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MIKA JUMPPONEN

OCCUPATIONAL EXPOSURE TO COMPONENTS OF BIOMASS-FIRED POWER PLANT ASH

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ABSTRACT

Renewable energy sources are the backbone of the electricity and heat generation system in power plants in Finland, and about 5000 workers are needed annually to keep these power plants running during wintertime.

To be able to evaluate the exposure of ash removal and maintenance workers to bottom and fly ash in biomass-fired power plants, we characterized the elements of fuel and ashes and clarified the sources of elemental concentrations. Workers' inhalation exposure to the most harmful elements of ash, as well as other particulate matter such as inhalable dust, respirable silica and polycyclic aromatic hydrocarbons (PAHs), were assessed. Their exposure to vaporous agents of PAHs, volatile organic compounds (VOCs) and inorganic gases were also measured. Workers' dermal elemental exposures were evaluated using new developed methods, and their total elemental exposure was measured using biomonitoring techniques. We also evaluated multiple exposure and exposure-associated health risks arising from elements of ash, vapors and gaseous agents, and assessed the usefulness of the results obtained from different methods of exposure assessments through different exposure routes. Finally, we evaluated the effects of the personal protective equipment (PPE) used by workers.

The results of this study showed that the fuels, and bottom- and fly ashes of biomass-fired power plants contained fifteen different elements {(iron (Fe), manganese (Mn), aluminum (Al), zinc (Zn), barium (Ba), copper (Cu), chromium (Cr), nickel (Ni), lead (Pb), cobalt (Co), arsenic (As), selenium (Se), thorium (Th), cadmium (Cd), and beryllium (Be)} that are potentially harmful to workers. Pellet bottom ash contained almost equally high amounts of these elements as fly ash. In wood and peat fly ashes, the amounts of Al, Pb, Co, and Se, and As and Cd were higher than in bottom ashes. Solid recovered fuel (SRF) fly ash contained higher amounts of Mn, Al, Zn, Cu, Cr, Pb, Co, As, Se, Cd, and Be than bottom ash. The results regarding fuels indicated that fuel processing, fuel additives, and soil additives may have effects on the elemental quality of the fuel. The combined element ash data,

and measured inhalable dust concentrations showed that environmental elemental ash data can be used in worker exposure assessments in biomass-fired power plants.

The results of this study showed that the median concentration of inhalable dusts was high in ash removal tasks (33 mgm^{-3}) and in maintenance tasks (120 mgm^{-3}). Workers' exposure to inhalable dust exceeded the occupational exposure limit value (OEL) for inorganic dust in 83% of the air samples in ash removal tasks and in 100% of the air samples in maintenance tasks. The OELs for Al, Mn, Pb, Cd, and Be were exceeded in 38%, 50%, 13%, 6% and 38% of the ash removal task samples, respectively, and the OELs for Al, Mn, and Be were exceeded in 40%, 80%, and 40% of the maintenance task samples, respectively. The average concentration of sulfur dioxide (SO_2) (0.42 ppm) was moderate, and the average concentrations of carbon monoxide (CO) (0.45 ppm), nitric oxide (NO) (0.06 ppm), nitrogen dioxide (NO_2) (0.05 ppm), ammonia (NH_3) (0.11 ppm), and hydrogen sulfide (H_2S) (less than 0.01 ppm) were low. However, the OELs for NO and SO_2 were exceeded slightly in 11% and 43% of samples, respectively. The combined concentration of measured PAHs was less than 7% of benzo[a]pyrene's OEL, and concentrations of VOCs were less than 3000 µgm^{-3}, turpentine being the most common VOC inside biomass-fired power plant boilers.

According to the Mixie program, the results of the exposure-associated multiple metal exposures were related to increased modeled exposure-associated risks of cancer, central nervous system disorders, and upper- and lower respiratory track irritation. Multiple gas exposures were also related to an increased exposure-associated risk of upper respiratory track irritation.

Dermal sample results clearly showed that workers' coveralls did not protect their bodies against Pb. Furthermore, As, Cd, Ni and Pb contaminated workers' hands. Some of the workers' urinary excretions of Pb, Mn, and Al; Al, Pb, Mn, and Se; As, Mn, and Pb; and Al exceeded the occupational non-exposed population reference values in the wood-, pellet-, and peat-fired power plants, respectively. Occupational health services were

guided in the assessment of the workers' elemental exposures using urine samples.

Exposure to ash elements was the lowest among the workers who used long leather gloves, coveralls and hoods, respirators with cartridges {(which protect against A; organic gases and vapors, B; inorganic gases and vapors, E; sulfur dioxide and acidic gases and vapors, K; ammonia and organic ammonia derivatives, and P; particles (A2B2E2K2-P)}, and full-face masks (TM3). These PPE and carbon monoxide gas detectors were thus recommended for workers during work tasks in biomass-fired power plants.

Universal Decimal Classification: 331.47, 613.63, 614.89, 621.311.22

National Library of Medicine Classification: WA 450, WA 465

CAB Thesaurus: occupational health; occupational hazards; exposure; inhalation; skin; power stations; combustion; boilers; biomass; workers; ash; particles; dust; silica; polycyclic hydrocarbons; aromatic hydrocarbons; volatile compounds; gases; elements; metals; heavy metals; safety devices; protective clothing

Medical Subject Headings: Occupational Exposure; Inhalation Exposure; Workplace; Power Plants; Particulate Matter; Dust; Polycyclic Aromatic Hydrocarbons; Volatile Organic Compounds; Gases; Elements; Metals; Environmental Monitoring; Personal Protective Equipment

TIIVISTELMÄ

Uusiutuvat energianlähteet ovat entistä tärkeämmässä asemassa sähkön- ja lämmön tuotannossa Suomen voimalaitoksissa, joiden huoltotöissä työskentelee noin 5000 työntekijää vuosittain, jotta voimalaitokset toimisivat moitteettomasti talviaikaan.

Jotta kattilan tuhkan puhdistajien ja kattilan korjaajien altistumista biomassaa polttavien voimalaitosten pohja- ja lentotuhkalle voitiin arvioida, voimalaitosten polttoaineen ja tuhkien alkuaineet karakterisoitiin ja alkuaineiden lähteet selvitettiin. Työntekijöiden hengitysteitse tapahtuvaa altistumista partikkelimaisille altisteille (haitallisimmat tuhkien alkuaineet, hengittyvä pöly, kvartsi ja PAH-yhdisteet) ja höyrymäisille altisteille (PAH- ja VOC-yhdisteet ja epäorgaaniset kaasut) arvioitiin tässä tutkimuksessa. Työntekijöiden ihon altistumista alkuaineille arvioitiin käyttäen tässä tutkimuksessa kehitettyjä uusia menetelmiä ja työntekijöiden kokonaisaltistumista alkuaineille arvioitiin biomonitorointitekniikoiden avulla. Monialtistumista ja altistumiseen liittyviä terveysriskejä arvioitiin tuhkan alkuaineiden, höyrymäisten altisteiden ja kaasujen osalta. Altistumisen arviointiin käytettyjen menetelmien tulosten hyödyllisyyttä, altistumisreittejä sekä työntekijöiden käyttämien henkilökohtaisten suojainten suojaavuutta arvioitiin tässä tutkimuksessa.

Tämän tutkimuksen tulokset osoittivat, että biopolttoaineet, pohja- ja lentotuhkat sisälsivät viittätoista alkuainetta (Fe, Mn, Al, Zn, Ba, Cu, Cr, Ni, Pb, Co, As, Se, Th, Cd, and Be), jotka voivat olla vaarallisia työntekijöille. Pellettilaitosten pohjatuhka sisälsi lähes yhtä suuret pitoisuudet alkuaineita kuin lentotuhka. Puuta polttavien laitosten lentotuhka sisälsi enemmän Al, Pb, Co ja Se ja turvetta polttavien laitosten lentotuhka enemmän As ja Cd alkuaineita kuin pohjatuhkat. Kierrätyspolttoainetta polttavan laitoksen lentotuhkassa oli suuremmat pitoisuudet alkuaineita Mn, Al, Zn, Cu, Cr, Pb, Co, As, Se, Cd, and Be kuin pohjatuhkassa. Polttoaineiden valmistuksella, polttoaineiden lisäaineilla ja maanparannusaineilla voi olla vaikutusta polttoaineiden

alkuainepitoisuuksiin. Tulokset osoittavat myös, että ympäristön suojeluun tarkoitettuja tuhkanäytteitä voidaan käyttää työntekijöiden altistumisen arvioimiseen.

Tutkimuksen tulokset osoittivat, että pölyn mediaani pitoisuudet ilmassa olivat korkeita kattiloiden tuhkan puhdistamisen (33 mgm^{-3}) ja kattiloiden korjaamisen aikana (120 mgm^{-3}). Työntekijöiden altistumien pölylle ylitti epäorgaanisen pölyn raja-arvon (10 mgm^{-3}) 83 prosentissa näytteissä kattilan tuhkan puhdistamisen aikana ja kaikissa näytteissä kattilalaitteiden korjaamisen aikana. Al, Mn, Pb, Cd ja Be pitoisuudet ylittivät raja-arvot (Al; 2 mgm^{-3}, Mn; 0,2 mgm^{-3}, Pb: 0,1 mgm^{-3}, Cd; 0,02 mgm^{-3} ja Be; 0,0001 mgm^{-3}) 38%, 50%, 13%, 6% ja 38% näytteissä kattilan tuhkan puhdistamisen aikana ja Al, Mn ja Be pitoisuudet olivat yli raja-arvon 40%, 80% ja 40% näytteissä kattilalaitteiden korjaamisen aikana. Rikkidioksidille altistuminen oli kohtalaista (0,42 ppm) ja altistuminen muille kaasuille (CO, 0,45 ppm; NO, 0,06 ppm; NO_2, 0,05 ppm; NH_3, 0,11 ppm; ja H_2S, alle 0,01 ppm) oli vähäistä. Typpioksidin ja rikkidioksidin pitoisuudet ylittivät työvaiheiden aikana (lyhytaikanainen altistuminen) kuitenkin näiden haitallisiksi tunnetut pitoisuudet (HTP) ($NO_{,HTP8h}$; 10 ppm ja $SO_{2,\ HTP15min}$; 4 ppm) 11% ja 43% näytteissä. PAH-yhdisteiden yhteenlasketut pitoisuudet olivat alle 7% bento[a]pyreenin raja-arvosta ja VOC-pitoisuude alle 3000 µgm^{-3}.

Mallinnetut alkuainealtistumiseen liittyvät metallien monialtistumistulokset antoivat viitteitä, että altistumiseen voi liittyä lisääntynyt riski syöpään, keskushermosto-oireisiin ja ylä- ja alahengitysteiden oireisiin ja mallinnetut kaasualtistumiseen liittyvät monialtistumistulokset antoivat viitteitä lisääntyneestä altistumiseen liittyvästä riskistä ylähengitysteiden ärsytykseen.

Ihoaltistumistulokset osoittivat selkeästi, että työntekijöiden käyttämät vaatteet eivät suojaa työntekijöitä tuhkapölyn lyijyltä ja tuhkapölyn As, Cd, Ni ja Pb voi kontaminoida työntekijöiden kädet työvaiheiden aikana käsineiden käytöstä huolimatta. Osa työntekijöiden biomonitorointinäytteistä ylitti altistumattomien viiteraja-arvot Pb, Mn ja Al osalta kierrätyspolttoainetta polttavassa laitoksessa, Al, Pb, Mn ja Se osalta puuta polttavissa laitoksissa, As, Mn ja Pb osalta pellettiä polttavissa laitoksissa ja

Al osalta turvetta polttavissa laitoksissa. Työterveyshuoltoja ohjeistettiin seuraamaan työntekijöiden altistumista kyseisten biomonitorointi näytteiden avulla.

Työntekijöiden altistuminen tuhkan sisältämille alkuaineille oli pienintä, kun työntekijät käyttivät pitkiä nahkakäsineitä, hupullisia työvaatteita ja kaasunaamarilla ja puhaltimella varustettuja hengityksensuojaimia, jossa on A2B2E2K2-P- luokan suodattimet. Lisäksi hiilimonoksidi kaasuhälyttimen käyttöä suositeltiin työntekijöille voimalaitoksilla tehtävien työvaiheiden aikana.

Yleinen suomalainen asiasanasto: altistuminen; altisteet; työympäristö; voimalat; biovoimalat; biopolttoaineet; tuhka; hengitys; iho; hiukkaset; pöly; alkuaineet; metallit; PAH-yhdisteet; haihtuvat orgaaniset yhdisteet; kaasut; monitorointi; suojaimet; suojavaatteet

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My special thanks go to my friends who took me out of my ‘office’ to go fishing and hiking in the wilderness of Finland.

Finally, I thank my late mother Alli, my father Veikko and my sister Arja for their care and the education that they provided for me. I thank also my dear wife and our children Antti and Jaakko for their positive attitude over the many days and nights when I was preparing this dissertation. Without their support, I would not have been able to complete this study.

Kuopio, October 2017 Mika Jumpponen

LIST OF ABBREVIATIONS

AAS	atomic absorption spectroscopy
A2B2E2K2-P	A; organic gases and vapors, B; inorganic gases and vapors, E; sulfur dioxide and acidic gases and vapors, K; ammonia and organic ammonia derivatives, and P; particles
ACGIH	American Conference of Governmental Industrial Hygienists
Al_2O_3	alumina
ANOVA	analysis of variance
AR	analytical recovery
ASA	register on employees exposed to carcinogens
ASTM	American Society for Testing and Materials
BFBC	bubbling fluidized bed combustor
CaO	calcium oxide
$CaCO_3$	calcium carbonate or limestone
$CaSO_4$	calcium sulfate
CEN	European Committee for Standardization
CFBC	circulated fluidized bed combustor
CO	carbon monoxide
COPD	chronic obstructive pulmonary disease
CNS	central nervous system
DOT	disruption of oxygen transport
EPA	Environmental Protection Agency
FBC	fluidized bed combustor
FF-P2/FF-P3	filtering face piece – particle classes 2 and 3
FLAA	flame atomic absorption spectrophotometry
GC	gas chromatography
GFAAS	graphite furnace atomic absorption spectrophotometry
GLM	generalized linear model
H_2S	hydrogen sulfide
HWR	hand-washing recovery
IARC	International Agency for Research on Cancer
IC	ion chromatography

ICP-AES	inductively coupled plasma atomic emission spectrometry
ICP-EOS	inductively coupled plasma optical emission spectrometry
ICP-MS	inductively coupled plasma mass spectrometry
INAA/EDX	instrumental neuron activation analysis/energy dispersive X-ray spectroscopy
IR	infrared spectroscopy
ISO	International Organization for Standardization
KCl	potassium chloride
K_2CO_3	potash
LRTI	lower respiratory tract irritation
MgO	magnesium oxide
MIXIE	mixtures of substances in the workplace
MS	mass spectrometry
NaCl	sodium chloride
NCV	net caloric value
NH_3	ammonia
NIOSH	The National Institute for Occupational Safety and Health
NIST	National Institute of Standards and Technology
NO	nitric oxide
NO_x	nitric oxides
NO_2	nitrogen dioxide
OEL	occupational exposure limit value
PAH	polycyclic aromatic hydrocarbon
PFA	pulverized fly ash
PPE	personal protective equipment
ppm	parts per million
SCG	coal gasification
SEM/EDX	scanning electron microscopy/energy dispersive X-ray spectroscopy
SiO_2	silicon dioxide or quartz
SO_x	sulfur oxides
SO_2	sulfur dioxide
SRF	solid recovered fuel
STEL	short-term exposure limit

TEF	toxic equivalency factor
TEQ	toxic equivalent of mixture
TM2/TM3	half mask or full-face mask, protection levels 2 or 3
TVOC	total volatile organic compound
U-	urine-
URTI	upper respiratory tract irritation
VOC	volatile organic compounds

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on data presented in the following articles, referred to by the Roman numerals I–IV.

I Jumpponen M. and Laitinen L. Usefulness of biomass-fired power plant ash in worker elemental exposure evaluations. Chem. Eng. Process Tech. 2(3): 1031, 2016.

II Jumpponen M., Rönkkömäki H., Pasanen P., Laitinen J. Occupational exposure to gases, polycyclic aromatic hydrocarbons and volatile organic compounds in biomass-fired power plants. Chemosphere 90, Pages 1289-1293, 2013.

III Jumpponen M., Rönkkömäki H., Pasanen P., Laitinen J. Occupational exposure to solid chemical agents in biomass-fired power plants and associated health effects. Chemosphere 104, Pages 25-31, 2014.

IV Jumpponen M., Heikkinen, P., Rönkkömäki, H., Laitinen, J. Workers' dermal and total exposure to metals in biomass-fired power plants. Review article. Biomonitoring 2015, Pages 1-15.

Unpublished data are also presented.

The above publications have been included at the end of this thesis with their copyright holders' permission.

AUTHOR’S CONTRIBUTION

The data of this thesis were collected during a project (109140) that was carried out in collaboration with the colleagues and authors reported in the original publications (I–IV), and in the acknowledgements.

I was responsible for the exposure assessments, including developing and testing the two new methods presented in this thesis; the selection of exposure assessment methods; the preparation of ‘field studies’; and taking the samples from the workers in all the power plants (field) reported in this thesis. Because of the challenging work environment in the power plants, samples were taken as group work, to ensure the safety of all the researchers. I also concluded and reported the results of the first draft of the project (109140). The final project report was written in collaboration with the authors reported in the project report.

I was responsible for writing the first drafts of all four articles, and was also the corresponding author in all these articles. However, all the authors presented in these original articles provided comments to improve the first drafts. Finally, I conducted the synthesis of the main results reported in articles I–IV, and I wrote this thesis, which was reviewed by my reviewers and supervisor.

Contents

1 Introduction

The bioenergy sector in Finland employs about 26 000 workers each year. It has been estimated that 5000 of these work in ash removal and maintenance tasks in biomass-fired power plants [10] per year. Most of these ash removal or maintenance workers (Group 1) work 12-hour days, five to seven days a week, March to October, at different power plants. Group 2 consisted of ash removal or maintenance workers (power plants' own workers), who work 12-hour days, five days a week, one to two weeks a year at one power plant. In many cases, these ash removal and maintenance operations are carried out (in summertime) inside the power plant boiler components after the power plant boilers are shut down. These operations usually start after the cool down of the power plant, when ash removal workers go inside the power plant components to remove ash accumulations. When the ash accumulations have been removed, maintenance workers begin their work. If ash removal work is done poorly, ash accumulations are still present during maintenance work tasks, which means that all these workers may be exposed to ash and its components [189].

Workers have been reported as being exposed to elements, to high dust concentrations, polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), chemicals, and unpleasant odors [1–6] during work tasks in coal-fired and thermoelectric power plants. Work-related high and long-term elemental (Al, As, Pb, Cd, Mn, and Se) exposure is suspected to increase the risk of numerous neurophysiological changes in workers, and may lead to symptoms resembling Parkinson's and Alzheimer's diseases or cancer [96–100]. However, there are no studies on worker exposure to elements, dust, silica, VOCs, PAHs, or gaseous agents during ash removal and maintenance tasks in biomass-fired power plants. Thus, we studied ash removal workers' and maintenance workers' exposure to these chemical agents in biomass-fired power plants boilers. Workers were guided to use personal protection equipment (PPE) during these work tasks. It was also recommended that occupational health care personnel assess workers' exposures during their working careers. The information reported in this study is needed urgently, because energy and heat production using biomass is a highly growing field of business in European counties. The information reported in this study can be used to control the possible exposure-associated health hazards among this growing number of workers [10].

2 Review of the literature

BIOMASS-FIRED POWER PLANTS

2.1.1 Introduction

In most countries, fossil-fueled power plants are the backbone of the power generation system. This is not so in Finland [7]. Altogether 41% of the electricity and heat produced in Finland in 2012 was produced by renewable energy sources. Twenty-one per cent (21%) of electricity and heat was produced by fossil fuels, 33% by nuclear power, 7% by wood, 5% by peat, and 3% by other energy sources [8]. The use of renewable energy sources was 25% of the total energy in 2008, and according to the national energy scenario of 2010, the final consumption of renewable energy sources in 2020 will account for 38% of total energy. In this scenario, forest energy plays a central role in renewable energy in heat and power production [9]. Finland has over 400 medium and large-scale biomass-fired power and heating plants that use renewable energy sources as fuel, and need 26 000 person-years (direct) to keep the renewable supply chain running [10]. The key to successful, sustainable biomass use is people's (customers') confidence in the entire supply chain, from the fuel itself through to the installation of efficient and reliable boiler systems and ongoing maintenance [11].

2.1.2 Grate boilers

Grate firing is the oldest firing principle used in boilers, and has been the most popular firing system in small-sized boilers (under 5 MW). In grate-fired boilers (Fig. 1), the fuel is usually fed automatically onto the grate by gravity. As the fuel bed moves, all fuels are first dried, then pyrolyzed, and finally, the char is burned on the grate and the ash is removed. In the stationary grate design, ashes fall into a pit for collection. In contrast, a travelling grate system drops the ash into a hopper. The combustion temperature of the same kind of fuel particles may vary, depending on their location on the grate. Temperatures above the bed and in the freeboard normally range between 800 °C and 1000 °C [7, 12].

