three weather stations were used in the measurements at the power plant sites. One was placed to the vicinity of fuel reception or even inside the reception hall as in the case of power plant B. Other two weather stations were placed to different sides of power plant area.

5 Results and discussion

5.1 Weather conditions during measurements

Weather conditions were measured at the power plant sites from the ground level by using VTT's weather stations. Wind directions, measured near fuel receptions at different power plant sites during the measurement rounds are presented in Table 7. The wind roses in Figures 12 – 14 show percentages of the wind direction from the measuring period. Background conditions are presented in Table 8. Weather data from other two locations at the power plant sites is presented in Appendix 1.

Table 7. Percentage of each wind direction of different compass points (N, NNE, NE…)at power plant sites A, B and C. Numbers 1 and 2 refer to measurement rounds and F means the location of weather station near the fuel reception.

Target\ Compass	**N**	NNE	NE	ENE	**E**	ESE	SE	SSE	**S**	SSW	SW	WSW	**W**	WNW	NW	NNW
A1F	2.1	2.8	7.6	56.9	29.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.7	0.7	0.0	0.0
A2F	0.0	6.3	53.1	3.1	0.0	0.0	0.0	37.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
B1F	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
B2F	0.0	0.0	1.3	0.0	25.0	55.3	11.8	0.0	6.6	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C1F	0.0	0.0	2.4	0.0	0.0	0.0	13.3	1.2	0.0	3.6	19.3	38.6	20.5	1.2	0.0	0.0
C2F	1.4	4.1	6.8	58.1	23.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.1	2.7

Table 8. Background conditions during wind measurements at different power plant sites, near the fuel reception. Numbers 1 and 2 refer to measurement rounds and F means the location of weather station near the fuel reception.

Target	N	V_{av} m/s	V_{min} m/s	V_{max} m/s	T_{av} ^{o}C	T_{min} ^{o}C	T_{max} ^{o}C	RH_{av} %	RH_{min} %	RH_{max} %
A1F	144	0.6	0.4	1.8	2.8	-4.8	9.4	89.0	66.0	97.0
A2F	32	-	-	-	2.1	1.6	3.9	95.0	70.0	97.0
B1F	-	-	-	-	-	-	-	-	-	-
B2F	76	0.2	0.0	1.3	4.4	-1.0	11.9	48.0	27.0	74.0
C1F	83	2.0	0.4	3.6	4.6	-0.1	6,4	93.0	69.0	96.0
C2F	74	0.5	0.4	1.3	-2.0	-2.8	-0.6	85.0	78.0	89.0

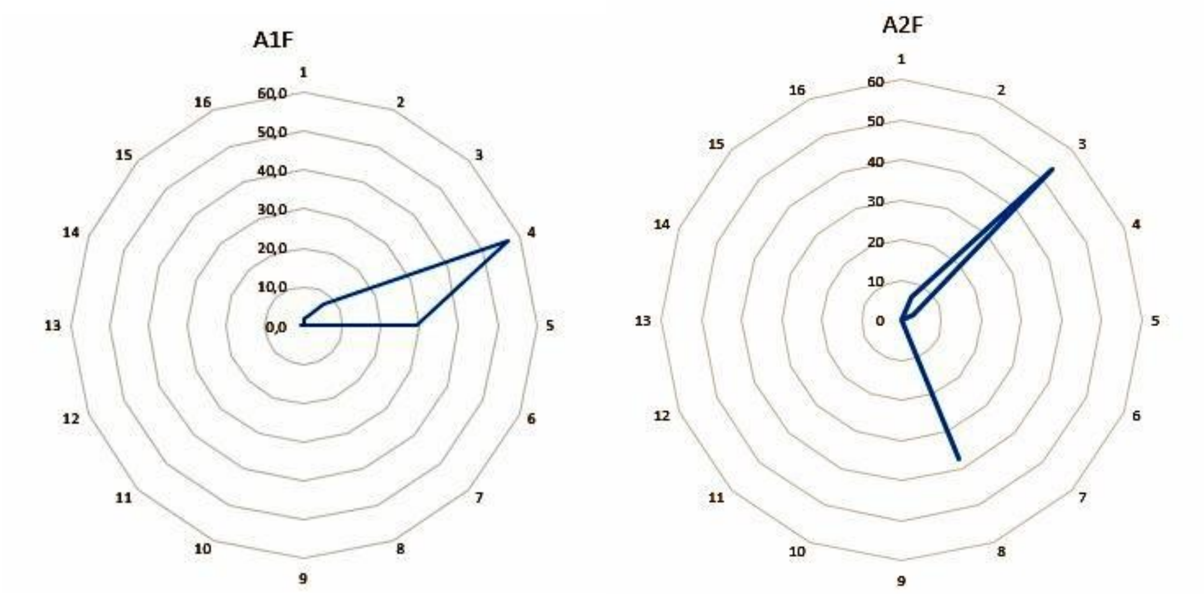

Figure 12. Wind directions near the fuel reception at the power plant A. E direction open.

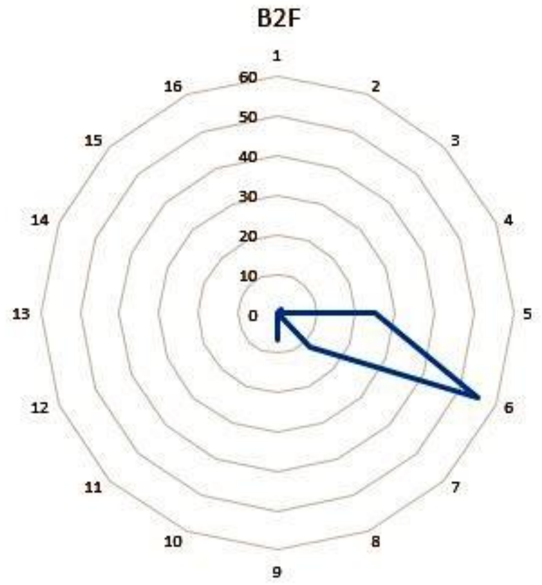

Figure 13. Wind directions near the fuel reception of the power plant B during the second round of HSE measurements (B1F data was invalid). W-direction open.

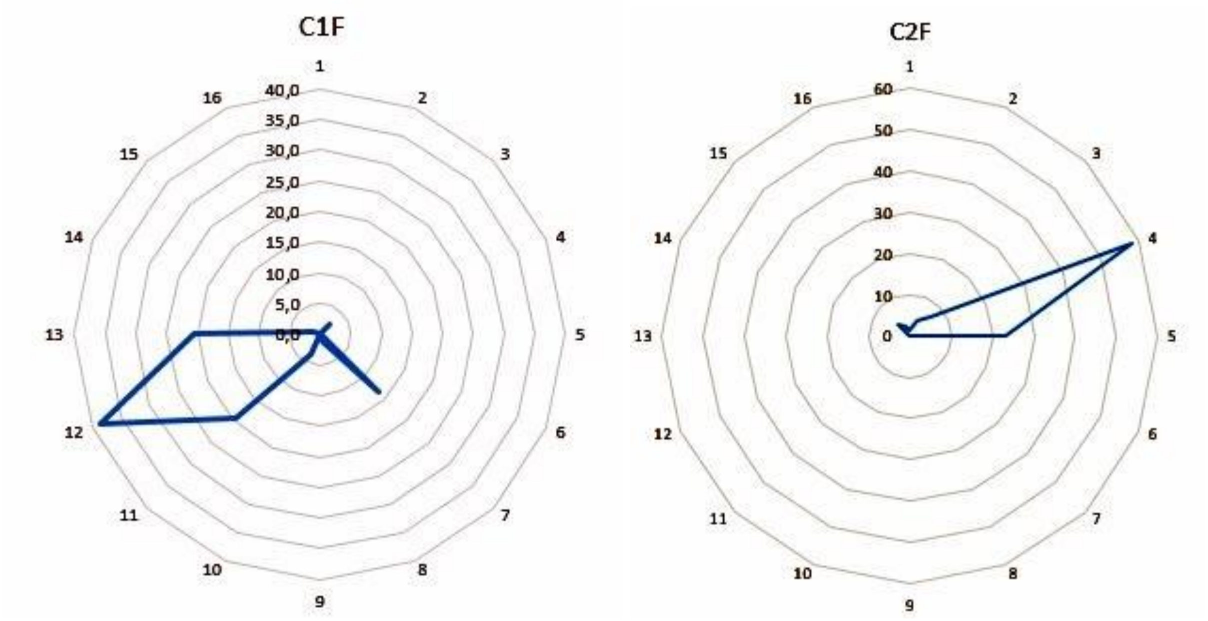

Figure 14. Wind directions near SRF reception of the power plant C during the first (12a) and second (12b) measurement rounds. N-S direction open.

The measured wind data was compared to the Finnish Wind Atlas (http://www.tuuliatlas.fi/en/index.html) 50 m wind level over the ground on the area of all three power plant sites. The wind data of the Wind Atlas at the 50 m level does not explain the conditions at the ground level of the site at all. As from the wind roses can be seen, practically in all cases (Figures 12, 13 and 14) there is certain similarity between 1st and 2nd measurement round. The shape of the roses between the rounds is quite similar except that the direction can vary about 180°. Maybe the reason is that the environment directs the wind significantly at the plant site.

At the sites there are several large and high buildings placed in the vague positions. Weather station location relative to buildings and surrounding environment (e.g. forest or hill) affected most significantly to the wind measurement results. Therefore, while planning new sites the relative location of buildings should be taken into account to be able to control ground level wind conditions.

In addition, from the environmental perspective this is relevant too. If e.g. dusts and microbes can easily be spread at the plant site, the environmental load can also grow. From this point of view, the location of the whole power plant site compared to the prevailing wind conditions and environment should be taken into account. In addition, the national databases like Finnish Wind Atlas can be helpful.

Many of the power plants are built very near to population centres, even inside the centres. If dust spreading at the power plant site or on the near environment is a problem, it could be controlled by using e.g. suitable wind nets or lightweight screens.

5.2 Biological exposure

5.2.1 Air concentrations of microbes

Air concentrations of bioaerosols such as fungi or bacteria and their endotoxins have been measured during processing of solid biofuels at power plants only in a few previous studies (Table 9). Large variation in exposure levels can be seen between the plants and interior of the plants also, due to differences in the fuels handled, the process equipment and work tasks.

Table 9. Concentrations of bioaerosols in processing biomass in other studies.

Bacteria	**Endotoxin EU/m^3**	**Fungi (moulds)**	**Sampling place or situation/material**
$2.6x10^4$-$5.7x10^4$ cfu/m^3		$2.0x10^5$ - $5.4x10^5$ cfu/m^3	Handling/chipping of logging residue logs[1]
$0.5x10^6$ cfu/m^3 (max)	1300 (max)	$8.6x10^6$ cfu/m^3 (max)	Handling/crushing of stumps, logging residue bundles and reed canary grass[2]
$8x10^4$ cfu/m^3 (Actinobacteria, max)	<0.3-440	$1.7x10^5$ cfu/m^3 (max)	Crushing stumps, logging residue bundles and reed canary grass[3]
$1.3x10^6$ cfu/m^3 (max)	1300 (max)	$2.1x10^6$ cfu/m^3 (max)	Solid biofuel plants using wood chips [4]
		$1x10^7$ cfu/m^3 (max)	Handling of wood chips[5]
$5.1x10^2$ - $2.0x10^4$ cfu/m^3		$2.2x10^2$ - $2.3x10^4$ cfu/m^3	Handling of wood chips and sunflower seed peel pellets[6]

[1]Jirjis and Norden 2005 [2]Ajanko and Fagernäs 2006 [3]Ajanko-Laurikko 2009 [4]Madsen 2006 [5]Surakka et al. 2004 [6]Ławniczek-Wałczyk et al. 2012

The large variation in air concentrations of microbes was also found in our study, especially in unloading (Table 10), and screening and crushing (Table 11), which were the most hazardous stages in processing of indigenous fuels. Measured bioaerosol levels of those stages were higher than in the corresponding plants of other studies (Table 9). The highest air concentrations of fungi were measured during handling of wood chips, while the highest airborne bacterial levels were in the unloading of fuel peat. Inside of the unloading halls were the biggest numbers of microbes compared to samples, which were collected from outside nearby a door of the hall.

A supervision of unloading from a control room reduced workers' exposure to bioaerosols, although in some cases it was noticed that the air may flow through the supervision hatches to a direct control room from the unloading hall. In addition, working in a cabin of wheel loader for example, decreased workers' exposure to bioaerosols. Those drivers, who had to visit inside the halls to take fuel samples and to clean the trucks and unloading areas, had high microbial levels in their breathing zones.

Table 10. Air concentrations of microbes (cfu/m^3) in the unloading hall during unloading fuels at the power plants.

Fuel (N)	Mesophilic fungi	Thermotolerant fungi	Mesophilic bacteria	Mesophilic actinobacteria	Thermophilic actinobacteria
Wood chips (6)	4.5×10^2– 1.4×10^7	$< 2.3 \times 10^2$– 1.1×10^7	2.3×10^2– 9.4×10^5	4.6×10^2– 8.9×10^5	$< 1 \times 10^2$– 1.2×10^4
Control room (2); (unloading of wood)	2.8×10^2 – 8.8×10^2	73–1.8×10^2	92–2.2×10^2	73– 92	< 92
Stump (1)	3.3×10^3– 5.7×10^3	2.6×10^2	2.1×10^3	2.9×10^3	$< 2.4 \times 10^2$
Peat (2)	3.7×10^4– 1.6×10^5	1.3×10^3–1.9×10^3	3.8×10^5– 2.3×10^6	1.7×10^4– 2.8×10^4	$< 6.3 \times 10^2$
SRF (1) (outside, but nearby a door of the hall)	7.5×10^2– 5.2×10^3	7.5×10^2	7.5×10^2	$< 7.5 \times 10^2$	$< 7.5 \times 10^2$
Driver (1); (unloading of SRF)	2.0×10^4 – 2.3×10^4	1.9×10^4	5.5×10^3	9.0×10^2	$< 8.3 \times 10^2$
Cabin of wheel loader (2); (unloading of SRF)	$< 2.8 \times 10^2$ – 6.1×10^2	$< 6.1 \times 10^2$	$< 2.8 \times 10^2$ – 1.2×10^3	$< 6.1 \times 10^2$	$< 6.1 \times 10^2$

N = number of samples

Table 11. Air concentrations of microbes (cfu/m^3) in other processing areas at the power plants.

Place/operation (N)	Mesophilic fungi	Thermotolerant fungi	Mesophilic bacteria	Mesophilic actinobacteria	Thermophilic actinobacteria
Screen, crusher (3)	$4.0x10^2$–$5.6x10^4$	$5.3x10^2$–$2.0x10^4$	$1.2x10^2$–$4.1x10^3$	$1.1x10^3$–$2.1x10^3$	< $1.2x10^2$–$3.4x10^3$
Conveyor (1)	$1.5x10^4$–$1.8x10^4$	$8.7x10^3$	$4.7x10^2$	$1.7x10^3$	$3.1x10^2$
Silo (2)	$8.4x10^3$–$7.0x10^4$	$4.3x10^3$–$1.3x10^4$	$1.2x10^2$–$6.5x10^4$	$3.4x10^2$-$4.8x10^4$	< $3.8x10^2$
Handling sludge (2)	< $1.9x10^2$	< $1.9x10^2$	< $1.9x10^2$–$4.6x10^2$	< $1.9 x10^2$	< $1.9 x10^2$
Other processing space (2)	< $1.2x10^2$–$2.3x10^2$	< $1.2x10^2$	< $1.2x10^2$	$2.3x10^2$	< $1.2x10^2$
Worker (visiting round) (3)	$3.5x10^2$–$2.8x10^3$	< $3.5x10^2$–$1.1x10^3$	< $3.5x10^2$ – $7.2x10^2$	< $3.5x10^2$ – $3.2x10^3$	< $3.5x10^2$–$7.2x10^2$
Worker (cleaning of power plant area) (1)	$1.2x10^4$–$2.1x10^4$	$8.7x10^3$	$7.6x10^3$	$4.7 x10^3$	$6.4 x10^2$
Worker (handling fuel samples) (1)	$1.3x10^3$–$1.6x10^3$	< $2.6x10^2$	$2.6x10^2$	$5.2x10^2$	< $2.6x10^2$
Power plant control room (3)	< 72–$3.2x10^2$	< 72–$6.4x10^2$	< 72–$6.4x10^2$	< $2.1x10^2$	< $2.1x10^2$

N = number of samples

5.2.2 Airborne endotoxin levels

Air concentrations of endotoxins in several samples exceeded 90 EU/m^3 that may cause adverse health effects for workers after short- or long-term occupational exposure. Endotoxin levels were the highest in unloading of indigenous fuels similarly with bacterial and fungal levels (Table 12). When the crusher and screen were processing, the concentrations of bioaerosols were much higher (endotoxin up to 130 EU/m^3 and fungi up to 56 000 cfu/m^3) than during the maintenance of the crusher, then the levels of endotoxin (< 5.6 EU/m^3) and fungi (≤ 660 cfu/m^3) were low in the working area (Table 13). Anyway during the maintenance and cleaning of a SRF screen, the concentration of endotoxin were very high (570 EU/m^3) in the breathing zone of the worker.

Air concentrations of endotoxins were low (< 14 EU/m^3) in control rooms and cabins, in the drying space of wastewater sludge, in the vicinity of conveyors and other enclosed processes. Also in the other study of sludge drying units, where dryers and conveyors in operation were closed, the monitoring task in the dryer room was associated with low levels of personal exposure to bioaerosols (Schlosser et al. 2011). However, cleaning and maintenance of the dryer and conveyors required the equipment to be opened, gave significantly higher task-based personal exposure levels in their study. This was also seen in our study during maintenance work in a silo of wood chips, where the concentration of endotoxin was 310 EU/m^3 in the breathing zone of the worker and the concentrations of fungi and bacteria were > 10^4 cfu/m^3.

Table 12. Air concentrations of endotoxin (EU/m^3) during unloading of fuels in the power plants. Suggested limit value for endotoxin is 90 EU/m^3.

Fuel	**Concentration in fuel reception halls EU/m^3**	**Concentration in the breathing zones of drivers EU/m^3**
	range (N, median)	**range**
Wood chips	< 2.8 – 6 700 (N = 5, median = 76)	36 – 140 (N = 2)
Stump (unloading and crushing hall)	450 (N = 1)	11 – 44 (N = 3)
Peat	96 (N = 1)	58 – 590 (N = 2)
SRF	16 (N = 1)	17 – 49 (N = 2)

N = number of samples

Table 13. Air concentrations of endotoxin (EU/m^3) in working area and in the breathing zones of workers in the power plants. Suggested limit value for endotoxin is 90 EU/m^3.

Place/operation (N)	**Concentration EU/m^3**
Control room (unloading of wood) (2)	0.76 – 1.1
Screen, crusher (3)	< 1.7 - 130
Conveyer (1)	3.8
Biosilo (1)	8.4
Drying sludge (2)	< 1.3 - 2.2
Other processing space (1)	1.7
Wheel loader cabin (handling of SRF) (2)	< 7.8
Worker (visiting round) (4)	< 5.6 - 14
Worker (cleaning power plant area) (1)	8.4
Worker (handling of fuel samples) (1)	27
Worker (handling of wood chips in silo) (1)	310
Worker (cleaning of screen) (1)	570
Power plant control room (3)	< 0.9 - 2.6

N = Number of samples

5.2.3 Microbes in the fuels

In the most of the indigenous solid fuels there were plenty of bacteria and fungi (Table 14) which are spread in large contents to the air during the emptying of the fuel load. The SRF fuels included the biggest numbers of microbes of the studied fuels, although the SRF caused lower bioaerosol levels to the air than other indigenous solid fuels. The peat, slowly renewable biomass fuel, included smaller amounts of mesophilic bacteria ($1.5 - 11 \times 10^6$ cfu/g) than the SRF, but the peat caused the largest concentrations of mesophilic bacteria to working area during unloading of the fuel (Table 10). A big part of those bacteria are apparently gram-negative bacteria, because high concentrations of endotoxin were also detected from the breathing zone of peat drivers (Table 12). In the Canadian study, bacterial levels up to 4.8×10^7 cfu/g were found in their peat samples and the presence of thermophilic bacteria was only sporadic (Mériaux et al. 2006). Reference studies from air concentrations of bioaerosols during use of peat as fuel are not available.

Thermotolerant fungi and thermophilic actinobacteria were more abundant in the wood chips, bark and SRF fuels than in the milled peat (Table 14). Also mixtures of fuels seemed to be very susceptible to microbial growth. *Streptomyces* spp., *Penicillium* spp., *Aspergillus fumigatus* and yeasts were the most common identified species. This may be due to self-heating of wood chips, bark, SRF and mixtures in storages causing growth of those microbes. Outdoor storage of solid biofuels has found to increase at least the microbial contamination of wood chips (Sebastian et al. 2006). When organic material with a sufficient moisture content is stored at ambient temperature for prolonged time, mesophilic micro-organisms may start to grow at first (Lacey & Crook, 1988). The metabolic activity produces heat, which may raise the temperature in the material and modulate thermotolerant fungal. Proliferation of thermophilic species may raise the temperature even further, up to 60-65°C. Thermotolerant fungi and thermophilic actinobacteria play an important role in transformation processes during the last phase of biomass decaying. The maximum temperature that stored material may reach mainly depends on the original moisture content. The material may eventually catch fire due to ignition of volatile organic compounds produced by the microorganisms (MVOCs). This multiplying process of microbes could be prevented by drying of fuel masses. One example about that in our study was the thermally dried sludge which included only few microbes (Table 14).

Table 14. Concentrations of microbes (cfu/g) in the fuel samples collected from the power plants.

Fuel (N)	Mesophilic fungi	Thermotolerant fungi	Mesophilic bacteria	Mesophilic actinobacteria	Thermophilic actinobacteria
Wood chips (6)	9.3x10^{4}–1.5x10^{7}	1.0x10^{3}–3.6x10^{6}	2.5x10^{5}–2.4x10^{8}	2.7x10^{4}–1.0x10^{6}	< 1.0x10^{2}–2.7x10^{4}
Hog fuel from stumps (1)	6.8x10^{5}	3.0x10^{4}	1.6x10^{6}	1.8x10^{5}	2.0x10^{2}
Bark (3)	9.3x10^{3}–5.2x10^{7}	5.6x10^{4}–1.5x10^{6}	4.2x10^{5}–1.6x10^{6}	< 1.0x10^{2}–1.8x10^{5}	1.0x10^{2}–3.0x10^{2}
Sawdust (1)	2.5x10^{5}–9.5x10^{5}	1.5x10^{3}	3.7x10^{7}	< 1.0x10^{2}	< 1.0x10^{2}
Thermally dried sludge (1)	1.0x10^{2}–4.0x10^{2}	< 1.0x10^{2}	1.4x10^{4}	1.8x10^{3}	< 1.0x10^{2}
Blend of fuels (5)	4.0x10^{2}–2.5x10^{7}	1.6x10^{3}–4.0x10^{7}	4.3x10^{4}–1.1x10^{8}	1.8x10^{3}–5.1x10^{6}	2.2x10^{3}–7.3 x10^{4}
Peat (3)	7.2x10^{4}–3.7x10^{5}	6.0x10^{2}–3.8x10^{4}	1.5x10^{6}–11x10^{6}	< 1.0x10^{2}–1.8x10^{5}	< 1.0x10^{2}–2.0x10^{2}
SRF (3)	5.4x10^{6}–4.8x10^{7}	5.9x10^{4}–7.1 x10^{5}	5.1x10^{7}–1.1x10^{10}	< 1.0x10^{2}–2.7x10^{4}	< 1.0x10^{2}–7.5x10^{6}

N = number of samples

5.2.4 Environmental levels of microbes

Outdoor environmental concentrations of bioaerosols were lower than in the vicinity of the power plants (Table 15). The median level of mesophilic fungi was 795 cfu/m^3 and the median concentrations of endotoxin were < 2.7 EU/m^3, which are normal concentrations of microbes outdoors. The highest concentrations are related to the transport or storage of biomass around the sampling point. These results are in accordance with measurements performed in the Danish study; fungi 320 cfu/m^3 and endotoxin 2.2 EU/m^3 (Madsen 2006). Especially in rainy weather, all the concentrations of the microbe samples and dust samples which were taken from the outdoor air were low. The differences between the times of the year were not perceived during the study period because winter resembled autumn and then hard frosts did not appear. Therefore, any situations where bioaerosols spread from the power plants to neighborhood were not detected.

Table 15. Outdoor environmental air concentrations of microbes (cfu/m^3) in the area of the power plants.

Place (N)	Mesophilic fungi	Thermotolerant fungi	Mesophilic bacteria	Mesophilic actinobacteria	Thermophilic actinobacteria
Upwind from fuel handling (5)	$< 1.6 \times 10^2$– 1.6×10^3	$< 1.6 \times 10^2$– 5.8×10^2	1.6×10^2– 1.1×10^3	$< 1.9 \times 10^2$	$< 1.9 \times 10^2$
Down-wind from fuel handling (5)	$< 2.0 \times 10^2$ – 1.8×10^3	1.7×10^2–8.1×10^2	$< 1.5 \times 10^2$– 4.0×10^4	$< 3.5 \times 10^2$	$< 3.5 \times 10^2$

N = number of samples

5.3 Exposure to particular, vaporous and gaseous agents

5.3.1 Workers' exposure in fuel reception

Organic inhalable dust concentrations were measured from stationary site near the place where solid biofuels were unloaded in fuel receptions hall (Figure 15). Also truck drivers' personal exposure to inhalable dust was followed by taking samples from their breathing zone during they steered the unloading process from control room (Figure 5) and visited the reception hall when needed. Unloading process took about 30 minutes, which also involves the cleaning of the reception hall.

Figure 15. Stationary sampling site near the place where solid biofuels were unloaded in fuel reception hall.

The highest inhalable dust concentrations were measured during unloading of peat, secondly unloading of logging residue chips and the thirdly unloading of stumps. The inhalable dust emissions during unloading of SRF were the lowest (Table 16). Measured results were compared to OEL$_{8hours}$ –value for organic dust not to the OEL$_{8hours}$ –value for wood dust, because measured dust consisted of many other inorganic and organic elements than wood.

Table 16. Measured concentration of inhalable dust in stationary site in reception hall and truck drivers' breathing zone during unloading of different indigenous solid fuels (OEL_{8hours}= 5 mg/m^3).

Fuel	Inhalable organic dust in reception hall, mg/m³	Inhalable organic dust in drivers' breathing zone, mg/m³
Logging residue chips	< 0.3 – 43 (n = 4)	1.5 (n = 1)
Stumps	0.5 – 25 (n = 2)	< 1.6 – 3.7 (n = 3)
Peat	33 – 87 (n = 2)	4.5 – 12 (n = 2)
SRF	< 1.6 (n = 1)	< 1.8 (n = 2)

The highest average inhalable dust concentration in stationary sites during unloading of peat, logging residues and stumps were 17, 8.6, and 5.0 –fold higher than Finnish eight hours exposure limit value ($OEL_{8\ hours}$) for organic dust, respectively (STM 2014). The measured levels of inhalable dust in unloading of SRF were below 30% of $OEL_{8\ hours}$ -value for organic dust. The measurements in control rooms of unloading process (n=4) showed that average concentrations were below 10% of $OEL_{8\ hours}$ -value for organic dust.

The personal measurements from truck drivers' breathing zone supported findings from stationary sites sampling. The highest average inhalable dust concentrations in drivers' breathing zone were measured during unloading of peat. The measured average value was 2.4 –fold higher than Finnish $OEL_{8\ hours}$-value for organic dust.

