



## Atmospheric chamber study of oil shale fly ash particles from circulating fluidized bed and pulverized firing processes

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Received 14 June 2011, revised 4 November 2011, accepted 5 November 2011, available online 20 November 2012

**Abstract.** Oil shale combustion fly ash collected to electric precipitators from pulverized firing (PF) and circulating fluidized bed combustion (CFB) processes was investigated in atmospheric chamber experiments. The aim of the work was to detect differences in the atmospheric behaviour of the fine particles from CFB and PF boilers of the Estonian Power Plant (PP), located close to Narva, Estonia. One series of experiments was performed in a dual outdoor Teflon film smog chamber (270 m<sup>3</sup>) at the University of North Carolina at Chapel Hill (USA) under normal weather conditions (temperature, humidity, sunlight). Parallel tests were carried out in an outdoor smog chamber (108 m<sup>3</sup>) at Tuulna, Harju County, Estonia, where the experiment was made under meteorological conditions similar to those at the location of the PP. The size distribution and number concentration of particles in the chamber were monitored during the experiment. The fractional distribution results demonstrate that the CFB aerosol in the chamber air had more fine particles than the PF aerosol. Approximately 2 h after injection the fly ash particles larger than 4 µm had settled out from both samples. The initial fly ash aerosol had a trimodal fractional distribution. Both PF and CFB fly ash formed stable aerosols 1–3 µm in diameter during the 6 h experiment and are therefore prone to long-range transport.

**Key words:** atmospheric pollution, PF, CFB, fly ash, fine particles.

### INTRODUCTION

Using oil shale as fuel for electricity production causes fly ash emissions. Estonia, remaining a leading producer of oil shale in the world, uses it mainly for electricity and thermal energy generation. As the content of organic matter in Estonian oil shale is relatively low (25–35%) [1,2], the amount of ash that remains after burning makes up 43–50% of the oil shale mass [2–4]. Pulverized firing (PF) technology was used in the Narva Power Plants (PPs) (the Estonian and the Baltic PP, together called Narva PPs) until 2004. One 200-MW power unit at the Baltic PP and one 200-MW power unit at the Estonian PP were upgraded to 215-MW with two circulating fluidized bed (CFB) boilers in 2004–2005 [5,6]. Both technologies (PF and CFB) are currently used in the Narva PPs. At present, 12 units (7 PF units and 1 CFB unit at the

Estonian PP and 3 PF units and 1 CFB unit at the Baltic PP) are running [1]. Hotta et al. [6] described in detail the technology of the new CFB boiler. The PF technology uses high burning temperature of up to 1500°C, whereas the CFB combustion optimum temperature in the furnace chamber is about 850°C [5].

Numerous works have been published that describe the properties and environmental behaviour of fly ash emitted from the PF combustion process [7–9]. However, the fly ash from the CFB process has received less attention so far.

Latest studies report that the total concentration of hazardous organic pollutants, for example polycyclic aromatic hydrocarbons (PAHs) in CFB ash is lower than in PF ash. However, a leaching test of fly ash has shown that the cumulative release of PAHs is more significant in the CFB process than in the case of the PF process [10,11]. Also the toxicity level of heavy metals in oil shale fly ash is significantly higher after CFB

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combustion [12]. Bityukova et al. [4] described in detail the compositional and morphological properties of PF and CFB ashes.