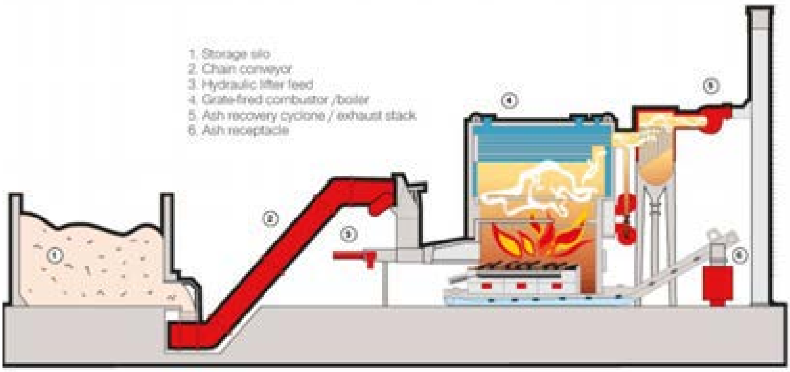

Figure 1. Biomass grate-fired boiler [13, modified].

2.1.3 Bubbling and circulated fluidized bed boilers

Fluidized bed combustion began its expansion at the beginning of the 1980s, and largely replaced grate firing. In Finland, most new solid fuel-fired boilers with a fuel input of over 5 MW are fluidized bed boilers (Fig. 2). Fluidized bed combustion is suitable for inhomogeneous fuels. There is no need to pulverize or dry the fuel; mechanical crushing is sufficient to facilitate feeding a boiler biofuels [14]. Sand, ash, and fuel are used as the bed materials in fluidized-bed combustors (FBC), in which biomass fuel burns in a 0.5–1.5 m high hot bed. The particle size distribution in the fluidizing bed material is typically 0.5–1.5 mm. Smaller particles are carried out with the fluidizing gas flow, and larger particles sink onto the distribution plate. Primary air (fluidizing velocity is about 1 m/s) is needed to keep the bed of sand in the 'air' [in bubbling fluidized bed combustion (BFBC)], whereas secondary air, and in some cases tertiary air, may be introduced higher up in the furnace to achieve a staged and more complete combustion. The bed is normally operated at 750–950 °C, which is a considerably lower temperature than that in grate-fired boilers [7, 12].

Circulating fluidized bed combustion (CFBC) differs from BFBC by two factors. The bed material particle size is 0.1–0.6 mm and the fluidizing velocity is 4–6 m/s. These change the fluidizing conditions so that part of the bed material is carried out from the bed, and transits through the furnace to the second pass of the boiler. These particles exiting the furnace are separated from flue gas flow by a cyclone, and circulated back to the fluidized bed. The separation can be done in the middle of the second pass and, in part, also at the outlet of the boiler pass, where electrostatic precipitators and fabric filters can also be used. In many respects, BFBC resembles grate firing. The main benefit for combustion is the better temperature control 'off grate'. CFBC resembles pulverized fuel combustion or burner combustion [7].

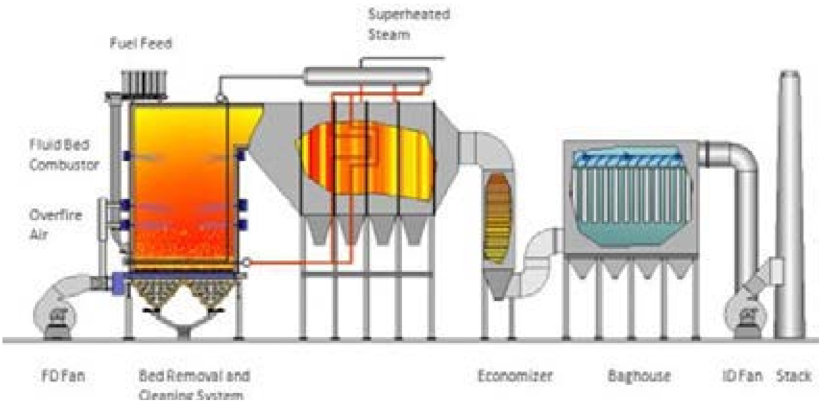

Figure 2. Fluidized bed boiler [15].

2.1.4 Biomass and fuel additives used in biomass combustion

Biomass is defined by the EU as "the biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal waste i.e. solid recovered fuels (SRF); it includes bio liquids and biofuels" [16]. In this work, biomass mainly means the biodegradable fraction of forestry products, i.e. wood pellets, saw dust, wood chips, and peat, and in small amounts, SRF which biomass-fired power plants use as a fuel.

Wood pellets are made by compressing dry sawdust or wood shreds under high pressure until the lining softens and binds the material together. The combination of their low moisture content (typically below 10%) and highly compressed material gives pellets a high volume of energy density, typically three to four times that of wood chips. Pellets also have significantly less storage requirements than wood chips. Pellets for industrial applications are typically 10–12 mm in diameter [17]. The quality of pellets is important: if high quality ash pellets are used, more boiler maintenance is required, as the ash must be removed from the boiler more frequently [18].

Sawdust is a byproduct of sawmills. The quality of sawdust is dependent on the saw type, method of sawing, tree species used, and the storage method of logs, including storage temperature, moisture and season [19, 20]. The particle size of sawdust is not uniform and its distribution is usually concentrated on the smallest size fractions, the average size of softwood sawdust being approximately 1.0–1.2 mm. Sawdust is used in power plants together with other fuels. The moisture content of sawdust varies greatly (air dry -70% of weight) [20].

Wood chips are made from whole wood (logs) or wood residues (stumps, branches) by chopping wood [21]. The quality of wood chips can vary from the best – manufactured exclusively from pure virgin wood – to chips made from roots and twigs. This also affects the content of ash [22]. The length of wood chips is typically 30–40 mm. Because the density of wood chips is high, they can be mixed with sawdust, which even further increases the density of this mixture [20].

Peat consists mainly of dead organic, plant-based matter that has accumulated in waterlogged conditions. The layers near the surface are recently formed, while the deeper layers are older. It is a slowly renewable biomass resource that has many uses, particularly in energy and horticulture. Fuel peat is a local, solid fuel, which is used in the form of milled peat, sod peat, peat briquettes or pellets [23]. It is mainly used in combined heat and power production, but is also used in power plants in combination with solid biofuels to improve combustion by reducing corrosion and the slagging of boiler components [24].

SRF is made from recycled, separately collected combustible wastes, which are blended and shredded to about 50 mm particle size before the magnetic separation of ferrous metals [25]. The European Recycled Fuel Organization has categorized SRF into different classes (1–5) [26], presented in EN15359. In EN15359, SRF classification consists of setting limits for Net Calorific Value (NCV), ash, moisture, Cl, Hg, Cd and Tl, and finding the sum of heavy metals for each class, so that SRF 1 is the best class and SRF 5 contains the highest amount of heavy metals [26]. Figure 3 presents wood pellets, wood chips, peat, and SRF fuels.

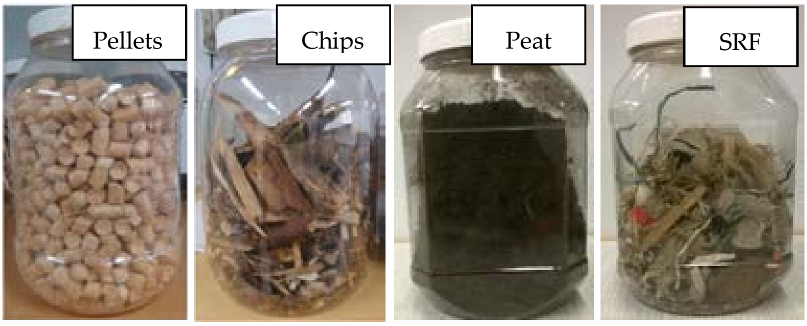

Figure 3. Wood pellets, wood ships, peat, and SRF fuels.

The corrosive environment in biomass or SRF combustion is generally worse than when burning fossil fuels, and therefore the need for maintenance of biomass boilers is greater than that of fossil fuel burning boilers. In biomass or SRF combustion, large amounts of ash may form on super heater tubes and other heat transfer surfaces, so ash removal is needed. The deposit-forming elements, i.e. the elements of fly ash, are in general S, Cl, K, Na, Ca and Al, and elements such as Pb, Zn and Sn may be enriched in the fly ash of SRF. Chlorides of these metals may, together with alkali chlorides (NaCl or KCl), form eutectic chloride, which melts at low temperatures thus accelerating corrosion to a catastrophic rate [25].

Biomass-fired power plants use heavy fuel oil as a support fuel during start-ups and under low loads [25]. Flue SOx and NOx gas sulfur emissions can be controlled by injecting limestone or dolomite into fluidized power plant boilers. At high temperatures in boilers, limestone or dolomite forms reactive CaO, the surface of which reacts with SOx, forming CaSO4. The flue gas then transports these CaSO4 particles to the electrical precipitator [27]. It should also be mentioned that limestone injections can affect the behavior of metals such as arsenic in coal-fired boilers. If limestone is added, the amount of arsenic decreases in flue gases [28], and probably increases in the ashes, which may increase worker exposure to arsenic in ash removal or maintenance tasks. Ammonia or urea can be injected into flue gases to reduce these flue gas emissions. When oxygen is present in flue gases, ammonia reduces NOx compounds to elemental nitrogen [29].

2.2 CHEMICAL FACTORS IN POWER PLANTS AND THEIR HEALTH EFFECTS

2.2.1 Ash

Biomass-fired power plant ash is formed from burned fuels and unburned residues of fuels. The ash content of different fuels varies and affects the ash content. Ash content is also dependent on the biomass harvesting time, harvesting method, and moisture content of the fuels. The inorganic emissions during the chipping of wood at the beginning of the biofuel supply chain are mainly due to the impurities in pure wood. These impurity emissions normally correlate with the soil composition of the forest in which the wood is collected. In peat collection fields, the mineral composition of the bogs also plays an important role in, for example, the emissions of crystalline silica. In the case of SRF, the most important factor in the levels of the ash dust emissions is the fuel itself. After the fuel has finally been transported to the power plants, it may be stored differently in different power plants, which also affects its quality and thus the workers' exposure to dusts. Power plant type, size, combustion temperature, fuel mixtures, and the fuel additives used vary, and this directly affects ash content. Because of these things, ash content may vary greatly, and therefore, power plant ash is a highly complex mixture of components for example metals, silica, and nutrients (P; 0.2–3%, K; 0.5–10%, Ca; 5–40%, and B; less than 0.1%) [181]. The ash removal and maintenance tasks inside the boilers are important work phases at the end of the bioenergy supply chain at the biomass power plant. In maintenance tasks, biofuel ash, ash removal techniques, processed materials, and tooling techniques greatly affect workers' exposure levels and the quality of inorganic dusts [30, 31].

Power plant ash can be divided into fly ash and bottom ash. Fly ash particles are very fine, and are carried in the flue gases of the power plant. Depending on flue gas temperatures, fly ash particles may condensate in boiler parts, if glue gas temperature decreases before the electrical precipitator. Finally, most of the fly ash particles are collected before entering the power plant pipe in the electrical precipitators or the baghouses. Larger particles fall through the power plant grate during combustion and are collected as bottom ash. Bottom ash can also contain larger noncombustible particles such as rocks or metals [21, 32].

Power plant ash has been reported to contain the major (Al, Ca, Fe, K, Mg, Na, P, Si, Ti) and minor (As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, TI, V, Zn) elements that are formed from solid biomass, together with Cl and S compounds [33, 34]. Elemental concentrations of fly ash and bottom ash in Finland have been reported in several studies in which forest residues were used as fuel [35-39]. Higher concentrations of elements such As, Cr, Cd, Cu, Pb, Zn, Co, Ni, Ba, Mn, and S have been detected in fly ash than in those in bottom ash, and the highest concentrations of V have been measured in bottom ash.

Table 1 presents the concentrations (mgkg^{-1}) of elements measured using EPA method 3051A [68], the ICP/MS methods [41, 42]; flame atomic absorption spectrophotometry (FLAA) [40], and atomic absorption spectroscopy (AAS) ASTM D3683-11 [43,167] in wood pellet-fired power plants' fly and bottom ashes. In wood pellet ashes, the highest concentrations of elements As, Ba, Cd, Co, Cr, Cu, Hg, K, Mo, Mn, P, Pb, Se, and Zn was measured in fly ashes, and the highest concentrations of elements Al, Ca, Fe, Mg, Na, and Ni in bottom ashes [40–43].

Table 1. *Elemental concentrations (mgkg^{-1}) in pellet-fired power plant ashes.*

Elements	**Fly ash (mgkg^{-1})**	**Bottom ash (mgkg^{-1})**	**n**	**Ref.**
Arsenic (As)	4–23	1.2	10	[41–43]
Aluminum (Al)	3000–7800	10700	10	[41–43]
Boron (B)	372–430	-	2	[42–43]
Barium (Ba)	1470–1930	1590	10	[42–43]
Calcium (Ca)	179000	100 000–196 000	9	[40–41]
Cadmium (Cd)	41–75	0.6	10	[41–43]
Cobalt (Co)	6.8–10	8.3	10	[41–43]
Chromium (Cr)	120–250	46	10	[41–43]
Copper (Cu)	156–900	23–130	11	[40–43]
Iron (Fe)	5200–7700	10 300	10	[41–43]
Mercury (Hg)	0.05–0.4	0.02	10	[41–43]
Potassium (K)	100 000–240 000	106 000	10	[41–43]
Magnesium (Mg)	21 000–42 000	16 500–44 000	11	[40–43]
Molybdenum (Mo)	<6–12	6.9	10	[41–43]
Manganese (Mn)	14 000–18 500	1370–17 800	10	[40–43]
Sodium (Na)	9390	5000–9800	9	[40–41]
Nickel (Ni)	21	23	8	[41]
Phosphorus (P)	6440	6290	8	[41]
Lead (Pb)	44–230	0.5	10	[42–43]
Selenium (Se)	5.9	0.7	8	[41]
Zink (Zn)	5900	108–350	9	[40–41]

n = number of samples, - = not reported.

Table 2 presents the concentrations (mgkg^{-1}) of elements measured in wood-fired power plant fly and bottom ashes using the EPA ICP/MS or ICP/EOS method 3051A [37, 44-48, 68], the AAS ASTM D3683-11 method [49-59,167], and AAS [60].

Table 2. *Elemental concentrations (mgkg^{-1}) in wood-fired power plant ashes.*

Elements	**Fly ash (mgkg^{-1})**	**Bottom ash (mgkg^{-1})**	**n**	**Ref.**
Arsenic (As)	< 3–150	< 2.5–62	207	[44–59]
Aluminum (Al)	10 000–84 000	22 400–46 000	109	[48–59]
Boron (B)	127–400	78	62	[48–53]
Barium (Ba)	109–4300	757–1600	196	[44–45, 48–50, 52–54]
Beryllium (Be)	1.2	0.9	156	[48]
Calcium (Ca)	113 000–212 000	34 400–842 000	125	[37, 44, 48]
Cadmium (Cd)	< 0.02–34	< 0.1–1.9	234	[44–59]
Cobalt (Co)	6.4–21	2.7–26	216	[45–46, 49–54]
Chromium (Cr)	10–290	15–91	202	[44–59]
Copper (Cu)	19–300	28–150	223	[37, 44–45, 47–48, 54–60]
Iron (Fe)	1988–26 900	4550–14 000	129	[45, 48, 54–59]
Mercury (Hg)	0.007–1.4	< 0.1	203	[44–45, 47–48, 54–59]
Potassium (K)	59 510–323 000	22 100–43 900	133	[37, 48, 60]
Magnesium (Mg)	20 230–194 000	15 390–124 000	125	[37, 48]
Molybdenum (Mo)	10–13	4.7	167	[44, 48]
Manganese (Mn)	2220–15 200	1700–17 000	137	[45–46, 48–61]
Sodium (Na)	9340–33 000	4864–9700	125	[37, 48]
Nickel (Ni)	25–77	30–71	193	[45–48, 61]
Phosphorus (P)	3400–13 700	1200–9000	129	[37, 48]
Lead (Pb)	10–350	6.3–72	235	[44–47, 49–61]
Sulfur (S)	15 560–24 000	550–2300	89	[37]
Antimony (Sb)	2.3–15	1.6	24	[44, 46]
Selenium (Se)	2.1–12	-	4	[44]
Zink (Zn)	61–4800	354–760	219	[37, 44-48, 60-61]
Vanadium (V)	35–110	26.6	190	[44, 46, 48]

n = number of samples, - = not reported.

The highest concentration of wood ash elements As, Al, B, Ba, Cd, Cr, Cu, Fe, Hg, K, Mg, Mo, Na, P, Pb, S, Sb, Zn, and V were measured in fly ashes, and the highest concentrations of elements Ca, and Mn in bottom ashes [37, 44–61].

Peat is normally combusted with wood fuels in biomass power plants. Table 3 presents the concentrations (mgkg^{-1}) of elements in peat-fired power plant fly and bottom ashes, when peat (50–100%) and wood fuels (0–50%) were used in these power plants.

The highest concentration of elements As, Al, Ba, Ca, Cd, Co, Cr, Cu, Hg, K, Mg, Mo, Mn, Na, Ni, P, Pb, S, Zn, and V were measured in the fly ashes of the power plants [40, 63-66]. Concentrations (mgkg^{-1}) of these elements were measured using the EPA FLAA Method 3051A [40, 68], the AAS ASTM D3683-11 method [63, 65,167] and AAS [64, 66].

Table 3. Elemental concentrations (mg kg^{-1}) in peat-fired power plant ashes.

Elements	**Fly ash (mgkg^{-1})**	**Bottom ash (mgkg^{-1})**	**n**	**Ref.**
Arsenic (As)	16–140	< 3	8	[39, 63–66]
Aluminum (Al)	13500	9200	2	[39]
Barium (Ba)	690–2000	330	3	[39, 65]
Calcium (Ca)	140 000	19 200	2	[39]
Cadmium (Cd)	0.5–9.1	< 0.3	8	[39, 63–66]
Cobalt (Co)	8	2.5	2	[39]
Chromium (Cr)	24–200	15	9	[39, 63–66]
Copper (Cu)	22–160	3.7	4	[39, 63, 65–66]
Mercury (Hg)	0.2–0.4	< 0.03	5	[39, 63–64]
Potassium (K)	9700	90	2	[39]
Magnesium (Mg)	17 000	2100	2	[39]
Molybdenum (Mo)	2–40	< 1	5	[39, 63, 65–66]
Manganese (Mn)	600–1500	180	5	[39, 64]
Sodium (Na)	1400	100	2	[39]
Nickel (Ni)	30–700	19	7	[39, 63–64, 66]
Phosphorus (P)	600	400	2	[39]
Lead (Pb)	< 12–970	< 3	9	[39, 63–66]
Sulfur (S)	17 300	200	2	[39]
Antimony (Sb)	< 4	< 4	2	[39]
Zink (Zn)	48–1600	41	5	[39, 63, 65–66]
Vanadium (V)	18–700	95	5	[39, 63, 65–66]

n = number of samples.

Table 4 presents the concentrations (mgkg^{-1}) of SRF in fly and bottom ash elements, measured using the AAS ASTM D3683-11 [65,167] method, and the AAS ICP-AES/GFAAS methods [66, 67, 69]. In these studies, SRF (10–45%) was combusted using peat (26–80%), sawdust (60–80%), and wood-based fuels (25–90%). The SRF ashes results indicated that the highest concentration of As, Cd, Cr, Mo, Mn, Pb, Sb, and Zn were in the fly ashes, and the highest concentration of Cu and V in the bottom ashes [65–67, 69].

Table 4. Elemental concentrations (mg kg^{-1}) in power plant, when SRF was used in mixed combustion.

Elements	**Fly ash (mgkg^{-1})**	**Bottom ash/sand (mgkg^{-1})**	**n**	**Ref.**
Arsenic (As)	< 30–200	40	11	[65–67]
Barium (Ba)	920–1000	-	2	[65]
Cadmium (Cd)	< 10–15	3.9	6	[65–66]
Cobalt (Co)	21–32	28	4	[66]
Chromium (Cr)	63–500	150	11	[65–67]
Copper (Cu)	400–1600	166–2200	15	[65–67, 69]
Molybdenum (Mo)	7–35	21	6	[65–66]
Manganese (Mn)	1700–7300	930–3500	8	[66, 69]
Nickel (Ni)	38–53	56	4	[66]
Lead (Pb)	55–1100	56–180	15	[65–67, 69]
Selenium (Se)	< 10	< 10	4	[66]
Antimony (Sb)	94	12	2	[66]
Zink (Zn)	380–3400	370–2000	15	[65–67, 69]
Vanadium (V	32–100	240	6	[65–66]

n = number of samples, - = not reported.

However, although a great deal of data is currently available on the elements in biomass-fired power plants, the literature has not reported elements in working areas inside the boilers.