In the Figures 16-20 are shown the variation of inhalable dust concentration in drivers' breathing zone during unloading of peat, logging residue chips, SRF, stumps and bark chips. Normally this process starts with the opening the door of truck trailer, which caused the first peaks in measured concentrations. In the end of the measurement there were also seen elevations in concentrations due to brushing and shovelling of fuel from the floor of the reception hall done by drivers. In Figure 21 is shown similar variation in control room of unloading process. The variation of inhalable dust concentration in the fuel reception near tipping hall during unloading of wood chips is shown in Figure 22.

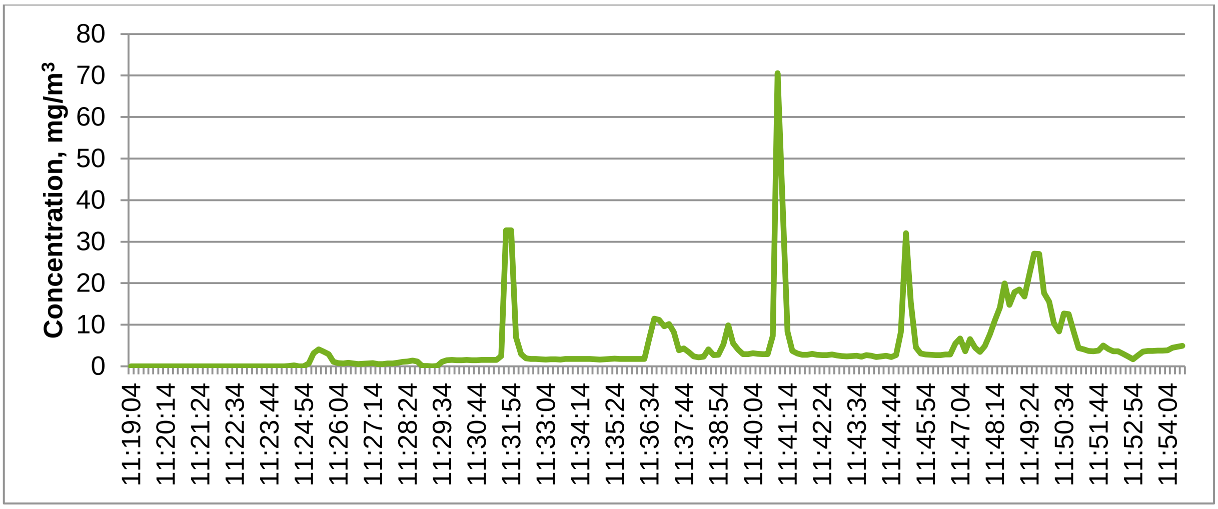

Figure 16. Variation of inhalable dust concentration in drivers' breathing zone during unloading of peat in Power Plant B ($OEL_{8\ hours}$= 10 mg/m^3).

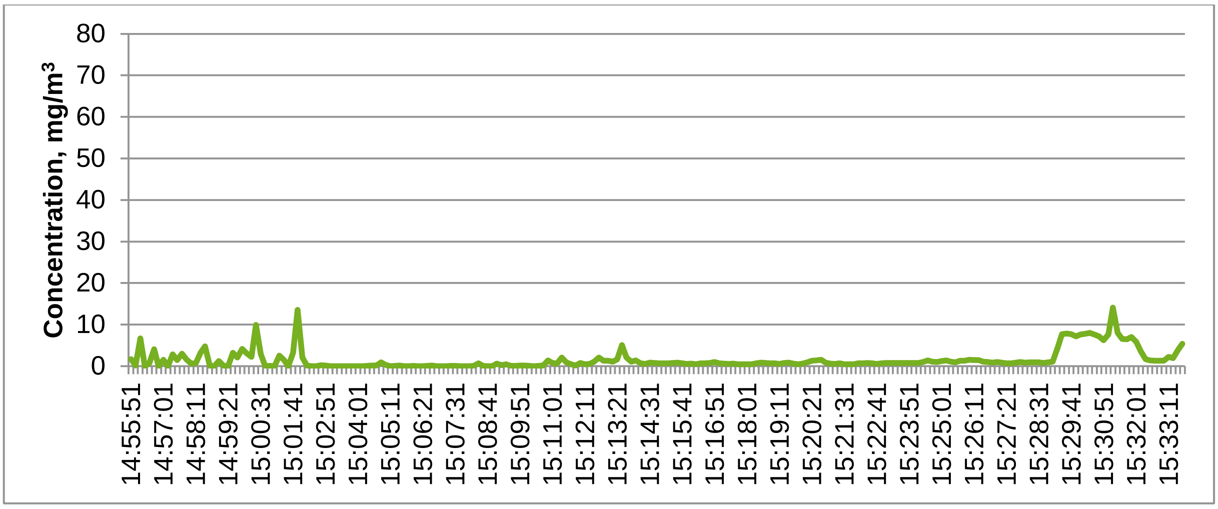

Figure 17. Variation of inhalable dust concentration in drivers' breathing zone during unloading of logging residue chips at Power Plant B ($OEL_{8\ hours}$= 10 mg/m^3).

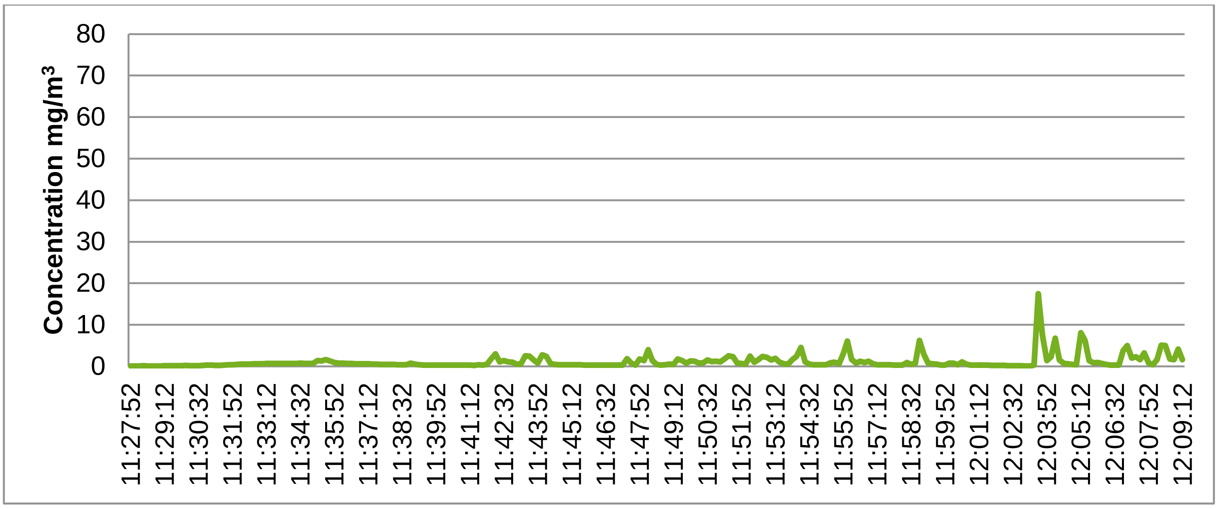

Figure 18. Variation of inhalable dust concentration in drivers' breathing zone during unloading SRF in Power Plant C ($OEL_{8\ hours}$= 10 mg/m^3).

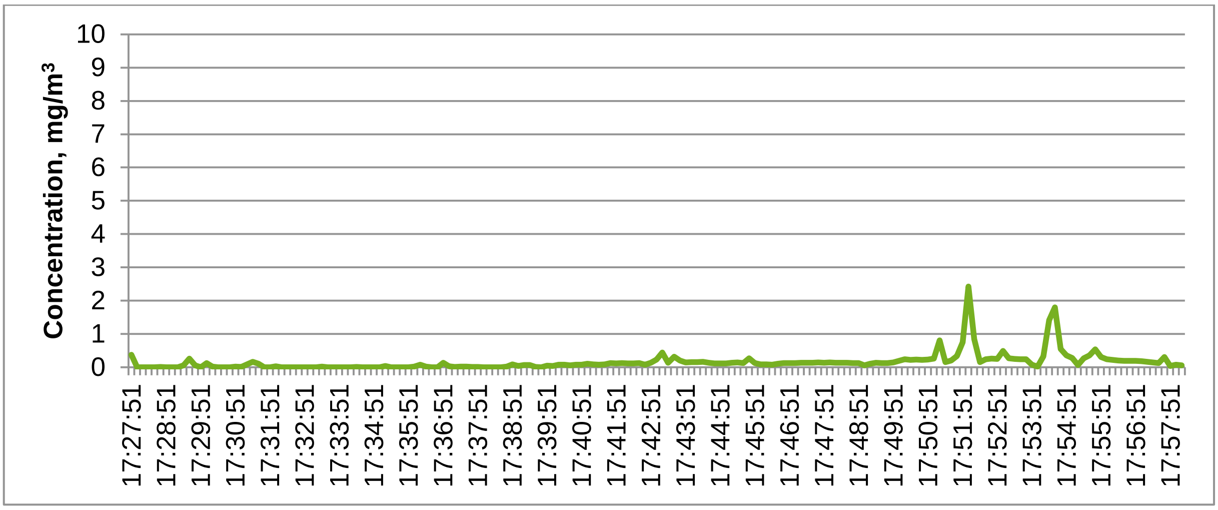

Figure 19. Variation of inhalable dust concentration in drivers' breathing zone during unloading and crushing stumps in crane cabin of the truck at Power Plant B ($OEL_{8\ hours}$= 10 mg/m^3).

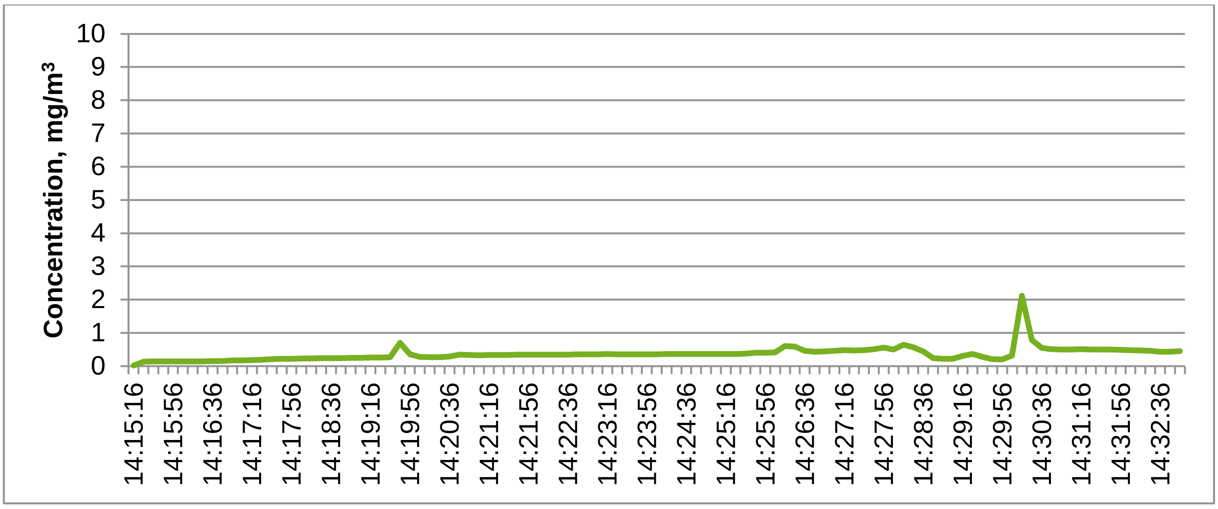

Figure 20. Variation of inhalable dust concentration in drivers' breathing zone during unloading bark chips in Power Plant A ($OEL_{8\ hours}$= 10 mg/m^3).

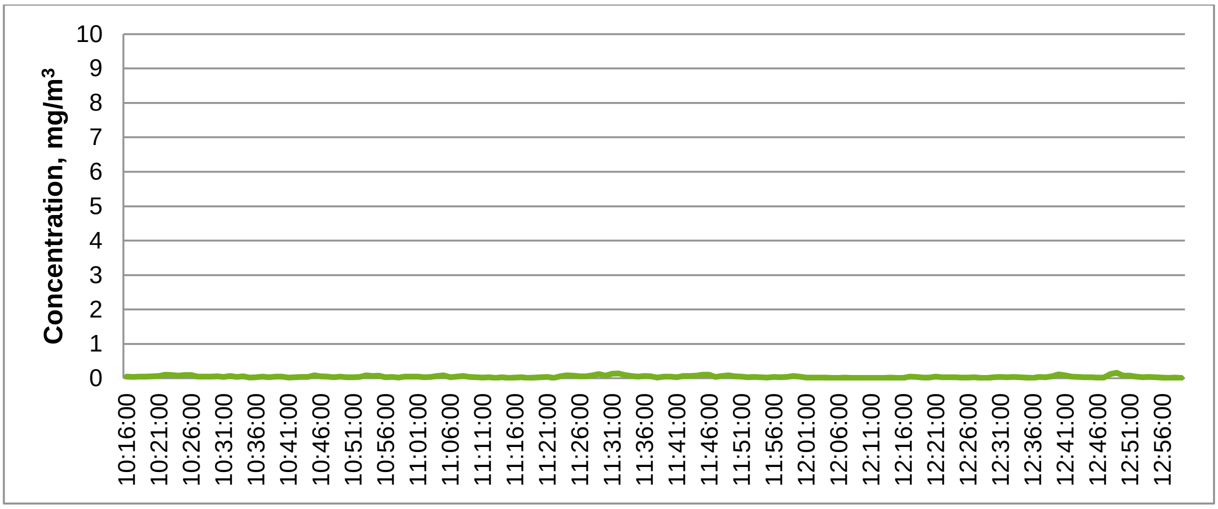

Figure 21. Variation of inhalable dust concentration in control room during unloading wood chips in Power Plant A ($OEL_{8\ hours}$= 10 mg/m^3).

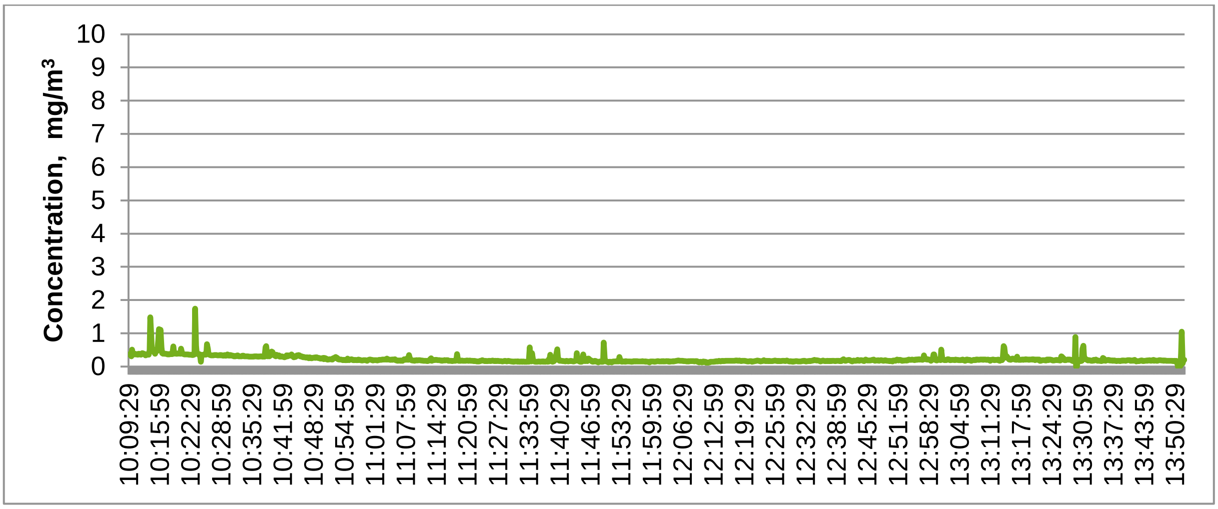

Figure 22. Variation of inhalable dust concentration in fuel reception near tipping hall during tipping of wood chips in Power Plant A ($OEL_{8\ hours}$= 10 mg/m^3).

Ajanko and Fagernäs (2006) have reported inhalable dust concentrations measured during loading and unloading of logging residue bundles and stumps. During loading of logging residues, measured inhalable dust concentrations in stationary sampling sites near operators were 1.1 mg/m^3 and during unloading from 2.2 to 4.6 mg/m^3. Corresponding values from loading and unloading processes of stumps were 1.6 mg/m^3 and 6.6 mg/m^3, respectively. The measured values in earlier studies have been very similar compared to the recorded values in our study (Figures 17 and 19). Ajanko-Laurikko (2009) has also found a crane cabin of truck very efficient for exposure reductions during unloading of logging residues. The inhalable dust concentration in the cabin during unloading logging residues varied from 0.3 to 0.5 mg/m^3. In a similar study in Sweden during loading of logging residues, the measured maximum values in the crane cabin varied from 0.2 to 1.4 mg/m^3 (Surakka et al. 2004). All findings mentioned above in both the studies were consistent with our results (Figure 19).

Workers' exposure to the components of diesel exhaust was also measured from fuel reception halls and from drivers' breathing zone. In Figure 23 is shown measured variation of *nitric oxide* concentrations during unloading of SRF in driver's breathing zone. In Figure 24 is presented variation of nitric oxide concentration in stationary site sampling in unloading hall. The highest short term concentration of nitric oxide was 62% of OEL$_{8\ \mathrm{hours}}$-value for nitric oxide in truck driver's breathing zone. Corresponding value in stationary sampling was 36% of OEL$_{8\ \mathrm{hours}}$-value for nitric oxide.

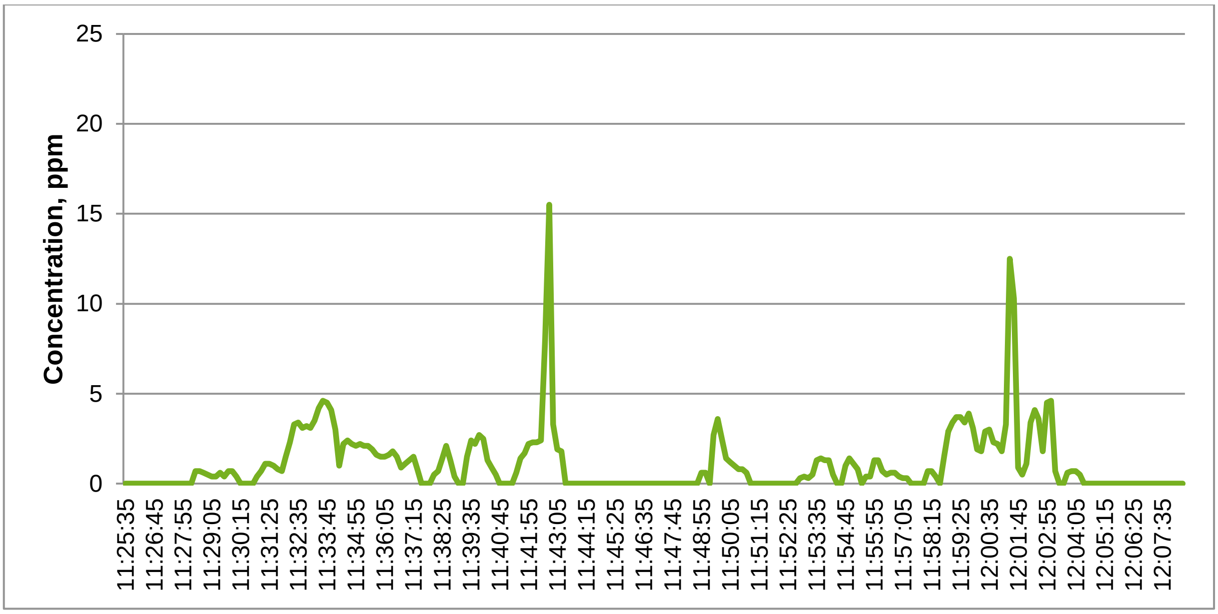

Figure 23. Variation of nitric oxide concentration in driver's breathing zone during unloading SRF in Power Plant C (OEL$_{8\ \mathrm{hours}}$= 25 ppm).

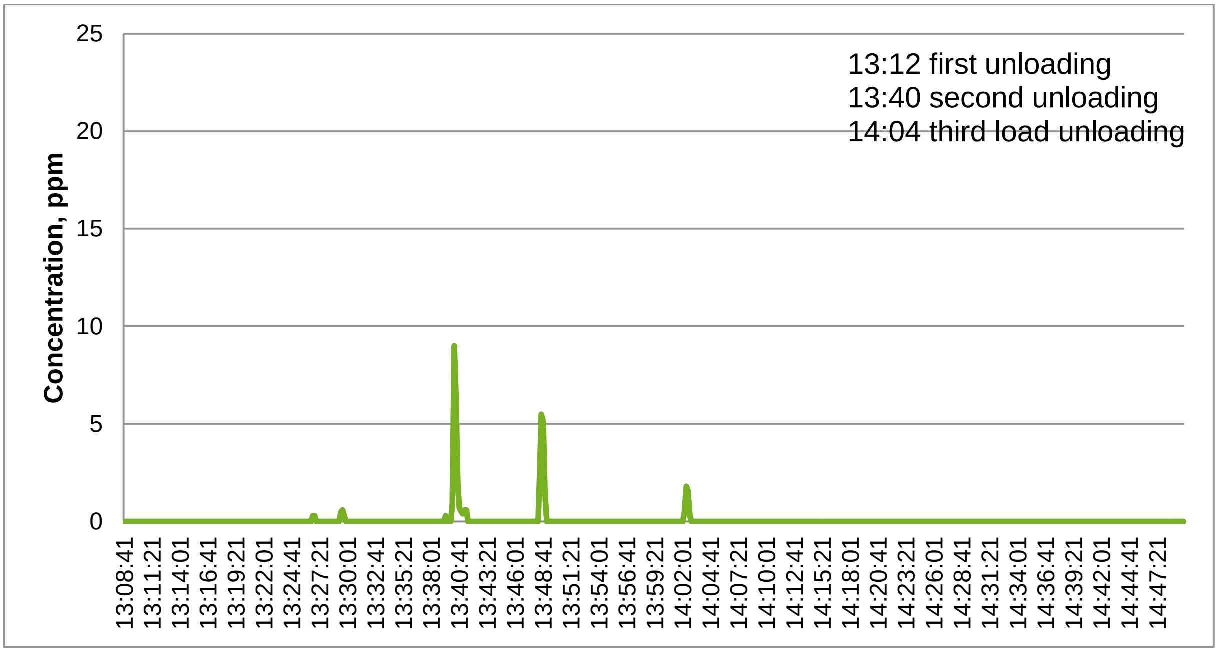

Figure 24. Variation of nitric oxide concentration in tipping hall during unloading wood chips in Power Plant A (OEL$_{8\ hours}$= 25 ppm).

The variation of *nitrogen dioxide* concentrations in reception hall during SRF unloading is shown in Figure 25. The highest short term concentration exceeded OEL$_{15\ minutes}$-value for nitrogen dioxide.

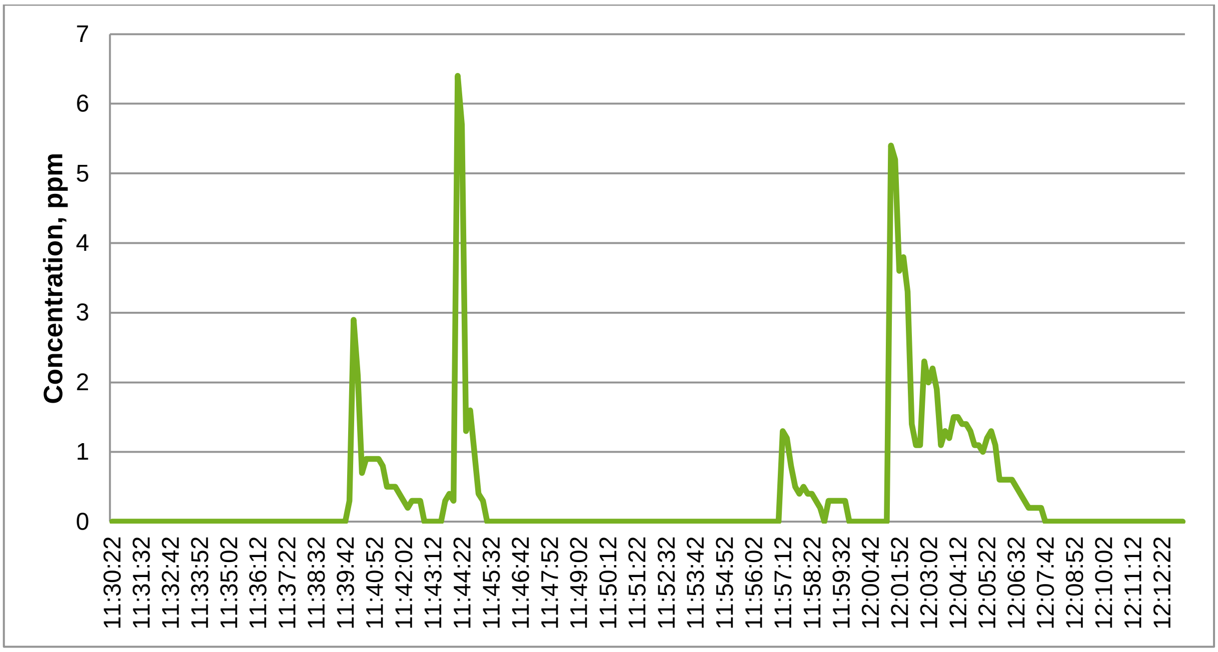

Figure 25. Variation of nitrogen dioxide concentration in reception hall during unloading SRF in Power Plant C (OEL$_{8\ hours}$= 6 ppm).

Variation of *carbon monoxide* concentration in reception hall during SRF unloading is shown in Figure 26. The highest short term concentration was 1.3 -fold higher than OEL$_{15\ minutes}$-value for carbon monoxide.

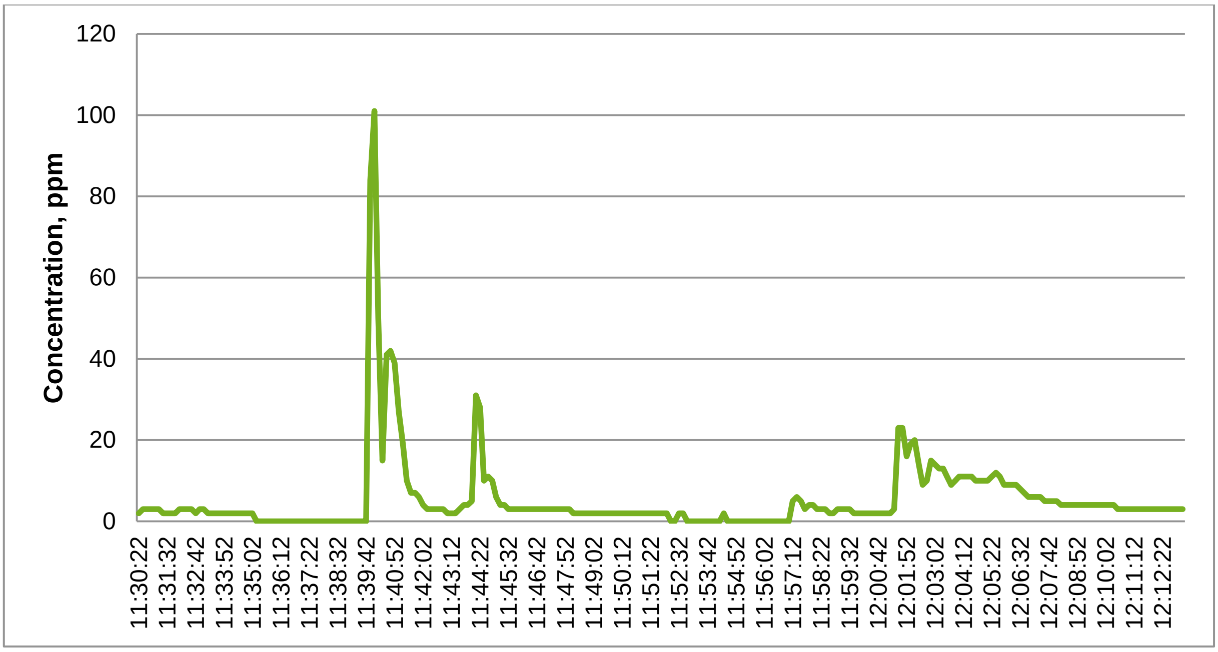

Figure 26. Variation of carbon monoxide concentration in reception hall during unloading SRF in Power Plant C. (OEL$_{15\ minutes}$= 75 ppm).