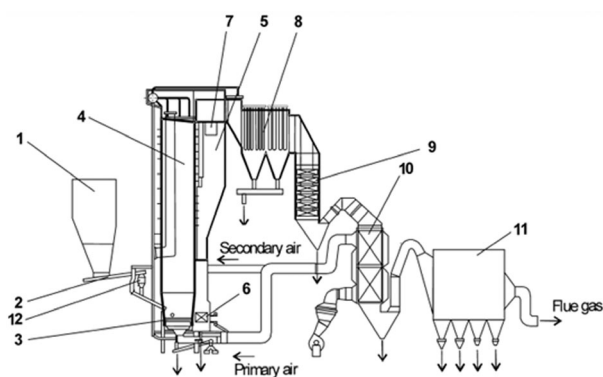
The Estonian PP, 20 km southwest of Narva, was connected to the grid in 1973. Its gross capacity today is 1615 MW per hour and the stack height is 250 m. The Baltic PP, 5 km southwest of Narva, has been in operation since 1966, the gross capacity today is 765 MW per hour and the stack height is 160 m [1,13]. Elevated elemental atmospheric aerosol concentrations are observed approximately 140 km north of the Narva PPs [14]. It is known that the potential hazard of solid particles present in inhaled air depends on particle size and number concentration [15]. In order to assess environmental and health effects of the fly ash emitted to the atmosphere from PF and CFB combustion processes, it is necessary to study the atmospheric behaviour of the fly ash.

From the environmental point of view not only the mass, but also the size of particles is relevant. Thus, the smaller aerosol could be more stable and its long-range transport more pronounced compared with larger particles.

The aim of the study was to investigate the difference in the atmospheric behaviour of the fine particles from CFB and PF boilers of the Estonian PP located close to Narva, Estonia.

## EXPERIMENTAL

Ash samples were collected at the last field of electrostatic precipitators at unit No. 5 (PF technology) and unit No. 8 (CFB technology) from the Estonian PP in 2008 and 2010 (Fig. 1) [16].



**Fig. 1.** Oil shale-fired CFB boiler and the sampling spot A. 1 – raw fuel silo, 2 – fuel feeder, 3 – grate, 4 – furnace chamber, 5 – separating chamber, 6 – fluidized bed internal heat exchanger (INTREX), 7 – separator of solids, 8 – convective superheater and reheater, 9 – economizer, 10 – air preheater, 11 – electrostatic precipitator, 12 – secondary fuel crusher, A – sample collection from the last unit of electrostatic precipitator.

Both combustors were operating in steady state during the sampling episodes. The sampling from both units was performed on the same day by specialists of the Estonian PP. The samples were transported to the laboratory the next day after sampling and stored hermetically before experiment.

Particle size distribution (PSD) and aging of the aerosols of fly ash formed by PF and CFB were studied in chamber experiments in the USA and Estonia.

The experiments started by the injection of a fly ash sample into the chamber. The particles size and number concentration were monitored with different analysers during the experiment. Knowledge of the size distribution of fly ash particles makes it possible to calculate the deposition characteristics of dry ash. On the basis of the dry deposition rate, the inclination of aerosol to long-range transport and environmental impact can be evaluated.

## Smog chamber in North Carolina, USA

The experiments with oil shale fly ash aerosol were performed in a dual outdoor Teflon film smog chamber (270 m<sup>3</sup>) at the University of North Carolina (UNC) Ambient Air Research Facility near Pittsboro, USA (Fig. 2) in 2008. The dual chamber was a Quonset hut in shape, width 8.53 m, length 9.75 m, and height 3.89 m [17,18]. A suspended 5 mil (125 microns) DuPont™ Teflon® FEP film (type C) curtain (Livingstone Plastics, Charlotte, NC) bisects the chamber into two parts with equal volumes. Sampling took place through collectors that run directly to a laboratory under the chambers, and aerosol in the chamber moves about 1.5 m to reach the aerosol sizing instruments.

The chamber experiments with oil shale fly ash were conducted under normal meteorological conditions (average temperature 16°C, average humidity 80%),



**Fig. 2.** The dual outdoor Teflon Film smog chamber of UNC at Chapel Hill, NC, USA.

which were comparable to average conditions in Estonia in summer. The chamber leak rate, including sampling, was 1–5% per hour, as measured by a sulphur hexafluoride tracer. The chamber was purged with rural background air prior to the experiments. The chamber was mixed for 2 min with the internal chamber fans after the fly ash particles had been added and then the fans were turned off.