The amount of total silica (SiO_2) in coal-fired power plant ashes has been reported as being between 40% and 60% of the total amount of ash [70]. Several studies have reported that biomass ash contains a greater amount of total silica, varying between 10.8% and 77.3% of the total amount of ash [70-71]. Total silica contains amorphous and crystalline fractions of silica, crystalline silica being the main focus of occupational hygiene samples, as it has been classified as carcinogenic to humans by the International Agency for Research on Cancer (IARC), which means that it may cause lung carcinoma [72]. Table 5 presents the total and crystalline silica content of coal ashes. The content of crystalline silica has been reported to vary between < 0.1% and 11.7% of the total amount of ash. However, its content in biomass-fired power plants ashes has not been reported. Although coal ashes can contain large (~10%) amounts of respirable fraction of free crystalline silica, the carcinogenic fraction have reported to be below 0.61% [62]. It has been concluded that the amount of free crystalline silica in coal ash is very small, because crystalline silica melts into silica glass at the combustion temperatures (1500–1600 ºC) of coal combustion boilers. In these studies, XRD [62, 70, 74, 76], SEM/EDX [62, 70, 73], ICP/MS [75], and AAS (pye-unicam) [71] methods were used to analyze total and crystalline silica.

Table 5. Total and crystalline silica content (%) of ashes.

Used fuel	**Sample type**	**Total amount of silica (%)**	**Content of crystalline silica (%)**	**n**	**Ref.**
Coal	Pulverized fly ash (PFA)	-	4.4–10.5	4	[73]
Coal	Pulverized fly ash (PFA)	-	0.1–0.6	4	[62]
Coal	Coal gasification (SCG) fly ash	-	< 0.1	2	[73]
Coal	Coal fly ash, ash silo samples	-	< 0.1–6.1	5	[74]
Coal	Coal fly ash, baghouse	-	< 0.1–4.0	2	[74]
Coal	Coal fly ash, boiler	--	2.3	1	[74]
Coal	Coal fly ash		4.1–11.7	12	[76]
Biomass	Cyclone ash	50.5	-	1	[75]
Biomass	Bottom ash	58.1	-	1	[75]
Biomass and coal	Co-combustion ash	28.5–77.3	-	4	[70]
Coal	Bottom ash	10.8–48.3	-	9	[71]
Coal	Fly ash	14.8–50.0	-	9	[71]

- = not reported.

Biomass has been reported as having a very high content of volatile matter. When biomass is poorly combusted at low temperatures, and the mixing of fuels with combustion air is poor, or the residence time of the combustible gas in the combustion zone has been too short, the volatile matter of fuel is not fully combusted [34]. For these reasons, coal and biomass ashes may contain a great number of PAHs [34, 77–78]. The total amount of PAHs in coal fly ash has been reported to be 26.9 mgm^{-3}, and the highest concentrations of PAH in coal fly ash have been reported as those of phenanthrene (7.57 mgkg^{-1}), fluoranthene (6.59 mgkg^{-1}) and trifenylene (2.44 mgkg^{-1}) [77]. It has also been claimed that in coal and biomass co-combustion, the PAH concentrations (measured by GC methods [77, 79–80]) in ashes in modern power plants are low (less than 1 mgkg^{-1}) [79–80], due to the effectiveness of the co-combustion of biomass and coal [80].

2.2.2 Dust

Workers' exposure to ash dust has mainly been reported in coal-fired power plants during routine work tasks, maintenance tasks and ash removal tasks [4, 81–82, 85]. Table 6 presents the dust concentrations. Total dust concentrations have been reported as high (even 73–200 mgm^{-3}) during boiler cleaning and during maintenance tasks in coal-fired power plants [81–82, 85]. Respirable dust concentrations have only been measured during operational work tasks in coal-fired power plants, and the concentrations of respirable dust have been also high (even 5–9 mgm^{-3}) [4, 81–82]. However, workers' exposure to inhalable ash dust has not been reported in maintenance and ash removal tasks in biomass-fired power plants.

Table 6. Workers' dust exposure (mg m^{-3}) *in work tasks in power plants.*

Used fuel	Work task	Concentration range of dust (mgm^{-3})	Dust fraction	n	Ref.
Coal	Boiler cleaning and attending to plant	< 0.1–98.6	Total dust	123	[81]
Coal	Doing electrical and mechanical fittings, unit adjustments	0.1–73.3	Total dust	78	[81]
Coal	Operating turbines	< 0.1–21.8	Total dust	56	[81]
Coal	Normal work duties in power plant	0.5–9.0	Respirable dust	-	[82]
		1.6–85.0	Total Dust	-	
Coal	Normal work duties in power plant	0.1–5.3	Respirable dust	203	[4]
Coal	Power engineering and boiler repairs	1–200	-	-	[81]
Coal	Boiler cleaning	1.3–19.1	Total dust	9	[85]
Coal	Boiler making	1.2–4.4	Total dust	13	[85]
Coal	Technicians' work	1.2–1.3	Total dust	18	[85]

- = not reported.

In biomass-fired power plants, exposure to wood dust (inhalable dust fraction) among workers has been reported; in pellet-fired power plants [86–88], where wood dust concentrations (n = 24) have been reported as ranging from 0.2 mgm^{-3} to 19 mgm^{-3} [86, 88]. Ajanko and Fagernäs, 2006 [87] reported 6.6 mgm^{-3} concentrations of wood dust when stumps were crushed in wood-fired power plants.

The American Conference of Governmental Industrial Hygienists (ACGIH), the International Organization for Standardization (ISO), and the European Standards Organization (CEN) have agreed on the definitions of the inhalable, thoracic and respirable fractions of dust. The sampling purposes of these conventions have been agreed in terms of the aerodynamic diameter of the particles, which indicates what fraction of dust should be collected as a dust sample, depending on the region of interest for the substance and hazard concerned. The inhalable particulate fraction is the fraction of a dust cloud that can be breathed in through the nose or mouth [89]. The critical effect of inhalable dust is generally harmful respiratory tract symptoms. The thoracic particulate fraction of dust is the fraction that can penetrate the head airways and enter the airways of the lungs. The respirable dust fraction is the fraction of inhaled airborne particles that can penetrate beyond the terminal bronchioles into the gas-exchange region of the lungs. The respiratory fraction of ash is sampled to assess worker exposure to crystalline silica. Regardless of where the particles are deposited, either in the airways or in the lungs, they have the potential to cause harm either locally or elsewhere in the body. Particles that have a harmful composition and remain in the body for a long time have a greater potential to cause disease – for example, asbestos. Thus, inhaled particles are important for occupational environmental evaluation and control [89].

2.2.3 Metals

Workers' exposure to metals has been reported in coal-, oil,- and SRF-fired power plants during normal work tasks, maintenance tasks, and ash removal tasks [4, 5, 79, 85, 90-91]. The results regarding the metals reported in these studies are presented in Table 7.

The highest arsenic concentrations were measured during operation and maintenance tasks in the coal-fired power plant, where they were very high (1.6–38 times higher than its Finnish OEL, 0.01 mgm^{-3}) [79, 85]. Boiler cleaners also had high arsenic concentrations (5.8–6.1 times its OEL) during boiler cleaning tasks in coal-fired power plants [85]. Technicians, baghouse cleaners, and workers in normal power plant duties were less exposed to arsenic than boiler cleaners and maintenance workers (0.4–33% of its OEL) [4, 85, 91] (Table 7).

Several articles have reported worker exposure to manganese [5, 90–93], as is shown in Table 7. The highest manganese concentrations (75% of its OEL) have been reported during baghouse cleaning tasks in coal-fired power plants [90]. Bagfilter workers' and boiler workers' exposure to manganese has been reported to be < 0.1–15% of the OEL for manganese in oil-, coal-, and SRF-fired power plants [5, 91–93] (Table 7).

Bagfilter workers' exposure to lead have been reported as high in coal-fired power plants; the highest lead concentrations have exceeded its OEL [92]. In SRF-fired power plants, 15% of lead samples have been 50% of its OEL, and lead concentrations have varied between < 0.1% and 25.5% of its OEL [91, 94]. During work tasks in coal-fired boilers, lead concentrations have been low (2–8% of its OEL [93] (Table 7).

Power plant workers have also reported being exposed to Be, Cd, Al, and Th during work tasks in coal- and SRF-fired power plants [90, 91, 93–94]. Baghouse cleaners have reported very high exposure to beryllium concentrations (2–24 times its OEL) during work tasks in coal-fired power plants [90]. Cadmium concentrations have been reported as moderate (less than 18% of its OEL) during normal duties in SRF-fired power plants [91, 94].

Aluminum and thorium concentrations (Al less than 4% of its OEL, Th less than < 0.00001 mgm^{-3}) have been reported as low during work tasks in boilers in coal-fired power plants [93] (Table 7). However, workers' exposure to metals or multiple metals (As, Al, Be, Cd, Mn, Pb, Se, Th) have not been reported in maintenance and ash removal tasks in biomass-fired power plants.

Table 7. Workers' exposure to metals (mg m^{-3}) in work tasks in power plants.

Used fuel	**Work task**	**Metal**	**Concentration range of metals (mg/m^3)**	**Method**	**n**	**Ref.**
Coal	Boiler cleaning	As	0.0582–0.0608	Total dust/I	9	[85]
Coal	Boilermaking	As	0.0159–0.0185	Total dust/I	13	[85]
Coal	Technicians' work	As	0.0009–0.0033	Total dust/I	18	[85]
Coal	Operators' work, maintenance	As	0.380 $^{2)}$	Total dust/II	-	[79]
Coal	Normal work duties	As	0.0004–0.0007	Total dust/III	128	[4]
Coal	Bagfilter workers' tasks	Mn	0.001–0.029	Total dust/III, IV	90	[92]
		As	< 0.063–< 0.069			
		Pb	< 0.032–0.139			
Coal	Boiler work tasks	As	< 0.0001	Total dust/V	2	[93]
		Pb	0.0016–0.0076			
		Mn	< 0.0007			
		Th	< 0.00001			
Coal	Baghouse cleaning	Al	0.040–0.080	Total dust/-		[90]
		As	0.0031–0.0070 $^{1)}$		45	
		Be	0.0002–0.0024 $^{1)}$		29	
		Mn	0.014–0.15 $^{1)}$		44	
SRF	Normal work duties	Pb	15% of samples over 0.050	-/III, VI	297	[94]
		cd	32% of samples 0.0004–0.0025		130	
SRF	Normal work duties	As	0.00004–0.00043	-/VII	20	[91]
		Cd	0.00001–0.00360		20	
		Pb	0.00009–0.0255		20	
		Mn	0.00026–0.00130		20	
Oil	Boiler maintenance	Mn	0.0005	PM10/VIII	13	[5]

$^{1)}$ = Variation of means, $^{2)}$ = highest concentration, Methods: I) = NIOSH method 7900, II) = NIOSH method 7901, III) = NIOSH method 7300, IV) = NIOSH Methods 0600, V) = INAA + EDX, VI) = NIOSH Methods 7048, VII) = AAS, NIOSH Methods 7048, VIII) = NIST 1643, - = not reported.

The total exposure of boilermakers to lead and manganese has also been reported during the overhaul of oil-fired boilers, when urine concentrations of lead and manganese exceeded those of the non-exposed population [95].

Total exposure to Al, As, Pb, Cd, Mn, and Se may increase the risk of numerous neurophysiological changes in workers, and may lead to symptoms resembling Parkinson's and Alzheimer's diseases. Skin exposure to inorganic arsenic and beryllium can also increase the risk of skin diseases. More precise examination of the metals measured has shown that arsenic and its inorganic compounds affect numerous systemic functions and organs, such as the nervous and hematopoietic systems, liver, kidneys, and skin. Short-term (acute) high-level inhalation exposure to arsenic dust or fumes has caused gastrointestinal effects, and central and peripheral nervous system disorders have occurred in workers acutely exposed to inorganic arsenic. Humans' long-term (chronic) inhalation exposure to inorganic arsenic is associated with irritation of the skin and mucous membranes, and causes effects in the brain and nervous system. Human exposure to inorganic arsenic via inhalation has shown to be strongly associated with lung cancer, and the ingestion of inorganic arsenic by humans has been linked to a form of skin cancer as well as to bladder, liver, and lung cancer. The EPA has classified inorganic arsenic as a human carcinogen [96–98].

Nervous system disorders are the critical effect of aluminum toxicity. Nervous system effects caused by aluminum, and the link between aluminum exposure and Alzheimer's disease have been examined a great deal in recent years, but no sufficient evidence that aluminum exposure could cause Alzheimer's disease has been reported. Effects resembling Alzheimer's disease (dialysis encephalopathy) have been reported in dialysis, when high amounts of aluminum (serum Al 3–7mmol/l) have accumulated in the patient's body i.e. brains via dialysis liquid [99–100]. Respiratory effects (asthma, repeated trouble with breathing), lung fibrosis, and signs of cholestasis have also been observed in workers exposed to aluminum dust or fumes [169].

Lead enters the body primarily through inhalation and ingestion. Workers are mainly exposed to lead by breathing in lead-containing dust during work tasks. Inhaled lead passes through the lungs into the blood, where it can harm many of the body's organ systems (nervous system, blood forming system, and kidneys). Inorganic lead compounds do not readily enter the body through the skin, but can enter the body through accidental ingestion (eating, drinking, and smoking) via contaminated hands, clothing and surfaces. Workers exposed to lead and its inorganic compounds may develop a variety of neurological symptoms, gastrointestinal effects, anemia, and kidney disease [103, 170]. The IARC has classified inorganic lead compounds as probably carcinogenic to humans (Group 2A) [104].

The kidney is the critical target organ of cadmium, because it accumulates primarily there, its biological half-life in humans being 10–35 years [101]. This accumulation may lead to renal tubular dysfunction, which is generally irreversible. Cadmium and its compounds are highly toxic and long-term occupational exposure to this metal is also known to cause cancer [102]; for example it contributes to the development of lung cancer, and may also cause cancers of the kidney and prostate. The IARC has classified cadmium and its compounds as carcinogenic to humans (Group 1), meaning that there is sufficient evidence of their carcinogenicity in humans [171].

Chronic, low-level occupational manganese exposure is also prevalent among smelters and welders, and leads to irreversible damage to neurological structures. The neurological signs and symptoms of manganism are similar to those of idiopathic Parkinson's disease (gait disturbances, clumsiness, tremor, speech disturbances, mask-like facial expression, and personality changes) [106]. Potential symptoms of manganese exposure are also, for example, irritation of the eyes, skin and respiratory system, and if contact with dust is prolonged, burning of the eyes and skin. Reported adverse effects are also blindness, dermatitis, weakness, sleepiness, kidney damage, and liver damage [105].

Selenium compounds can also be toxic in excessive quantities in the long term. The central nervous system (CNS), liver, heart, and lungs seem to be the target organs for selenium compounds. The most frequent symptoms described are skin and scalp lesions, nail problems and hair abnormalities, including loss [107–108]. Selenium may prevent or alleviate the toxic effects of As, Cd and Hg. Conversely, some of these metals protect against selenium toxicity [107].

Beryllium may cause dermatitis, acute pneumonitis (lung inflammation), and chronic pulmonary granulomatosis (berylliosis - multiple nodular inflammatory lesions) in humans [98]. The IARC has classified beryllium and beryllium compounds as carcinogenic to humans (Group 1), because they cause lung cancer [171].

Thorium exposure has been associated with increased incidence of lung cancer, pancreatic cancer, colorectal cancers, liver damage, and chronic respiratory diseases. Skeletal sarcomas, thorotrastomas, and sarcomas of the reticuloendothelial system were reported in a study of patients receiving intravenous injections of a colloidal solution of thorium [109–110].

However, small amounts of Se and Mn are important minerals for humans. The recommended daily intake is 50–60 μg and 280–350 μg, respectively. The estimated maximum daily intake level (levels of minerals that are unlikely to cause a risk of adverse health effects to humans) of Se is 300 μg per day [182].

2.2.4 Respirable silica

Worker exposure to respirable crystalline silica has been reported in coal-fired power plants during normal operations, maintenance tasks and ash removal tasks [74, 90, 111]. Table 8 presents the results regarding respirable crystalline silica. The highest respirable crystalline silica concentrations have been reported during ash vacuuming and maintenance tasks, when respirable crystalline silica concentrations have been between 0.0071 mgm^{-3} and 96 mgm^{-3} and between 0.0080 mgm^{-3} and 13 mgm^{-3}, respectively [74, 90, 111]. The highest measured concentrations in these tasks have been extremely high (260–1920 times higher than the Finnish OEL for respirable crystalline silica). The average concentrations of respirable crystalline silica have exceeded the OEL for respirable crystalline silica during bag changing in the baghouses of bituminous and sub-bituminous coal-fired power plants [90]. During the normal operations of coal-fired power plants, the highest respirable crystalline silica concentrations have exceeded the OEL for respirable crystalline silica in work tasks in ash silos [111]. However, the lowest concentrations (14–18% of the OEL) of respirable crystalline silica have been reported as 0.0071 mgm^{-3}, 0.0080 mgm^{-3}, and 0.0092 mgm^{-3} during ash vacuuming, maintenance, and the normal operations of power plants, respectively [74, 111].

Table 8. Workers' exposure to respirable crystalline *silica (mgm^{-3}) in* work tasks in power plants.

Used fuel	**Work task**	**Respirable crystalline silica (mgm^{-3})**	**Method**	**n**	**Ref.**
Coal	Vacuum crew's tasks	0.0071–3.9	I	21	[74]
Coal	Maintenance task	0.0080–13	I	31	[74]
Coal	Baghouse bag changing	0.182 [1)]	-	33	[90]
Coal	Baghouse bag changing	0.069 [1)]	-	12	[90]
Coal	Normal operations, Ash silo operator's tasks	< 0.1–0.18	I	14	[111]
Coal	Normal operations, Ash silo operator's tasks	0.0092–0.39	I	7	[111]
Coal	Vacuum crew/laborer's tasks	0.0071–96	I	34	[111]
Coal	Mechanic's tasks Maintenance task	0.017–5.9	I	23	[111]

[1)] = Geomean, I) = NIOSH method 7500, - = not reported.

The IARC has classified crystalline silica as carcinogenic to humans. This means that it may cause lung carcinoma [112]. In the case of crystalline silica, the particle distribution of inorganic dust is the most important factor as regards health effects. Chronic silicosis is the disease most often associated with long-term exposure to low-level respirable crystalline silica. Epidemiologic studies have found that chronic silicosis may develop or progress even after occupational exposure has ceased [113-118]. Symptoms of acute silicosis may also develop shortly after exposure to high concentrations of respirable crystalline silica. Silicotics may also be at a higher risk of lung cancer than workers who do not have silicosis [119]. Furthermore, strong epidemiological evidence supports an association between long-term exposure to crystalline silica and severe health effects such as chronic obstructive pulmonary diseases (COPD), cardiovascular disease and rheumatoid arthritis [120–125]. The chemical impurities in inorganic dust have been found to be highest at the end of the bioenergy supply chain, during ash removal and maintenance tasks in power plants.

2.2.5 Gases, PAHs, and VOCs

Gases such as NH_3, CH_4, CO_2, CO and sulfur compounds may be present in closed biomass silos and warehouses, especially if the fuel has decomposed [126–127]. Hazardous CO concentrations have been reported in warehouses of the silo type, when the degradation of pellets has occurred [88]. The highest CO concentrations have been reported to be several times higher than the OEL for CO. Gas concentrations in biomass-fired power plants have been reported to be very high during fuel transportation system failures between the silos and the boiler, and have even caused fires or explosion accidents in power plants [127–128]. During maintenance and ash removal work inside biomass-fired power plant boilers, fuel may still be burning, or burned ash may still be hot. If fuel is burning or smoldering inside the boilers, workers may be exposed to the gases and volatile agents of hot ash. Ash may still be present when workers weld and grind materials inside the boilers, and its ingredients may evaporate or be released by the high temperatures of these maintenance tasks. Liu et al., 2005 [129] have reported that boilermakers ($n = 13$) are exposed to low (0.06 ppm) NO_2 concentrations during flame or plasma cutting and the welding of boilers in oil-fired power plants. High SO_2 (over 1.8 ppm) and NO_x (NO_2, 2.7 ppm) concentrations have been reported in thermoelectric power plants during the normal use of boilers, when combustion gases have entered the boiler room [130]. Levy et al., 1984 [131] have also reported high SO_2 concentrations (1–35 ppm) during the torch cutting of expansion joints in oil-to-coal conversion power plants. However, we know no studies exist on maintenance and ash removal workers' exposure to gases in biomass-fired power plants.

Exposing gases can be categorized as irritating, asphyxiant or anesthetic. One toxic effect of primary irritating gases is local inflammation in exposed cells in the lungs, on the skin or in the eyes. The most water-soluble gases, i.e. ammonia, interact with the upper part of the respiratory system such as the nose, pharynx and larynx, causing laryngitis and rhinitis. In addition, ammonia and air mixture may explode, and cause coughing, shortness of breath and a sore throat when inhaled in high concentrations [132]. Median water-soluble gases i.e. SO_2 interact with the upper respiratory system, such as the region of the bronchial tubes, causing bronchitis or pneumonia. Low water-soluble, but very reactive gases such as NO_2, interact directly with the lower parts of the respiratory system such as the bronchial tubes and alveoli, causing pulmonary edemas at high concentration levels [133].