Also variation of *ammonia* during unloading of SRF was measured in fuel reception hall. The highest short term ammonia concentration was 1.7% of OEL$_{15\ minutes}$-value for ammonia (Figure 27). This might be originated from the activity of microbes in biomass or from reduction techniques of nitrogen oxides in diesel engines. The use of selective catalytic reduction (SCR) in diesel engine might also produce small amount of ammonia to the diesel exhaust. The content of ammonia in the air may be an indicator of clostridia and enterobacteria growth in the biomass. Organic matter biodegradation via ammonification of organic nitrogen is responsible for the release of ammonia (Pagans et al. 2006).

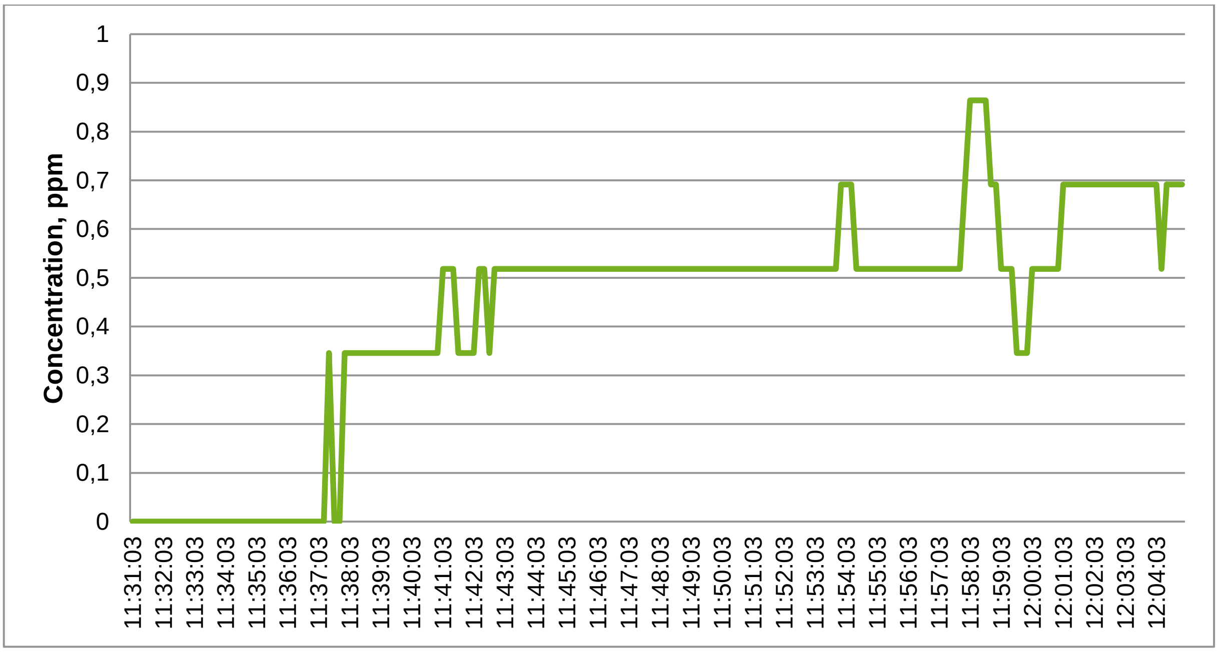

Figure 27. Variation of ammonia concentration in fuel reception hall during unloading SRF in Power Plant C (OEL$_{8\ hours}$= 50 ppm).

To be able to achieve enough low detection limit for *respirable crystalline silica*, very long sampling times are needed due to its' very low OEL$_{8\ hours}$ limit value 0.05 mg/m^3 (STM 2014). All unloading processes were too short for this requirement to be able to collect data separately from each of them. To be able to get estimations of the levels of crystalline silica in fuel reception, concentration levels of respirable crystalline silica were measured during tipping of logging residues, which includes all kind of wood chips in Power plant A. The measured average level was less than 0.01 mg/m^3, which was below 20% of OEL$_{8\ hours}$-value for respirable crystalline silica.

The highest *TVOC* concentration in our study was 6 fold higher during unloading of wood chips in fuel reception than the recommended reference value (3000 µg/m^3) (Table 17). The most important single VOCs were terpene compounds such as *α-pinene, 3-carene, β-pinene and limonene*. Also ketone compounds such as *acetone* was detected from the air. The source for these single volatile compounds was very logical, pine and spruce wood. We were also able to detect *sulphur dioxide* from the air of reception hall. Diesel gasoline contains certain amounts of sulphur, which might be responsible for sulphur dioxide emissions in trucks exhausts (Table 17). During the unloading and crushing of stumps measured TVOC concentrations exceeded easily reference limit value of FIOH. Single measured VOCs were very similar as in unloading of wood chips (Table 17). More details of the VOCs results are given in Appendix 2.

Table 17. The concentration of TVOC and examples of the most important VOC compounds in fuel reception hall.

Place/operation (N)	TVOC, µg/m^3	Examples of compounds	Concentration µg/m^3
Unloading of wood chips (n= 3)	80 – 18 000	α-Pinene 3-Carene β-Pinene Limonene Monoterpene $C_{10}H_{16}$ Acetone Sulphur dioxide 1-Propanol Camphene	120 - 5 300 48 - 3 900 3 500 23 - 2 200 2 000 54 45 28 9
Unloading and crushing of stumps (n = 1)	580	α-Pinene β-Pinene 3-Carene Limonene Camphene	430 140 130 22 18

Fagernäs et al. (2003) have concluded that the most abundant volatile organic compounds in the air of storages of logging residues were α-pinene, β-pinene and 3-carene. Rupar and Sanati (2005) have noticed that the highest emissions of logging residues were available after two to three months storage time. According to the Edman and his co-authors (Edman et al. 2003), the measured concentration level of monoterpenes in pellet storages has been from 640 µg/m^3 to 28000 µg/m^3. Our findings from fuel reception during unloading of wood chips supported the earlier results of fuel emissions, where the most important VOCs were α-pinene, β-pinene and 3-carene (Table 17).

5.3.2 Workers' exposure during the processing of indigenous solid fuels

Inhalable organic dust concentration was measured from different locations during the processing steps of indigenous solid fuels at the power plants. The aim of the measurements was to cover with stationary site sampling all important places, where workers had to continuously visit. The highest average inhalable dust concentration was measured from handling of fuel samples in the laboratory (Figure 28). The measured concentration was 52% of $OEL_{8\ hours}$-values for organic dust. The second dustiest stage of the process was in bio silo building (Figure 29), where concentration was 20% of $OEL_{8\ hours}$-value for organic dust. In other stationary sites measured concentrations were under 24% of $OEL_{8\ hours}$-value for organic dust (Table 18).

Figure 28. Handling of solid biofuel samples in the laboratory.

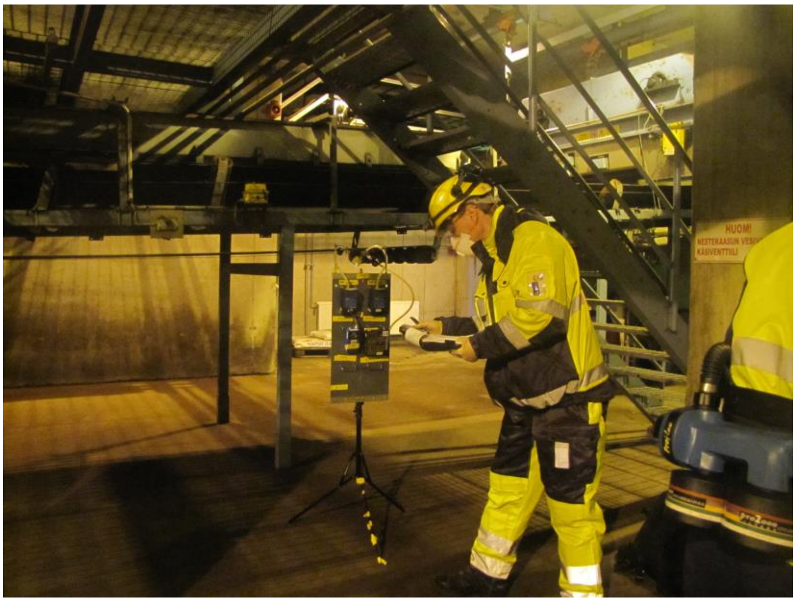

Figure 29. Stationary site sampling in bio silo building.

The highest *TVOC* concentration was measured from the conveyor (Figure 30), where bark and sludge was conveyed. Measured concentrations were 12 fold higher than reference value for good air quality in industry. The main detected VOCs were *acetic acid, ethanol and different terpenes*. The second worst situation was near the bio silo (Figure 29) where TVOC –concentration was 5.3 fold higher than reference value. The main detected VOCs were different terpenes. Measured TVOC concentrations from other parts of the process fulfilled the reference value for good air quality in industry (Table 18).

Figure 30. Stationary site sampling near conveyor.

All measured inhalable dust, TVOC and single VOC concentrations in different parts of the power plants are presented in Table 18. More details of the VOCs results are given in Appendix 2.

Table 18. Measured inhalable dust, TVOC and single VOC concentrations in stationary sampling sites in different parts of power plant.

Place/operation	**Inhalable organic dust mg/m³**	**TVOC µg/m³**	**Single VOCs**	**VOCs, µg/m³**
Screen, crusher	< 0.7 (n = 2)	280 – 330 (n = 2)	α-Pinene Ethanol Pentane β-Pinene 3-Carene Limonene Camphene	130 – 140 130 120 48 – 69 68 34 – 45 28
Conveyer (bark, sludge)	not measured	37 000 (n = 1)	Acetic acid Ethanol 3-Carene α-Pinene Monoterpene $C_{10}H_{16}$	23 000 7 200 4 000 3 900 3 600
Biosilo	1.0 (n = 1)	16 000 (n = 1)	3-Carene α-Pinene β-Pinene Monoterpene $C_{10}H_{16}$ Myrcene	3 700 3 600 2 100 1 900 1 300
Boiler room	< 0.3 (n = 3)	30 (n = 1)	α-Pinene β-Pinene	21 18
Wheel loader cabin (handling of SRF)	< 1.2 (n = 1)	not measured	not measured	not measured
Fuel sample handling room	< 0.5 – 2.6 (n = 2)	190 (n = 1)	α-Pinene β-Pinene 3-Carene Limonene Camphene	78 38 38 24 15
Heat recovery	not measured	30 (n = 1)	α-Pinene β-Pinene Benzoic alcohol	21 15 14
Power plant control room		20 – 50 (n = 3)	Ethanol α-Pinene Benzoic alcohol β-Pinene	89 13 – 21 13 6 - 11

n= number of samples

Some bacteria and yeasts, especially anaerobic bacteria such as clostridia, are capable of converting a wide range of carbon sources of biomass via fermentation to chemicals and fuels such as carboxylic acids (*e.g.* acetic acid), acetone, butanol, and ethanol (Patakova et al. 2013). These compounds were found from the air samples taken in unloading and crushing halls, and indoors of conveyors and silos, which shows the rate of the fermentation process of solid biofuels (Table 18).

Personal samples were also collected from workers, who did surveillance work and walked around of the power plant to do operator's works such as checking, cleaning and sampling during their work shift. Workers' personal exposure to *inhalable inorganic dust* was also followed with direct reading instrument during cleaning of screen (Figure 31) and changing of a sulphur sack.

Figure 31. Cleaning of the recycled fuel screen at the power plant C.

Variation of Inhalable dust concentration in worker's breathing zone during these work tasks is described in Figure 32. The highest short term exposures to inhalable dust during the cleaning of screen (15:57-16:05) and changing of the sulphur sack (16:16-16:19) were 1.25 and 2.75 fold higher than $\text{OEL}_{15\ \text{minutes}}$-value for organic dust, respectively. The average inhalable dust concentration during the whole working period was 4.3 mg/m^3, which was 86% of $\text{OEL}_{8\ \text{hours}}$-value for organic dust.

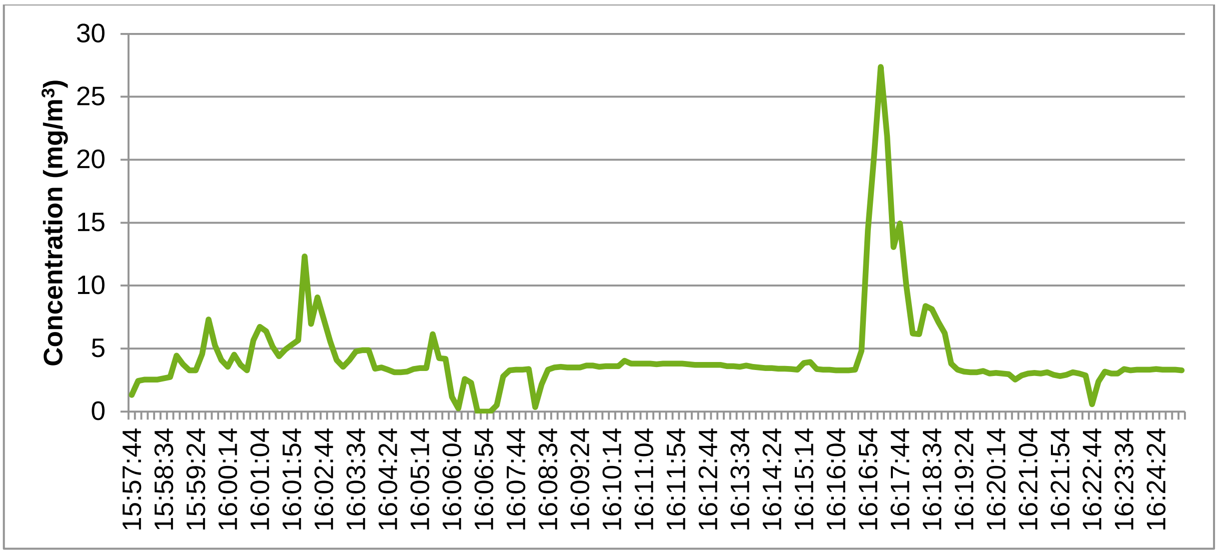

Figure 32. Variation of inhalable dust concentrations in worker's breathing zone during cleaning of screen and changing of sulphur sack in power plant C (OEL$_{8\ hours}$= 10 mg/m^3).

Worker's exposure to inhalable dust was followed when he pretreated solid biofuel samples in the laboratory. During the opening of the barrel containing fuels (15:06-15:09), inhalable dust concentration achieved OEL$_{15\ minutes}$-value for organic dust in worker's breathing zone. The average inhalable dust concentrations in worker's breathing zone was 2.6 mg/m^3 during the whole working period, which is 52% of OEL$_{8\ hours}$-value for organic dust (Figure 33). It was also interesting to note that concentration of inhalable dust increased in the laboratory during the measurement.

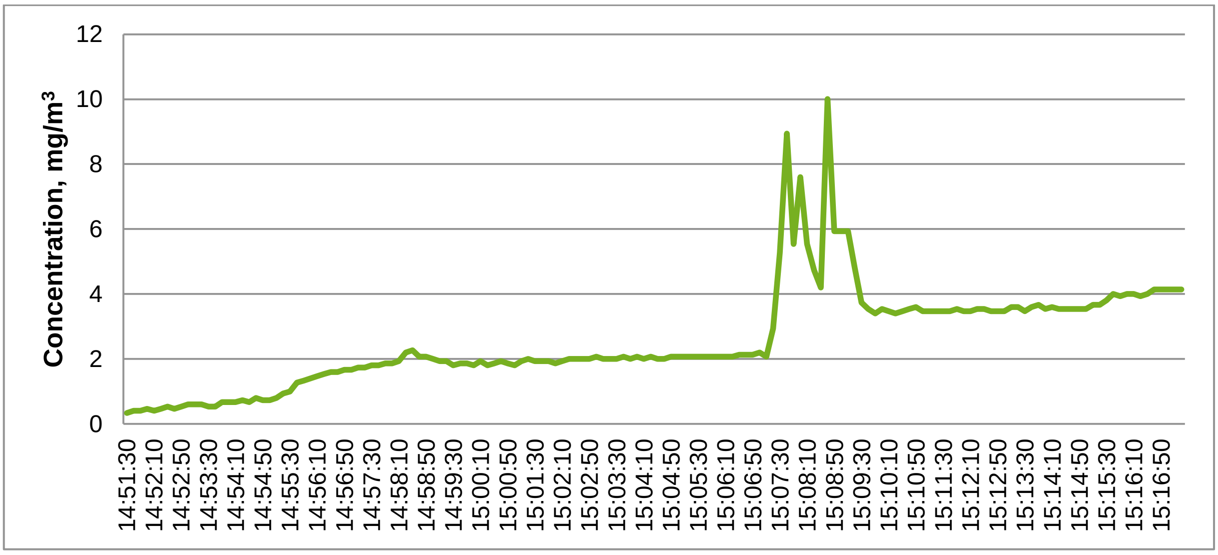

Figure 33. Variation of inhalable dust concentration in worker's breathing zone during pretreatment of solid biofuels in the laboratory (OEL$_{8\ hours}$= 10 mg/m^3).

In Figure 34 is shown variation of inhalable dust concentration in surveillance operator's breathing zone during walking around at the power plant C. The highest inhalable dust concentrations were recorded during the visit in screening (8:45 - 8:52) and crushing (9:19 - 9:23) of SRF. The average concentration during the whole surveillance period was 75% of OEL$_{8\ hours}$-value for organic dust.

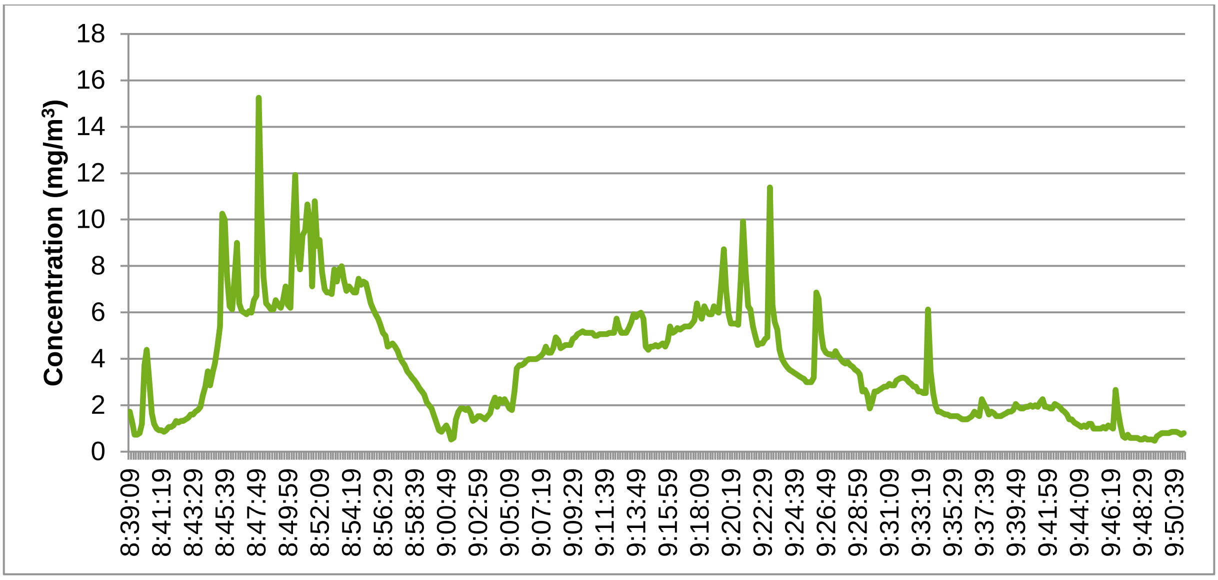

Figure 34. Variation of inhalable dust concentration in the surveillance operator's breathing zone during surveillance walking around at Power Plant C (OEL$_{8\ hours}$= 10 mg/m^3).

In Figure 35 is shown variation of *carbon monoxide* in boiler room in the stationary sampling site at the power plant C. The highest short term concentrations were 63% of OEL$_{15\ minutes}$-value for carbon monoxide.

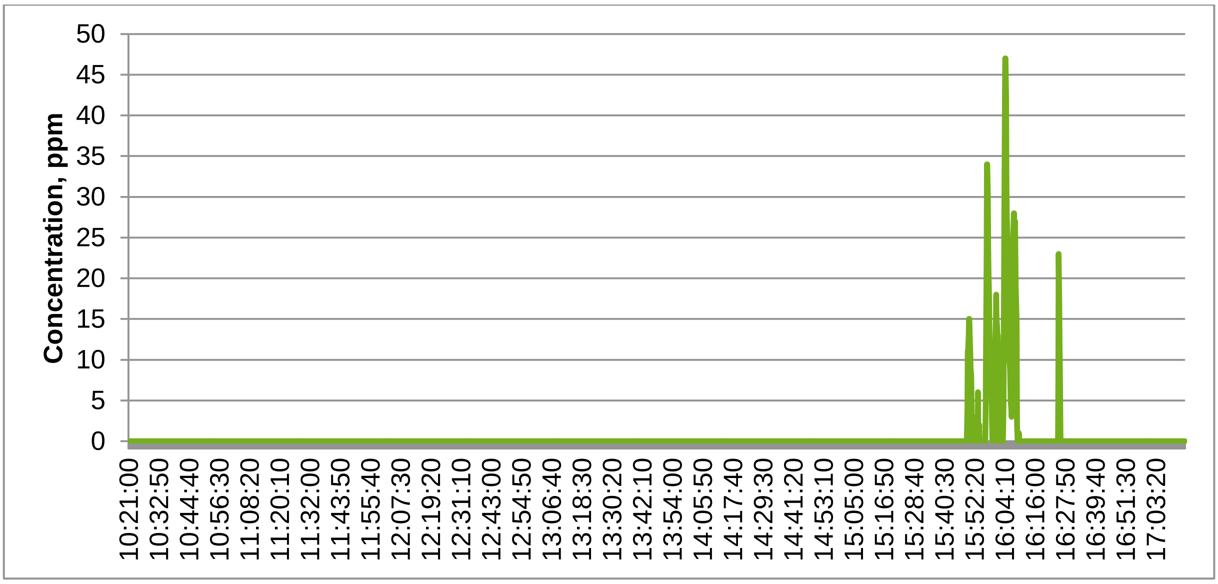

Figure 35. Variation of carbon monoxide concentration in boiler room in the stationary sampling site at the power plant C (OEL$_{8\ hours}$= 75 ppm).

Concentration of *respirable crystalline silica* was under 20% of OEL$_{8\ hours}$-value for respirable crystalline in boiler room in both measurements at Power Plant C. Also concentrations of *polycyclic aromatic compounds* in the same boiler room were low. The measured concentrations of single PAHs were far below their OEL$_{8\ hours}$-value (*naphthalene* and *bentzo[a]pyrene*) (Appendix 3).

Variation of *ammonia* was measured in the upstairs of heat recovery department. The highest short term ammonia concentrations were 3.2% of its' OEL$_{15\ min}$-value (Figure 36).

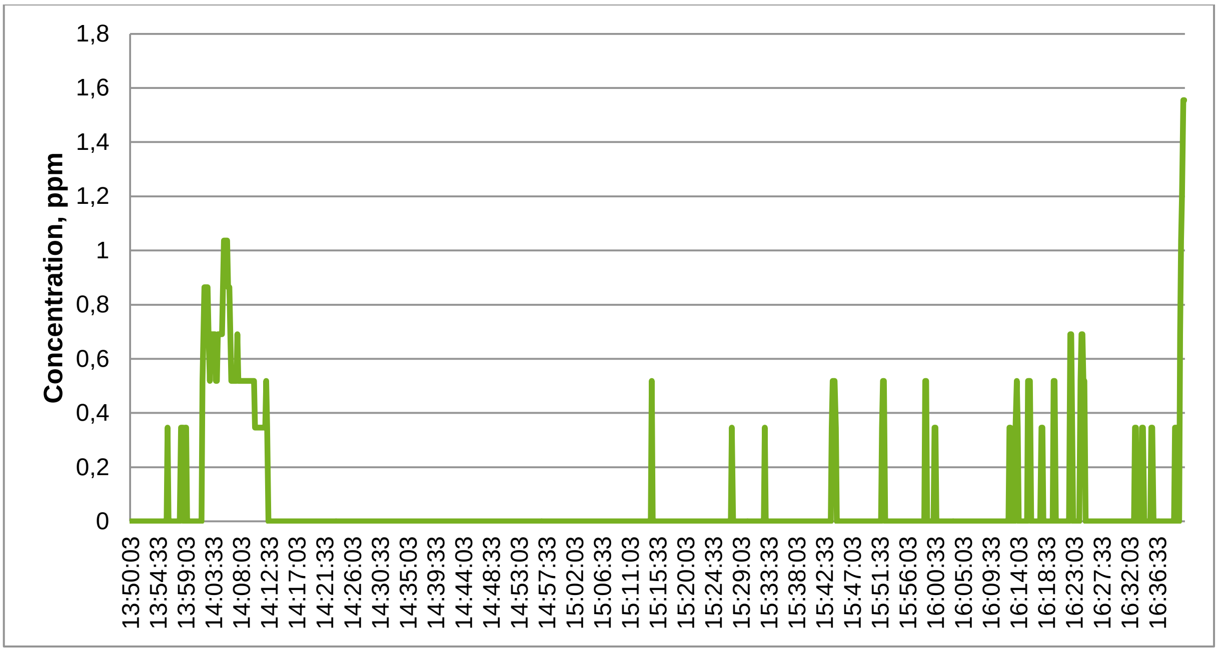

Figure 36. Variation of ammonia concentration in the stationary sampling site in heat recovery department at the power plant C (OEL$_{8\ hours}$= 50 ppm).

The variation of *hydrogen sulphide* concentration was measured by direct reading instrument in the upstairs and downstairs of heat recovery department. The short term exposure levels of hydrogen sulphide were in the upstairs and downstairs over 60% and below 1% of OEL$_{15\ minutes}$-value for hydrogen sulphide, respectively. The average hydrogen sulphide concentration during measurement period was 6% of its' OEL$_{8\ hours}$-value (Figure 37).