Particle size and number were monitored during the experiment using four different aerosol particle counters:

- TSI model 3071 connected with Ultrafine Condensation Particle Counter TSI model 3025A (14 nm–600 nm)
- TSI model 3080 Electrostatic Classifier connected with TSI model 3022A Condensation Particle Counter (20 nm–900 nm)
- TSI model 3321 Aerodynamic Particle Sizer® (APSTM) spectrometer (500 nm–20  $\mu\text{m}$ )
- Grimm aerosol spectrometer, Model 1.109 (250 nm–32  $\mu\text{m}$ ).

The experiment started with injecting 1 g of PF and 1 g of CFB oil shale fly ash into the two separate chambers. During the experiment the particle mass and number concentration were measured for the particles whose size ranged from 14 nm to 32  $\mu\text{m}$  using different analysers and sampling systems.

### Smog chamber at Tuulna, Estonia

For the local study and for a comparison of the results obtained at the smog chamber at the UNC in 2008, a 108 m<sup>3</sup> outdoor smog chamber was built at Tuulna, Harju County, Estonia (Fig. 3). The chamber is a cube in shape, width 6 m, length 6 m, and height 3 m. The inside of the chamber walls and the ceiling were covered with 2 mil (50 microns) DuPont™ Tedlar®



**Fig. 3.** The outdoor smog chamber at Tuulna, Harju County, Estonia.

PVF film. Tedlar® 2 mil film was used because of its non-stick and chemically inert properties. The outside of the chamber was covered with 1-mm thick PVC to avoid the breakup of the Tedlar film by wind. As the sunlight does not have any effect on the particle size distribution, the outside cover was negligible.

The sampling system was similar to the construction in the smog chamber at the UNC, but the aerosol moved about 1.0 m before reaching the aerosol sizing instruments. The chamber was purged with filtered rural background air prior to the experiment. The chamber was mixed for 2 min with the internal chamber fans after fly ash had been added and then the fans were turned off.

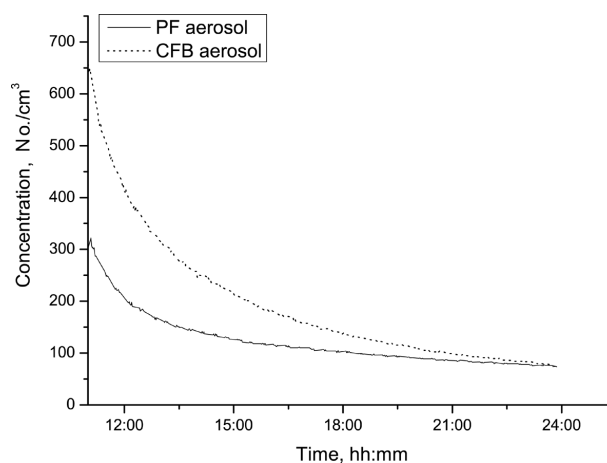
Particle size and number distribution were measured using two different aerosol particle counters:

- Dekati Electrical Low Pressure Impactor (ELPI™) (30 nm–10  $\mu\text{m}$ ) connected with vacuum pump Sogevac SV65B
- Grimm aerosol spectrometer, Model 1.109 (250 nm–32  $\mu\text{m}$ ).

## RESULTS AND DISCUSSION

Deposition of fly ash particles, determined through the fractional size distribution, enables to assess the behaviour of the aerosol in the atmosphere. It allows calculating the lifetime of the different aerosol fractions in the atmosphere and assessing the possible impact on human health and ecosystems.

The particle count data obtained from the aerosol sizing instruments showed that the total settling of fractions with particle diameter less than 10  $\mu\text{m}$  takes several hours (Figs 4 and 5). The number concentration of the fine fractions (particle diameter less than 0.5  $\mu\text{m}$ ) was higher than of larger fractions (diameter of particles between 0.5  $\mu\text{m}$  and 10  $\mu\text{m}$ ) (Fig. 5).