The toxic effects of secondary irritating gases, for example, H_2S are local inflammation in exposed cells in the lower part of the respiratory system and systemic effects such as inhibition of the respiratory chain [133]. H_2S is also an easily flammable gas and is classified as fatal if inhaled [134]. The first category of asphyxiant gases, for example CO_2, only become dangerous in very high concentrations when they start to replace oxygen and reduce the partial pressure of oxygen in inhaled air. CO_2 can cause fatigue, headaches and suffocation in high concentrations [135]. The second category of asphyxiant gases, for example CO, are chemically suffocating gases [133]. CO is also an easily flammable gas and can cause headaches and harm to an unborn child [136]. The third group of gases are chemicals with the potential to cause neurological symptoms. These kinds of vapors are hydrocarbons [133].

Of the PAHs, fluorene (detected in all samples, $n = 59$) and naphthalene (detected in 50% of samples) have been reported as the two most commonly detected compounds that workers are exposed to in coal-fired power plants. Air concentrations of these have been very low, at 1.8–4.0 μgm^{-3} and < 0.1–40 μgm^{-3}, respectively. Concentrations of acenaphthene, pyrene, phenanthrene, and anthracene have been reported to be less than 2 μgm^{-3}, and detected in less than 10% of samples [111].

Bentso(a)pyrene concentrations have also been reported as low (<0.1 µg m^{-3}) in SRF-fired power plants [91]. However, no studies have examined maintenance and ash removal workers' exposure to PAHs in biomass-fired power plants. PAHs are classified as carcinogenic to humans and suspected of causing harm to both mother and unborn child [137].

High hexanal concentrations (even 230000 µgm^{-3}) have been reported in warehouses of the silo type, in which the degradation of pellets has occurred. VOC concentrations have been reported to be less than 200–16600 µgm^{-3} in warehouses of the silo type [88]. Worker exposure to total VOCs have been reported to be 3600 µgm^{-3} in thermoelectric power plants [3], and between 220 µgm^{-3} and 8400 µgm^{-3} in SRF-fired power plants [91]. VOCs are harmful to humans in high concentrations and can cause irritation to the eyes and respiratory system when inhaled. VOCs are also flammable in high concentrations [138].

2.2.6 Recommendations for PPE

The possible health hazards of workers working with biomass fly ash have led to recommendations for PPE [139]. However, these recommendations are given in the knowledge that biomass fly ash contains particles of limestone ($CaCO_3$), potash (K_2CO_3), alumina (Al_2O_3), ferric oxide (Fe_2O_3), magnesium oxide (MgO), and manganese (Mn), but not the other elements presented in Tables 1–4. In addition, power plant ash has been reported to be alkaline or very alkaline, pH 9.2–13.5 [139-144]. Worker exposure to airborne fly ash or ash dust may cause immediate or delayed irritation or inflammation in the eyes, and if ash becomes wet, it becomes corrosive (because of its high pH) and causes feeling of burning of the eyes. Skin contact with fly ash may cause dry skin, discomfort and irritation in susceptible individuals, or dermatitis. Moreover, wet ash will cause burning of the skin, because of the corrosive nature of ash. A single, short-term exposure episode to dry ash may cause only little or no acute inhalation hazard. However, high concentrations of fly ash may cause unpleasant obstruction to the nasal passages, and cause nosebleeds and/or headaches, minor chemical irritation to the membranes of the upper respiratory tract, and lung irritation. These hazards depend on, for example, the duration and level of the worker's exposure. Large quantities of fly ash can cause distress to the digestive tract if ingested, although ingestion of small quantities is not known to be harmful [139].

Precautions must also be taken when handling and storing biomass fly ash. The use of proper PPE (coveralls, gloves and goggles) is recommended when handling biomass fly ash. Leather gloves are recommended for workers when handling dry ash, to minimize potential mechanical irritation of skin, and if ash becomes wet, neoprene, butyl, or nitrile gloves are recommended. Loading and unloading fly ash may generate excessive airborne ash dust, and facepiece dust respirators are recommended when exposure limits may be exceeded. However, specific respiratory classes of respirators have not yet been recommended. It is recommended that fly ash be kept dry, because of the corrosive nature of ash [139].

2.3 OCCUPATIONAL EXPOSURE LIMITS AND EXPOSURE ASSESSMENT

2.3.1 Air sampling of chemical agents and reference values

The chemical agents present in work environment air are commonly measured, because inhalation is the main route of many chemical agents (dusts, metals, respirable silica, PAHs, VOCs, and gases) into workers' bodies. There is a long tradition of measuring these agents in the air, and many methods are available for sample analysis. Most of these methods are highly sensitive, and low concentrations may be measured at a particular moment. Sample results can be compared to the OEL values for each agent, which enables conclusions regarding how hazardous they are. The purpose of conclusions in many cases is to clarify the magnitude of worker exposure levels, and to determine whether respirators, for example, are needed [145].

Table 9 presents the Finnish OEL values for the chemical agents measured in this study [138].

Table 9. OEL values for gases, metals, PAHs, dust, and silica.

Chemical agent	**OEL_{8h} value (ppm)**	**OEL_{8h} value (mgm^{-3})**	**OEL_{15min} value (ppm)**	**OEL_{15min} value (mgm^{-3})**
Gases				
Ammonia	20	14	50	36
Carbon monoxide	30	35	75	87
Hydrogen sulfide	5	7	10	14
Nitric oxide	10	12.5		
Nitrogen dioxide	1	1.9	2	3.8
Sulfur dioxide	1	2.7	4	11
Metals				
Aluminum, soluble compounds		2		
Arsenic, inorganic compounds		0.01		
Beryllium, compounds		0.0001		
Cadmium, compounds		0.02		
Lead		0.1		
Manganese, inorganic compounds		0.2		
Selenium, compounds		0.1		
Others				
Benzo[a]pyrene		0.01		
Inorganic dust		10		
Respirable silica		0.05		

In this study, the air concentrations of total volatile organic compounds (TVOCs) were compared to the Finnish normal industrial reference level of 3000 $\mu g\ m^{-3}$ [146]. To evaluate the total effect of PAHs, their toxic equivalency factors were used in the calculation of their total concentration [147]. The results of total PAHs were compared to the OELs for benzo[a]pyrene in this study.

2.3.2 Dermal exposure measurement methods

Workers' skin can be exposed to chemical agents through contact with either solid or liquid agents. Solid agents such as dusts and metals can attach onto workers’ clothing and penetrate it, causing irritation of the skin surface. Contamination of work environment surfaces with dusts or metals can also lead to exposure of the skin. Gaseous agents can be absorbed through the skin and cause adverse health effects. Worker exposure via the skin can be evaluated by attaching samples to the skin and skin wiping samples, which provide information regarding the agents that can cause, for example, irritation of the skin. There are currently no reference values for dermal samples, but comparing sample results can indicate, for example, which work task causes the highest skin exposure [145].

2.3.3 Biomonitoring and reference values

Workers’ exposure to chemical agents, for example, metals can be measured from workers’ urine or blood samples. These methods are called biomonitoring methods, and provide information regarding workers’ total exposures to chemical agents. This means that biomonitoring results unify the inhalation, skin, and oral exposure routes of workers. Biological monitoring results are very useful for obtaining information on worker exposures in cases when respirators are used. Biomonitoring methods also take into account physical work environment factors such as heat. Chemical agents that accumulate in workers’ bodies can only be measured by biomonitoring methods. Reference values for concluding biomonitoring results are given to common exposure agents such as lead, but not as many reference values are available as for air sampling reference values [145]. Table 10 presents the biomonitoring reference values of the Finnish Institute of Occupational Health (FIOH) [148] for the urine concentrations of metals measured in this study.

Table 10. Biomonitoring reference values of metals (μmol l^{-1}, nmol l^{-1}, and mg g^{-1} creatinine).

Metals and analysis codes	**Non-exposed population limit**	**Action limit**	**Units**
Aluminum, U-Al	0.6	3.0	μmol l^{-1}
Arsenic, inorganic, U-As-i	30	70	nmol l^{-1}
Beryllium, U-Be	15	-	nmol l^{-1}
Cadmium, U-Cd	5(1 and 10(2	20	nmol l^{-1}
Manganese, U-Mn	10	-	nmol l^{-1}
Lead, U-Pb	0.008	0.1	μmol l^{-1}
Selenium, U-Se	0.07		mg g^{-1} creatinine

(1 reference value for non-smokers (2 reference value for smokers.

3 Aims of the study

The aims of the study were:

I To characterize the elements of bottom and fly ashes in biomass-fired power plants, in order to determine the sources of the elements, and to test the usefulness of the analyzed material ash results in occupational exposure assessment settings.

II To measure maintenance and ash removal workers' multiple exposure to vapors and gaseous agents, and to evaluate their exposure-associated health risks during work tasks in pellet-, wood-, peat-, and SRF-fired power plants.

III To measure maintenance and ash removal workers' multiple exposures to particulate agents, and to evaluate their exposure-associated health risks during work tasks in pellet-, wood-, peat-, and SRF-fired power plants.

IV To develop methods for evaluating hand-washing and whole body dermal exposure to the elements of ashes, to evaluate workers' total exposure to the elements of ashes, and to assess different personal protection level effects on workers' dermal and total elemental exposure.

4 Materials and methods

Figure 4 presents the project's flowchart. Phase I characterized the elements of ashes and classified the sources of elements. In Phase II and III, we selected exposed worker groups and observed their work tasks. Possible exposure routes were detected and the required measuring methods were chosen or developed. In the field phase, we measured workers' exposure to vapors and gaseous and particulate agents during work tasks in biomass-fired power plants. After this, risk assessment was carried out and multiple exposures and exposure-associated health risks were determined. In Phase IV, we evaluated methods to be able to give recommendations for biomass-fired power plant workers' elemental exposure assessments. The effectiveness of the PPE used by the workers was also assessed to be able to give recommendations to workers regarding the type of PPE they should use during work tasks in biomass-fired power plants to minimize their exposure to ash elements.

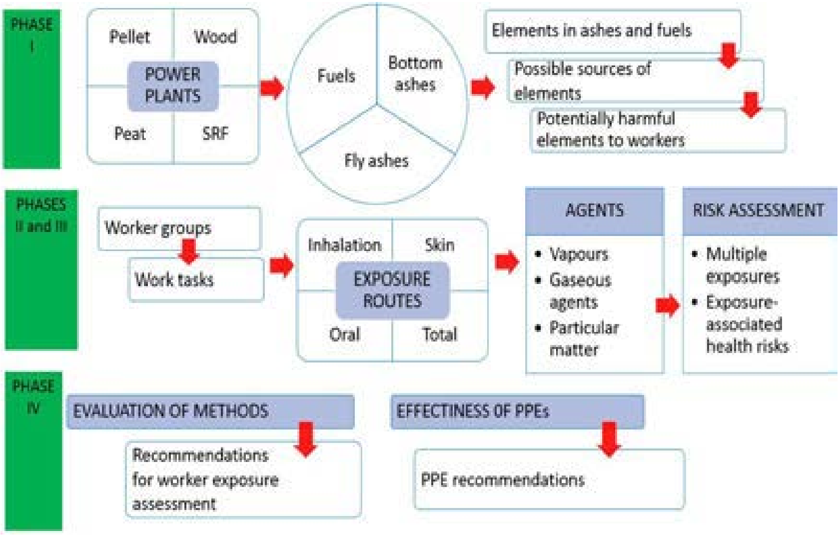

Figure 4. Project's flowchart.

4.1 BIOMASS-FIRED POWER PLANTS

The study was conducted at eight Finnish biomass-fired power plants during the summer of 2010. The plants were randomly selected from different Provinces (two from Eastern Finland, two from Western Finland, one from Southern Finland, and three from Lapland). Pellets were the main fuel in two of the power plants (total thermal input 0.3–0.7 MW), wood was the main fuel in three (total thermal input 17–40 MW), and peat in two (total thermal input 4.5–110 MW) power plants. Recycled wood was only used in one biomass-fired power plant (70 MW) in which peat was nevertheless the main fuel. Table 11 presents the power plant types, fuels used, total thermal inputs, and combustion techniques and temperatures of the power plants.

Table 11. Power plant types, fuels used, total thermal inputs, and combustion techniques and boiler temperatures of power plants.

Power plant type	**Fuels (%)**	**(MW [1])**	**Combustion technique**	**(°C [2])**
Pellet-fired	Pellets 100%	0.7	Grate-fired boiler	*
Pellet-fired	Pellets 100%	0.3	Grate-fired boiler	*
Wood-fired	Wood chips 80% Saw dust and bark 15% Peat 5%	40	Bubbling bed boiler	900
Wood-fired	Saw dust 65% Wood chips 30% Peat 5%	20	Bubbling bed boiler	*
Wood-fired	Saw dust 70% Bark 30%	17	Circulated bed boiler	740–812
Peat-fired	Peat 75% Wood chips 22% Saw dust and bark 3%	110	Circulated bed boiler	760–830
Peat-fired	Peat 100%	4.5	Grate-fired	630
SRF-fired	Recycled wood 25% Wood chips 25% Peat 50%	70	Bubbling bed boiler	850

1) = total thermal input, 2) = combustion temperatures in boilers,

* = information not available.

4.2 TEST GROUP

The exposure of 35 male workers (with an average age of 37 and standard deviation of 11 years) to ash and its components was assessed during the summer of 2010 in biomass-fired power plants in Finland. The Ethics Committee of the Hospital District of Helsinki and Uusimaa approved the study (reference number 62/13/03/00/2010). Written informed consent was obtained from all volunteering participants. The ash removal workers' ($n = 18$) occupational exposure to inhalable dusts, metals, respirable crystalline silica, gases, PAHs, and VOCs inside the boilers were measured first. The same measurements were then taken from maintenance workers ($n = 17$) during their tasks in the boilers. The work tasks performed were recorded during direct observation of the workers' activities.

4.3 SAMPLING AND ANALYSIS OF FUELS AND ASH SAMPLES

The elements of the samples were analyzed in Labtium Oy. Labtium Oy, T025, is an accredited test laboratory (FINAS accreditation services EN ISO/IEC 17025), which specializes in the element analysis of ash and solid biofuels. A total of 32 ash samples (bottom ash, $n_{tot} = 21$; fly ash, $n_{tot} = 11$) were collected from the places in which the workers performed their tasks.

Each power plant delivered mixed fuel samples ($n_{tot} = 9$) to our laboratory for fuel ashing procedures and further elemental analysis. Biofuel samples were dried, crushed, and ashed at 815 °C before element analysis.

Ash and fuel elements were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS), using the ISO 11466 method [150], the average detection limit being 0.1 mg kg^{-1} (± 10–55%) in Labtium Oy.

4.4 AIR SAMPLING METHODS

Air samples of inhalable dust, metals, respirable crystalline silica, gases, PAHs, and VOCs were analyzed in the laboratory of the Finnish Institute of Occupational Health (FIOH). FIOH's Client Services, T013, is an accredited test laboratory that specializes in chemical exposures and aerosol specification in work environments/indoor air. The sample collection and laboratory analysis method of inhalable dust, metals, volatile organic compounds, and respirable crystalline silica mentioned in this article falls under the purview of accreditation.

The sampling pumps were calibrated before sampling. Air samples were collected from the breathing zones of the workers or from stationary sampling points during ash removal and maintenance tasks. The sampling periods varied from 53 minutes to 464 minutes, because some of the work tasks only took a short time (partial shifts), whereas others constituted full shifts. The inhalable dusts and metals were collected in an IOM sampler (Millipore-filter, 25 mm AAWP, pore size 0.8 μm), and respirable crystalline silica in an IOM foam sampler (Millipore-filter, 25 mm AAWP, pore size 0.8 μm, foam (MultiDust Foam Discs for Respirable Sampling, SKC Inc.) at a calibrated flow rate of 2.0 L min-1. After sample collection, IOM filters were weighed for quantification of dust concentration. Metal and crystalline silica were analyzed in accordance with the standards presented in Table 12.

The concentrations of the gases (CO, n = 16; NO, n = 9; NO_2, n = 8; SO_2, n = 7; H_2S, n = 2; NH_3, n = 6) were collected at stationary sampling points next to the workers during ash removal and maintenance tasks. TSI and X-am 7000 (Dräger) gas monitors were used to measure concentrations of CO, NO, NO_2, SO_2, H_2S, and NH_3. The gas monitor sensors for CO, NO, and NO_2 were calibrated before the measurements, using calibrating gases (AGA) with known concentrations (CO = 30 ppm, NO = 5 ppm, NO_2 = 3 ppm). The gas monitor sensors for SO_2, NH_3, and H_2S

were also calibrated using known concentrations (SO_2 = 10 ppm, NH_3 = 100 ppm, and H_2S = 15 ppm) [Table 12].

Vaporous PAHs (n = 24) were collected at stationary sampling points next to the workers into Supelco Orbo 43 tubes at a calibrated flow rate of 0.1 L min-1. The particulate PAHs were collected in a glass fiber filter at a calibrated flow rate of 2.0 L min-1. The analysis of both samples used the methods presented in Table 12.

VOCs (n = 13) were collected at stationary sampling points next to the workers using Tenax TA tubes at a calibrated flow rate of 0.1 L min-1. The samples were analyzed using (TD-GC-MS, detector Agilent 5975C, column Agilentin HP-5ms) and the method presented in Table 12.

An overview of the air sampling and analysis methods of the air samples used in this study are presented in Table 12.

Table 12. Sampling and analysis methods of air samples.

Analyses	**Sample types**	**Detection limit/sample**	**Method**	**Ref.**
Dust	Inhalable dust	0.1 mg	Gravimetric /EN 481/1993	[155]
Metals	Inhalable dust	Al, 9.3 µg; As, 0.075 µg; Cd, 0.3 µg; Mn, 0.1 µg; Pb, 1.75 µg; Se, 1.6 µg	ICP-MS/NIOSH 7303	[156]
Respirable silica	Respirable dust	5 µg	IR/NIOSH 7602	[152]
Gases	NO, CO, NO_2, NH_3, SO_2, and H_2S	NO, CO, NO_2, NH_3, and SO_2 0.1 ppm, H_2S 1 ppm	Electro chemical sensor	[153-154]
PAH	Vaporous and particulate PAHs	Vaporous PAHs ~ 0.01 μgm^{-3}, (0.1 m^3 sample), particulate PAHs ~ 0.001 μgm^{-3} (1 m^3 sample)	GC/MS/EPA 610	[157]
VOC	VOCs (boiling point between 60 °C and 280°C)	~ 0.4 μgm^{-3} (10 dm^3 sample)	TD-GC-MS/SFS-EN ISO 16017-1	[158,168]

4.5 CORRESPONDENCE BETWEEN MEASURED AND CALCULATED METAL CONCENTRATION CALCULATIONS

The correspondence between the measured and calculated metal concentrations was determined to ensure that elemental ash data can be used to assess the risk posed to workers by power plant elements. The following measured inhalable dust air concentrations (C_{Is}; 0.5–290 mgm^{-3}) and amounts of elements [C_{As}; (Mn (440–23000 mgkg^{-1}), Th (1.1–6.2 mgkg^{-1}), Al (8300–32000 mgkg^{-1}), Cd (0.1– 46 mgkg^{-1}), Pb (0.7–3900 mgkg^{-1}), and As (3.2–410 mgkg^{-1})] were used to determine the concentrations of the calculated air elements (C_C). After this, these calculated results were compared to the measured air elemental concentrations (Mn, 0.002–3.1 mgm^{-3}; Th, 0.0001–0.0024 mgm^{-3}; Al, 0.01–5.1 mgm^{-3}; Cd, 0.0001–0.019 mgm^{-3}; Pb, 0.0001–2.5 mgm^{-3}; and As, 0.0001–0.027 mgm^{-3}). The C_C were calculated using the measured average concentrations of inhalable dust in the boilers (C_I), and the results of the elemental analysis of the material ash samples (C_A) (Equation 1).

$$C_C = C_I \times (C_A \div 1000000) \qquad \text{(eq. 1.)}$$

, where

C_C = Concentration of calculated air elements (mgm^{-3})

C_I = Concentration of inhalable dust (mgm^{-3})

C_A = Element amount of ash (mgkg^{-1})

4.6 DERMAL SAMPLING METHODS

4.6.1 Hand-washing samples

Wood-fired power plant ash was used for testing analytical recovery (AR) and hand-washing recovery (HWR) in the hand-washing method. Used ash was selected for testing due to its highest amount of measured elements.

The AR of the metals from the cellulose ester towels was tested by adding (weighted by Mettler AT261 DeltaRange, Mettler-Toledo) 0.0 mg (n = 3, zero samples), 20.0 mg (n = 3), 40.0 mg (n = 3), and 80.0 mg (n = 3) of wood-fired power plant ash, and 3 ml of sunflower oil (Keiju, Burge Finland Oy) to cellulose ester towels (Serla, Metsä Tissue, Mänttä, Finland). The towels were analyzed using the ICP-OES and ICP-MS methods [150], and the levels of elements (Al, As, Ba, Be, Cd, Co, Cu, Cr, Fe, Mn, Mo, Ni, Pb, Sb, Se, Th, U, and Zn) were measured. These elements were selected on the basis of their harmfulness to workers.