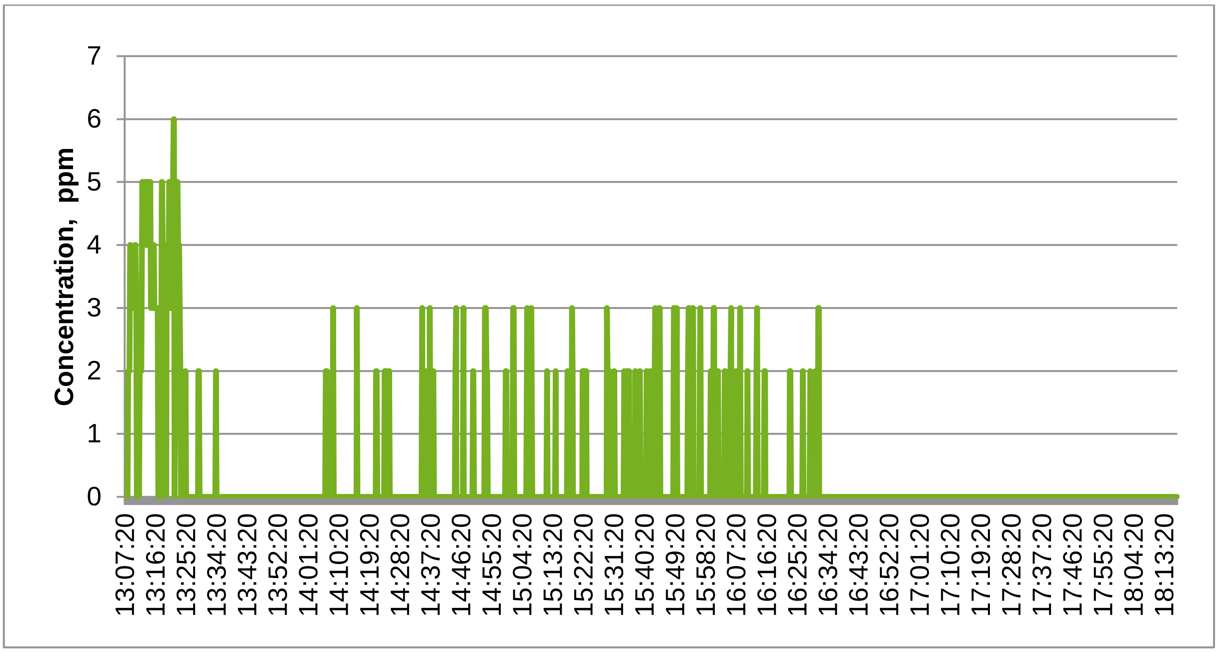

Figure 37. Variation of hydrogen sulphide concentration in the stationary sampling site in the upstairs (13:07-16:30) and in the downstairs (16:30-18:09) of heat recovery department at the power plant C (OEL$_{8\ hours}$= 10 ppm).

In addition to hydrogen sulphide measurements by direct reading instruments, *reduced sulphur compounds* were measured more extensively from heat recovery and wet scrubber sludge drying process from stationary sampling sites. Each measurement represented the average concentration of the measurement period (5 minutes). The average *hydrogen sulphide* concentrations in heat recovery and wet scrubber sludge drying department were 24% and under 2% of $OEL_{8\ hours}$-value for hydrogen sulphide, respectively. Corresponding values for *methyl mercaptan* were 60% and 20% of its' $OEL_{8\ hours}$-value. We were also able to find the concentration 0.1 ppm of *dimethyl sulphide* from both departments. *Dimethyl disulphide* concentrations were under detections of our measurement method in both departments. It was not able to compare the latter two reduced sulphur compound values to Finnish OEL-values, because there are no established values available for those compounds. *Sulphur dioxide* concentrations were very low in both departments being under 0.5% of its' $OEL_{8\ hours}$-value (Table 19).

Table 19. The measured reduced sulphur compounds in stationary sites at the heat recovery and wet scrubber sludge drying process at the Power Plant C. 1 ppm = 0.0001%

Reduced sulphur compound	Heat recovery	Sludge drying
Sulphur dioxide (mg/m³)	0.013	< 0.007
Dimethyl disulphide (ppm)	< 0.05	< 0.1
Dimethyl sulphide (ppm)	0.1	0.1
Methyl mercaptan (ppm)	0.2 – 0.3	0.1
Hydrogen sulphide (ppm)	0.1 – 1.2	< 0.1

Surveillance operator's exposure to carbon dioxide was measured when he washed the floors near bio silo department in order to find out possible risk caused by fermentation of solid biofuels (Figure 38). Also ability of carbon dioxide to replace oxygen at these concentrations levels was measured. The highest measured short term exposure level of *carbon dioxide* exceeded $OEL_{8\ hours}$-value for carbon dioxide. Interesting was also to note that during the highest carbon dioxide concentrations also *oxygen concentration* started to decrease, which might reflect ability of carbon dioxide to replace oxygen in the air already at measured concentration levels (Figure 39). The measured decrease of oxygen concentration was not so high that it did not have any effects on worker. The ratio of oxygen should decrease to the level of 18% after that workers start to suffer lack of oxygen (STM 2014).

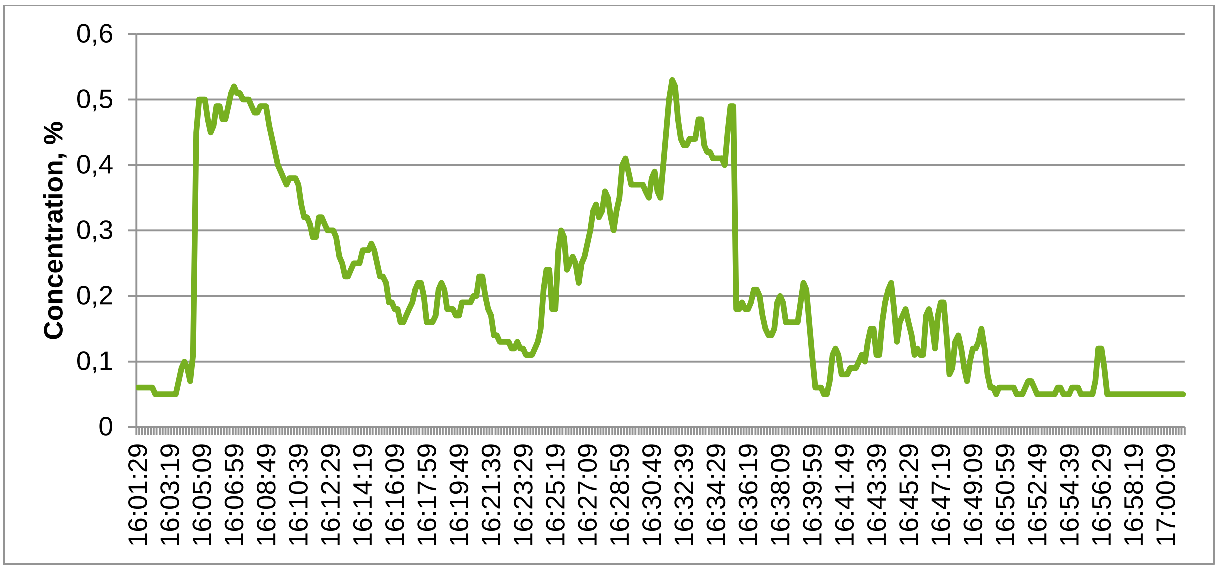

Figure 38. Variation of carbon dioxide concentration in surveillance operator's breathing zone during the washing of floors in the bio silo building at the power plant B ($OEL_{8\ hours}$= 5000 ppm).

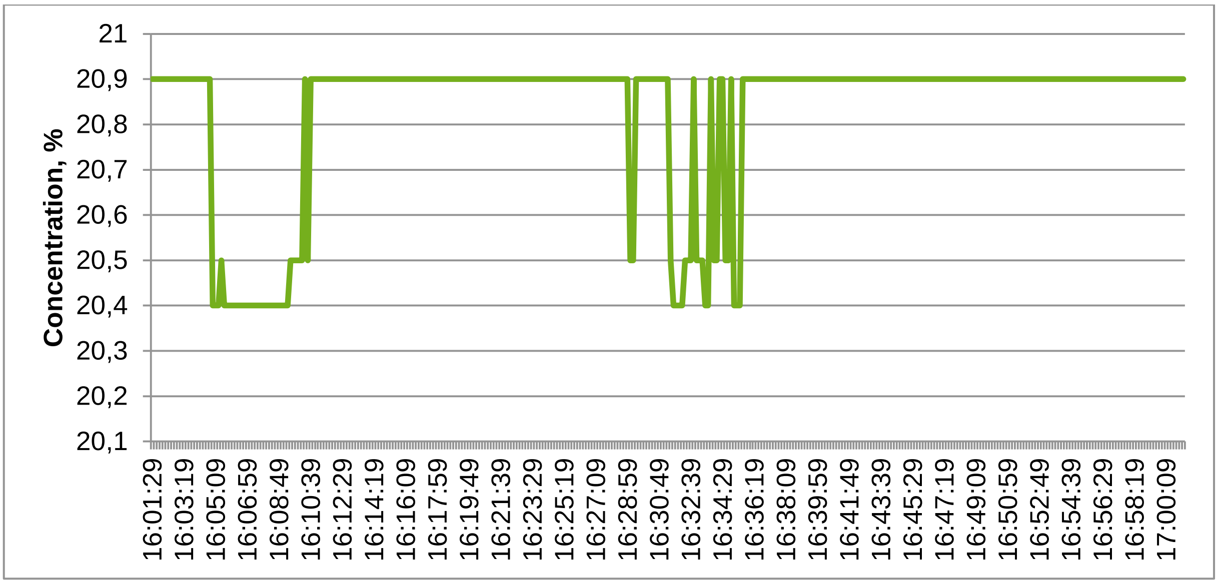

Figure 39. Variation of oxygen concentration in surveillance operator's breathing zone during the washing of floors in the bio silo building at the power plant B (critical level 18%).

Also *inorganic acids* (*sulphuric, hydrochloric* and *hydrofluoric acids*) and sodium hydroxide concentrations from department of heat recovery, drying of sludge and regeneration at power plant C were measured. All measured concentrations were under 8% of their $OEL_{8\ hours}$-values.

5.3.3 Workers' exposure in ash loading

Truck drivers' and operators' exposure to *inhalable dust, crystalline silica* and *nitric oxide* was evaluated from stationary sampling sites. The loading process was done in closed and at open loading stations (Figure 8). The moistening of the ash during loading was in use at both measured power plants.

The variation of *inhalable inorganic dust* concentrations in the closed loading station is shown in Figure 40. The highest short term exposure levels were over 10 fold higher than $OEL_{8\ hours}$-value for inorganic dust. The inhalable dust concentrations decreased to the level of 10% of $OEL_{8\ hours}$-values within 75 minutes after the end of ash loading. The average inhalable concentrations during loading and two hours after that varied from 69% to 130% of its' OEL-value in closed loading hall. Average *respirable crystalline silica* concentration was 30% of its $OEL_{8\ hours}$-value.

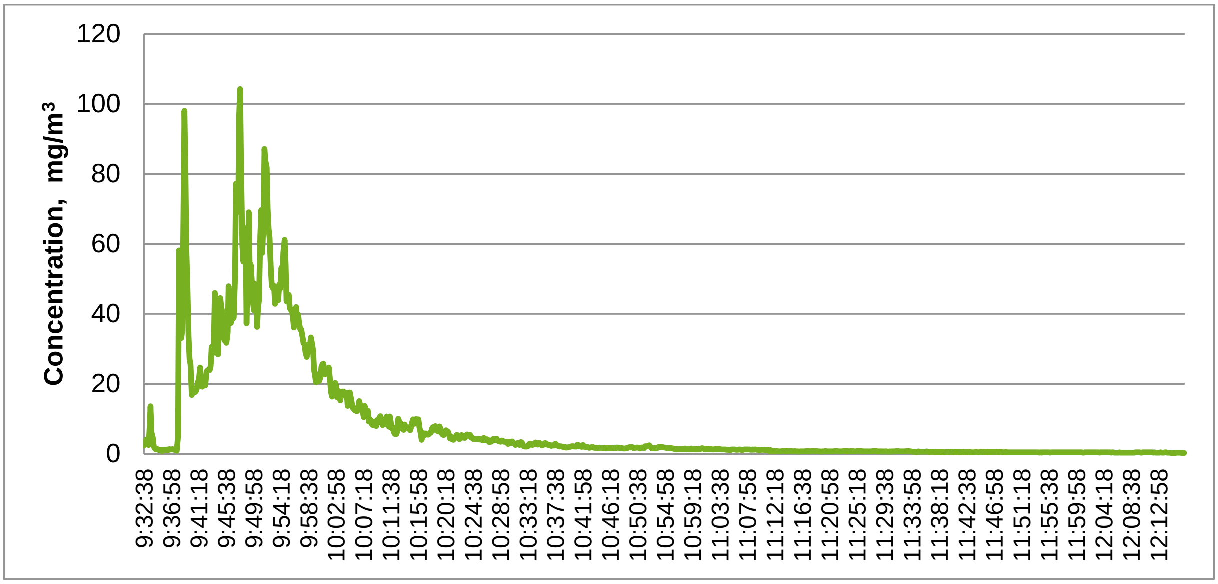

Figure 40. Variation of inhalable dust concentration during loading of moistened ash in closed hall at Power Plant B (OEL$_{8hours}$= 10 mg/m^3).

In Figures 41 - 43 are shown the calculated (from metal content of material samples in fine ash, see chapter 5.4.2) metal concentrations during loading of moistened ash in closed hall at power plant B. Short term exposure levels of chromium, manganese and nickel exceeded their $OEL_{8\ hours}$-limit value during the loading of ash.

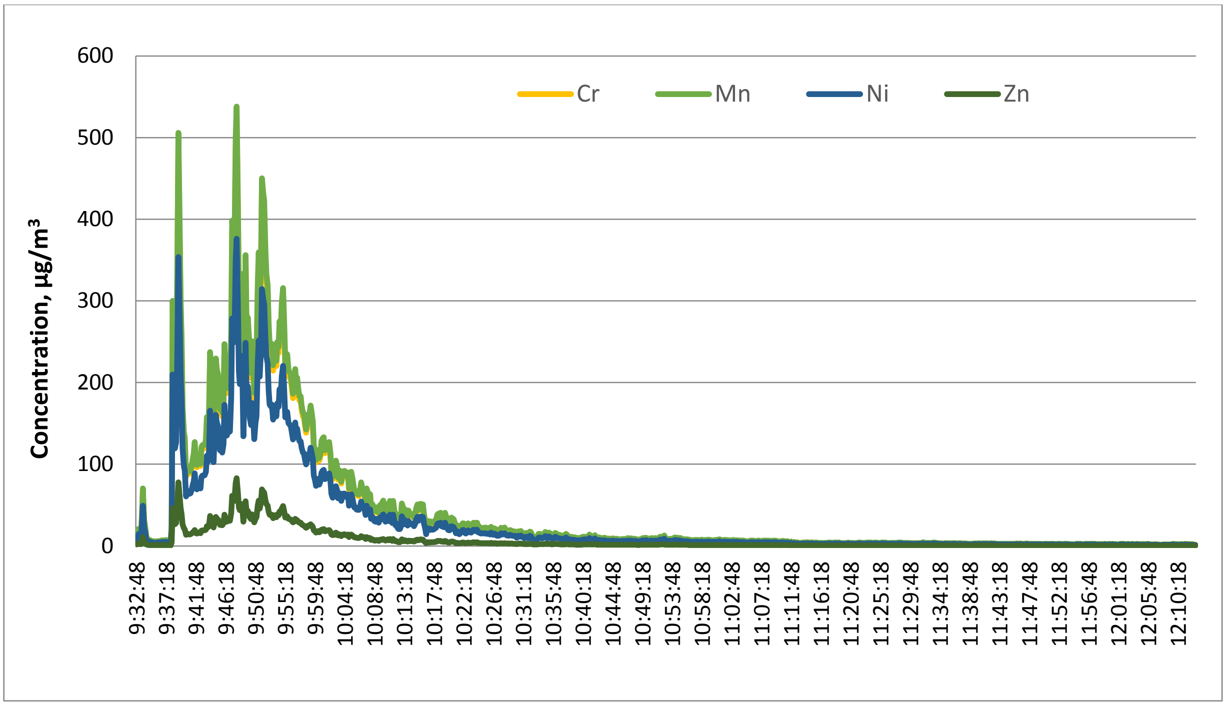

Figure 41. Variation of calculated metal concentrations during loading of moistened ash in closed hall at Power Plant B ($OEL_{8\ hours}$ –values for chromium, manganese, nickel and zinc are 500 µg/m^3, 200 µg/m^3, 50 µg/m^3 and 2000 µg/m^3 respectively).

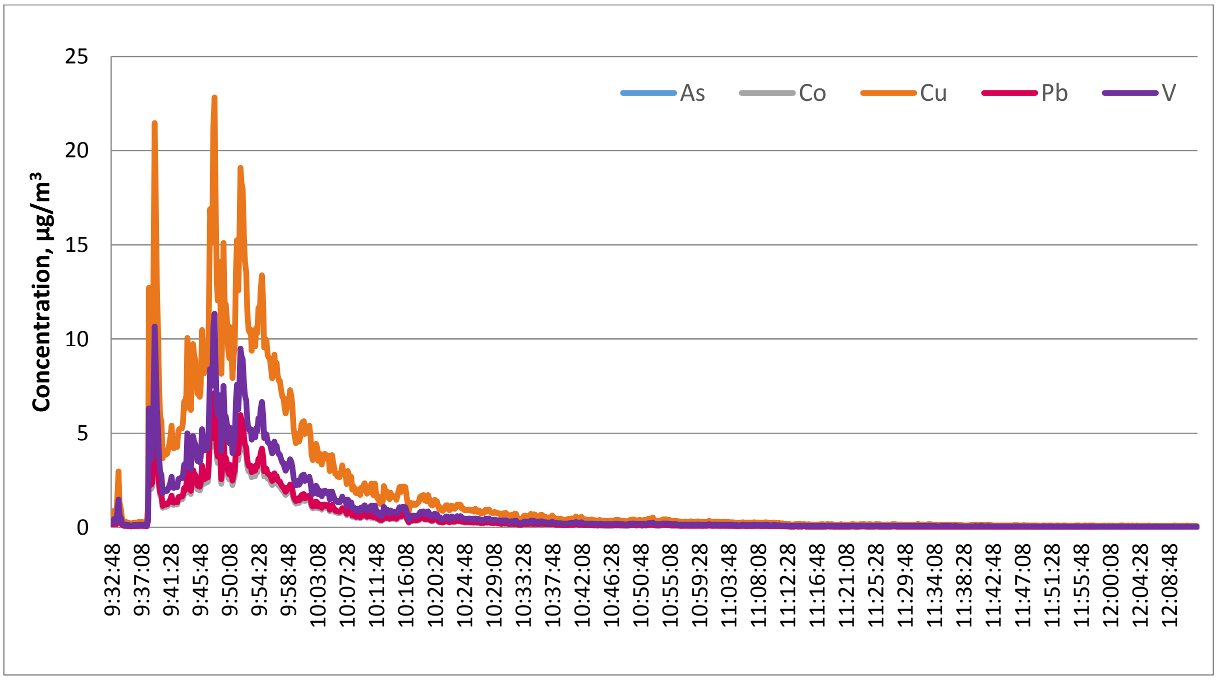

Figure 42. Variation of calculated metal concentrations during loading of moistened ash in closed hall at Power Plant B ($OEL_{8\ hours}$ –values for arsenic, cobalt, copper, lead and vanadium are 10 µg/m^3, 20 µg/m^3, 1000 µg/m^3, 100 µg/m^3 and not available, respectively).

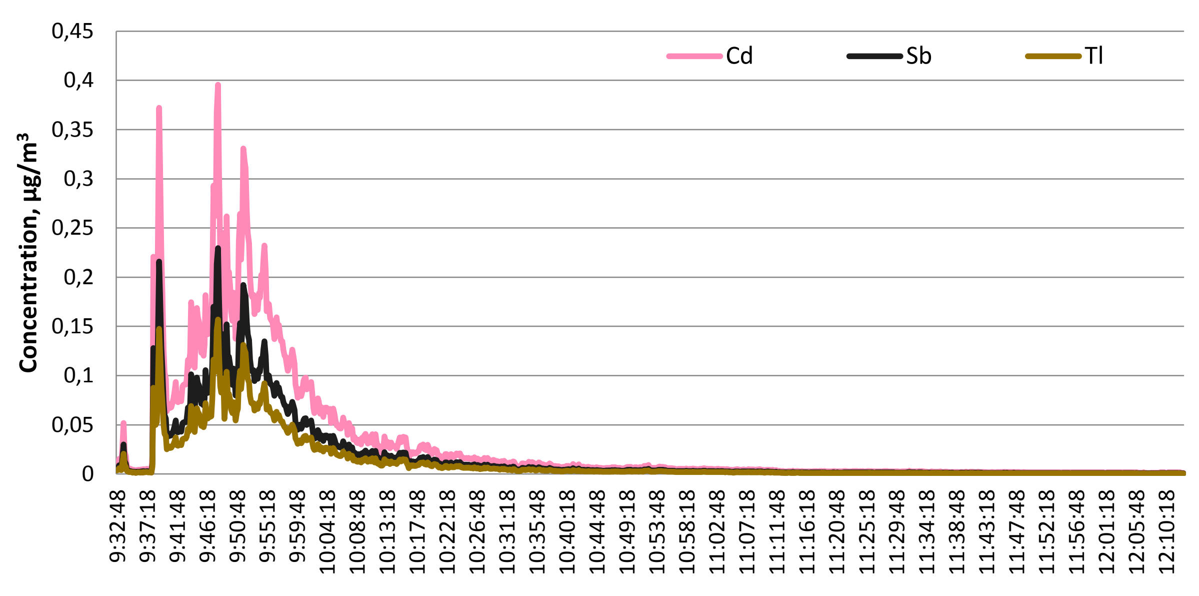

Figure 43. Variation of calculated metal concentrations during loading of moistened ash in closed hall at Power Plant B ($OEL_{8\ hours}$ –values for cadmium, antimony and titanium are 20 µg/m^3, 500 µg/m^3 and not available, respectively).

The variation of inhalable dust concentrations in the open loading station is shown in Figure 44. The highest short term exposure levels were over 1.7 fold higher than $OEL_{8\ hours}$-value for inorganic dust. The average inhalable concentrations during loading and two hours after that in open loading station was 73% of $OEL_{8\ hours}$-value for inorganic dust.

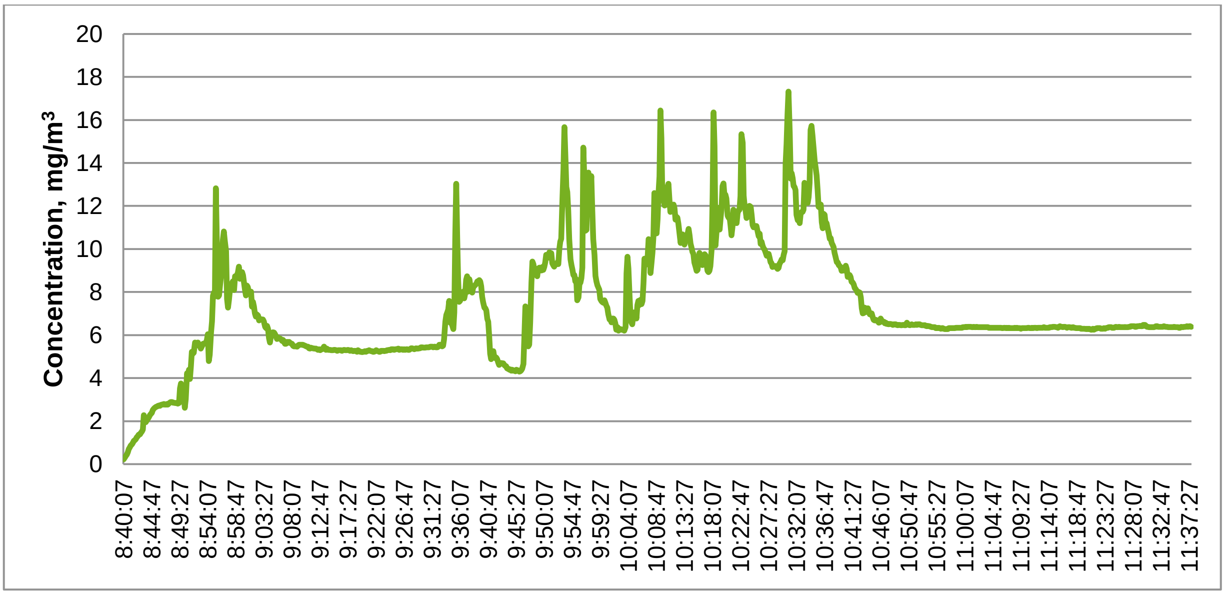

Figure 44. Variation of inhalable dust concentration during loading of moistened ash in the open loading station at Power Plant C (OEL_{8hours}= 10 mg/m^3).

In Figures 45 -47 are shown calculated (from metal content of material samples in fine ash) metal concentrations during loading of moistened ash in the open loading station at power plant C. Short term exposure levels of metals did not exceeded their $OEL_{8\ hours}$-limit values during loading of ash.

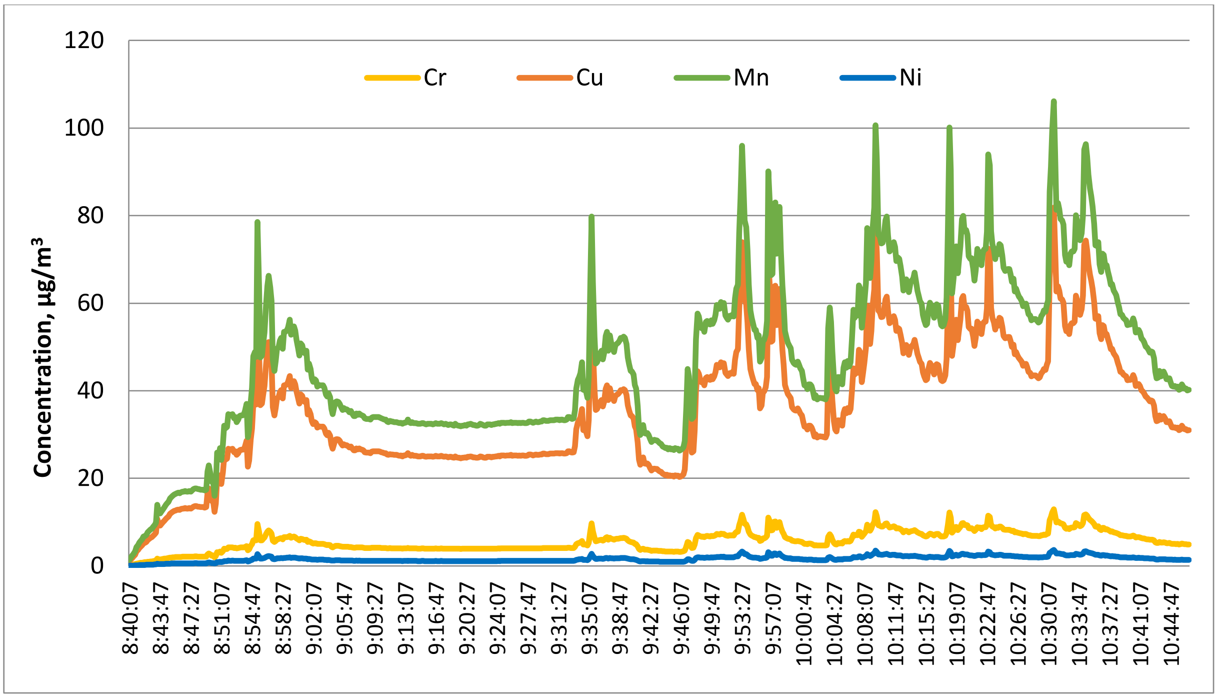

Figure 45. Variation of calculated inhalable metal concentration during loading of moistened ash in the open loading station at Power Plant C (OEL_{8hours} –values for chromium, copper, manganese and nickel are 500 µg/m^3, 1000 µg/m^3, 200 µg/m^3 and 50 µg/m^3 respectively).