Next, the HWR of the hand-washing method was tested by adding a known amount (0.8 g) of ash with sunflower oil to the participants' (n = 9) hands. Zero samples (n = 3) were also made, and treated like other samples, without adding known ash to them. The participants washed their hands according to the standard hand-washing procedure [159], and the levels of elements (Al, As, Ba, Be, Cd, Co, Cu, Cr, Fe, Mn, Mo, Ni, Pb, Sb, Se, Th, U, and Zn) in the cellulose ester towels were measured using the ICP-OES and ICP-MS methods [150]. Both the AR and the HWR of the samples were calculated using Equation 2.

AR or HWR (%) =

$$\frac{[(C_{Ash+towel+oil} \times m_{Sample}) - (C_{Zero} \times m_{Zero\,sample})]}{C_{Wood\,ash} \times m_{Sample}} \times 100 \qquad \text{(eq.2.)}$$

, where

$C_{Ash+towel+oil}$ = Amount of elements in sample ($\mu g g^{-1}$)
m_{Sample} = Amount of ash that was added to towels or hands (g)
C_{Zero} = Amount of elements in zero sample ($\mu g g^{-1}$)
$m_{Zero\ sample}$ = Dry mass of zero sample (g)
$C_{Wood\ ash}$ = Known amounts of elements in wood ash ($\mu g g^{-1}$)

The masses of elements (µg) for which the AR results were between 65% and 120% of the expected masses of elements were taken into account. The minimum and maximum masses of these elements defined the lower and upper analytical ranges.

The AR and HWR were combined, and the total recovery of the elements was estimated. The total recovery (TR) of the hand-washing method was determined using Equation 3.

$$\mathrm{TR} = \left\{\frac{AR\ (\%)}{100\ (\%)} \times \frac{\mathrm{HWR}\ (\%)}{100\ (\%)}\right\} \times 100\ (\%) \qquad \text{(eq. 3.)}$$

, where
TR = Total recovery of method (%)

A TR of 65% to 120% of the metals was classified as quantitatively sufficient. The background elemental content of cellulose ester towels and sunflower oil was taken into account in the calculation of TR.

After testing the hand-washing method, we collected hand-washing samples (sample area 820 cm^{-2}, n =19) to identify elemental contaminants on the workers' hands, and to assess the workers' actual exposure to the elements in the power plants. Zero samples (n = 6) were also made, and the results of these were taken account when workers' hand-washing results were calculated. Workers' hand-washing sample results were calculated using Equation 4.

$$A = \left\{\frac{m_{\text{Elements in analyzed towel}} \times 1000}{\text{Sample area}}\right\} \qquad \text{(eq. 4.)}$$

, where
A = Amount of elements (ngcm^{-2})
$m_{\text{Elements in analyzed wipes}}$ = Amount elements in analyzed towel (µg)

The workers washed their hands with sunflower oil in accordance with the standard hand-washing procedure before lunch and immediately after the working day. Correct hand-washing was demonstrated to the workers beforehand. Total washing time was limited to 60 seconds [18]. Elements (Al, As, Ba, Be, Cd, Co, Cu, Cr, Fe, Mn, Mo, Ni, Pb, Sb, Se, Th, U, and Zn) were analyzed using the same method as that used in the earlier AR and HWR test [150].

4.6.2 Chest patch samples

Wood-fired power plant ash was used for testing AR and chest patch recovery in the chest patch method. We tested the AR of the elements from the chest patch samples (zero samples, n = 2) by adding 2.0 mg (n = 3), 20.0 mg (n = 3), and 50.0 mg (n = 3) of ash to nine chest patch samples. The elemental concentrations from all the chest patch samples were measured using the ICP-OES and ICP-MS methods [150], and the levels of elements (Al, As, Ba, Be, Cd, Co, Cu, Cr, Fe, Mn, Mo, Ni, Pb, Sb, Se, Th, U, and Zn) were analyzed. The ARs of the method were calculated using Equation 5.

$$\text{AR } (\%) = \frac{[(c_{Ash+chest\ patch\ sample} \times m_{Sample}) - (c_{Zero} \times m_{Zero\ sample})]}{c_{Wood\ ash} \times m_{Sample}} \times 100$$

(eq. 5.)

, where

$C_{\text{Ash+chest patch sample}}$ = Amount of elements in sample ($\mu g g^{-1}$)

m_{Sample} = Amount of ash that was added to chest patch sample (μg)

C_{Zero} = Amount of elements in zero sample ($\mu g g^{-1}$)

$m_{\text{Zero sample}}$ = Dry mass of zero sample (g)

$C_{\text{Wood ash}}$ = Known amounts of elements in wood ash ($\mu g g^{-1}$)

The masses of the elements (μg) for which the AR results were between 65% and 120% of the expected masses of elements were taken into account, and an AR of 65% to 120% was classified as quantitatively sufficient. The minimum and maximum masses of these elements defined the lower and upper analytical ranges.

We did not perform chest patch sample recovery tests because we were unable to simulate the same circumstances in the laboratory as those inside the biomass-fired boilers.

The workers' chest patch samples (sampling area 18.1 cm^2) (n = 15) were collected to identify the elemental contaminants on the skin of the workers' bodies in the power plants. We also took zero samples (n = 5) into account when calculating the workers' chest patch results. The sampling time was one whole work shift. The levels of Al, As, Ba, Be, Cd, Co, Cu, Cr, Fe, Mn, Mo, Ni, Pb, Sb, Se, Th, U, and Zn were analyzed using the ICP-OES and ICP-MS methods [150]. Workers' chest patch sample results were calculated using Equation 6.

$$A = \left\{\frac{m_{\text{Elements in analyzed chest patch}} \times 1000}{\text{Sample area}}\right\} \qquad \text{(eq. 6.)}$$

, where

A = Amount of elements (ngcm^{-2})

$m_{\text{Elements in analyzed chest patch}}$ = Amount of elements in analyzed chest patch (μg)

4.7 BIOMONITORING

Workers' biomonitoring (urine) samples were analyzed in the FIOH's laboratory, Client Services, T013, which is an accredited test laboratory (FINAS accreditation services EN ISO/IEC 17025) that specializes in chemical exposures and aerosol specification in work environments/indoor air. The analysis of biomonitoring of metals falls under the purview of accreditation.

Workers' total metal exposure was assessed by biomonitoring urine. The urine spot samples were collected (according to the biomonitoring laboratory's instructions) in acid-washed plastic sample containers before the working week began, after two days of no work (Al); immediately after each working day (Pb, Mn, As, Se, Cd, Be, Th); and in morning before each working day (Hg). These metals were chosen for biomonitoring on the basis of their carcinogenic and neurological effects. We were unable to obtain all the biomonitoring samples from all the ash removal and maintenance workers in this study.

ICP-MS (Thermo X Series) was used for urinary Pb (n = 23), Mn (n = 24), Cd (n = 23), Hg (n = 14), Be (n = 14), Th (n = 21), and Se (n = 21) analysis. An AAS Varian SpectrAA 800 graphite furnace was used for urinary aluminum (n = 21) analysis, and liquid chromatography (Agilent 1200), atomic fluorescence detectors (Excabur) and columns (Supelguard Discovery C18, 2 cm x 4.9 mm, 5µm, and Discovery C18, 15cm x 4.6 mm, 5 µm, Supelco) for urinary arsenic (As^{3+} and As^{5+}) analysis (n = 21). The urinary results of Pb, Mn, Cd, Hg, Be, Th, and As were corrected with the specific gravity of each urine sample measured by a refractometer (Atago USR 20), to reduce the variability of the urinary metal results. For the selenium results, a similar correction was made with the creatinine concentration of each urine sample analyzed by the picric acid method. Urine samples were stored in the freezer before metal analysis. We performed calibration using aqueous solutions and standard addition. The quality procedures included the daily use of commercial reference materials and regular participation in external quality assessment schemes [151, 160–165, 178–180].

4.8 MULTIPLE EXPOSURE ASSESSMENT

The American Conference of Industrial Hygienists (ACGIH®) and Finnish Ministry of Social Affairs and Health recommends that the presence of all contaminants that have similar effects on the same organs or systems of the human body should be taken into account in exposure assessment [138, 149]. These exposures should be added together (multiple exposure assessment) rather than considered individually.

We used the MIXIE program for evaluating (modeling) the health risks of multiple exposures to chemical agents [149]. First, the average metal (Al, As, Pb, Cd, Mn, Se, Be) concentrations, maximum gas (CO, NO, NO_2, SO_2, H_2S, NH_3) concentrations, and their percentages of the Finnish OELs were calculated by Excel. After this, these metal and gas concentrations were fed into MIXIE. Because MIXIE uses Canadian OEL values, which are either higher or lower than the Finnish ones, the concentrations of metals and gases were fed into MIXIE were fixed so that the results (percentages of the OEL values) were equal to the Finnish ones. When the results were fed into MIXIE, the first-level analysis was of the fed agents (metals or gases). This analysis gave combinations for the different adverse health outcomes of the fed agents, reported which agents may have exposure-associated combined effects (Rm), and gave their numerical results. The Rm values were calculated by MIXIE using Equation 7. These Rm values were also calculated using Excel to verify the MIXIE results.

$$Rm1 = \frac{Cs1}{OELs1} + \frac{Cs2}{OELs2} + \frac{Cs3}{OELs3} \qquad \text{(eq. 7.)}$$

$$= 1\% \quad + 10\% + 1\%$$

$$= \mathbf{12}\%$$

, where
Rm1 = Result of exposure-associated combined effect (%)
Cs = Concentration of substances
OEL = Occupational exposure limit value

MIXIE also gave a second-level analysis, which is based on MIXIE's scientific literature reports. This analysis demonstrates interactions between two agents, and provides a brief literature review and the conclusions of this analysis.

The MIXIE results revealed the exposure-associated combined effects of the analyzed chemicals (in our case, cancer, CNS disorders, or irritation of the upper and lower respiratory tract), and the chemicals responsible for these effects. The second-level analysis of the MIXIE primary literature results also provided information on the interactions (additive and supra-additive effects) of the analyzed chemicals [149].

The toxic equivalency factors (TEF) of the PAHs were used for evaluating multiple exposure to PAHs. The TEFs of the PAHs were used for evaluating the carcinogenic effects of PAHs related to benzo[a]pyrene [83]. The TEFs of the PAHs used are presented in Table 13 [147].

Table 13. Toxic equivalency factors of PAHs.

PAH compounds	Toxic equivalency factors of PAHs
Naphthalene	0.001
Acenaphthene	0.001
Fluorene	0.001
Phenanthrene	0.001
Fluoranthene	0.001
Pyrene	0.001
Benzo[a]anthracene	0.1
Chrysene	0.01
Benzo[b]fluoranthene	0.1
Benzo[k]fluoranthene	0.1
Benzo[a]pyrene	1.0
Dibenzo[a,h]anthracene	1.0
Benzo[g,h,i]perylene	0.01
Indeno[1,2,3-c, d]pyrene	0.01
Dibenzo[a,h]anthracene	1.0

Equation 8 presents the equation for toxic equivalent of mixture (TEQ) [84].

$$\text{TEQ} = \sum(C_i \times TEF_i) \qquad \text{(Eq. 8.)}$$

, where
C = Concentration of individual PAHs (μgm^{-3})
TEF = Toxic equivalency factors of individual PAHs

4.9 STATISTICAL ANALYSIS OF DATA

4.9.1 Comparison of ashed fuel and ash

The median amounts of the elements in ashed fuel samples, bottom ashes, and fly ashes were calculated, and the elemental (Mn, Al, Fe, Ba, Cu, Cr, Ni, Pb, Co, As, Se, Th, Cd, and Be) amounts of pellet-, wood-, peat-, and SRF-fired power plants were presented separately after elemental analysis of the ashed fuels and ashes. The data of these elements are presented only, except for Th, they all have occupational exposure values (OEL).

4.9.2 Comparison of calculated and measured elemental concentrations

The correlation between the measured and calculated elemental concentration data was determined using a linear regression fit. The p-values and 95th percentiles of the data were also reported.

4.9.3 Multiple exposure assessment of metals and gases

The exposure-associated adverse health effects of the average concentrations of metals (Al, As, Pb, Cd, Mn, Se and Be) were determined using the MIXIE program. These average concentrations (mgm^{-3}) of each metal were converted into percentage values using the metals’ Finnish OELs. SAS for Windows 9.2, and one-way ANOVA were used to analyze the differences between the means of the groups (biomass-fired power plants), according to the generalized linear model (GLM) procedure. Tukey's multiple comparison method was used to determine any significant differences [$p < 0.05$ (*)] between the health hazards of different biomass-fired power plants, classified by their hazard and type.

The ten highest peak values (ppm) of each gas (CO, NO, NO_2, SO_2, H_2S and NH_3) responsible for acute health hazards in the biomass-fired power plants were converted into percent values using the Finnish short-term exposure limits (OEL_{15min}) for gases and the OEL_{8h} for nitric oxide. SAS for Windows 9.2, and one-way ANOVA were used to analyze the differences between the means of the groups (biomass-fired power plants), according to the generalized linear model (GLM) procedure. Tukey's multiple comparison method was used to determine any significant differences [$p < 0.001$ (*)] between the acute health hazards of different biomass-fired power plants, classified by their hazard and type.

4.9.4 Comparison of protection levels of gloves and coveralls

The effectiveness of the protection level of gloves was calculated in glove groups of long leather gloves, short leather gloves, and other gloves. First, the average concentrations (%) of metals in hand-washing (As, Cd, Cu, Ni, Pb, and Zn) were calculated. Then, standard deviations and the standard error of means of each glove group were calculated. After this, the best detected protection level of gloves was set to the value of 100%. The results of the other average concentrations of gloves were proportioned to this value. The effectiveness of the protection of coveralls and hoods, coveralls without a hood, and open coveralls during the work tasks inside the power plant boilers were calculated in the same way as that of the gloves. Chest patch sample metal (As, Cd, Cu, Ni, and Pb) average concentrations (%) were used in these calculations, and the results of these calculations were used for recommendations regarding gloves and coveralls.

5 Results

5.1 ASHED FUELS, AND BOTTOM- AND FLY ASH ELEMENTS

Figures 5a–5d compare the median amounts of elements in fuel-, bottom- and fly ash of pellet-, wood-, peat-, and SRF-fired power plants. The median amounts of Cr, Ni and Se were higher in the pellet fuel ashes than in the bottom and fly ashes of pellet-fired power plants. There were no significant differences in the levels of elements in pellet bottom and fly ashes; Mn, Al, and Fe were the highest, and their amounts varied between 11800 mgkg^{-1} and 24000 mgkg^{-1}. The median amounts of other elements in bottom and fly ashes decreased in the following order Ba>Zn>Cu>Cr>Ni>As>Co>Pb>Cd>Th>Se>Be, and Zn>Ba> Cu>Cr>Ni>Pb>As>Co>Cd>Th>Se>Be, respectively (Study I).

The median amounts of elements in wood fuels were at the same level as those in the bottom and fly ashes of wood-fired power plants. Al, Fe, and Mn (2400-19000 mgkg^{-1} had the highest median amounts in bottom and fly ashes; however, the amount of Mn was lower in the bottom and fly ashes from wood-fired power plants than in the bottom and fly ashes from pellet-fired power plants. The median amounts of other elements in the bottom and fly ashes decreased in the following order Zn>Ba>Cu>Cr>Ni>As>Pb>Co>Th>Be>Se>Cd, and Zn>Ba>Pb> Cu>Cr>Ni>As>Co>Cd>Th>Se>Be, respectively (Study I).

In peat fuels, the median amounts of Al, Fe, Th, and Be were higher than those in the bottom and fly ashes from peat-fired power plants. Fe, Al, and Mn (440–66000 mgkg^{-1}) had the highest median amounts in bottom and fly ashes. The median amounts of As and Cd in fly ashes were higher than those in the bottom ashes from peat-fired power plants, and the amounts of Mn, Al, Fe, Zn, Ba, Cu, Cr, Ni, Pb, Co, Se, Th, and Be were within the same range in both bottom and fly ashes (Study I).

In SRF fuels, the median amounts of Ba and Ni were higher than those in the bottom and fly ashes from the SRF-fired power plant. Fe, Al, and Mn (640–10500 $mgkg^{-1}$) had the highest median amounts in the bottom ashes, whereas Al, Fe, Zn, and Pb (3900–21200 $mgkg^{-1}$) had the highest median amounts in the fly ashes from SRF-fired power plants. The median amounts of other elements in bottom and fly ashes decreased in the following order Zn>Cu>Ba>Cr>Pb>As>Ni>Th>Co>Se>Be>Cd, and Cu>Mn>As> Cr> Ba> Cd>Ni>Co> Se>Th>Be, respectively (Study I).

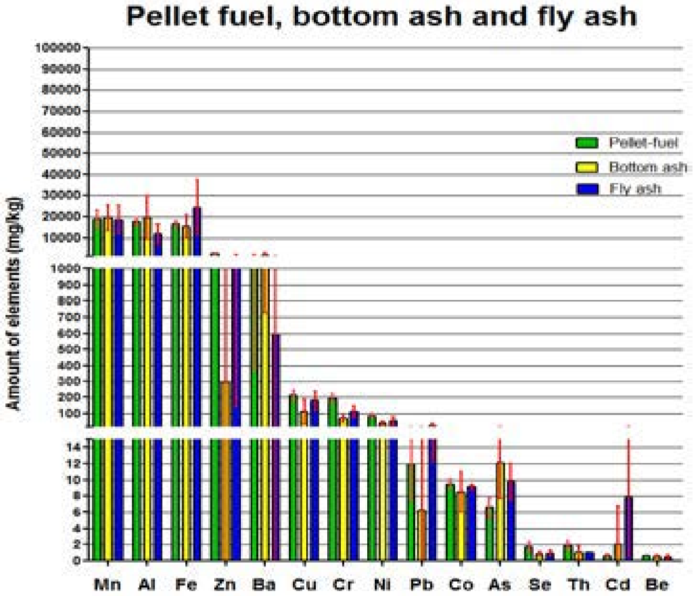

Figure 5a. Median amounts (mgkg^{-1}*) and standard deviation of pellet fuel (n = 2, pellet bottom ash (n = 6), and pellet fly ash (n = 2) elements (mg/kg) in pellet-fired power plants.*

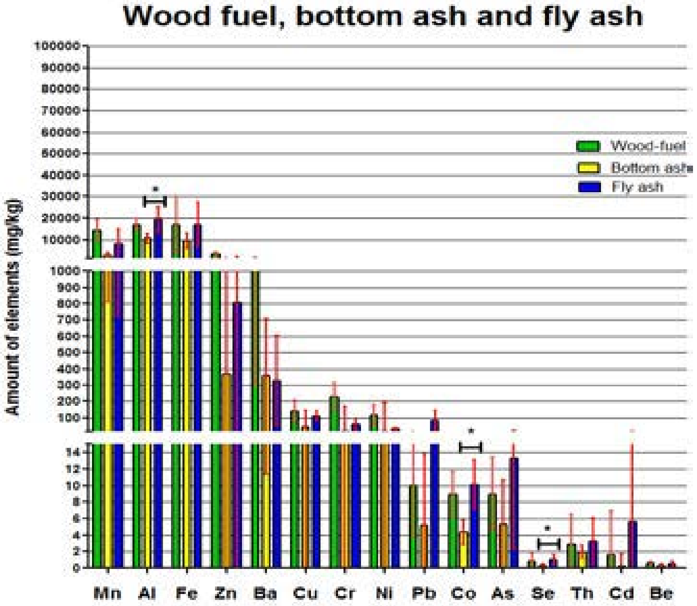

Figure 5b. Median amounts (mgkg^{-1}*) and standard deviation of wood fuel (n = 3), wood bottom ash (n = 10), and wood fly ash (n = 4) elements (mg/kg) in wood-fired power plants.*

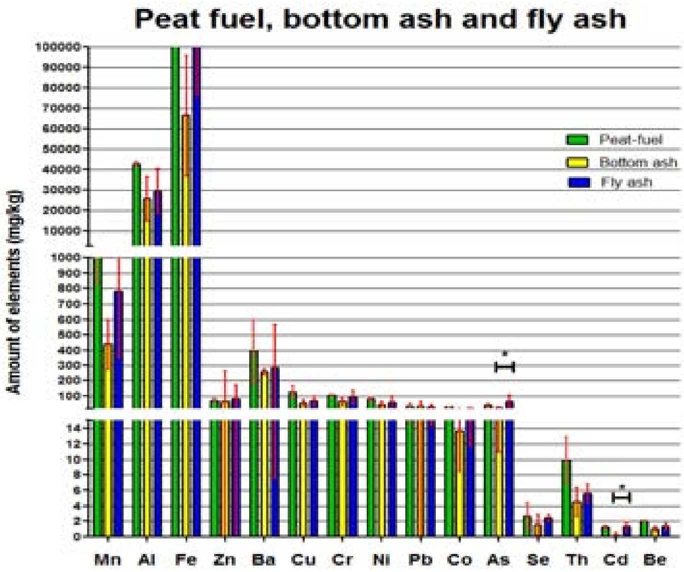

Figure 5c. Median amounts (mgkg^{-1}*) and standard deviation of peat fuel (n = 2), peat bottom ash (n = 3), and peat fly ash (n = 3) elements (mg/kg) in peat-fired power plants.*

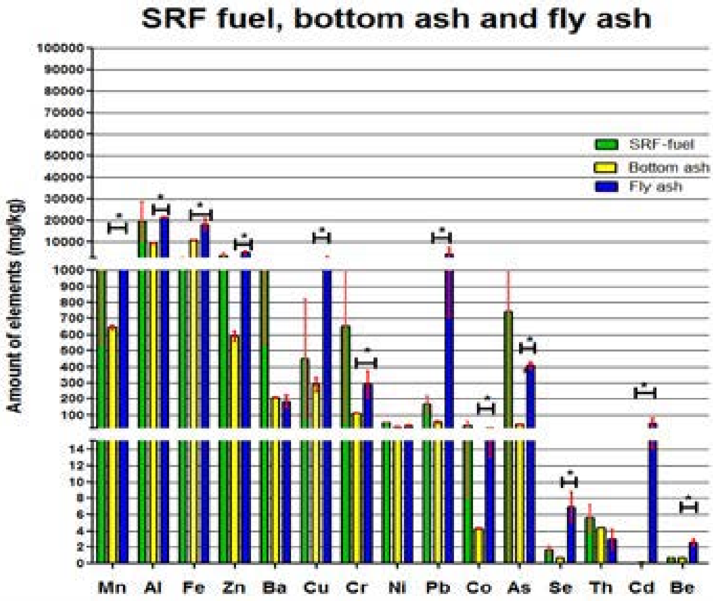

Figure 5d. Median amounts (mgkg^{-1}*) and standard deviation of SRF fuel (n = 2), SRF bottom ash (n = 2), and SRF fly ash (n = 2) elements (mg/kg) in SRF-fired power plants.*

The sources of the increased amounts of chromium and nickel in pellet fuel may be metal alloys, which are used in many processes when wood logs are processed to sawdust. A possible source of selenium in pellet fuel may be wood pellet additives, which are added to saw dust in the pellet-making process. The amounts of aluminum and iron in peat fuel may be due to aluminum and iron additives, which are added to peat soils to bind fertilizer phosphorous to minimize leaching. Peat itself can contain thorium and beryllium, and soil in the peat layers can contain thorium: these are possible sources of thorium and beryllium in peat fuel. The nickel in SRF fuel may be due to the fuel itself or impurities such as metal alloys and steel dust, which get into fuel during its processing. Sources of barium in SRF fuel may be recycled building materials used in SRF fuel, or concrete impurities in wood fuels (Study I).