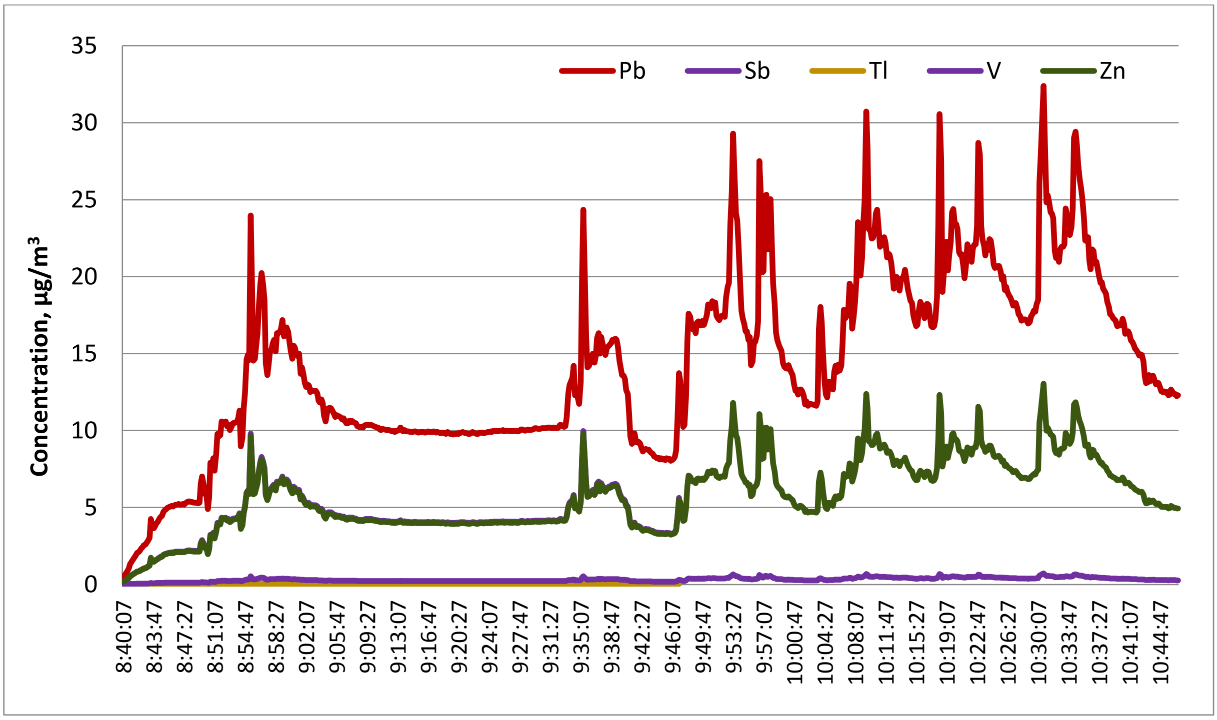

Figure 46. Variation of calculated inhalable metal concentration during loading of moistened ash in the open loading station at Power Plant C ($OEL_{8\ hours}$ –values for lead, antimony, titanium, vanadium and zinc 100 µg/m^3, 500 µg/m^3, not available, not available and 2000 µg/m^3, respectively)

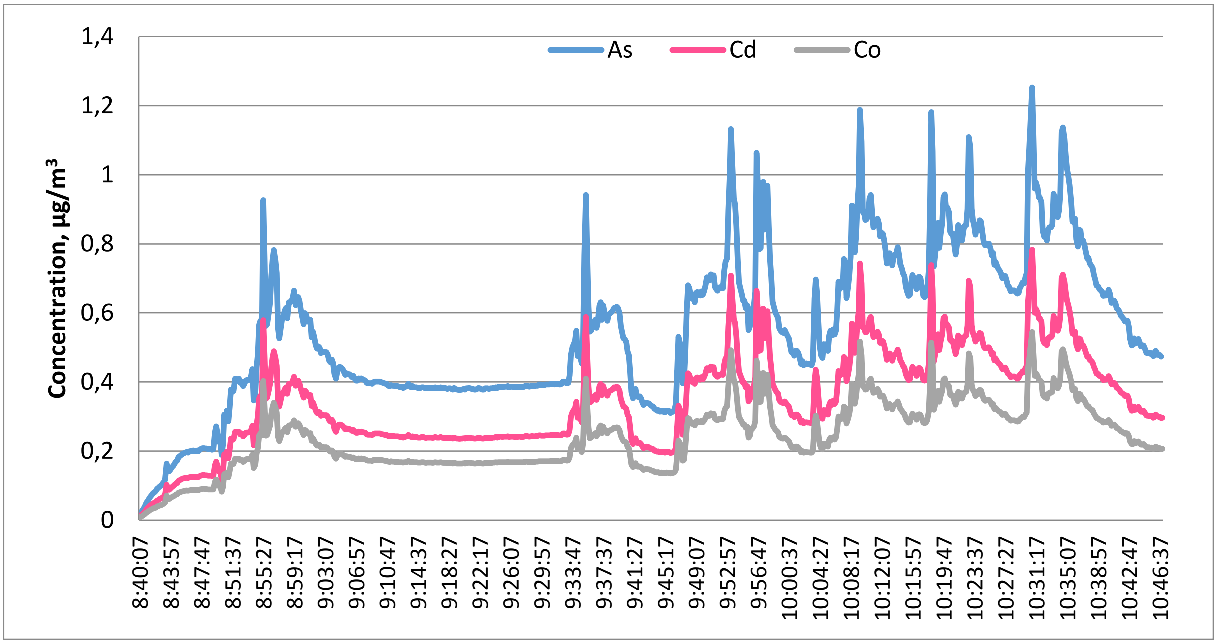

Figure 47. Variation of calculated inhalable metal concentration during loading of moistened ash in the open loading station at Power Plant C (OEL$_{8\ \text{hours}}$ –values for arsenic, cadmium and cobalt are 10 µg/m^3, 20 µg/m^3 and 20 µg/m^3, respectively)

In Figure 48 is shown *nitric oxide* concentration during loading moistened ash in closed hall, when diesel engine of the truck was idling during loading. The highest short term nitric oxide concentration was 1.6 fold higher than OEL$_{8\ \text{hours}}$ –value for nitric oxide. Nitric oxide concentrations decreased to the level of 10% of OEL$_{8\ \text{hours}}$-values within 15 minutes after end of ash loading. The average nitric oxide concentration during loading was 73% of OEL$_{8\ \text{hours}}$-value for nitric oxide. The nitric oxide concentration decreased to the level of 10% of OEL$_{8\ \text{hours}}$-value within 15 minutes after end of ash loading.

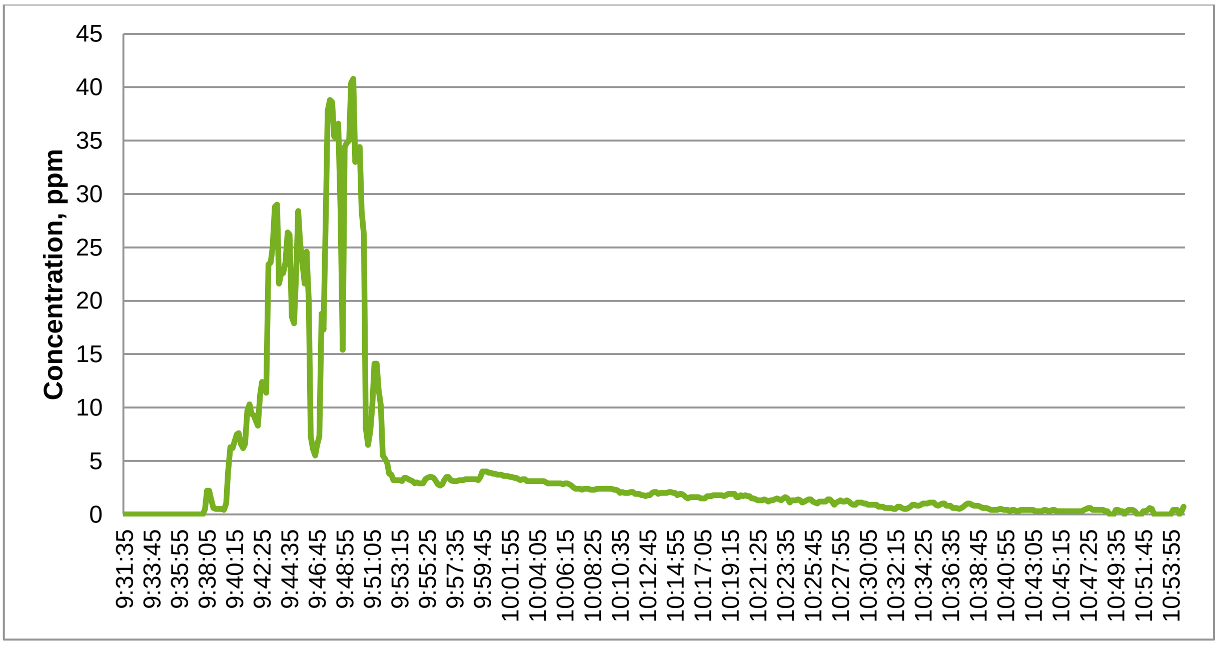

Figure 48. Variation of nitric oxide concentration during loading of moistened ash in closed loading station hall at Power Plant B (OEL$_{8\ \text{hours}}$= 25 ppm).

5.4 Ash chemical composition and morphology

5.4.1 Particle size

Both the fly and the bottom ashes consisted mainly of coarse particles, < 10 µm particles were the minor fraction (less than 4% in the fly ashes and less than 0.5% in the bottom ashes). The fly ashes included a lot of coarse particles and thus the fly and bottom ashes were partly the same matter.

5.4.2 Chemical composition (ICP-MS, IC & ICP-OES)

Main components

In the first round samples, the chemical composition was analysed with the ICP-MS and the ICP-OES. The composition of the fly ashes was similar with each other, including 19-23% Si and 13-18% Ca. Other main components (>1%) were Al, Fe, K, Na and Mg. All are typical compounds for biomass combustion ashes (Sippula et al. 2007). The bottom ashes contained more Si (33-34%) than fly ashes. The other main components were Al, Ca, Fe and Na (Figure 49, Appendix 4).

The chemical composition of the second round samples were analysed with the ICP-MS and the IC. Breathable fraction, <10 µm, was used in analyses to reflect better health effects of the ashes. The differences between the fly and bottom ashes were not so clear than in the first round samples. Like the first round samples (unsieved fractions), all the samples contained Ca (10-24%), Si (5-19%) and Al (1-6%) as main components, the bottom ashes more Si and Al than the fly ashes. The power plant C ashes contained some more Ca than the power plant A and B ashes. The power plant B ashes contained more Si than the power plant A and C ashes (Figure 50, Appendix 5).

SO_4^{2-} was also one main component in the power plant A and C ashes (3-16%), but not in the power plant B ashes. The difference is probably because sulphur is added to combustion process in the power plants A and C, but not in the power plant B.

All the samples contained also Fe, K, Mg and Na (1-8%). The power plant B ashes contained some more Fe than the power plant A and C ashes.

When comparing the unsieved fractions (first round samples) and <10 µm fractions (second round samples), there was less Si in <10 µm fractions in relation to unsieved samples. It seems that Si is in most part in coarse particles; however this can partly be because of incomplete digestion of Si in < 10 µm samples and also differences between the measurement rounds. Si is probably ended up to the ashes from bedsand.

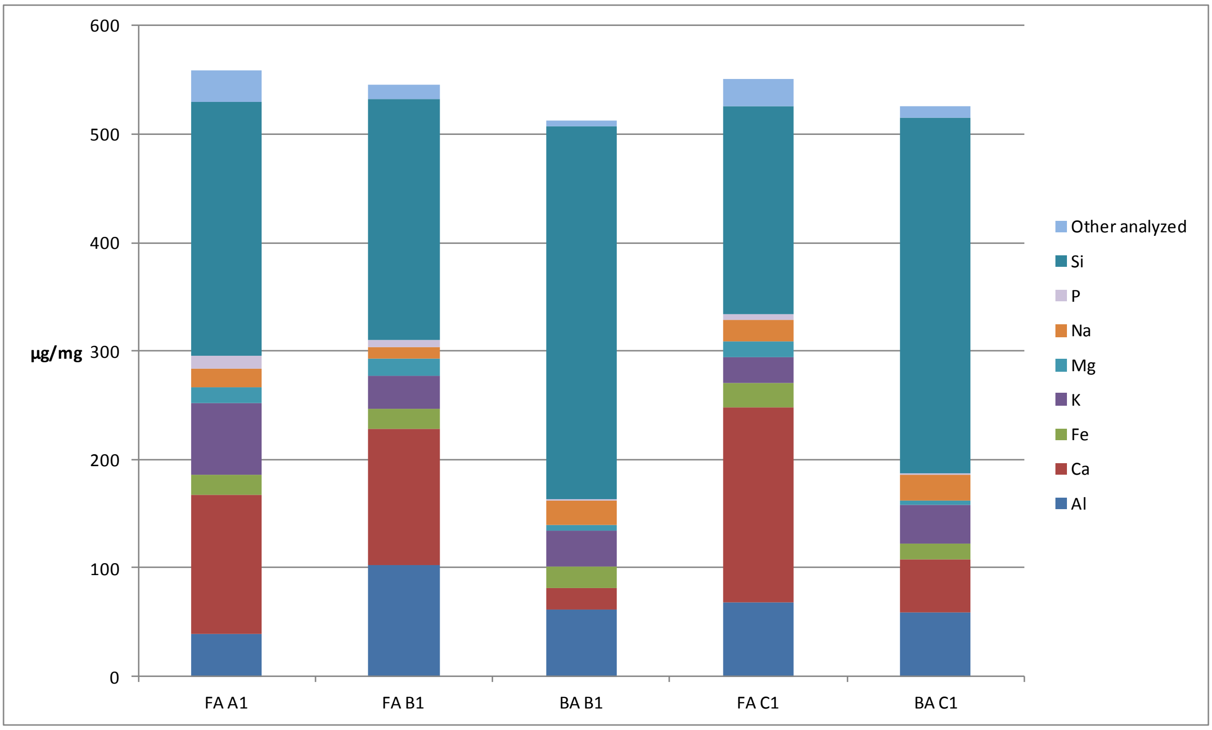

Figure 49. Chemical composition of first round samples (FA=fly ash, BA=bottom ash, number codes 1 and 2 describe different measurement rounds and letters A, B and C different power plants).

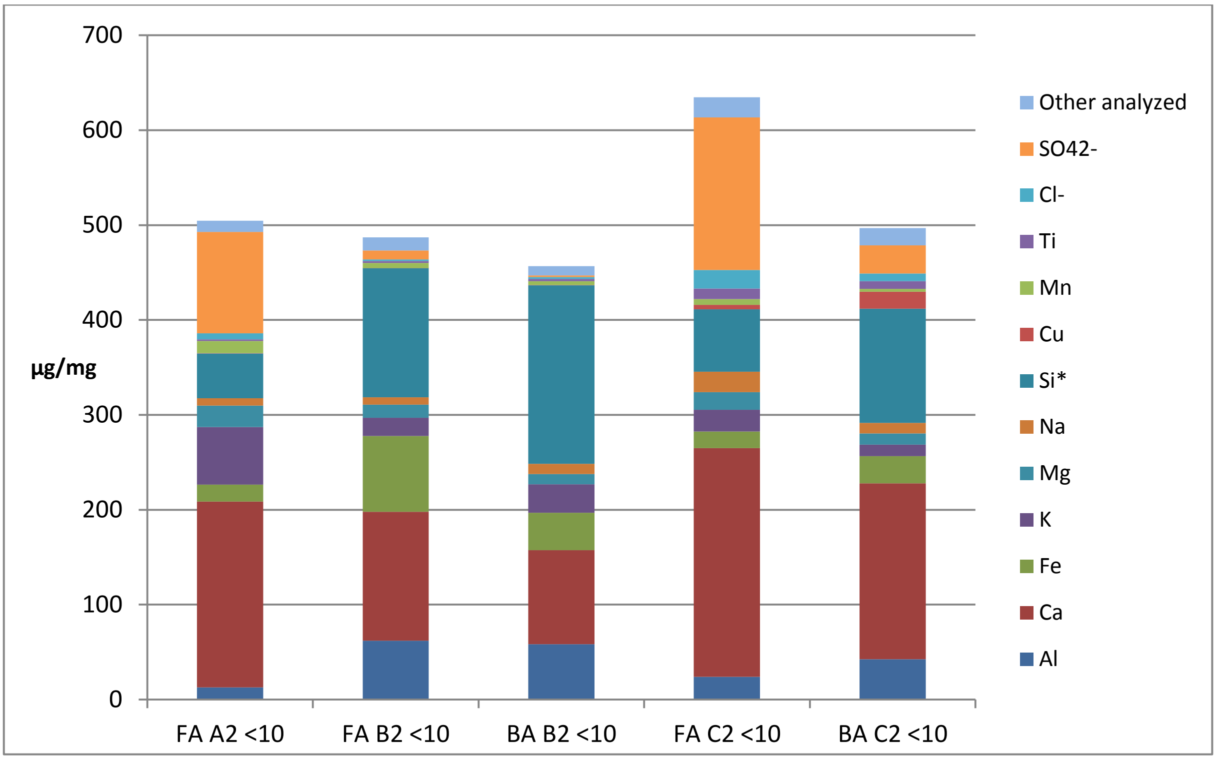

Figure 50. Chemical composition of <10 µm fractions of second round samples (FA=fly ash, BA=bottom ash, number codes 1 and 2 describe different measurement rounds and letters A, B and C different power plants).

Heavy metals

The first round samples contained 0.1-1% heavy metals. Mn was the main component (0.1-0.8%) and all the samples contained also Zn (0.02-0.2%). Mn content is typical for wood combustion ashes (Alakangas 2000). Power plant C ashes contained more Cu (0.2%) than other power plant ashes, probably due to SRF used. The amount of As, Cd, Co, Cr, Cu, Ni, Pb and Sb were also higher. The fly ashes contained more Cd and Pb and also some more Sb and As than the bottom ashes (Figure 51), which is consistent as these species are known to volatilize and enriched in fly particle fraction in the biomass combustion processes (Sippula 2010).

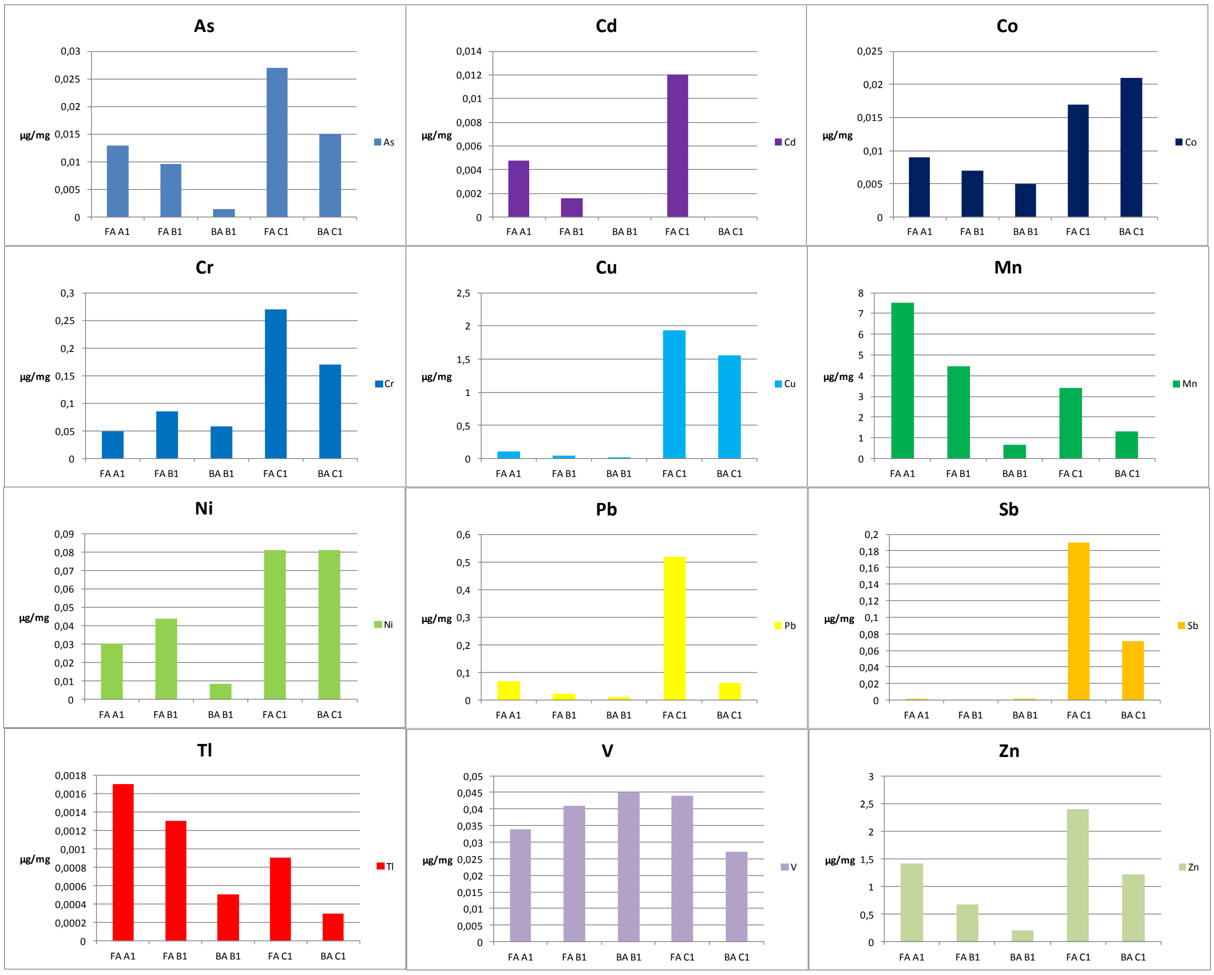

Figure 51. Heavy metal composition of first round samples (FA=fly ash, BA=bottom ash, number codes 1 and 2 describe different measurement rounds and letters A, B and C different power plants). 1 µg/mg = 1000 mg/kg.

The second round samples (< 10 µm fractions) contained more heavy metals (0.7-3.3%, Figure 52) than the first round samples (unsieved fractions). This is partly because of smaller proportion of Si in <10 µm fractions, but also shows that at least some heavy metals exist mostly in the small particles. In previous studies it has been found out that, in some cases, heavy metals tend to vaporize in combustion and form species in sub-micrometer sizes (Sippula 2010).

In the second round samples (< 10 µm fractions), Mn and Zn were again the main heavy metals in the power plant A ash, as can be expected on the basis of fuels used. Probably due to SRF used, the power plant C ashes contained more heavy metals (Cd, Cu, Pb, Sb and Zn) than the other power plant ashes, such as the unsieved fractions. When comparing to the unsieved fractions, there were differences in Cr, Ni and Co contents; the < 10 µm fractions of the power plant B fly ashes contained more of them than the < 10 µm fractions the power plant A or C ashes. Based on SEM-EDS figures (later in report, Figure 57), one option for Ni and Cr is that e.g. in fuel crushing process some stainless steel ends up to the fuel.

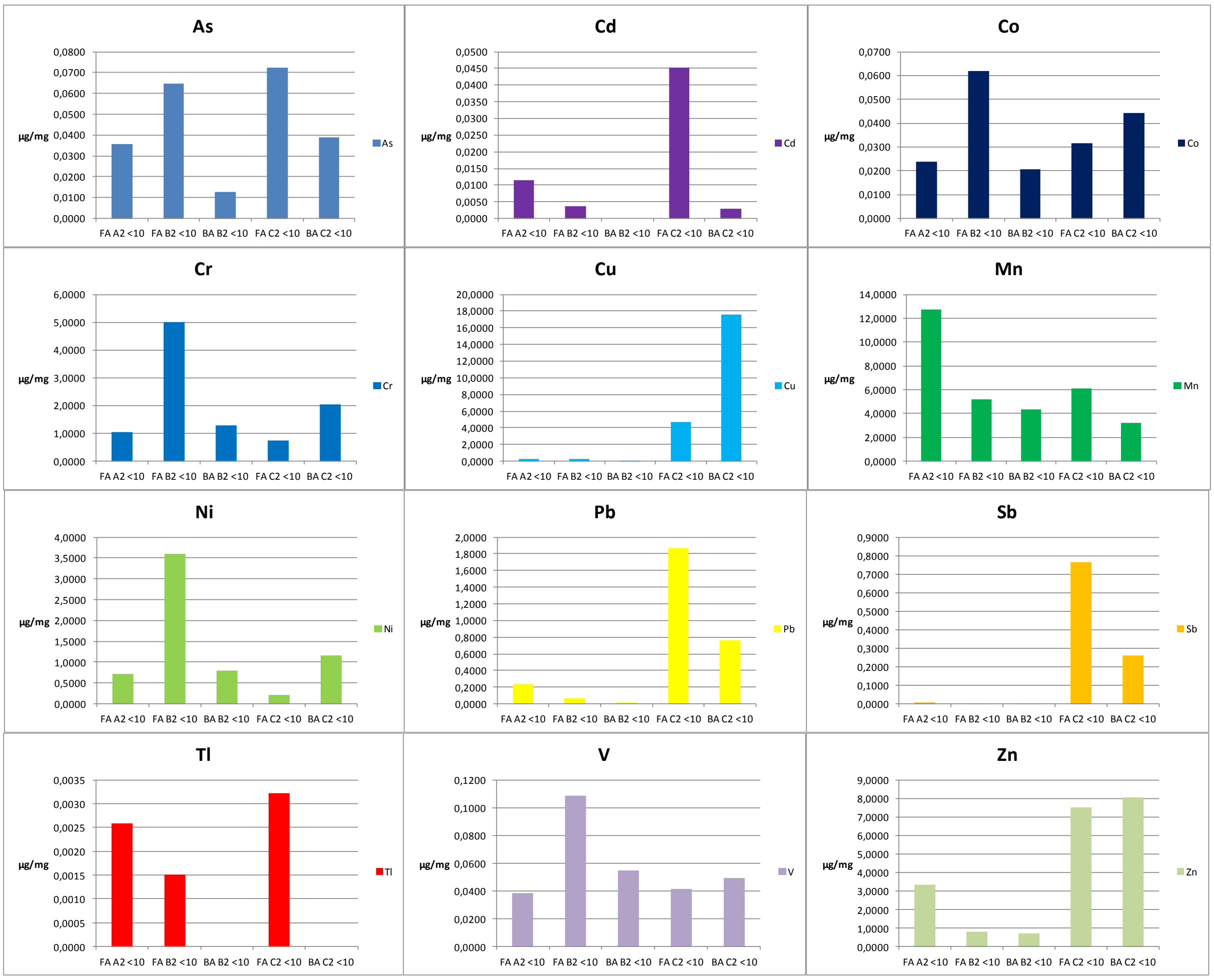

Figure 52. Heavy metal composition of < 10 µm fractions of second round samples (FA=fly ash, BA=bottom ash, number codes 1 and 2 describe different measurement rounds and letters A, B and C different power plants). 1 µg/mg = 1000 mg/kg.

5.4.3 Particles chemical structure (XRD)

In XRD analyses, objective was to identify compounds linked to the main chemical components analysed with ICP-MS, ICP-OES and IC, and also to identify compounds related to heavy metal components. The detection limit of the XRD analysis is highly dependent on the sample properties (e.g. number of compounds, degree of crystallinity and crystallite size) but generally falls in the range of 0.1 to 1%. The heavy metals exist in the samples in low quantities. As such, unambiguous identification of the compounds was not possible.