5.2 INHALABLE DUST

Workers' potential exposure to inhalable dust was measured during ash removal and maintenance tasks in biomass-fired power plants. Table 14 summarizes the inhalable dust concentrations (mgm^{-3}) in workers' personal samples and at stationary sampling points, and the percentages of samples that were over the OEL for inorganic dust (Study III).

Table 14. Summary of concentrations of inhalable dust (mgm^{-3}).

Sample	**n**	**Median**	**Range**	**Mean ± SD**	**Agent over OEL (%)**
Ash removal tasks					
Personal samples	18	33	1.3–290	93±104	83
Stationary samples inside boilers	10	20	0.8–120	46±47	80
Stationary samples outside boilers	17	0.5	0.2–9.1	1±2	0
Maintenance tasks					
Personal samples	5	120	20-260	122±105	100
Stationary samples inside boilers	4	4.8	0.5–14	6±6	25
Stationary samples outside boilers	10	2.0	0.2–53	7±16	10

The median concentrations of the maintenance workers' exposure to inhalable dust were 3.6 times higher than those of the ash removal workers (personal samples). During these dust measurements, the maintenance workers' tasks included flame cutting of boiler tubes and detaching boiler walls using angle grinders, whereas the ash removal workers vacuumed boiler ash, which explained the differences in their exposures to inhalable dust. The median concentrations of inhalable dust (at stationary samples inside the boilers) during ash removal tasks were 4.2 times higher than those during maintenance tasks. Ash removal workers vacuumed boiler ash, whereas maintenance workers welded boiler tubes, which explained the differences in inhalable dusts inside the boilers. The smallest median concentrations of inhalable dusts were measured outside the boilers.

5.3 METALS

Table 15 summarizes the metal concentrations (mgm^{-3}) and the percentages of metals that were over their OEL (agents over the OEL) in the breathing zone samples of workers during ash removal and maintenance tasks in biomass-fired power plants (Study III).

Table 15. Summary of concentrations of metals (mg m^{-3}) in breathing zone samples of workers in biomass-fired power plants.

Sample	n	Median	Range	Mean ± SD	Agents over OEL (%)
Ash removal					
Al	16	1.35	0.013–5.3	2.0±2.0	38
Mn	16	0.185	0.008–3.1	0.7±1.1	50
Pb	15	0.018	0.0002–0.53	0.07±0.2	13
Cd	16	0.0004	< 0.0001–0.03	0.003±0.007	6
As	16	0.0007	< 0.0001–0.08	0.007±0.02	0
Se	16	0.0004	< 0.0001–0.01	0.002±0.003	0
Be	16	0.0001	< 0.0001–0.0002	0.0001±0.00003	38
Th	16	0.0005	< 0.0001–0.002	0.0006±0.0005	
Maintenance					
Al	5	0.42	0.12–4.5	1.9±2.2	40
Mn	5	0.31	0.08–0.8	0.4±0.3	80
Pb	5	0.0053	0.002–0.05	0.02±0.02	0
Cd	5	0.0002	0.001–0.002	0.0007±0.0009	0
As	5	0.003	0.001–0.005	0.003±0.001	0
Se	5	0.0001	< 0.0001–0.0001	0.0001±0	0
Be	5	0.0001	< 0.0001–0.0001	0.0001±0	40
Th	5	0.0013	< 0.0001–0.003	0.001±0.001	

The highest median metal concentrations in the breathing zone samples of workers during ash removal and maintenance tasks were those of Al and Mn. Some of the Al, Mn, Pb, Cd, and Be concentrations exceeded their OELs during ash removal tasks, and some of the Al, Mn and Be OELs were exceeded during maintenance tasks.

Figure 6 shows the median concentrations (mgm^{-3}) of metal in the breathing zone samples of workers during ash removal (AR) and maintenance (M) tasks in biomass-fired power plants (Study III).

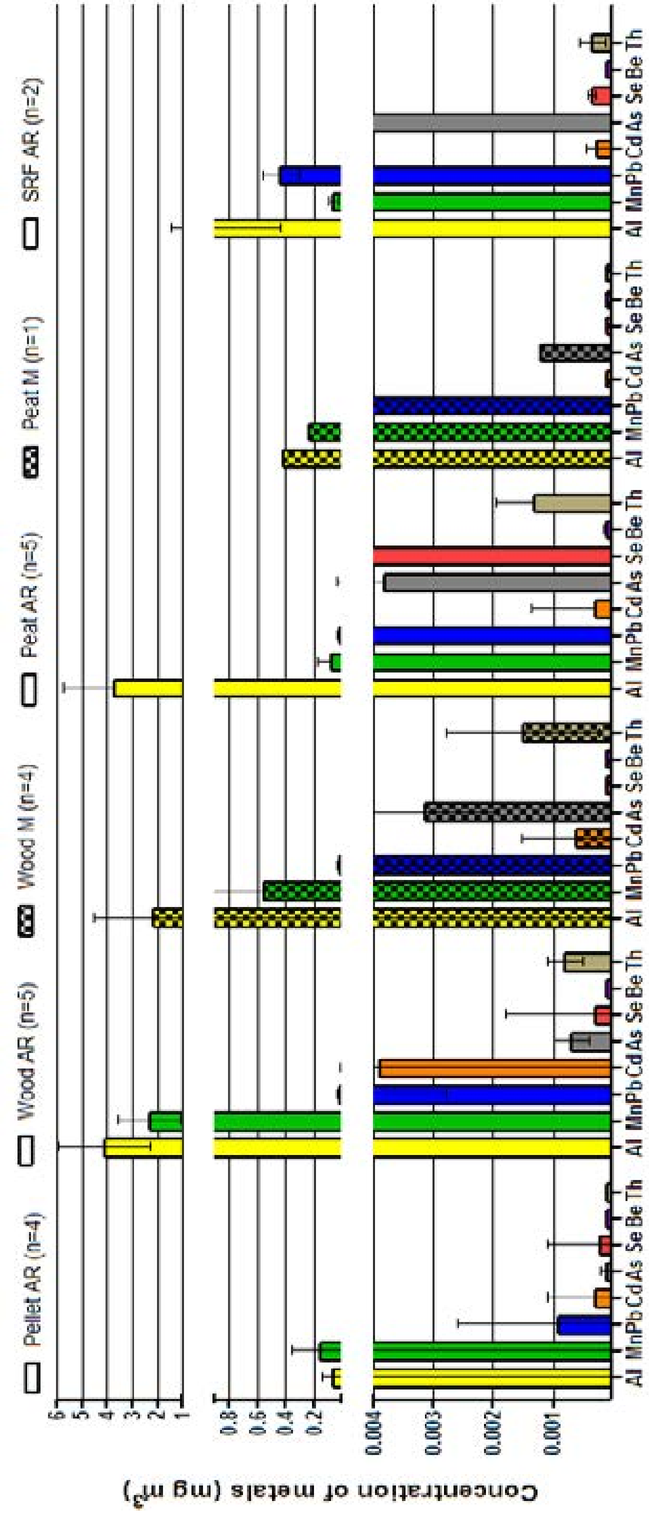

Figure 6. Median concentrations (mgm^{-3}) and standard deviation of metals in workers' breathing zone samples.

The highest median Al, Mn, Cd, and Th concentrations in workers' breathing zone samples were in the wood-fired power plants during ash removal tasks. The highest median Pb and Se concentrations were in the SRF-fired power plants. The highest median concentrations of Be were almost at the same level in all breathing zone samples in the biomass-fired power plants.

The highest median Al, Mn, Pb, Cd, As, and Th concentrations in workers' breathing zone samples were in the wood-fired power plants during maintenance tasks. Median concentrations of Se and Be were almost at the same level in all breathing zone samples in the biomass-fired power plants.

5.4 COMPARISON OF MEASURED AND CALCULATED ELEMENTAL CONCENTRATIONS

The differences between the measured and calculated elemental concentrations were determined to ensure that elemental ash data can be used to assess the risk posed to workers by power plant elements. Figure 7 presents the comparison of the measured and calculated elemental air concentrations of Mn, Th, Al, Cd, Pb, and As. The results concerning Mn ($r = 0.9031$), Th ($r = 0.8829$), Al (0.8228), and Cd (0.6128) showed good correlations (r) with the calculated and measured data, and the p-values ($p < 0.0001$) of these elements were also statistically significant. The measured air concentrations of Mn, Al, and Cd were 1.0–1550%, 0.5–255%, and 0.5–95% of their Finnish OELs, (Mn = 0.2 mgm^{-3}, Al = 2.0 mgm^{-3}, and Cd = 0.02 mgm^{-3}), respectively. Pb and As results showed weaker correlations, at 0.6026 and 0.5400, respectively, and their p-values also had the same trend (Pb, $p = 0.0018$ and As, $p = 0.0056$). The measured air concentrations of Pb and As were 0.1–2500% and 1.0–270% of their Finnish OELs, (Pb = 0.1 mgm^{-3} and Cd = 0.02 mgm^{-3}), respectively (Study I).

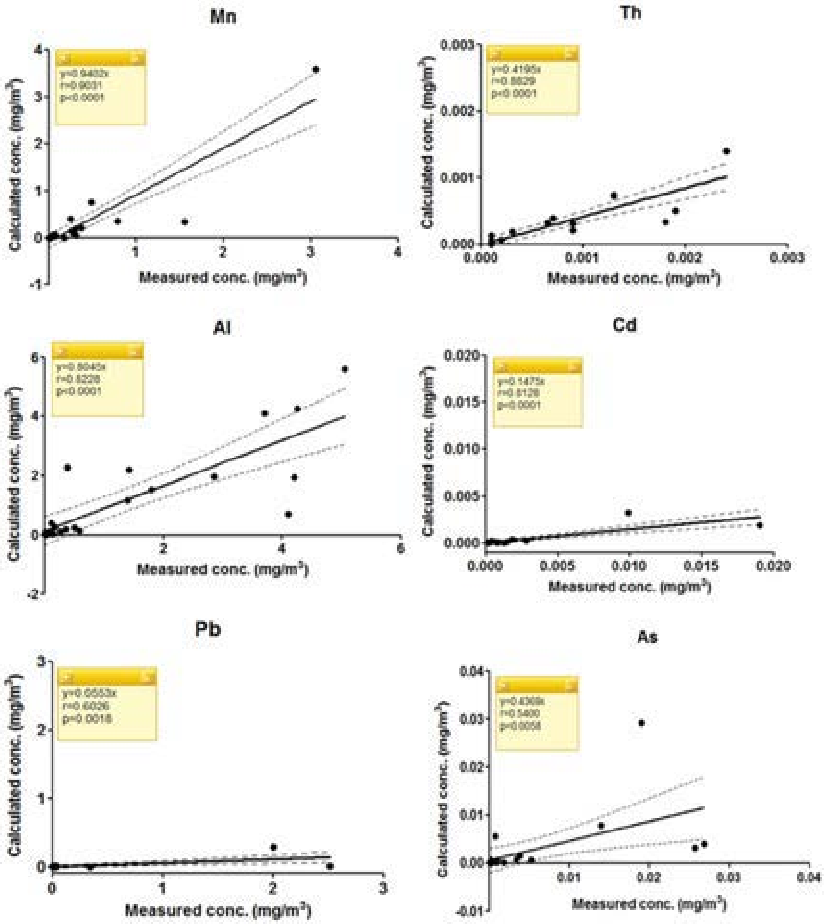

Figure 7. Comparison of measured and calculated elemental (Mn, n = 24; Th, n = 22; Al, n = 24; Cd, n = 24; Pb, n = 24; As, n = 24) concentrations (mg/m³) in air, 95th percentiles, correlations, and p-values of data (Study I).

5.5 RESPIRABLE SILICA

The average total amount of respirable crystalline silica in stationary samples inside the biomass-fired boilers (including amorphous and crystalline silica) was 0.2 mgm^{-3}, and the total amounts of respirable silica ranged between below 0.2 mgm^{-3} and 0.5 mgm^{-3} (Study III).

5.6 GASES

Workers' exposure to gases was measured during work tasks in biomass-fired power plants. Table 16 summarizes the gas prevalences, concentrations (ppm), and the mean and maximum concentrations of the gases' OELs in biomass-fired power plants (Study II).

Table 16. Summary of concentrations (ppm) and prevalences of gases in biomass-fired power plants.

Gas	**n**	**Prevalence**	**Mean±SD (ppm)**	**Max (ppm)**	**Mean/Max of OEL (%)**
CO	16	7/8	0.45±1.7	46	1.5/61
NO	9	4/8	0.06±0.4	30	0.6/300
NH_3	6	4/8	0.11±0.6	11	0.6/22
SO_2	7	3/8	0.42±1.3	17	42/425
NO_2	8	2/8	0.05±0.07	0.5	5/25
H_2S	2	2/8	<0.01±0.03	2	<1/100

The most commonly found gas inside the power plant boilers was carbon monoxide (CO), the mean and maximum concentrations of which were 1.5% and 61% of its OEL, respectively. CO was present in seven boilers out of eight during work tasks inside the boilers. The second most commonly found gases were NO and NH_3, the mean concentrations of which were 0.6%, and maximum concentrations 300% and 22% of their OELs, respectively. SO_2 was found in three boilers out of eight, but its mean and maximum concentrations were the highest (42% and 425% of their OELs, respectively). NO_2 and H_2S were found in two boilers out of eight.

5.7 PAHs

Only 6 of the 16 PAHs that had concentrations (μgm^{-3}) over the limit of quantification were found in the stationary sampling points in the biomass-fired power plants. The mean air concentrations of phenanthrene and naphthalene were 0.02 μgm^{-3} and 0.23 μgm^{-3}, respectively, and the highest air concentrations of benzo[g,h,i]perylene, acenaphthene, fluoranthene, and pyrene were 0.08 μgm^{-3}, 0.01 μgm^{-3}, 0.002 μgm^{-3}, and 0.002 μgm^{-3}, respectively. Phenanthrene and naphthalene were the most commonly found PAHs in the air of the boilers; these were found in four and three boilers out of eight, respectively. The second most commonly found PAHs in the air of boiler rooms were benzo[g,h,i]perylene, acenaphthene, fluoranthene, and pyrene, which were found in one boiler room out of eight. The concentrations of all 16 PAHs were combined with the toxic equivalent of the mixture value, using toxic equivalency factors of different PAHs so that the carcinogenic effect of the PAH mixture could be assessed. The maximum concentration of the carcinogenic effect of the PAH mixture was less than 7% of the benzo[a]pyrenes' OEL value, measured inside a peat-fired power plant boiler. The concentrations of the carcinogenic effect of the PAH mixture was less than 2%, less than 6.5%, and less than 5% in the SRF-, wood-, and pellet-fired power plants, respectively (Study II).

5.8 VOCs

The mean TVOC value at the stationary sampling points in the biomass-fired power plants was 430 μgm^{-3}, the highest TVOC value being 2900 μgm^{-3}. Toluene, α-pinene, dodecane, Δ-carene, benzene, xylenes (o,p,m), β-pinene, tetradecane, and undecane were the main agents in all VOC samples ($n = 13$). Their air concentrations were 2.7 μgm^{-3}, 56 μgm^{-3}, 1.9 μgm^{-3}, 53 μgm^{-3}, 2.4

μgm^{-3}, 3.7 μgm^{-3}, 32 μgm^{-3}, 1.4 μgm^{-3}, and 6.4 μgm^{-3}, respectively (Study II).

5.9 HAND-WASHING AND CHEST PATCH SAMPLES

Workers' hand-washing samples and chest patch samples were taken after work tasks in the biomass-fired power plants to assess workers' hand and body exposure to metals when using gloves and coveralls. In the hand-washing samples, the analytical ranges (n = 9) of Pb, As, Cd, and Ni were 0.7–130 $ngcm^{-2}$, 0.2–30 $ngcm^{-2}$, 0.01–5.0 $ngcm^{-2}$, and 0.9–50 $ngcm^{-2}$, respectively All measured amounts of hand-washing sample Pb in the SRF-fired power plants were over the analytical range of the method (130 $ngcm^{-2}$). The analytical range (n = 9) of chest patch sample Pb was 4.9–300 $ngcm^{-2}$. (Study III).

Figure 8 presents the concentrations of the metals in the hand-washing and chest patch samples, and the ARs and HWRs of Pb, As, Cd, and Ni in hand-washing and chest patch methods are presented in Table 17 (Study III).

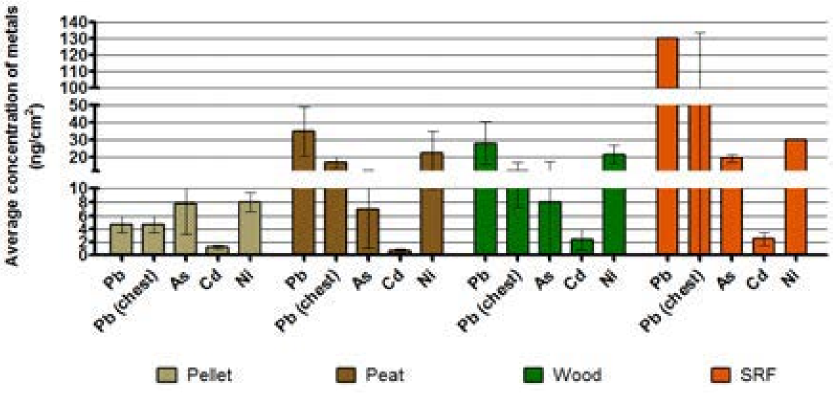

Figure 8. Average (±SD) concentrations of Pb, As, Cd and Ni in hand-washing samples (pellet, n = 2; peat, n = 7; wood, n = 7; and SRF, n = 3), and Pb (chest) in chest patch samples (pellet, n = 2; peat, n = 5; wood, n = 6; and SRF, n = 2) (Study III).

The highest average concentrations of Pb, As, Cd, and Ni in the hand-washing samples were in the SRF-power plant, where their average concentrations were 130 $ngcm^{-2}$, 19 $ngcm^{-2}$, 3 $ngcm^{-2}$, and

30 ngcm^{-2}, respectively. The highest average concentration of Pb (58 ngcm^{-2}) in chest patch samples was also found in the SRF-power plants. Average concentrations of Pb, As, Cd, and Ni in the hand-washing and chest patch samples were almost at the same level in the peat-, and wood-fired power plants (Pb; 35 ngcm^{-2} and 28 ngcm^{-2}, Pb (chest); 17 ngcm^{-2} and 12 ngcm^{-2}, As; 7 ngcm^{-2} and 8 ngcm^{-2}, Cd; 1 ngcm^{-2} and 2 ngcm^{-2}, and Ni; 23 ngcm^{-2} and 22 ngcm^{-2}), respectively. The smallest average Pb concentrations in the hand-washing- and chest patch samples were in the pellet-fired power plants.

Table 17. Analytical and hand-washing recoveries of methods.

	Hand-washing method		Chest patch method
Metals	Analytical recovery (%)	Hand-washing recovery (%)	Analytical recovery (%)
Pb	88	73	74
As	86	77	68
Cd	96	84	96
Ni	108	101	75

The Analytical recoveries of hand-washing and chest patch methods, and the hand-washing recovery of hand-washing method were good at the tested ranges.

5.10 BIOMONITORING

Workers' urine samples were biomonitored to assess their total exposure to metals (U-Al; µmol l^{-1}, U-As; nmol l^{-1}, U-Mn; nmol l^{-1}, U-Pb; µmol l^{-1}, and U-Se; mg g creat. $^{-1}$). Figure 9 presents the prevalence of the measured metals that had concentrations exceeding the non-exposed population value (%) (Study III).

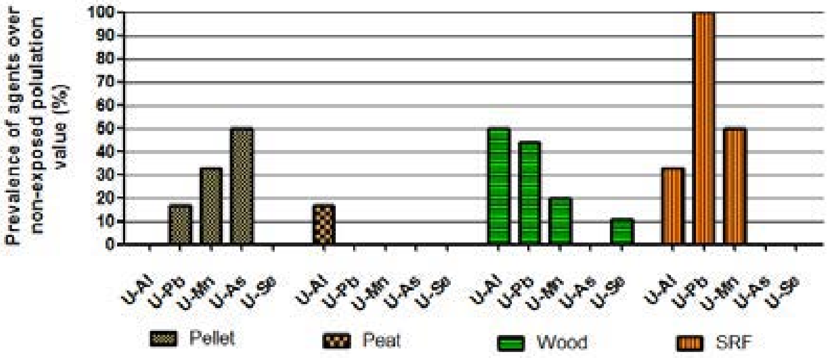

Figure 9. Biomonitoring results of metals over non-exposed population value in pellet- (n = 8), peat- (n = 6), wood- (n = 12), and SRF- (n = 3) fired power plants (%).

The urinary excretions of Pb exceeded the reference value of the non-exposed population in all urine samples in the SRF-fired power plants, in 44% urine samples in the wood-fired power plants, and 17% urine samples in the pellet-fired power plants. The urinary excretions of Mn exceeded the reference value of non-exposed population in 50%, 33%, and 20% of the samples in the SRF-, pellet-, and in wood-fired power plants. The urinary excretions of Al exceeded the reference value of the non-exposed population in 50%, 33%, and 17% of the samples in the wood-, SRF-, and peat-fired power plants, and those of Se in 20% of the samples in the wood-fired power plants. These results indicate that biomass-fired workers are more exposed to these metals than the non-exposed working population.

5.11 EFFECT OF PPE ON WORKERS' EXPOSURE TO METALS

The effects of PPE on worker metal exposures were assessed, so as to provide workers with recommendations as to the type of PPE they should use to minimize hand, body and total exposures to metals.

The average concentration (%) of metals in workers' hand and chest patches (hands: As, Cd, Cu, Ni, Pb, and Zn; chest patches: As, Cd, Cu, Ni, and Pb), when workers used PPE during work tasks inside power plant boilers are presented in Figure 10 (Study III).

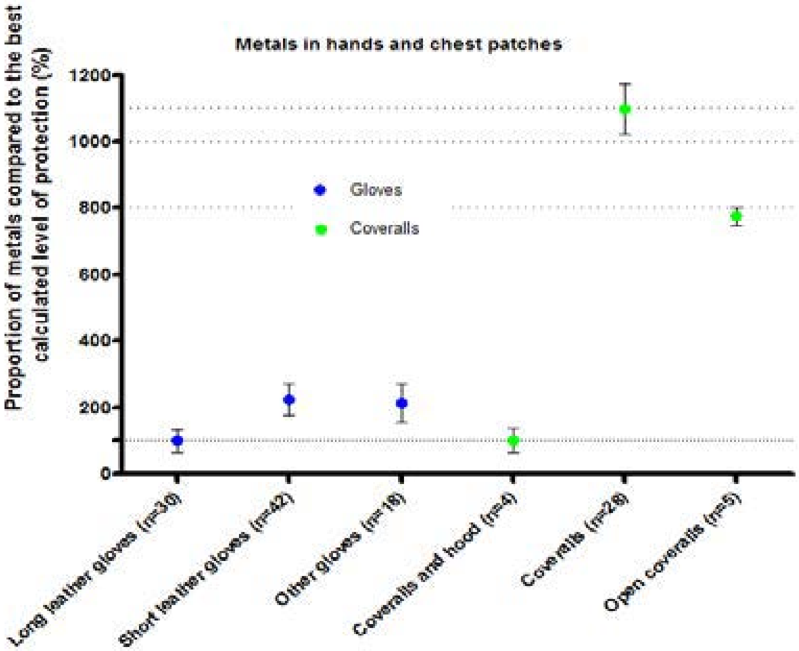

Figure 10. Effect of glove and coverall usage on workers' hand and body exposures (mean+ standard error of the mean) to metals (hands: As, Cd, Cu, Ni, Pb, and Zn; chest patches: As, Cd, Cu, Ni, and Pb) during work tasks inside power plant boilers.

The results in Figure 10 show that long leather gloves protected the workers' hands during work tasks (against As, Cd, Cu, Ni, Pb, and Zn) 2.1 and 2.2 times more effectively than short leather gloves and other gloves. When the workers used coveralls with hoods, their bodies were protected (against As, Cd, Cu, Ni, and Pb) 11 and 7.7 times better than when they used coveralls with no hoods or open coveralls.

The effects of using respirators with filters (respirator/filter types: TM3-A2B2E2K2-P; TM3-P and FF-P3; TM2-P and FF-P2) and the effects of using no respirators were assessed in workers' urine samples for metals (Al, Cd, Pb, Mn, As, and Se). Figure 11 presents these and average urinary excretions (Study III).

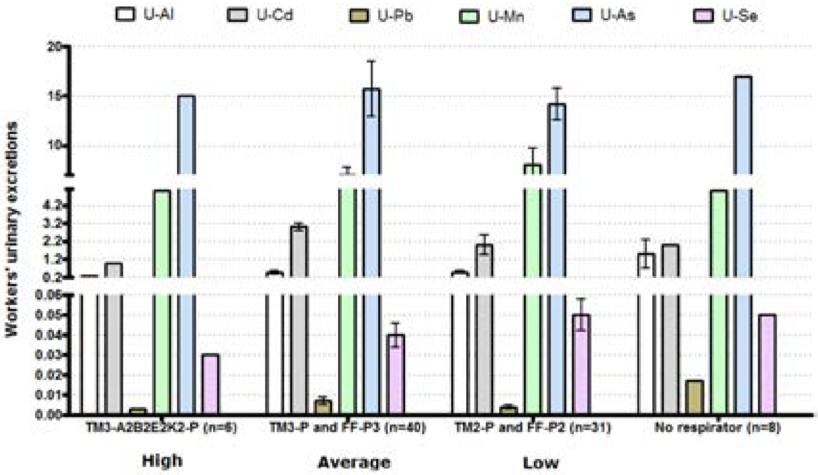

Figure 11. Workers' urinary excretion of Al: µmol l^{-1}*, Cd: nmol l*$^{-1}$*, Pb: µmol l*$^{-1}$*, Mn: nmol l*$^{-1}$*, As: nmol l*$^{-1}$*, and Se: mg g creat.* $^{-1}$ *(±SD), when workers wore respirators with filters (TM3-A2B2E2K2-p; TM3-P and FF-P3; TM2-P and FF-P2) or did not wear respirators during work tasks inside power plant boilers. Respiratory classification is selected according to filtering efficiency.*

Average urine excretions of Al, Cd, Pb, and Se were the smallest, at 0.3 µmol l^{-1}, 1 nmol l^{-1}, 0.003 µmol l^{-1}, and 0.03 mg/g kreat., respectively, when workers used 'high' class respirators and filters. Urinary excretion of Al was 0.5 µmol l^{-1} when workers used 'average or low' class respirators and filters, and three times higher (1.5 µmol l^{-1}) when respirators were not used.

Average urine excretions of Cd were 2-3 nmol l^{-1} when workers used 'low or average' class respirators or none at all, and 1 nmol l^{-1} when workers used 'high' class respirators and filters. Average urine excretions of Pb were 0.003 µmol l^{-1} when workers used 'high' class respirators and filters, 0.004-0.007 µmol l^{-1} when they used 'low or average' class respirators and filters, and increased clearly (0.017 µmol l^{-1}) when respirators were not used. The average urine excretions of Mn were 5-8 nmol l^{-1} regardless of whether or not respirators were used. Workers' excretions of As were almost at the same level (14.2-15.7 nmol l^{-1}) when they used respirators, and slightly higher (17.0 nmol l^{-1}) when respirators were not used. The highest Se urinary excretions were measured in the urine samples of workers who did not use respirators.

5.12 MULTIPLE EXPOSURE ASSESSMENT

Workers in biomass-fired power plants were exposed to more than one metal during work tasks inside power plant boilers. The risk of exposure to more than one metal (multiple exposures) was assessed using the MIXIE program. This program provides rough estimations of the exposure-associated combined effects of the agents (Rm) that are fed into this program, based on its scientific literature analysis. Further analysis of the fed data also provided information regarding the interactions (additive and supra-additive effects) of the analyzed agents. In this study, the average concentrations of the metals (Al, As, Pb, Cd, Mn, Se, Be), and the maximum concentrations (worst-case) of the gases (CO, NO, NO_2, SO_2, H_2S, NH_3) were used to obtain information on the multiple exposure-associated health risks of these in the different work tasks in biomass-fired power plants (Studies II, III).

Figure 12 presents the results of the Mixie program (Rms) that exceeded the combined OELs for metals and gases. According to Mixie, these multiple exposures were associated with an increased risk of upper respiratory tract irritation (URTI), lower respiratory tract irritation (LRTI), cancer, and central nervous system disorders (CNSD). When multiple exposures to agents exceed 100%, this indicates that the combined OEL for agents is exceeded, and that adverse health effects caused by occupational exposure to the mixtures may occur (Studies II, III).

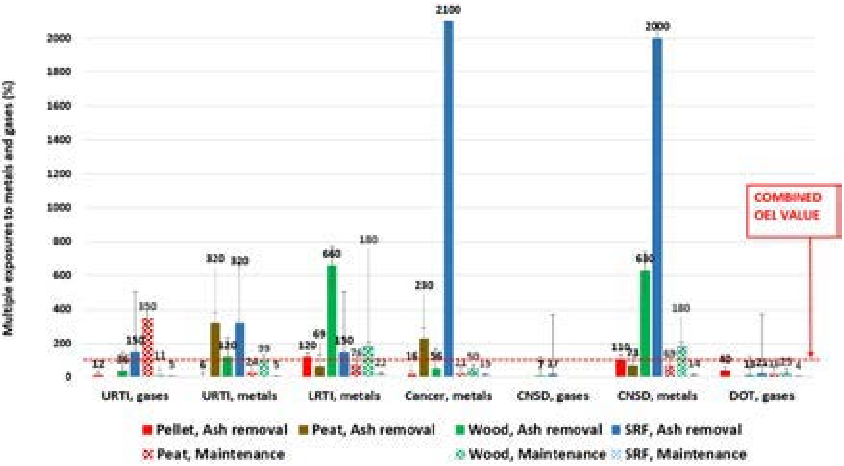

Figure 12. Results of exposure-associated combined effect (Rm; %) of metals and gases (±SD) that were over the combined OELs, and exposure-associated health effects according to Mixie program (Studies II, III).

According to Mixie, the highest combined exposure-associated metal concentration that was associated with an increased risk of cancer was in the SRF-fired power plant during ash removal tasks. This combined metal concentration was 21 times higher than the combined OEL value. In the peat-fired power plants, combined metal concentration was 2.3 times higher than the combined OEL value during ash removal tasks. The highest combined exposure-associated metal concentration that was associated with an increased risk of CNSD was also in the SRF-fired power plant during ash removal tasks. This combined metal concentration was 20 times higher than the combined OEL value. During ash removal and maintenance tasks in the wood-fired power plants, and during ash removal in the pellet-fired power plants, the combined metal concentrations were 6.3, 1.8, and 1.1 times higher than the combined OEL value, respectively. Combined exposure-associated metal concentration, which was related to an increased risk of LRTI was the highest in the wood-fired power plants during ash removal and during maintenance tasks, and the combined metal concentration of these were 6.6 and 1.8 times higher than the combined OEL value, respectively. During ash removal in the SRF- and the pellet-fired power plants, the combined metal concentrations were 1.5 and 1.2 times higher than the combined OEL value, respectively. The combined exposure-associated metal concentration that was related to an increased risk of URTI was the highest in the peat-fired power plants and the SRF-fired power plants during ash removal, the combined metal concentrations of which were 3.2 times higher than the combined OEL value. During ash removal in the wood-fired power plants, the combined metal concentrations were 1.2 times higher than the combined OEL value. According to Mixie, the combined exposure-associated gas concentration was related to an increased risk of URTI, and the combined gas concentrations were 3.5 and 1.5 times higher than the combined OEL value in the peat-fired power plants during maintenance and in the SRF-fired power plants during ash removal, respectively.

6 Discussion

6.1 SIGNIFICANT EXPOSING AGENTS IN ASH

When this study started, I was interested in the elements of ash that may increase the worker exposure-associated risk of cancer, and neurological risks which may lead to symptoms resembling Parkinson's or Alzheimer's disease, because several research groups have reported metal exposures to be associated with these symptoms [96–100]. However, the epidemiological evidence supporting the association between occupational metal exposure and Parkinson's and Alzheimer's diseases is not clear [176–177]. Biomass bottom and fly ashes have been reported as containing a great deal of different elements [35–61, 63–67, 69], the amounts of which may vary among power plants for many reasons [18–22, 32]. However, the main reason for analyzing these elements in many studies [35–61, 63–67, 69] has been environmental issues rather than worker occupational exposure assessment, which in contrast is the main purpose of this study. To be able to assess the possible harmful elements in biomass ashes, this study analyzed a wide range of different elements from the ash samples. The ash sample analysis of elements revealed that biomass-fired power plant ashes contained 15 occupationally meaningful elements (Fe, Al, Mn, Zn, Ba, Cu, Pb, Cr, Ni, Cd, As, Co, Th, Se, and Be). Of these, As, Be, and Cd are classified as human carcinogens [96–98, 171], and Pb is probably carcinogenic to humans [104]. Neurologically harmful effects have been reported to arise from As, Al, Mn, Pb, and Se [96–100, 103, 106–108, 170].

The median amounts of Cr, Ni and Se were higher in fuel pellets than in the bottom and fly ashes from pellet-fired power plants. The median amounts of elements in wood fuels were at the same level as those in the bottom and fly ashes from wood-fired power plants. In peat fuels, the median amounts of Al, Fe, Th, and Be were higher than those in the bottom and fly ashes from peat-fired power plants. In SRF fuels, the median amounts of Ba and Ni were higher than those in the bottom and fly ashes of the SRF-fired power plant (Study I).

Possible sources of Cr and Ni in pellet fuel may be metal alloys [64], used in wood log processing. A possible source of Se can be potatoes, used as a binding agent in the pellet-making process [184]. Large amounts of Al and Fe in peat fuel may be due to Al and Fe additives, which are added to peat soils to bind fertilizer phosphorous to minimize leaching [183]. Peat itself can contain Th and Be, and soil in the peat layers can also contain Th, which is a possible source of Th and Be in peat fuel [184,185]. High amounts of Ni in SRF fuel may be due to the fuel itself [187,188] or impurities such as metal alloys and steel dust [186], which may enter the fuel during its processing (Figure 5). The high amount of Ba in SRF fuels may be due to the recycled building materials used in SRF fuels [186] or concrete impurities in wood fuels [187] (Study I).

Generally speaking, although the fly ashes of power plants have been reported to contain higher amounts of many elements (Al, Pb, As, Cd, Co, Cr, Cu, Fe, Mn, Na, Ni, Zn, and V) than bottom ashes [37, 40, 44–61, 63–66], because most fine fly ash particles are supposedly enriched into fly ash fractions [194, 195], this is not always so, as the results of this study show. A clear enrichment of elements (Mn, Al, Fe, Zn, Ba, Cu, Cr, Ni, Pb, Co, As, Th, Cd, and Be) in pellet bottom or fly ash was not observed in this study. A few studies have reported that pellet fly ash contains higher amounts of As, Cd, Co, Cr, Cu, Mn, Pb, Se, and Zn than bottom ash, and that pellet bottom ash contains higher amounts of Al, Fe, and Ni than fly ash [40-43]. These findings show that the potential risk of worker exposure to bottom or fly ash elements (Mn, Al, Fe, Zn, Ba, Cu, Cr, Ni, Pb, Co, As, Th, Cd, and Be) may be equal, regardless of whether workers are exposed to bottom or fly ashes in pellet-fired power plants (Figure 5).

The median amounts of Al, Pb, Co and Se in the fly ashes were higher than those in the bottom ashes from wood-fired power plants, showing that the potential risk of workers being exposed to these may be higher if they are exposed to fly ashes in wood-fired power plants. The literature has reported wood fly ash to contain more elements (Al, Pb, As, Cd, Cr, Cu, Fe, Zn, and V), with amounts being higher in fly ashes than in bottom ashes [37, 44–61].

The median amounts of As and Cd in the fly ashes were higher than those in the bottom ashes from peat-fired power plants. The median amounts of As in peat fly ashes were clearly higher than those in pellet and wood fly ashes. These findings show that the potential risk of workers being exposed to As and Cd may be higher if they are exposed to fly ashes in peat-fired power plants. The literature has reported peat fly ashes to contain higher amounts of As, Al, Cd, Co, Cr, Cu, Mn, Na, Ni, Pb, Zn, and V than bottom ashes [40, 63–66].

Fly ashes from SRF-fired power plants contained higher median amounts of Mn, Al, Zn, Cu, Cr, Pb, Co, As, Se, Cd, and Be than SRF bottom ash, which means that workers' potential risk of exposure to these fly ash elements may be much higher if they are exposed to fly ashes in SRF-fired power plants. The median amounts of Cu, Pb, and Cd were several times higher in the fly ashes than in the bottom ashes from SRF-fired power plants (Study I). A few studies have reported similar findings regarding SRF fly ashes with higher amounts of As, Cd, Cr, Mo, Mn, Pb, Sb, and Zn than bottom ashes [65–67, 69].

6.2 INHALABLE DUST

The inhalable dust concentrations of this study show that workers are exposed to very high dusts concentrations. The median concentration of inhalable dust was 33 mgm^{-3} in ash removal tasks (while workers vacuumed boiler ash), and 120 mgm^{-3} in maintenance tasks (while workers performed flame cutting of boiler tubes and detached boiler walls using angle grinders). These concentrations were 330% and 1200% of the Finnish OEL (10 mgm^{-3}) for inorganic dust during these tasks, respectively. Workers' exposure to inhalable dust exceeded the OEL for inorganic dust in 83% of the air samples in ash removal tasks and in 100% of the air samples in maintenance tasks (Table 14).

The highest median air concentration of inhalable dust at the stationary sampling points was measured during ash removal tasks inside the boilers (boilers' air and superheaters' air), where the median concentration of inhalable dust was 200% of the Finnish OEL for inorganic dust. During maintenance tasks inside the boilers, the median concentration of inhalable dust was 48% of the Finnish OEL for inorganic dust. Outside the boilers, the median air concentrations of inhalable dust ranged from 5% to 20% of the Finnish OEL for inorganic dust. At stationary sampling points, air concentrations of inhalable dust exceeded the OEL for inorganic dust in 80%, 25%, 10% and 0% of the air samples in ash removal tasks inside the boilers, during maintenance tasks inside the boilers, during maintenance tasks outside the boilers, and during ash removal tasks outside the boilers, respectively (Study III). Liu et. al. (2005) reported workers' exposure to dust in power plants and thermoelectric power stations and found that the mean concentration of respirable dust exceeds its hygienic standard value in 64% of power plant samples [5]. Equally high dust concentrations have also been reported in pulverized fuel ash stations where different exposure groups of workers are exposed to high dust concentrations (low exposure group 0.1–22 mgm^{-3}; medium exposure group 0.1–73 mgm^{-3}; and high exposure group 0.1–99 mgm^{-3}) [81]. In coal-fired power plants, boiler cleaners' exposure to dust has been reported [85] to be over the OEL for dust (19 mgm^{-3}), which is clearly smaller than the inhalable dust concentration (33 mgm^{-3}) results reported in this study. This difference may be explained by the wet ash removal methods in coal-fired power plants as opposed to the dry ash vacuuming in our study. Boiler makers' exposure to dust has been reported to be 4.4 mgm^{-3} [85].