Silicon compounds

Si exists mainly in SiO_2. Other main Si compounds were $KAlSi_3O_8$ and $NaAlSi_3O_8$ in the bottom ashes and probably also $Ca_2Al_2SiO_7$ in both the fly and the bottom ashes. In smaller amounts, $Ca_3Mg(SiO_4)_2$, Ca_2SiO_4, $NaCaAl(Si_2O_7)$, $NaSi_3AlO_8$ and $(Na, Ca)Al(Si,Al)_3O_8$ are possible compounds in the fly ashes and K_2MgSiO_4 in the bottom ashes. SiO_2 were also found by Enestam et al. (2011) from aerosol particles collected from combustion of recovered waste wood, and SiO_2, $KAlSi_3O_8$ and $NaAlSi_3O_8$ by Lindström et al. (2010) from bottom ashes of combustion of woody biomass pellets.

The power plant B ashes contained more Si than the other samples and due to that the ashes from the power plant B contained more SiO_2 than ashes from power plants A and C. The power plant B bottom ash contained also more $KAlSi_3O_8$ and $NaAlSi_3O_8$ than the power plant C bottom ash.

The unsieved samples contained more SiO_2 and also slightly more $NaAlSi_3O_8$ than < 10 µm fractions, so SiO_2 and also partly $NaAlSi_3O_8$ likely exists for the most part in the coarse particles. Especially in the unsieved bottom ash samples, high SiO_2 content “overruns” the other components in XRD spectrums.

Calcium compounds

In the fly ashes, main Ca containing compounds were $CaSO_4$, CaO and probably also $Ca_2Al_2SiO_7$ and $Ca_3Al_2O_6$. In the bottom ashes, $Ca_2Al_2SiO_7$ were the main Ca containing component. In smaller amounts, $Ca_3Mg(SiO_4)_2$, Ca_2SiO_4, $NaCaAl(Si_2O_7)$, $K_3CaH(PO_4)_2$ and $(Na, Ca)Al(Si,Al)_3O_8$ are possible compounds. $CaSO_4$ and CaO were also found by Enestam et al. (2011). Fernandez-Turiel et al. (2004) found some $Ca_2Al_2SiO_7$ and probably some calcium aluminate in different form ($CaAl_2O_4$) from ash deposits of Ca-rich lignite combustion.

The fly ashes from the power plants A and C contained more Ca (Figure 50) and also some more $CaSO_4$ and CaO than the power plant B fly ash.

Sulphates

Majority of SO_4^{2-} was in form $CaSO_4$ in fly ashes. In small amounts, the fly ashes contained probably also $K_2Na_2(SO_4)_2$ and the bottom ashes $K_2Ca_2(SO_4)_3$. The fly ashes from the power plants A and C contained more $CaSO_4$ than the fly ashes from the power plant B. This is probably due to, in addition to the higher Ca content, bigger amount of sulphates in the power plant A and C ashes due to the sulphur addition processes.

Aluminium compounds

Majority of Al exists in $Ca_2Al_2SiO_7$ and $Ca_3Al_2O_6$ in the fly ashes and in $AlSi_3O_8$, $NaAlSi_3O_8$ and $Ca_2Al_2SiO_7$ in the bottom ashes.

Potassium compounds

In the bottom ashes, K exists mainly in $KAlSi_3O_8$ and in small amounts probably also in $K_2Ca_2(SO_4)_3$ and K_2MgSiO_4. $KAlSiO_4$ and $K_2Ca_2(SO_4)_3$ are typical compounds in bottom ashes (Sippula 2010). In the fly ashes, no K containing compound were identified for sure with XRD, but possible compounds are $K_2Na_2(SO_4)_2$ and $K_3CaH(PO_4)_2$. Typical K containing compounds in fine fly ashes are e.g. K_2SO_4 and KCl (Sippula 2010), and it is possible that they exist in amorphous form in the samples and are therefore not seen with XRD.

Sodium compounds

Na exists mainly as NaCl in fly ashes and as $NaAlSi_3O_8$ in bottom ashes. In addition to them, $K_2Na_2(SO_4)_2$, $NaCaAl(Si_2O_7)$ and $(Na, Ca)Al(Si,Al)_3O_8$ are possible compounds in the fly ashes and $Na_{2x}Ca_{3-x}Al_2O_6$ in the bottom ashes.

Magnesium, chlorine and iron compounds

Mg-containing compounds cannot be identified for sure, but possible compounds are $Ca_3Mg(SiO_4)_2$ in the fly ashes and K_2MgSiO_4 in the bottom ashes. Cl^- were found to be in NaCl in the fly ashes. Fe was probably in Fe_2O_3 in both the fly and the bottom ashes.

Heavy metals

Heavy metal compounds of the ashes cannot be defined definitely because of small amount of heavy metals and big amounts of other components in the samples. In literature (put together by Enestam et al. 2011), Zn has been found to be e.g. in forms Zn_2SiO_4, $ZnAl_2O_4$, $Zn(OH)_2$, ZnO and K_2ZnCl_4 (in bottom ashes, aerosols and fly ashes). ZnO is the most thermodynamically probable form (Jones et al. 2013). In both fly and bottom ashes, it seems that no single Zn compound dominates but Zn exists in many compounds. In bottom ashes, Zn probably does not exist in forms Zn_2SiO_4 or K_2ZnCl_4. Existence of $ZnAl_2O_4$, $Zn(OH)_2$ and ZnO cannot be excluded because their spectrums fit to data. Anyway, if they exist in samples, the amounts are quite small. In fly ashes, $Zn(OH)_2$ and K_2ZnCl_4 probably not exist, but $ZnSiO_4$, ZnO and $ZnAl_2O_4$ are possible in small amounts. $K_2Zn_2(SO_4)_3$ fit to spectrum in the power plant A and C fly ashes, but not in the power plant B fly ashes or in the bottom ashes. The difference can be because of sulphur addition processes in power plants A and C. Zn has not been found in this form in literature, but $ZnSO_4$ has been found in literature from aerosols and deposits (Enestam et al. 2011).

Hsiao et al. (2002) found out Cu existing in forms $CuCO_3$, $Cu(OH)_2$ and CuO in fly ash of municipal solid waste combustion. Both in the fly and the bottom ashes of the power plant C, Cu exists probably in many compounds. Part of Cu can exist in forms CuO or CuO_2, but not in big amounts. Cu seems not to exists in forms $CuCO_3$ or $Cu(OH)_2$. Cu seems not to exists in $CuSO_4$ also, at least not in crystalline form, although in earlier study Cu have found to exist in $CuSO_4$ in the fly ashes from the same power plant (Bajamundi et al. 2014).

5.4.4 Morphology (SEM)

Fly ashes

The fly ash sample FA B2 <10 and the bottom ash sample BA B2 <10 were pictured and analysed with SEM and EDS. The fly ash particles varied with morphology containing both bigger (size more than few micrometres) and smaller (size some hundred nanometres) particles. The smaller particles seem to exist partly in the surfaces of the bigger particles. Shapes of the particles varied, the bigger particles included e.g. (hollow) spherical particles (cenosphere-like particles), and the small particles e.g. fibrous particles (Figure 53 and Figure 54).

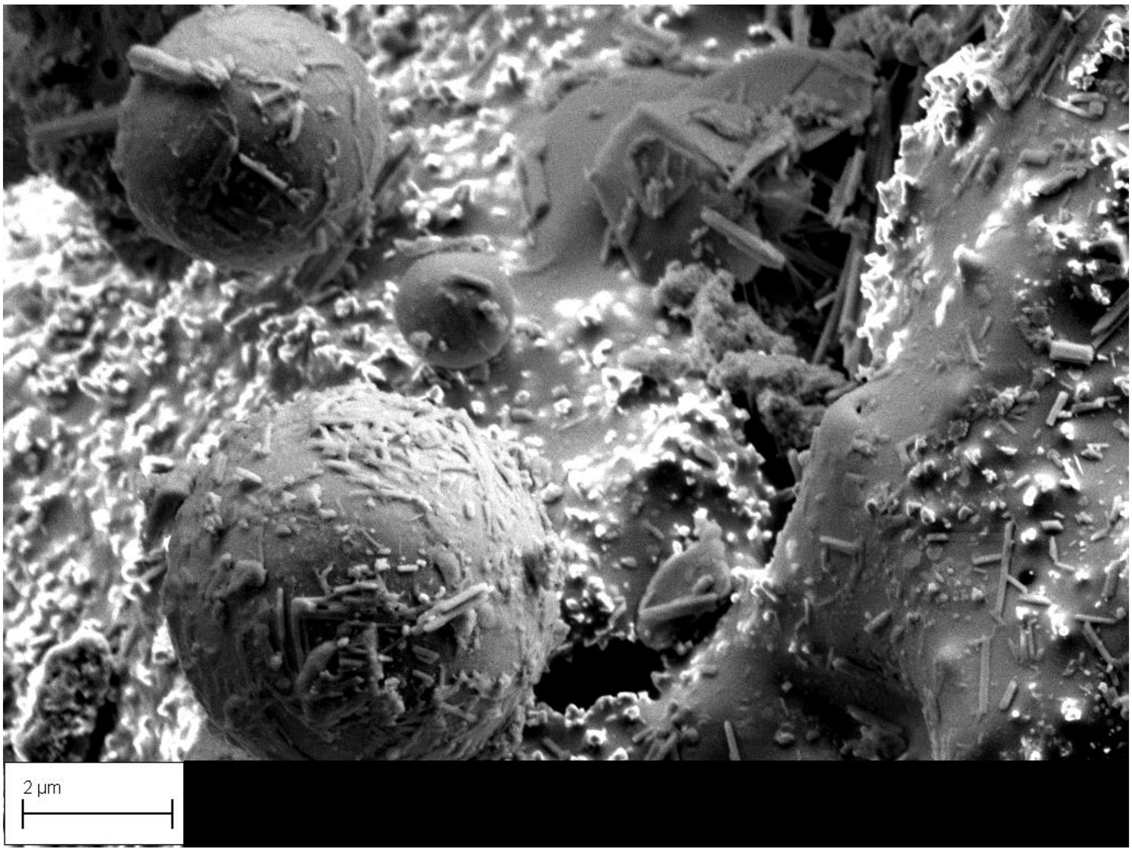

Figure 53. SEM image of fly ash particles with various shapes (sample FA B2 <10).

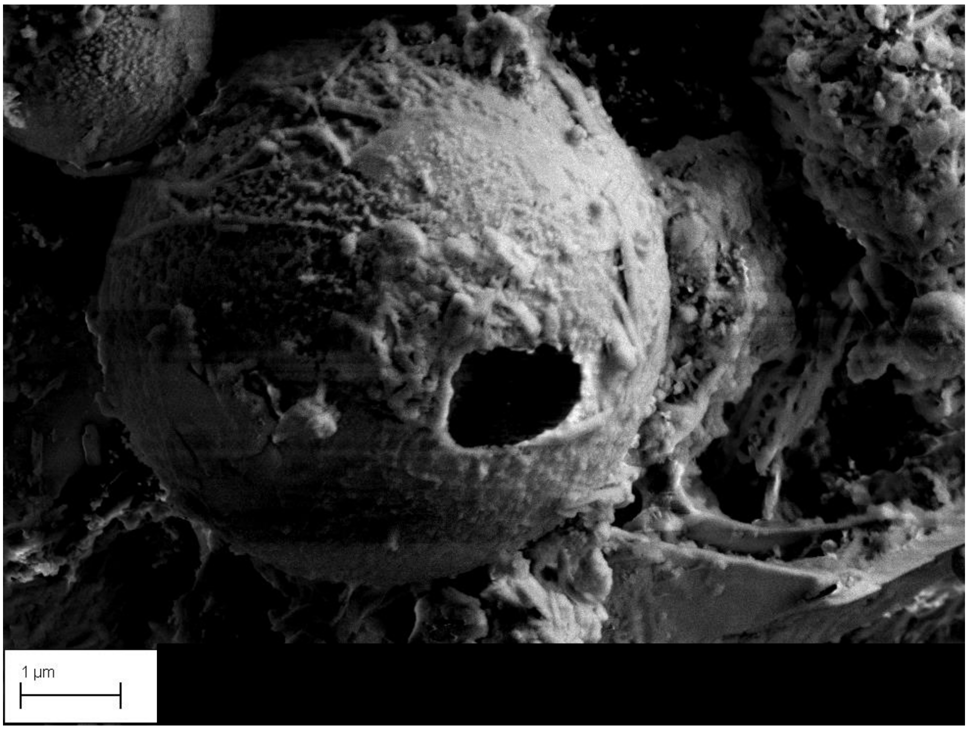

Figure 54. SEM image of hollow spherical particle (cenosphere) (sample FA B2 <10).

One agglomerate of the fly ash sample FA B2 <10 was analysed with SEM-EDS (Figure 55 and Figure 56). The biggest particle seems to contain O, Al, Si and Ca (possibly $Ca_2Al_2SiO_2$), the particle on left O, Al, Si, K and Na (possibly $KAlSi_3O_8$ and $NaAlSi_3O_8$) and the middle area of agglomerate Si and O (possibly SiO_2), and Ca, O, Al and S (possibly $Ca_3Al_2O_7$ and $CaSO_4$). Kutchko et al. (2006) found also Si, Al, Fe, Ca and O in various compound from fly ashes of coal combustion analysed by EDS, however the ashes from the coal combustion are quite different compared to the biomass combustion ashes. They concluded that the fly ashes consisted mostly of alumino-silicate spheres and also iron-containing spheres, and that Ca is not associated with Si or Al. However, in this case Ca in the spherical particle seems to be associated with Al, Si and O (possibly $Ca_2Al_2SiO_7$).

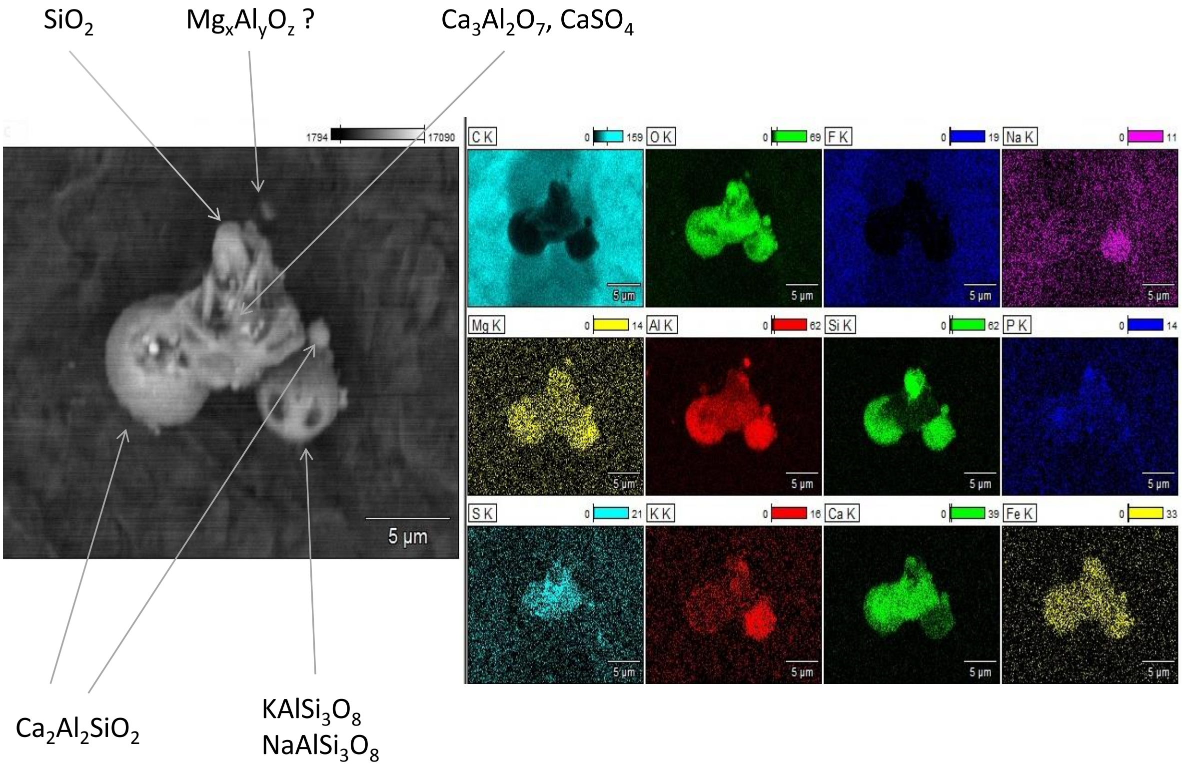

Figure 55. SEM-EDS image of fly ash particles and possible compounds they included (sample FA B2 <10).

Bottom ashes

The bottom ash sample contained mainly non-spherical particles with various shapes. Smaller particles (< 1 µm) exist partly in surfaces of bigger particles (~10 µm), as in the fly ashes (Figure 56). The bigger particles in the Figure 50 are possibly SiO_2 (quartz) (Kutchko et al. 2006).

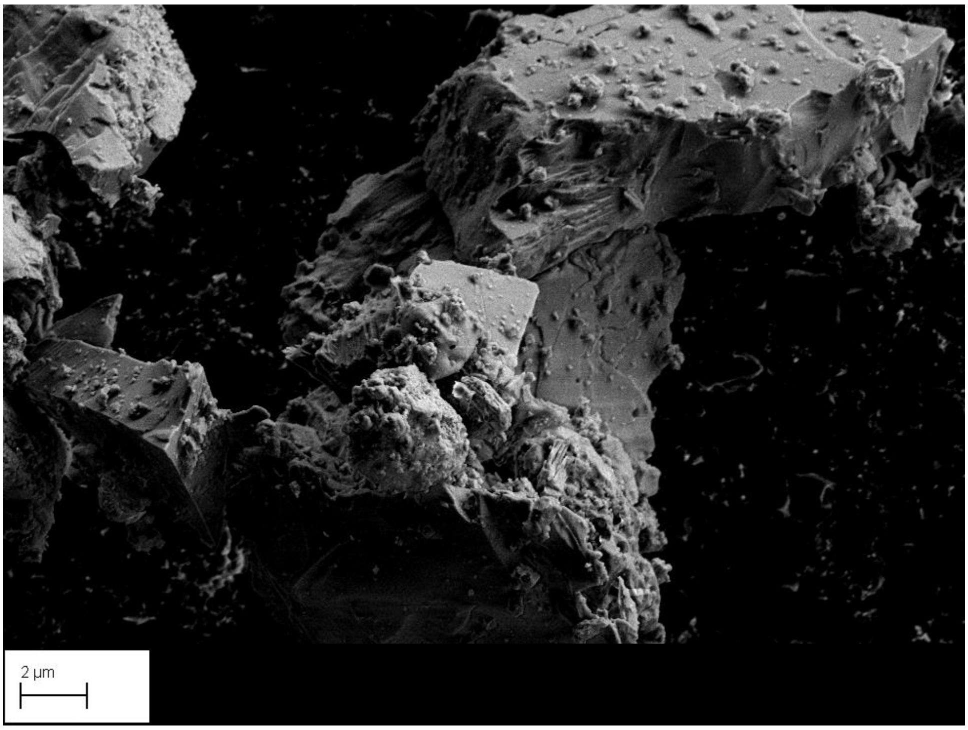

Figure 56. SEM image of bottom ash (BA B2 <10) particles (big particles possible SiO_2).

From the <10 µm fraction of the bottom ash sample BA B2, one part (size some hundred micrometres) was analysed with SEM-EDS (Figure 57). Particle on right side of the picture contained Cr, Fe and Ni, and is probably stainless steel from e.g. the fuel crushing processes. Particle on left side of the picture contained O, Na, Al and Si and is possibly $NaAlSi_3O_8$ (albite, ended up to the process possibly from the ground). The rest small particles contained at least O, Al, Si, K, Ca and also small amounts of Na, Mg, S, Ti, Cr, Mn, Fe and Ni. Carbon area on left side of the picture is from carbon varnish.

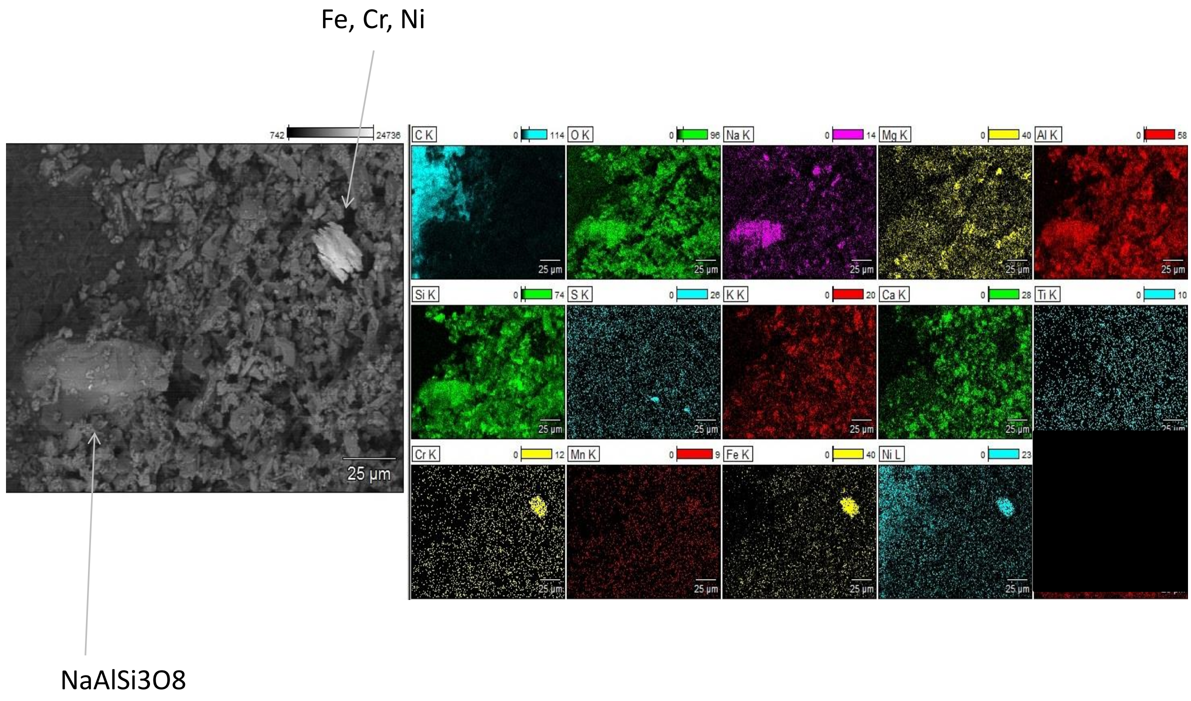

Figure 57. SEM-EDS image of bottom ash particles (sample BA B2 <10) and possible compounds they included.

6 Conclusions

The main occupational exposure associated health risks for workers at the biomass fired power plants are bacteria and fungi, which are easily spread to the air during heavy biomass processes. The measured exposure levels of endotoxin, actinobacteria and fungi were very high especially during reception of indigenous solid fuels. The highest exposure levels from reception hall and drivers' breathing zone were measured during the unloading of peat and logging residue chips. In addition to that, workers were exposed to mechanical irritation caused by organic dust, chemical irritation caused by volatile organic compounds and components of diesel exhausts. Multiple exposures to these agents simultaneously may cause synergistic health effect on workers' lower and upper respiratory tract.

During the solid biofuel operations at the power plant sites workers were also exposed to endotoxin, actinobacteria and fungi, especially during cleaning and handling of wood chips in silo and working near screens or crushers. Measured concentrations exceeded proposed limit values of these agents. The highest concentration of volatile organic compounds (VOCs) was measured near conveyors. The measured profile of VOCs contained many metabolites of bacteria and fungi. Near the silo carbon dioxide concentrations exceeded its' $\text{OEL}_{8\ \text{hours}}$-value reflecting the fermentation of solid biofuels. The increase of carbon dioxide concentrations near solid biofuel silos might end up to the situation where carbon dioxide can start to replace oxygen in the air. The reason for that is generally inadequate ventilation compared to the production of carbon dioxide during fermentation process. Reduced sulphur compounds concentrations in the heat recovery department were at the significant level and needs to be addressed as one occupational hazard in biomass fired power plant processes. Also high short term exposure to carbon monoxide in boiler room seemed to be possible during the malfunctions of boilers, according to the data recorded from boiler room during the whole work shift.

Truck drivers and power plant workers can also be exposed to ash in loading of ash at closed or open loading stations. The highest exposure risk seems to be at closed loading stations. The highest short term exposure levels of inorganic dust were 10 fold higher than $\text{OEL}_{8\ \text{hours}}$-value. Due to very fine particle size of fly ash, the inhalable inorganic dust concentrations at the loading stations decreased very slowly after end of ash loading. It took about 75 minutes after end of the ash loading to reach the 10% level of $\text{OEL}_{8\ \text{hours}}$-value for inorganic dust. Also calculated short term levels of chromium, manganese and nickel exceeded their $\text{OEL}_{8\ \text{hours}}$-values during loading of ash. Idling of diesel engine during the loading at closed loading station posed high concentrations of nitric oxide in the air of the loading hall. At the open ash loading stations all above mentioned problems were clearly lower than those in closed loading stations.

The spreading of contaminants from the power plant to the environment was estimated with endotoxin, bacteria and fungi outdoor measurements. This measured data was combined with wind data obtained from Wind Atlas at the 50 meter level and also from three weather stations at the ground level. The levels of above mentioned agents in outdoor measurements were reflecting low spreading of contaminants to the environment during the measurements. To be able to estimate the most contaminated area outside the power plant, wind data was refined to the wind roses. Wind Atlas at the 50 m level did not explained the wind conditions at the ground level of the site at all. As from the wind roses can be seen, practically in all cases (Figures 12 - 14 and Appendix 1) certain similarity between 1st and 2nd measurement rounds was found. The shape of the roses between the rounds was quite similar except that the direction could vary about 180°. Maybe the reason was that at the plant site the environment directed the wind significantly. At the sites there were several large and high buildings placed in the vague shape. The relative location of the weather station to buildings and the surrounding environment (e.g. forest or hill) affected most significantly the wind measurement results.

Altogether 3 fly ash and 4 bottom ash samples were analysed by using ICP-MS, IC, ICP-OES, XRD and SEM-EDS. The samples were collected from three different power plants, in which two were operated with sulphur addition into the combustion chamber. The main components of the ashes were Si, Ca, Al, Fe, K, Na and Mg, which is typical in biomass combustion. The main Si compound observed with XRD was SiO_2 and SiO_2 seems to exist for the most part in the coarse particles and is probably ended up to the ashes from bedsand. The other main compounds observed with the XRD were $CaSO_4$, CaO, $Ca_2Al_2SiO_7$, NaCl and $Ca_3Al_2O_6$ in the fly ashes and $KAlSi_3O_8$, $NaAlSi_3O_8$ and $Ca_2Al_2SiO_7$ in the bottom ashes. All (except $Ca_3Al_2O_6$) are typical compounds in the biomass combustion ashes according to literature.

It seems that some heavy metals are enriched in the respirable particle fraction (PM10). Mn and Zn were the main heavy metals, what is typical for woody biomass fuels. In addition to the SRF co-firing plant, relatively high concentration of Cu was found from the ashes. The fly ashes generally contained more Cd and Pb and also some more Sb and As than the bottom ashes, which is consistent with the fact that these species are known to volatilize and enrich in the fly particle fraction in biomass combustion processes. The ashes from the power plant co-firing SRF contained more As, Cd, Co, Cu, Pb, Sb and Zn than the other ashes.

The effect of sulphur addition was observed as existence of crystalline $CaSO_4$ in the fly ashes. In addition, according to XRD analyses, Zn possibly exists in $K_2Zn_2(SO_4)_3$ in the fly ashes of the power plants using the sulphur addition, while without sulphur addition Zn compounds were not detected with XRD. However, due to a small amount of Zn in the samples, the existence of $K_2Zn_2(SO_4)_3$ cannot be confirmed without further studies. Interestingly, Zn seems not to exist as ZnO, which is thermodynamically the most probable form, at least not in big amounts and in crystalline form, in the ashes.