6.3 METALS

The median concentrations of aluminum and manganese in workers' breathing zones in ash removal tasks were 68% and 95% of their Finnish OEL, and in maintenance tasks 21% and 155% of the OEL, respectively. However, The OELs for aluminum and manganese were exceeded in 38–50% of the ash removal task samples and in 40–80% of the maintenance task samples, respectively. Aluminum concentrations have been reported as low (less than 4% of the OEL for Al) during work tasks in boilers in coal-fired power plants [93]. Manganese concentrations (less than 0.4–14.5% of the OEL for Mn) in total dusts and in PM_{10} dust have been mainly reported as low during work tasks in coal-, SRF-, and oil-fired power plants [5, 91-93]. Equally high manganese concentrations to those in this study (75% of the OEL for Mn) in total dusts have been reported during baghouse cleaning operations [90] in coal-fired power plants. The results of this study indicate that aluminum and manganese concentrations in biomass-fired power plants are at the same level or higher than the reported aluminum and manganese concentrations in coal-, SRF-, and oil-fired power plants [5, 91-93].

The median concentration of beryllium reached the OEL for Be in the workers' breathing zone samples in ash removal and maintenance tasks, and the OEL for beryllium were exceeded in 38% and in 40% of these samples, respectively (Study III). Very high beryllium concentrations (2–24 times the OEL for Be) have also been reported in coal-fired power plants during baghouse cleaning tasks [90].

The median concentrations of cadmium and lead in workers' breathing zone samples were 0.0002–0.0004 mgm^{-3} and 0.0053–0.018 mgm^{-3}, respectively. Their OELs were exceeded in 6–13% of the samples in ash removal tasks only; the OELs for these metals were not exceeded in maintenance task samples. The median concentrations of cadmium and lead were 2% and 18% of the Finnish OEL for these metals in ash removal tasks, and 1% and 5% of their OELs in maintenance tasks, respectively (Study III).

Similar concentrations of cadmium have been reported in SRF-fired power plants during normal operations [91, 94], and similar lead concentrations in coal and SRF-fired power plants during normal duties and during work tasks in baghouses and boilers [91–94]. (Study III)

The median concentrations of As, Se, and Th in workers' breathing zone samples were 0.0007–0.003 mgm^{-3}, 0.0001–0.0004 mgm^{-3}, and 0.0005–0.0013 mgm^{-3}, respectively, and the OELs for these metals were not exceeded during the work tasks. However, the median concentrations of arsenic were 7% and 30% of the Finnish OEL in maintenance and ash removal tasks, respectively (Study III). Elevated concentrations of arsenic have been reported in many studies in coal- and SRF-fired power plants during different work tasks [4, 79, 85, 92, 93, 90–93], and concentrations of arsenic have varied widely (0.00004–0.38 mgm^{-3}). Similar arsenic results to those in this study have been reported in coal-fired power plants during normal and maintenance tasks [4, 85]. One study of coal-fired power plants has reported low thorium concentrations (less than 0.00001 mgm^{-3}) [93]. Concentrations of selenium have not been reported during ash removal or maintenance tasks in power plants. The results concerning metals in the workers' breathing zones indicated that it the most important metal exposures to assess among workers are those to Be, Mn, Al, Pb, and Cd in biomass-fired power plants.

6.4 COMPARISON OF MEASURED AND CALCULATED ELEMENTAL CONCENTRATIONS

The comparison of measured and calculated data concerning elemental concentrations (Mn, $r = 0.9031$; Th, $r = 0.8829$; Al, $r = 0.8228$; and Cd, $r = 0.6128$) showed that these elements had good correlations (r), and p-values ($p < 0.0001$). This finding suggests that material sample element data on Mn, Th, Al, and Cd can provide valuable information regarding workers' exposure assessments when inhalable dust concentrations are known and elemental ash data are present. The calculated elemental results predicted high concentrations of Mn, Al, Pb and As. Despite this, elemental data concerning power plant ashes are still rarely used in workers' exposure assessments. Routine available information regarding the elemental composition of ash should be used more often in occupational risk evaluations in biomass-fired power plants.

6.5 RESPIRABLE SILICA

An analysis of crystalline silica revealed that amorphous silica was a disturbing factor when the concentration of the respirable dust was over 5.3 mgm^{-3}. Due to analytical problems with the FT-IR technique, we only obtained the sum results concerning amorphous and crystalline silica (Study III), and it was impossible to accurately assess workers' exposure to crystalline silica. Respirable crystalline silica concentrations have been reported in coal-fired power plants [74, 90, 111], and concentrations of crystalline silica have ranged widely between 0.0071 mgm^{-3} and 96 mgm^{-3}, which exceeds the OEL for crystalline silica during vacuuming of ash and during maintenance tasks [74, 111].

6.6 GASES

Gases were present in the air of biomass-fired power plants during ash removal and maintenance tasks. CO was found in seven boilers out of eight, NO and NH_3 in four boilers out of eight, SO_2 in three boilers out of eight, and NO_2 and H_2S in two boilers of out eight. The average concentration of CO was low, at 1.5% of the Finnish OEL, and the maximum concentration was 61% of the Finnish STEL. Average concentrations of NO and NH_3

were low, 0.6% and 0.6% of their Finnish OELs, respectively, and the average concentration of SO_2 was moderate, at 42% of the Finnish OEL. The maximum concentrations of NO, NH_3, and SO_2 gases were 300%, 22%, and 425% of their Finnish OELs and STELs (Finnish STEL value for nitric oxide not available), respectively. The average concentrations of NO_2 and H_2S were also low, at 5% and below 0.2% of their Finnish OEL, respectively. Their maximum concentrations were 17% and 20% of their Finnish STELs, respectively (Study II). When the Finnish OELs $_{\text{(8h and 15min)}}$ of gases are exceeded, the effect of the gases is harmful. In this study, the maximum concentrations of NO and SO_2 exceeded their OELs for a short time (less than 10 min) by 3.0 and 4.3 times, which can cause respiratory system irritation among workers if they do not use PPEs during work tasks.

Only a few studies have reported gas (NO_2 and SO_2) concentrations during maintenance tasks and the normal use of thermal, oil-fired, and oil-to-coal conversion power plants [129–131]. Equally low (2% of OEL for NO_2) NO_2 results have been reported during maintenance tasks in oil-fired power plants [129]. High results that exceed the OEL for SO_2 have been reported during the normal use of thermal power plants and during maintenance tasks in oil-to-coal conversion power plants [130–131]. No CO, H_2S, NO, NH_3 gas concentrations during work tasks in biomass-fired power plants have been previously reported.

6.7 PAHS

Phenanthrene, naphthalene, benzo[g,h,i]perylene, acenaphthene, fluoranthene, and pyrene were found in the air of boilers and superheaters. All their air concentrations were low. PAH TEFs were used in the calculation of combined PAH concentrations to assess the worker exposure-associated risk of cancer [147]. The combined concentrations of all PAH samples were less than 7% of the Finnish OEL for benzo[a]pyrene

(10 μgm^{-3}) in ash removal and maintenance tasks, and indicates only a moderate exposure-associated risk of cancer (Study I). Fluorene and naphthalene have been reported as the two most commonly detected PAHs in coal-fired power plants [111]. Equally high concentrations of naphthalene (< 0.1–40 μgm^{-3}), acenaphthene and pyrene (concentrations under 2 μgm^{-3}) have also been reported in coal-fired power plants [111]. However, no combined PAH exposures have been reported during work tasks in power plants.

6.8 VOCS

Turpentines (α-pinene, β-pinene and Δ-carene), aromatic hydrocarbons (toluene, benzene and xylene) and aliphatic hydrocarbons (dodecane, tetradecane and undecane) were the most commonly found VOCs in the boilers' air, in boiler rooms, and in the superheaters' air (found in five to eight boilers out of eight). The average concentrations of all these agents were low. All measured TVOC air concentrations were below the Finnish normal industrial reference level of 3000 μgm^{-3} (Tuomi et al., 2012), and thus insignificant in terms of health risks compared to the other chemical agents in this study (Study I). Higher TVOC results have been reported inside thermoelectric power plants (3600 μgm^{-3}). The author suspects that the main source of the VOCs inside the thermoelectric power plant was residual fuel oil [3]. SRF-fired power plant TVOC results (220–8421 μgm^{-3}) have been reported at the same level or higher than those reported in this study [91].

6.9 HAND-WASHING AND CHEST PATCH

The ARs for Pb, As, Cd, and Ni were 88%, 86%, 96%, and 108%, respectively, and the HWRs were 73%, 77%, 84%, and 101%, respectively. As, Cd, Ni, and Pb had the lowest detection limits, ranging from 0.01 ngcm^{-2} to 0.9 ngcm^{-2}. The analytical ranges of these metals were wide enough to quantitatively assess workers' hand exposure to these metals in most biomass-fired power plants. However, in recycled fuel-fired power plants, every lead concentration exceeded the method analytical range. The highest As (19.4 ngcm^{-2}), Ni (30.3 ngcm^{-2}), and Pb (> 130 ngcm^{-2}) median concentrations were found on workers hands in SRF-fired power plants, and the highest Cd (2.8 ngcm^{-2}) median concentrations in wood-fired power plants. In pellet-, peat-, and wood-fired power plants, the median concentrations of As, Ni, and Pb varied between 4.8 ngcm^{-2} and 7.8 ngcm^{-2}, 8.0 ngcm^{-2} and 20.7 ngcm^{-2}, and 4.7 ngcm^{-2} and 33.2 ngcm^{-2}, respectively, and the Cd concentrations in pellet-, peat-, and SRF-fired power plants between 0.7 ngcm^{-2} and 2.5 ngcm^{-2}. Similar or slightly higher concentrations of As (5-28 ngcm^{-2}), Ni (7-43 ngcm^{-2}); similar or slightly smaller concentrations of Pb (12-95 ngcm^{-2}), and similar or slightly smaller concentrations of Cd (less than 0.1-2 ngcm^{-2}) to those found in this study on workers' hands have also been reported elsewhere in Finnish coal-fired power plants [190]

The ARs of the chest patch method for Pb, As, Cd, and Ni were 74%, 68%, 96%, and 75%, respectively. The AR for Pb was good (74%) in the chest patch samples, and the analytical range of lead was wide enough to assess workers' body exposures in all biomass-fired power plants (Study IV). The highest median Pb concentrations (58.4 ngcm^{-2}) were found in workers' chest patch samples in SRF-fired power plants. Median concentrations of Pb varied between 4.5 ng cm^{-2} and 17.0 ng cm^{-2} in pellet-, peat- and wood-fired power plants (Study IV).

The results of the chest patch samples clearly showed that workers' coveralls do not totally protect their whole bodies against Pb. The results showed that power plant ash can also contaminate workers' hands. The biomonitoring results supported these finding. Metal contaminations can increase the risk of exposure through the gastrointestinal route. The hand-to-mouth route of metals was assessed to be the next exposure route after the inhalation of As and Pb (Study IV), and this may increase workers' exposure-associated risks of harmful neurological and skin effects [98, 191]. Skin effects from nickel (nickel contact dermatitis and nickel allergy) are quite common in the general population. It has been estimated that 30% of people have nickel sensitivity (more prevalent among females)[191], which may lead to skin effects, if the skin is in contact with nickel-containing dust or nickel objects. The results concerning nickel in this study indicated that the Ni concentrations found on workers' hands may increase the risk of skin effects from nickel, especially among of nickel-sensitive workers. Skin exposure to cadmium is low, because of the low degree of its absorption through the skin. Cadmium can cause changes in the skin and skin dermatitis [193], but this has been reported as rare (only one case of dermatitis in 1996–2002 in Finland) [192]. Workers' hand-washing and chest patch results in biomass-fired power plants have not been previously reported in the literature.

6.10 BIOMONITORING

In the SRF-fired power plant, some of the workers' urinary excretions of Pb, Mn, and Al exceeded the occupational non-exposed population reference values. In the wood-fired power plants some of the excretions of Al, Pb, Mn, and Se also exceeded the reference values. In the pellet-fired power plants, some of the workers' urinary excretions of As, Mn, and Pb, and in peat-fired power plants the excretion of Al, exceeded the reference values of the non-exposed population. These results indicate that biomass-fired power plant workers are exposed to these metals to a greater extent than the non-exposed working population. This means that they are at a higher exposure-associated risk of adverse effects from these elements than the non-exposed population. However, the magnitude of this risk is small if the workers rarely perform ash removal and maintenance tasks, and use proper respirators and protective gloves and clothes.

If workers perform only ash removal and maintenance tasks and neglect the use of PPE, they are more exposed to contaminants in boilers.

Similar biomonitoring results have been reported during maintenance tasks in oil-fired boilers where worker exposure to Pb and Mn have exceeded the limits of non-exposed population [95]. A few (2.4% of samples) slightly elevated cadmium levels have also been reported [94] during work tasks in SRF-fired power plants.

The most suitable biomonitoring indicators of exposure to ash in pellet-fired power plants were Mn, Pb and As. In peat-fired power plants, Al was the most important indicator of exposure to ash. In the wood-fired power plants, the most recommendable indicators of exposure to ash were Al, Pb, Mn and Se, and for the SRF-fired power plant, the best indicators of exposure to ash seem to be Al, Pb and Mn.

6.11 EFFECT OF PPE ON WORKERS' EXPOSURE TO METALS

Long leather gloves protected workers' hands 2.1 and 2.2 times better than short leather gloves and other gloves, respectively. Coveralls and hoods were 7.7 and 11 times more effective in protecting workers' bodies against these metals than open coveralls and coveralls without a hood, respectively. Average urinary excretions of Al, Cd, Pb, and Se were lowest, at 0.3 µmol/l, 1 nmol/l, 0.003 µmol g^{-1}, and 0.03 mg g^{-1} creatinine, respectively, when workers used TM3-A2B2E2K2-P class respirators.

6.12 MULTIPLE EXPOSURE ASSESSMENT

6.12.1 Multiple exposures to gases and exposure-associated health risks

Ash removal and maintenance workers are simultaneously exposed to more than one gas during their work in biomass-fired power plants. The average concentrations of gases were low, but high and short 'peak' gas exposures were also recorded during work tasks. Multiple exposures to these peak gas exposures were assessed using Mixie (worst-case scenarios), which is a theoretical model and provides rough estimates of the agents fed into its program. Adverse health outcomes of gases were not elicited from the workers.

The MIXIE program provided first-level analysis of gases. This showed the combinations of different adverse health outcomes of the fed agents, which were CNSD, disruption of oxygen transport, and URTI. CNSD was explained by the combined exposure-associated effects of CO and H_2S, the disruption of oxygen transport by the combined effects of CO and NO, and URTI by the combined effects of SO_2, NO, NO_2, NH_3, and H_2S.

The most evident adverse health outcome of multiple exposures to gases in the model was upper respiratory track irritation, when the combined OEL values for gases were exceeded during maintenance tasks in peat-fired power plants (3.5 times the OEL) and during ash removal tasks in the SRF-fired power plant (1.5 times the OEL). The multiple gas concentrations did not exceed the combined OEL values for the gases that were responsible for the disruption of oxygen transport and CNSD.

6.12.2 Multiple elemental exposures and exposure-associated health risks

The adverse health outcomes of multiple elemental exposures were cancer, CNSD, and upper and lower respiratory track irritation, according to the results of the Mixie program's first-level analysis. Cancer was explained in this model by the combined exposure-associated effects of As, Be, Cd, and Pb; CNSDs by the combined effects of Mn, Pb and Se; irritation of the upper respiratory tract by the combined effects of Al, As and Se; and irritation of the lower respiratory tract by the combined effects of Be, Cd, Mn, and Se.

The Mixie program also suggested that exposure to a mixture of As and Cd may have a supra-additive effect on the kidneys. Simultaneous exposure to Mn and Pb may have a supra-additive effect on the blood-forming system and the liver, whereas simultaneous exposure to As and Se also may have a supra-additive effect that may lead to mammary cancer [149] (Study II). One should note that these results regarding combined effects and interactions are based on rough data and the evaluation of interactions in the model. The combined effects and interactions of metals are complex, and depend case by case on the levels of the exposing metals, the order of exposure, etc., i.e. on the factor which contributes to the effects. Therefore, the results regarding combined effects must only be considered as possible worst-case scenarios.

The most evident exposure-associated adverse health outcome of multiple exposures to metals in this model was cancer, and OELs were exceeded in SRF- (21 times OEL) and peat-fired power plants (2.3 times OEL) during ash removal. Although the exposure level is high enough to indicate a risk, it is typically regular long-term exposure that causes cancer. The second most significant exposure-associated adverse health outcome CNSD, and the OELs were exceeded in the SRF-fired plant during ash removal tasks (20 times the OEL), in wood-fired power plants during ash removal and maintenance tasks (6.3 and 1.8 times the OEL), and in pellet-fired power plants during ash removal (1.1 times the OEL). CNSD may manifest as acute effects when exposure is high enough. The third most significant exposure-associated adverse health outcome was lower respiratory tract irritation, and the OELs were exceeded in wood-fired power plants during ash removal and maintenance tasks (6.6 and 1.8 times the OEL), in the SRF-fired plant during ash removal (1.5

times the OEL), and in pellet-fired power plants during ash removal (1.2 times the OEL). Irritation of the respiratory tract was the most commonly found adverse effect, after exposure to enough high dust and gas concentrations. Finally, the fourth adverse health outcome from metals was URTI, and the OELs were exceeded during ash removal tasks in the peat- (3.2 times the OEL), SRF- (3.2 times the OEL), and wood-fired power plants (1.2 times the OEL) (Study III). Multiple exposures to gases and metals during work tasks in power plants have not been previously reported.

The results of this study indicate that ash removal and maintenance workers' potential exposure to components of biomass-fired power plant ash is partly high, and the results of the modeled multiple exposures to metals and gases are associated with several adverse health outcomes among workers. On the basis of these results, we recommend further research (medical research/survey studies) to find out more about the adverse health outcomes among ash removal and maintenance workers of biomass-fired power plants reported in this study.

7 Conclusions

I. The results of this study showed equally high elemental median amounts and estimated exposure in bottom and fly ashes from pellet-, wood- and peat-fired power plants; and clearly higher median fly ash element amounts and higher estimated fly ash element exposure in an SRF-fired power plant. The results of combined element ash data, and measured inhalable dust air concentrations showed good correlations and p-values ($p < 0.0001$) for Mn, Th, Al, and Cd. These results show that it would be valuable to use environmental elemental ash data in worker exposure assessments in biomass-fired power plants.

II. The results of this study show that biomass-fired power plant workers are simultaneously exposed to moderate average SO_2 and low average CO, NO, NO_2, NH_3, and H_2S concentrations (working day exposure). Short-term high gas concentrations were measured during maintenance tasks in peat-fired power plants and during ash removal in the SRF-fired power plant, resulting in a higher exposure-associated risk of upper respiratory track irritation.

All the measured air PAH concentrations were low, and suggest only moderate exposure-associated risk of cancer. All the measured TVOC concentrations were insignificant in comparison to the other chemical agents measured in this study, and are not likely to pose health risks to workers.

III. The results of this study indicated that the median concentration of inhalable dust in workers' breathing zone samples was high or extremely high during ash removal and maintenance tasks. The OELs for Al, Mn, Cd, Pb, and Be were exceeded in the breathing zone samples of workers during ash removal tasks; and the OELs for Al, Mn, and Be were exceeded during maintenance tasks. The exposure-associated multiple exposures to metals suggested, as modeled, an increased risk of cancer, CNSDs, and upper- and lower respiratory track irritation. To avoid these inevitable risks from dust and the increased risks from metals, workers should use respirators during work tasks inside biomass-fired boilers. I recommend further study to find out more about the adverse health outcomes among biomass-fired power plant workers.

IV. The results of this study showed that workers' urinary excretions of some metals (Al, As, Mn, Pb, and Se) partly exceeded the occupational non-exposed population reference values and indicated slightly increased exposure-associated risks of adverse health effects from these metals, despite the use of PPE during work tasks. The dermal exposure results clearly showed that power plant ash can significantly contaminate workers' hands and bodies during work tasks inside power plant boilers.

Biomass-fired power plant workers, especially those who work inside power plant boilers or superheaters should routinely use powered air respirators with TM3-A2B2E2K2-P cartridges and face masks, hooded one-piece coveralls, over-wrist long leather protective gloves, and carbon monoxide gas detectors to minimize their exposure to the components of biomass-fired power plant ash.

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MIKA JUMPPONEN

The current thesis attempts to evaluate workers' exposure to components of biomassfired power plants ash. Inhalation and dermal exposure to inorganic dust and elements of ash, and multiple exposure-associated health risks of metals and gases were evaluated. The concentrations of inorganic dust, Mn, Al, Pb, Cd, NO, and SO_2 were exceeded the OEL levels and thus use of powered respirators, face masks, gas detectors, hooded one-piece coveralls, and protective leather gloves were recommended.

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