The morphology of individual ash particles, analysed with SEM-EDS varied from spherical to irregular shape and fibre-like particles. In general, size, shape and surface structure of ash particles affect their health related properties. Of particular importance might also be the attachment of the fine particles on the surfaces of the coarse particles because this affects largely the dispersion and lung deposition of the ashes which are suspended in the air. It should be noted that the health effects of the ash particles are difficult to assess if they are not suspended as aerosol. To get a realistic picture of lung deposition of the ashes and thus the health effects they induce, more information about size distributions and compounds existing in different size fractions is needed. One option is to suspend the samples using an aerosol generator and fractionate them for example with a low-pressure impactor system. This enables analysis of the particle size distribution and chemical composition under realistic conditions. This kind of setup can also be further extended for health studies, utilizing for example cell tests for determining toxicological properties of the particles.

The model of sequential technical surveys and occupational hygiene measurements at selected power plant sites, planned for the execution of the research worked well. Lot of information about possible exposures during the operations at the power plant sites were collected widely and productive conversations were carried out between VTT, FIOH and representatives of power plants. Unfortunately the winter 2014 was warmer than normally and the weather nearly corresponded to autumn and therefore the effect of cold and dry period on the biological and chemical exposure was not seen in measurements performed. More information is still needed about the effect of possible occupational exposure and its significance to employee’s health at different parts of bioenergy supply chain.

7 Best practices

In order to prevent exposure associated respiratory impairment among truck drivers and fuel reception workers, who may inhale large amounts of bioaerosols during unloading process, the key issue is to improve the quality of the solid biofuels. The measured exposure levels of endotoxin, actinobacteria and fungi are mostly dependent on the quality of the fuels. The whole biomass supply chain has the main influence on the quality of fuels. In designing of the storages the elimination of microbial generation is the first step, which should be taken into account. To be able to prevent the microbial growth and microbial contamination in solid biofuels, strict control of moisture content, storage time and temperature are needed. Temperature has a major influence on the growth of micro-organisms. Therefore, by reducing moisture content and preventing particularly self-heating of the fuel mass, microbe growth can be reduced at the working area. For example, the quality improvement of solid biofuels by thermal drying reduces the amount of viable microbes in biomass and thereby the risk of exposure, which was seen in our study from the results of thermally dried sludge. If particularly waste heat energy is available, it could be used for the drying of biomass.The better quality of solid biofuels ensures also higher energy content.

As a preventive technical measure, isolation of the spaces reduces spreading of bioaerosols and other agents to the environment. For example, closing the doors in fuel reception halls and use of hoods around crushers and screens may reduce spreading of bioaerosols into the surroundings. On the contrary, contaminants may concentrate into the air of unloading hall and cause even more severe health effects for the workers. This risk can be minimised if worker can supervise unloading from a control room (Figure 58) or crane cabin of the truck (Figure 59). If fuel samples from the load can also be taken from the control room (Figure 60) it would reduce drivers’ exposure to bioaerosols compared to the fact that the workers have to enter to the unloading hall and take samples personally from the fuel load. The central vacuum cleaners could be less dust spreading solution to the cleaning of the unloading premises and trucks after unloading than shovelling or brushing. The favourable solution for the rear-unloading trucks could be automatic cleaning systems.

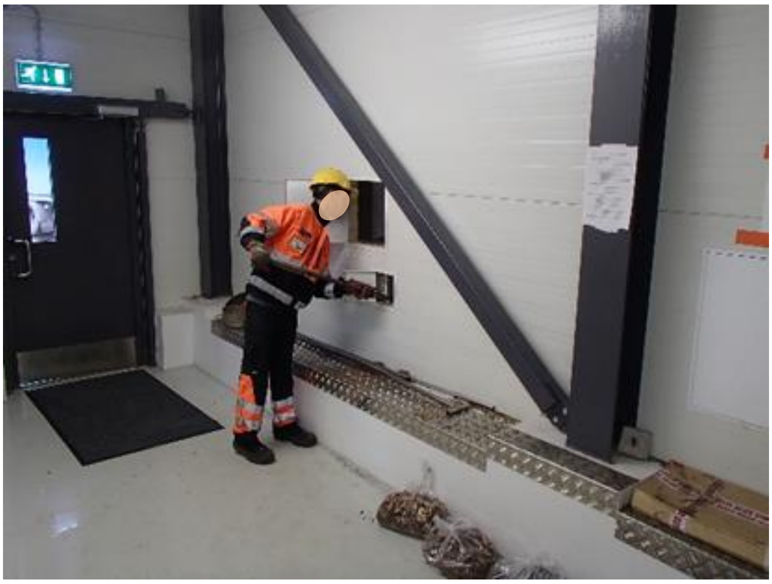

Figure 58. Supervising of unloading.

Figure 59. Crane cabin of the truck.

Figure 60. Fuel sampling from control room.

Well-designed ventilation in control rooms is an essential requirement for above mentioned improvements in fuel reception and reduction of exposure to contaminants originated from solid biofuels and exhausts of diesel engine. The first requirement for ventilation is right location for the supply of fresh incoming air. It should be placed on the clean side of the building that contaminants do not enter directly into the ventilation and eventually to the indoor air of control room. To avoid that problem it is possible to install the effective particulate air filters into the ventilation machine, which removes all particles from the fresh air. If also vaporous and gaseous agents are needed to be removed, active carbon filters are also available. It is also important to address that ventilation in the control room has to be adjusted such a way that there is positive pressure in the room compared to that in the unloading hall. This prevents the flow of contaminated air from the unloading hall into the control room through the supervision hatches. Positive pressure is also needed in crane cabins of the truck to provide an adequate protection for drivers.

There are two principles in exposure reduction, which both are useful in handling of fuel samples. The first one is to remove contaminants immediately from the place where they are born and the second one is to reduce exposure time by automation. According to the first principle local hoods are very recommendable in indoor spaces where workers are opening and handling fuel samples. The second principle can be applied to fuel sampling in unloading stage by replacing manual fuel sampling with automated one (Figure 61). As in all technical solutions, their regular maintenance, for example exchange of filters in ventilation systems, is extremely important.

Figure 61. Automated fuel sampling system at a power plant.

During processes of indigenous solid fuels at power plant sites, to be able to avoid a sudden exposure to toxic gaseous agents, workers should use a personal gas detector to get warning about too high concentration of carbon dioxide during working near bio silos or too high concentrations of carbon monoxide in boiler rooms, and too high a concentration of hydrogen sulphide in departments of the heat recovery and the flue gas scrubber sludge drying.

During ash loading a lot of ash is spread to the hall at the loading stations. More attention should be put into moistening process of ash to prevent ash spreading. Another important point is to give recommendations, how much drivers can idle their diesel engine during the ash loading process.

All valuable preventive technical measures should be taken on use at biomass fired power plants to keep the occupational exposure as low as possible (Occupational Safety and Health Act 738/2002 8 §). It is important to take into account all the working techniques and tools in future designing which can ensure lowest possible exposure to bioaerosols and other contaminants (BAT principle). Nevertheless it is valuable to compare preventive power of actions and impact of actions on workers’ health before decision making of new possible preventive options (Figure 62).

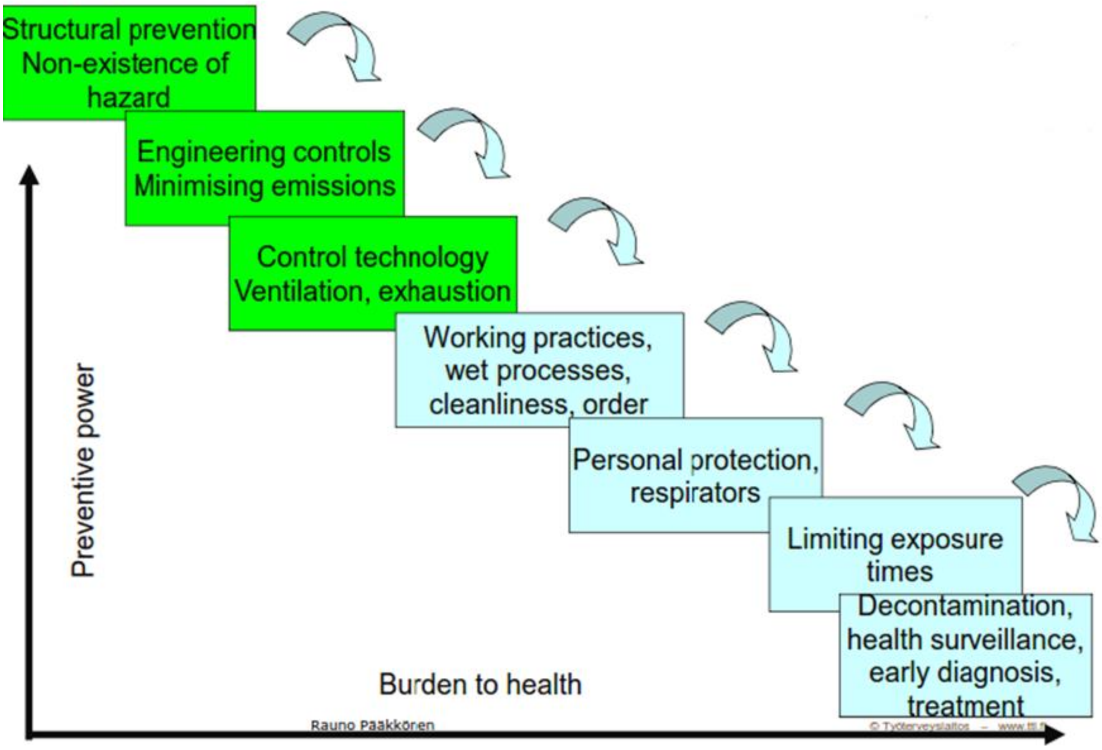

Figure 62. Hierarchy of preventive principles (FIOH, Rauno Pääkkönen).

If workers are still, after technical preventive measures, exposed to harmful substances at the bioenergy plants, this needs to be prevented by using personal protective equipment. In this case, the workers have to be trained in its appropriate use. When one works especially in the unloading hall of fuels or in the ash loading station, in the maintenance work of solid biofuel processes such as cleaning and handling of wood chips in silos, and in the working near screens or crushers, the worker must use the personal protective equipment. It is important to choose appropriate requirements and select respiratory protective equipment fitting well onto the face of the individual worker. The selection will be done carefully by fitting a person with a variety of options. The best option for workers is fan-assisted respiratory protection device system equipped with combined P3 particle filters, of which the protection class is TH3 or TM3. These systems protect workers’ face and eyes at the same time against bioaerosols and other particles. If one wants to protect oneself also from the irritating terpenes (from the VOC compounds), a combination filter A2-P3 must be used. The filtering face piece classified as FFP3 and marked with the letter R (reusable) is suitable if used in the short-term duration, up to a maximum of 2 hours, and only for protection against bioaerosols and other particles.

Workers’ exposure to potential infectious microbes through hands to the mouth in handling wastewater sludge and SRF fuels should be minimized by using protective gloves and adhering to good personal hygiene. The mechanical strength of gloves is very important for manual operation conducted by workers to prevent infectious punctures through the skin.

Workers’ exposure to carbon monoxide in boiler room, carbon dioxide near silos, nitric oxide and nitrogen dioxide in fuel reception and ash loading poses a problem, because these gases could not be filtrated from the breathing air. In protection against these gases a pressurized protective breathing apparatus is needed especially in accident cases. For that reason a personal detector could be the solution for these kinds of cases and workers can leave the place, before the gases have effects on them. For hydrogen sulphide there is available gas filter B, which removes hydrogen sulphide from breathing air.

How wind results should be taken into account in future power plant designing? While planning new sites, the buildings relative location should be taken into account to be able to control ground level wind conditions. In addition, from the environmental perspective this is relevant too. If e.g. dusts and microbes can easily be spread at the plant site, the environmental load can also grow. From this point of view, the location of the whole power plant site compared to the prevailing wind conditions and environment should be taken into account. In addition the national databases like Finnish Wind Atlas can be helpful. Many of the power plants are built very near population centres, even inside the centres. If dust spreading at the power plant site or onto the near environment is a problem it could be controlled by using e.g. suitable wind nets or lightweight screens.

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Appendix 1 Weather conditions during the measurements at the power plant sites

Two of three weather stations were located to the power plant sites so that the collected information would represent the background conditions at the site area as well as possible. On Tables A1.1 and A1.2 are the results of those measurements. Respectively, wind roses are presented in Figures A1.1, A1.2 and A1.3.

Table A1.1. Measured background wind conditions at the power plant sites during the measurement rounds. Percentage of each wind direction of different compass points (N, NNE, NE etc.) are presented. Targets are power plant sites A, B and C. Measurement rounds are 1 and 2 and location of weather stations are N, S, E and W (See Figures A1.1, A1.2 and A1.3).

Target/Compass	**N**	NNE	NE	ENE	**E**	ESE	SE	SSE	**S**	SSW	SW	WSW	**W**	WNW	NW	NNW
A1S	0.0	11.2	1.6	6.4	2.7	9.6	22.3	20.2	13.8	8.5	3.7	0.0	0.0	0.0	0.0	0.0
A1N	1.2	0.0	2.4	0.6	3.0	10.2	35.9	27.5	14.4	4.2	0.6	0.0	0.0	0.0	0.0	0.0
A2S	0.0	0.0	6.8	20.5	27.3	0.0	20.5	15.9	0.0	9.1	0.0	0.0	0.0	0.0	0.0	0.0
A2N	0.0	0.0	0.0	2.2	15.2	17.2	30.4	10.9	19.6	0.0	4.3	0.0	0.0	0.0	0.0	0.0
B1E	0.0	0.7	0.7	1.1	4.2	5.7	2.1	2.1	18.4	5.3	42.0	8.5	7.1	0.7	1.4	0.0
B1W	0.0	0.0	0.0	0.0	0.4	0.0	0.8	0.4	2.0	4.5	2.5	15.6	34.0	21.3	15.2	3.3
B2E	5.1	8.1	21.1	24.2	9.1	12.1	0.0	0.0	0.0	0.0	0.0	0.0	1.0	13.1	3.0	3.0
B2W	1.2	15.5	0.0	20.4	19.0	36.9	17.9	0.0	0.0	0.0	1.2	0.0	1.2	0.0	1.2	3.6
C1S	0.0	0.0	0.0	14.8	0.0	0.0	0.0	2.5	58.0	14.8	7.4	1.2	0.0	0.0	1.2	0.0
C1N	0.0	1.2	0.0	0.0	0.0	4.8	45.8	47.6	0.0	0.0	0.6	0.0	0.0	0.0	0.0	0.0
C2S	1.3	18.2	20.8	28.6	29.9	2.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C2N	10.3	0.0	0.0	0.0	0.0	0.0	5.1	15.4	3.8	5.1	5.1	6.4	5.1	9.0	12.8	21.8

Table A1.2. Measured wind speeds, temperatures and relative humidities at the places where the weather stations for background conditions were located during the measurements at the power plant sites. Location of weather stations were N, S, (Power plants A and C) and E, W (Power plant B). Measurements were carried out the power plants named A, B and C. Numbers 1 and 2 refer to measurement rounds.

Target	n	V_{av} m/s	V_{min} m/s	V_{max} m/s	T_{av} ^oC	T_{min} ^oC	T_{max} ^oC	HR_{av} %	HR_{min} %	HR_{max} %
A1S	188	1.6	0.4	2.7	1.6	0.0	2.7	89.0	67.0	94.0
A1N	167	1.4	0.9	3.1	2.0	-5.9	8.9	90.0	66.0	98.0
A2S	46	-	-	-	2.5	0.9	3.9	94.0	76.0	98.0
A2N	46	-	-	-	1.8	1.2	5.8	97.0	76.0	93.0
B1E	283	1.4	0.4	3.1	5.4	-2.4	12.8	86.0	44.0	99.0
B1W	244	0.9	0.4	2.7	5.6	-2.1	12.8	85.0	62.0	98.0
B2E	99	0.8	0.0	2.2	2.8	-3.4	8.0	55.0	30.0	84.0
B2W	84	1.1	0.0	2.7	2.4	-3.9	8.7	54.0	28.0	84.0
C1S	81	1.7	0.4	3.1	4.3	-0.3	6.2	91.0	70.0	94.0
C1N	168	2.7	0.4	4.5	4.3	-0.6	6.2	92.0	70.0	96.0
C2S	77	0.6	0.4	1.3	-2.2	-2.9	-0.9	85.0	79.0	92.0
C2N	78	07	0.4	1.3	-2.5	-3.2	-1.3	84.0	78.0	92.0

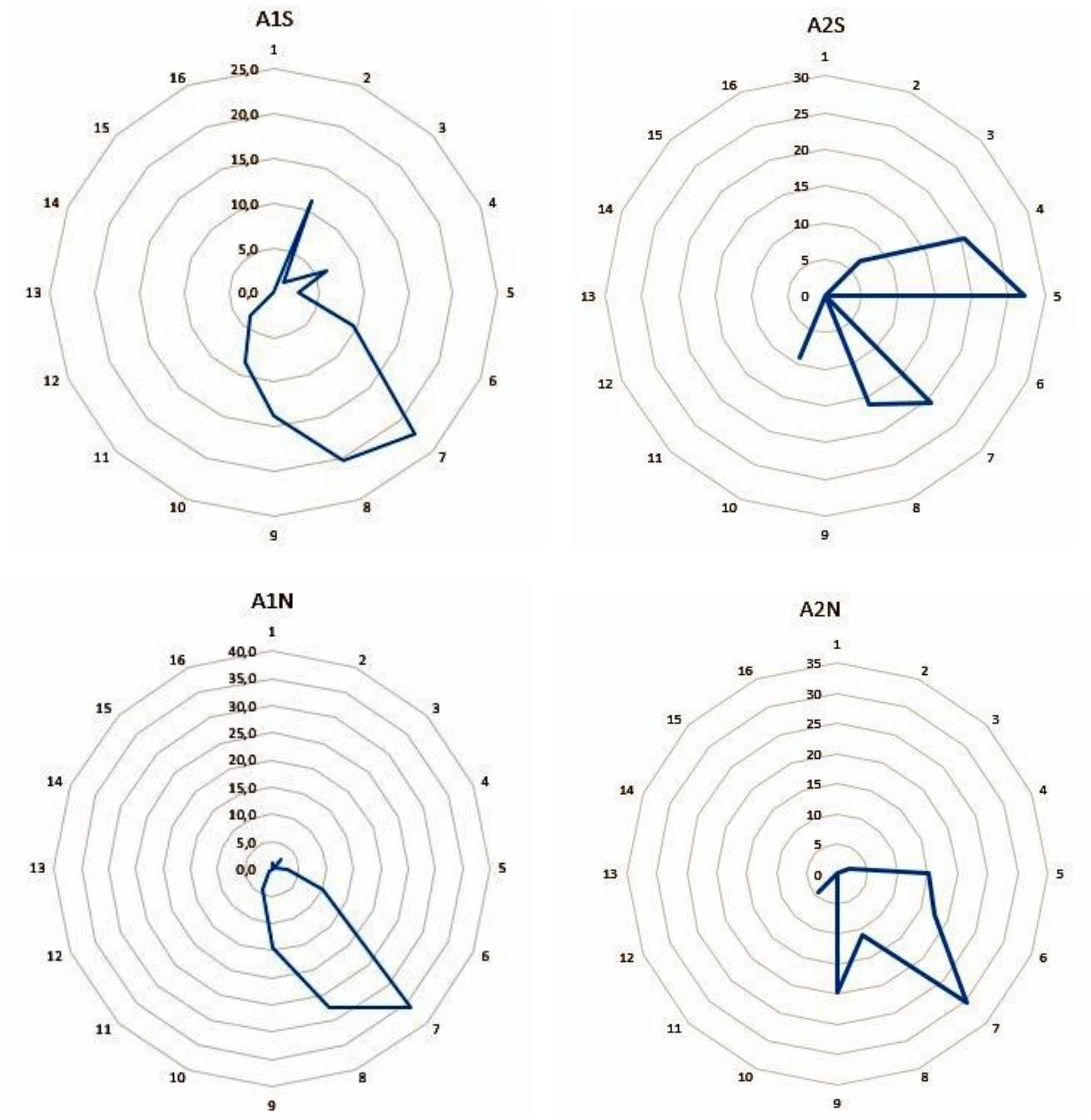


Figure A1.1. Power plant site A. Measurement rounds 1 and 2, weather station locations South and North.

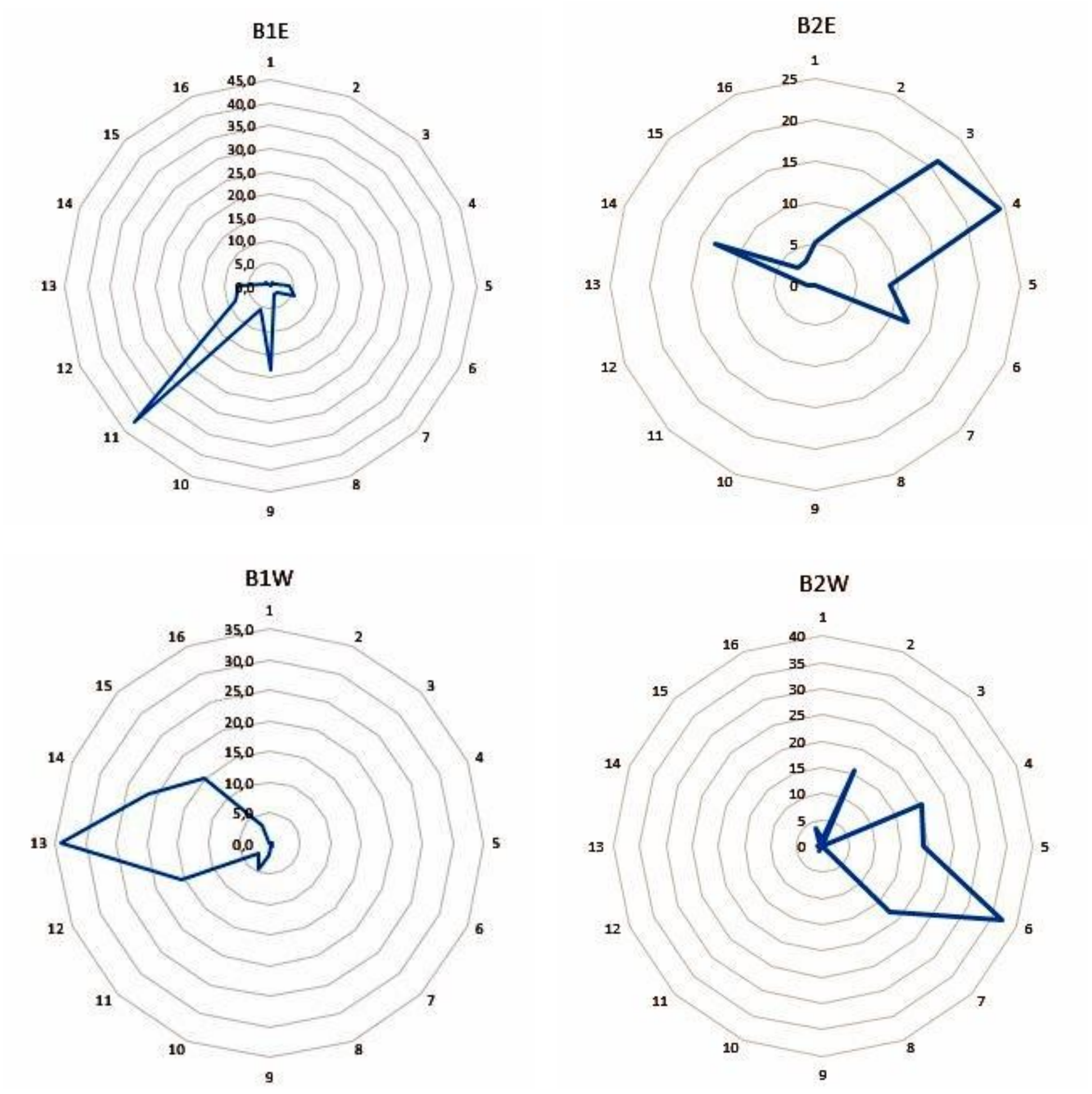


Figure A1.2. Power plant site B. Measurement rounds 1 and 2, weather station locations East and West.

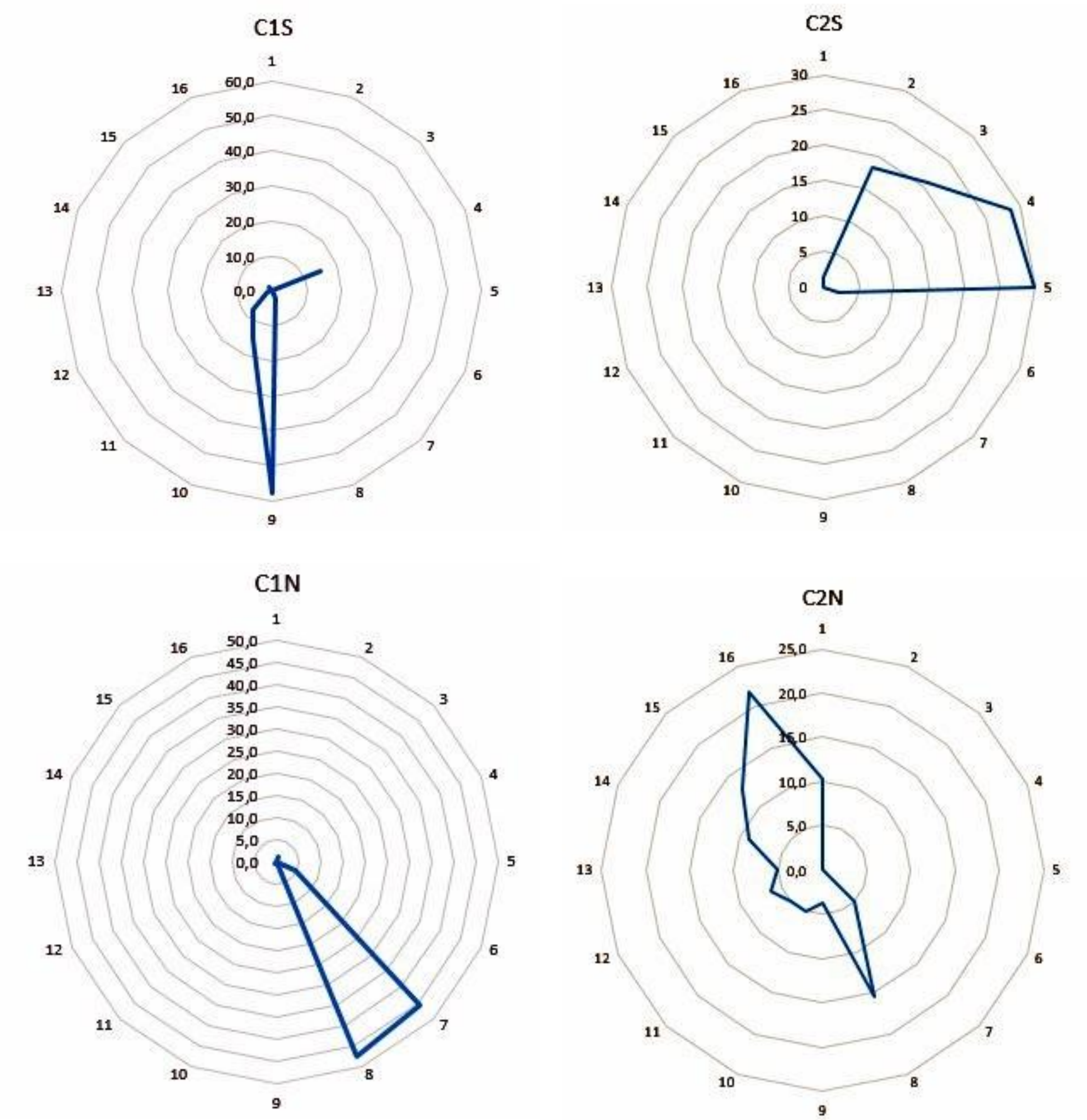


Figure A1.3. Power plant site C. Measurement rounds 1 and 2, weather station locations South and North.

Appendix 2, Volatile organic compounds (VOCs) at the power plant sites

VOCs and average concentrations at the power plants. Only compounds with at least one concentration >50µg/m^3 are shown.

Compound	Fuel reception (N = 4)	Average concentration µg/m^3	Processing of fuels (N = 7)	Average concentration µg/m^3	Control room (N = 3)	Average concentration µg/m^3
Pentane			n = 1	120		
C_4-alkylbenzene*	n = 4	53	n = 4	406		
Styrene			n = 4	22		
Toluene	n = 2	13	n = 6	39	n = 2	1
Germacrene*			n = 2	435		
Junipene*			n = 3	278		
Camphene*	n = 4	336	n = 6	172		
3-Carene	n = 3	1 359	n = 7	1 119	n = 2	4
Limonene	n = 3	748	n = 7	473	n = 2	5
a-Longipinene*			n = 2	230		
Monoterpene $C_{10}H_{16}$*	n = 2	1 002	n = 5	1 102	n = 1	1
Myrcene*	n = 1	1 500	n = 6	718		
a-Pinene	n = 3	1 950	n = 7	1 127	n = 2	17
b-Pinene	n = 3	1 217	n = 7	755	n = 2	9
Pinocarvone*	n = 1	150	n = 2	53		
Sabinene*	n = 1	290	n = 2	70		
Terpinolene*	n = 1	180	n = 2	515		
1-Butanol	n = 1	4	n = 5	100	n = 2	2
Ethanol	n = 1	190	n = 3	2 610	n = 1	89
1-Hexanol	n = 1	13	n = 2	66		
3-Methyl-1-butanol			n = 2	335		
2-Methyl-1-propanol			n = 2	33		
1-Pentanol			n = 1	110		
2-Pentanol			n = 2	69		
1-Propanol	n = 1	28	n = 3	197		
2-Propanol			n = 4	62		
2-Furfural			n = 2	46	n = 1	1
Acetone	n = 4	112	n = 6	83	n = 3	2
2-Hexanone			n = 2	51		
2-Heptanone			n = 2	125		
2-Butanone	n = 2	13	n = 4	116		
2-Pentanone	n = 1	18	n = 2	126		
Butyric acid			n = 2	567		
Acetic acid			n = 2	11 605		
Hexanoic acid			n = 1	300		
Valeric acid			n = 1	530		
Propionic acid			n = 2	448		
Ethyl acetate	n = 1	27	n = 4	657	n = 1	1
Ethyl butanoate*			n = 1	200		
Methyl acetate*	n = 1	14	n = 2	104		

N = total number of samples
n = number of samples containing compound
* Compound identified with Wiley or NIST mass spectrum database, concentration quantified as toluene equivalent.

Appendix 3, Polycyclic aromatic hydrocarbons (PAHs) in air samples

PAHs (µg/m³) in air samples from downstairs and upstairs of boiler room at Power Plant C.

Compound	**Downstairs**		**Upstairs**		**OEL$_{8hours}$**
	Gas phase µg/m³	**Particle phase µg/m³**	**Gas phase µg/m³**	**Particle phase µg/m³**	**µg/m³**
Naphthalene	1.6	<0.17	<0.0015	<0.0032	5 000
Acenaphthylene	<0.05	<0.06	<0.0015	<0.0032	-
Acenaphthene	0.11	<0.07	<0.0015	<0.0032	-
Fluorene	<0.04	<0.06	<0.0015	<0.0032	-
Phenanthrene	0.06	<0.06	0.0097	<0.0032	-
Anthracene	<0.11	<0.06	<0.0015	<0.0032	-
Fluoranthene	<0.03	<0.06	0.0043	<0.0032	-
Pyrene	<0.03	<0.06	0.0016	<0.0032	-
Benzo[a]anthracene	<0.03	<0.06	<0.0015	<0.0032	-
Chrysene	<0.03	<0.06	0.0039	<0.0032	-
Benzo[b]fluoranthene	<0.03	<0.06	<0.0015	<0.0032	-
Benzo[k]fluoranthene	<0.03	<0.06	<0.0015	<0.0032	-
Bentzo[a]pyrene	<0.03	<0.06	<0.0015	<0.0032	10
Indeno[1,2,3-cd]pyrene	<0.03	<0.06	<0.0015	<0.0032	-
Dibenzo[a,h]anthracene	<0.03	<0.06	<0.0015	<0.0032	-
Benzo[ghi]perylene	<0.03	<0.06	<0.0015	<0.0032	-

Appendix 4, Chemical composition of first round ash samples

		DL	FA A1	FA B1	BA B1	FA C1	BA C1
Dry matter	(%)	0,1	99,8	100	100	100	99,9
TOC *	(µg/mg)	1	8	2	<DL	2	<DL
TIC **	(µg/mg)	1	8	2	<DL	4	<DL
Sb	(µg/mg)	0,001	0,002	0,001	0,002	0,190	0,071
As	(µg/mg)	0,0008	0,0130	0,0096	0,0015	0,0270	0,0150
Be	(µg/mg)	0,0002	0,0011	0,0022	0,0016	0,0010	0,0013
Bi	(µg/mg)	0,0002	0,0010	0,0026	0,0011	0,0030	0,0015
Pb	(µg/mg)	0,002	0,067	0,023	0,010	0,520	0,063
B	(µg/mg)	0,001	0,160	0,200	0,013	0,510	0,310
Cd	(µg/mg)	0,0002	0,0048	0,0016	<DL	0,0120	<DL
Cr	(µg/mg)	0,001	0,050	0,085	0,058	0,270	0,170
Co	(µg/mg)	0,001	0,009	0,007	0,005	0,017	0,021
Cu	(µg/mg)	0,001	0,110	0,048	0,014	1,930	1,560
Li	(µg/mg)	0,005	0,014	0,044	0,015	0,015	0,011
Mn	(µg/mg)	0,001	7,540	4,440	0,650	3,400	1,330
Mo	(µg/mg)	0,002	0,002	0,004	<DL	0,012	0,005
Ni	(µg/mg)	0,0001	0,0300	0,0440	0,0086	0,0810	0,0810
Rb	(µg/mg)	0,001	0,210	0,150	0,066	0,083	0,058
Se	(µg/mg)	0,001	<DL	<DL	<DL	0,001	<DL
Ag	(µg/mg)	0,001	<DL	0,007	0,003	0,005	0,002
Sr	(µg/mg)	0,002	0,650	0,490	0,270	0,420	0,310
Tl	(µg/mg)	0,0002	0,0017	0,0013	0,0005	0,0009	0,0003
Th	(µg/mg)	0,0002	0,0042	0,0100	0,0038	0,0006	0,0028
U	(µg/mg)	0,0002	0,0018	0,0040	0,0018	0,0017	0,0011
V	(µg/mg)	0,001	0,034	0,041	0,045	0,044	0,027
Zn	(µg/mg)	0,001	1,410	0,670	0,210	2,400	1,220
Al	(µg/mg)	1	40	103	62	69	59
Ba	(µg/mg)	1	2	1	1	2	2
Ca	(µg/mg)	1	127	125	20	179	49
Fe	(µg/mg)	1	19	19	20	23	14
K	(µg/mg)	1	66	30	32	23	36
Mg	(µg/mg)	1	15	16	6	15	5
Na	(µg/mg)	1	17	10	22	19	23
P	(µg/mg)	1	12	7	1	6	2
Si	(µg/mg)	1	234	222	344	191	327
Ti	(µg/mg)	1	2	2	2	8	4
Tot	(µg/mg)	1	559	546	512	551	525

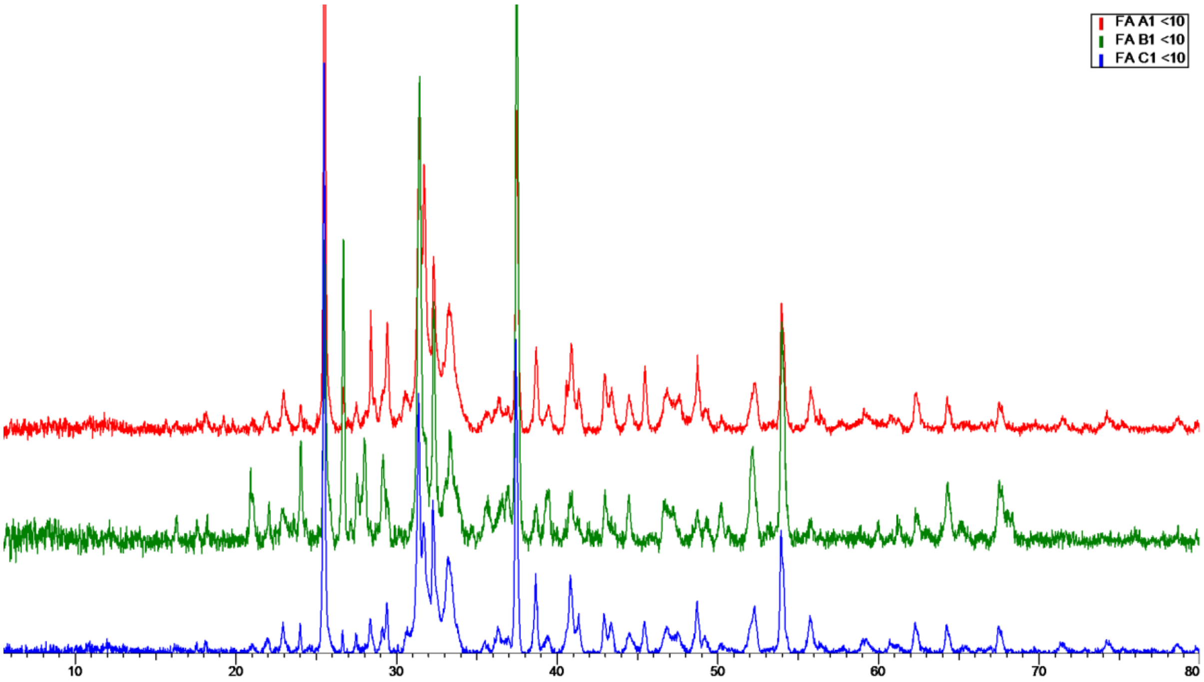
DL=detection limit * noncarbonate carbon ** carbonate carbon

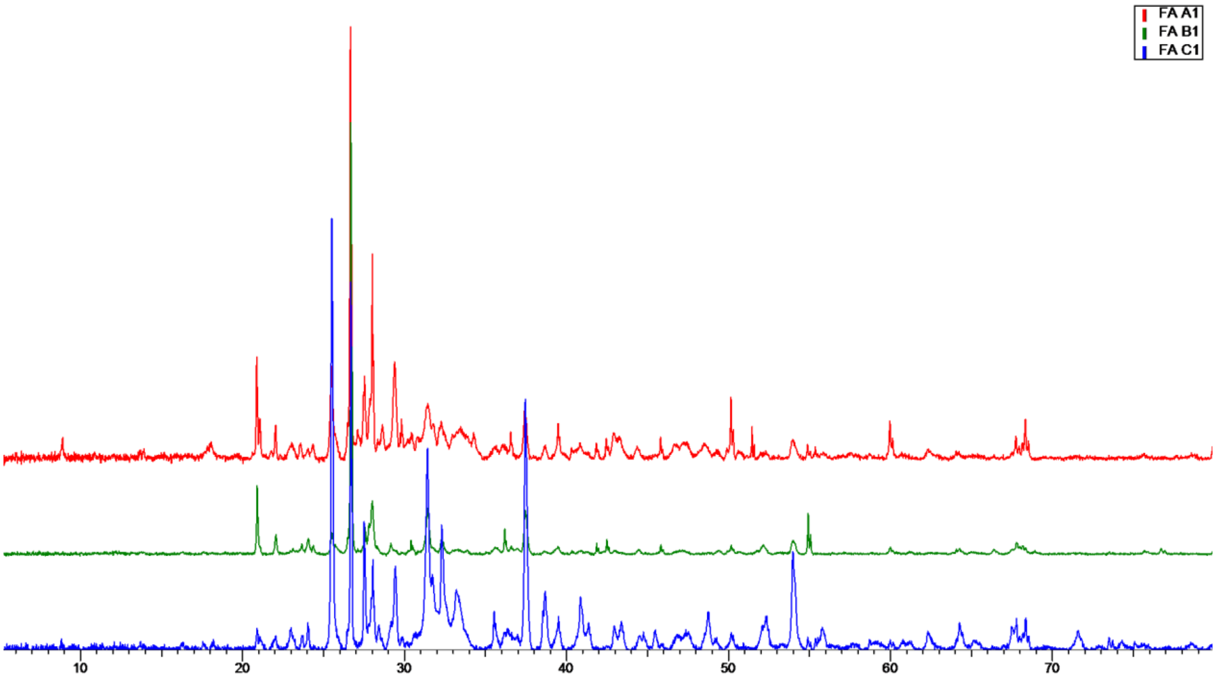
Appendix 5, Chemical composition of second round ash samples

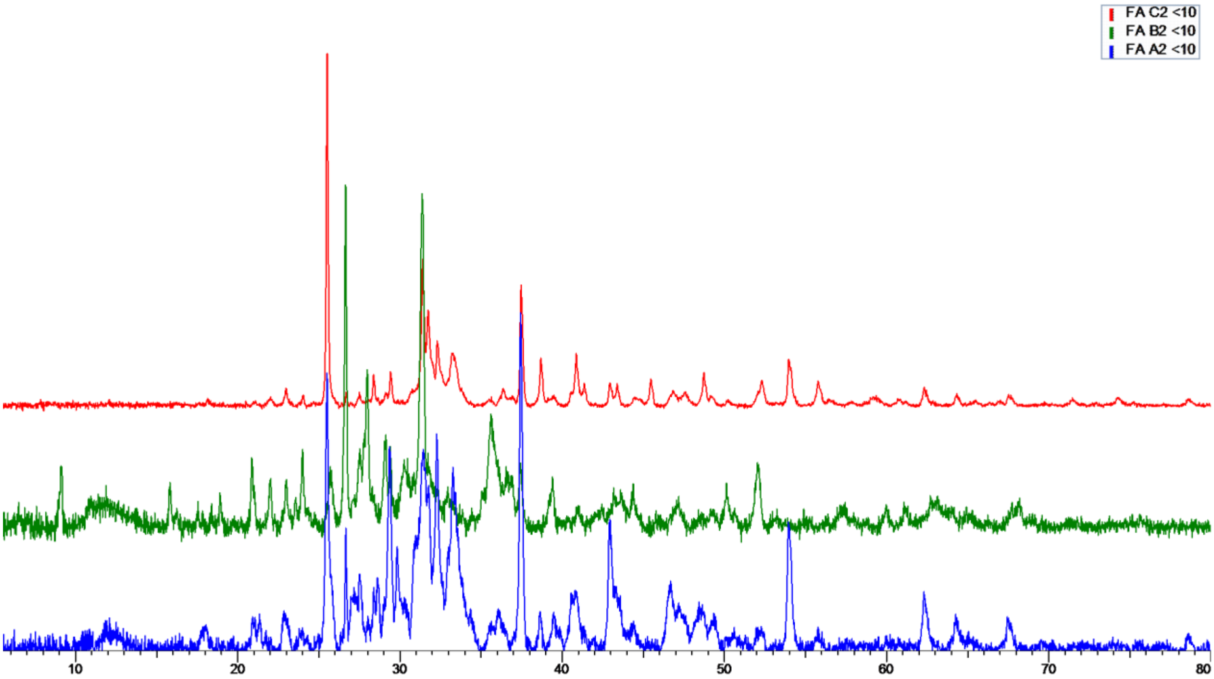
		DL	FA A2 <10	FA B2 <10	BA B2 <10	FA C2 <10	BA C2 <10
Ag	µg/mg	0,002	0,013	<DL	<DL	0,050	0,021
Al	µg/mg	0,002	12,745	62,136	58,416	24,074	42,593
As	µg/mg	0,0005	0,0357	0,0648	0,0127	0,0723	0,0388
B	µg/mg	0,0005	0,2874	0,0639	0,0646	0,7865	0,4092
Ba	µg/mg	0,0005	2,4151	1,4567	1,6974	4,3318	2,9939
Be	µg/mg	0,0005	0,0008	0,0033	0,0024	0,0006	0,0010
Bi	µg/mg	0,0005	0,0007	0,0210	0,0013	0,0344	0,0019
Ca	µg/mg	0,02	196,08	135,92	99,01	240,74	185,19
Cd	µg/mg	0,0005	0,0116	0,0038	<DL	0,0452	0,0028
Co	µg/mg	0,0005	0,0239	0,0621	0,0206	0,0314	0,0444
Cr	µg/mg	0,0005	1,0423	5,0070	1,2853	0,7486	2,0511
Cu	µg/mg	0,0005	0,2766	0,2189	0,0798	4,7222	17,5926
Fe	µg/mg	0,007	17,647	79,612	39,604	17,593	28,704
K	µg/mg	0,1	60,8	19,4	29,7	23,1	12,0
Li	µg/mg	0,002	0,017	0,034	0,029	0,023	0,024
Mg	µg/mg	0,02	22,55	13,59	10,89	18,52	12,04
Mn	µg/mg	0,002	12,745	5,162	4,313	6,124	3,228
Mo	µg/mg	0,0005	0,0108	0,0424	0,0134	0,0297	0,0356
Na	µg/mg	0,1	7,8	8,0	10,9	21,3	11,1
Ni	µg/mg	0,0005	0,7227	3,6068	0,7926	0,2114	1,1593
Pb	µg/mg	0,0005	0,2363	0,0684	0,0169	1,8695	0,7635
Rb	µg/mg	0,0005	0,2562	0,1177	0,1264	0,1338	0,0399
Sb	µg/mg	0,0005	0,0064	0,0022	0,0009	0,7648	0,2614
Se	µg/mg	0,0005	0,0014	0,0041	<DL	0,0049	<DL
Sr	µg/mg	0,0005	1,2745	0,6759	0,5950	0,8264	0,5274
Th	µg/mg	0,0005	0,0019	0,0196	0,0126	0,0032	0,0045
Ti	µg/mg	0,002	1,720	2,306	2,106	11,111	8,174
Tl	µg/mg	0,0005	0,0026	0,0015	<DL	0,0032	<DL
V	µg/mg	0,0005	0,0384	0,1089	0,0546	0,0412	0,0491
U	µg/mg	0,0005	0,0019	0,0290	0,0088	0,0018	0,0021
Zn	µg/mg	0,002	3,325	0,795	0,696	7,528	8,063
Si*	µg/mg	0,1	47,1	135,9	188,1	65,7	120,4
Br^-	µg/mg	0,1	<DL	<DL	<DL	1,5	<DL
Cl-	µg/mg	0,1	6,5	1,6	2,0	19,6	7,9
SO_4^{2-}	µg/mg	0,1	106,8	9,4	1,8	160,7	29,8
F^-	µg/mg	0,2	0,4	0,3	0,3	0,7	<DL
PO_4^{3-}	µg/mg	0,1	<DL	<DL	2,3	<DL	<DL
NO_3^-	µg/mg	0,1	1,7	1,5	1,6	1,3	1,4
Tot	µg/mg	0,1	504,5	487,2	456,7	634,5	496,7

DL=detection limit   * incompleate digestion

Appendix 6 XRD spectra of fly and bottom ash samples (normalised to maximum intensity)



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FA A2 <10
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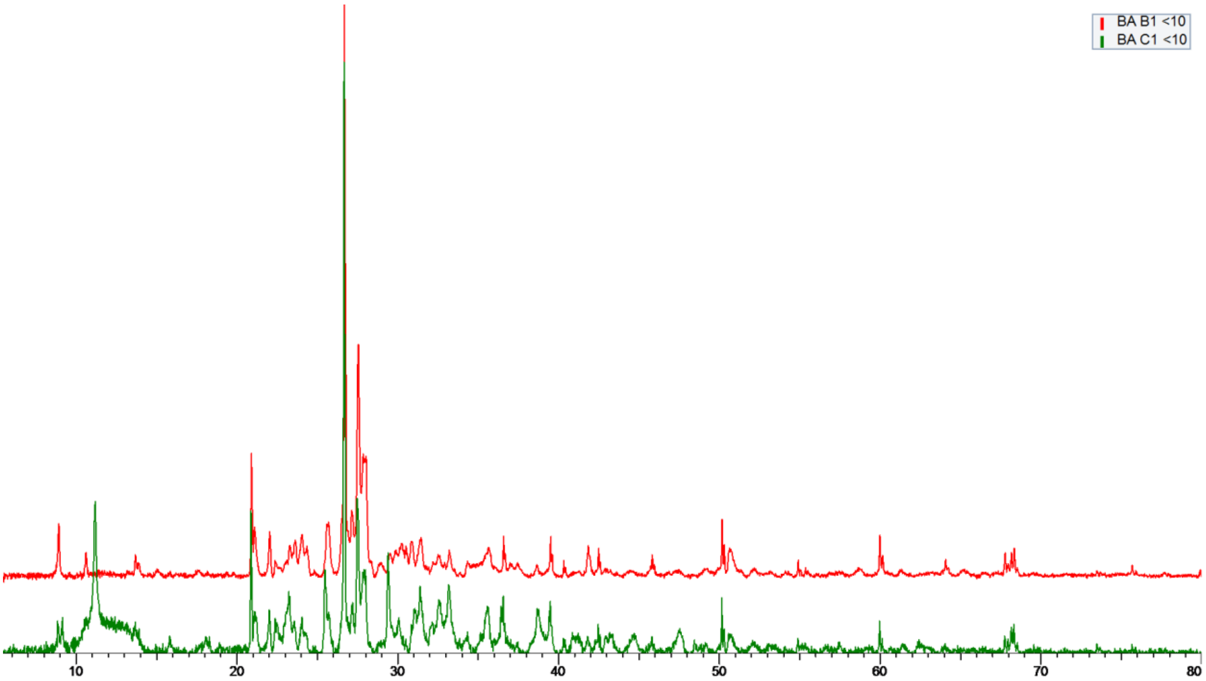
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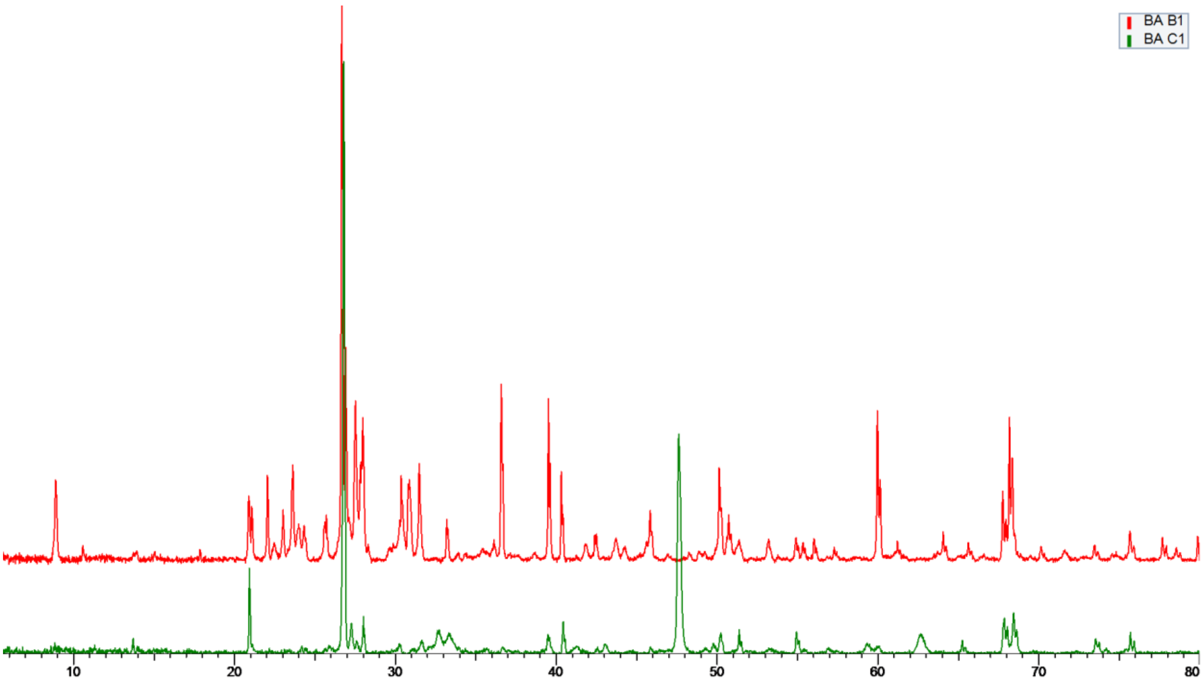
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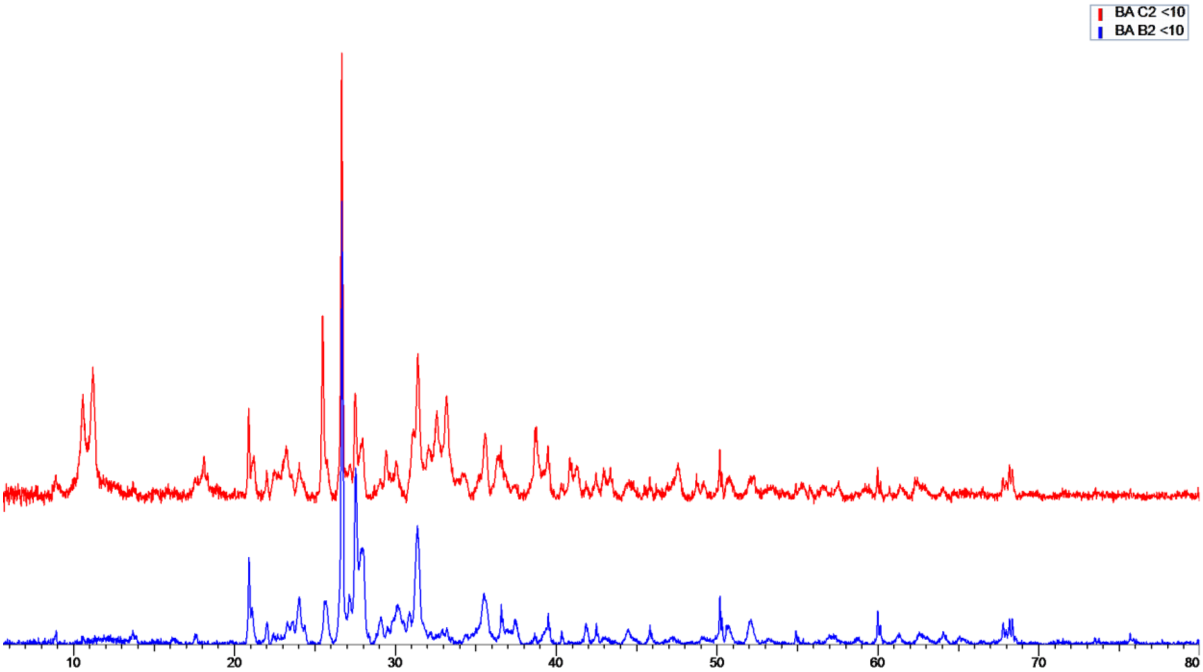
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