**Fig. 4.** Number concentration of PF and CFB aerosols of less than 10  $\mu\text{m}$  in diameter.

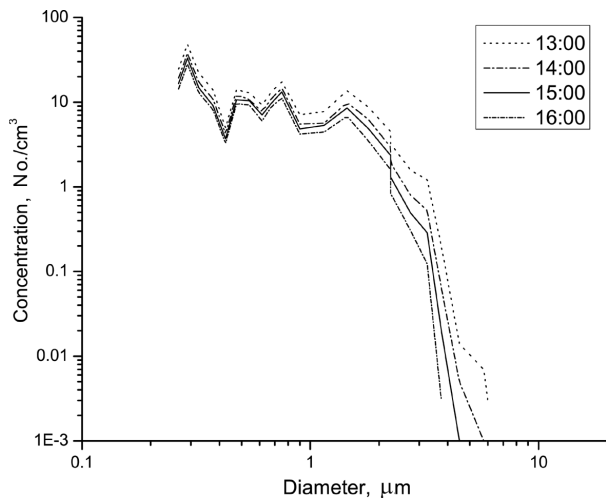


Fig. 5. Number concentration of CFB fly ash.

For a better understanding, the particle count data were calculated into mass units. The initial aerosol mass concentration decreased quickly due to the deposition of larger particles (Figs 6 and 7). The fractional distribution of CFB fly ash showed a trimodal PSD (Fig. 6). The highest concentration was measured for the particles with diameters around 4 µm, and high concentrations were determined for the particles with diameters around 2 µm and 3 µm. It can be also seen that particles larger than 4 µm in diameter settled during about 2 h, but particles of about 2 µm were still hovering after 4 h, although their concentration had decreased about 5 times, from 250 µg/m<sup>3</sup> to 50 µg/m<sup>3</sup> (Fig. 6). For PF fly ash the fractional distribution (Fig. 7) was similar to the distribution of CFB fly ash.

The fractional distribution obtained from the experiments in the smog chamber at Tuulna in 2010 slightly deviates from the 2008 experiments (Fig. 8). The highest concentration was found for particles around 4 µm in diameter in both chamber experiments, but

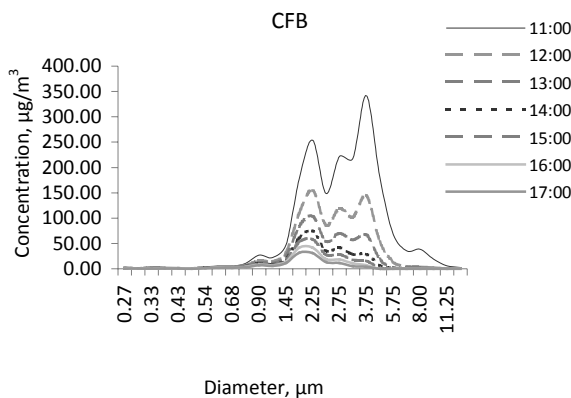


Fig. 6. Fractional distribution of CFB fly ash in 2008.

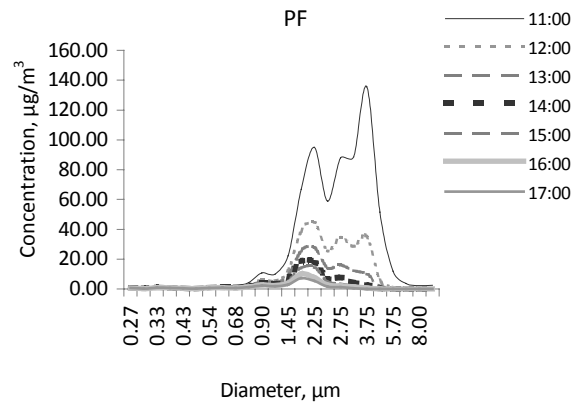


Fig. 7. Fractional distribution of PF fly ash in 2008.

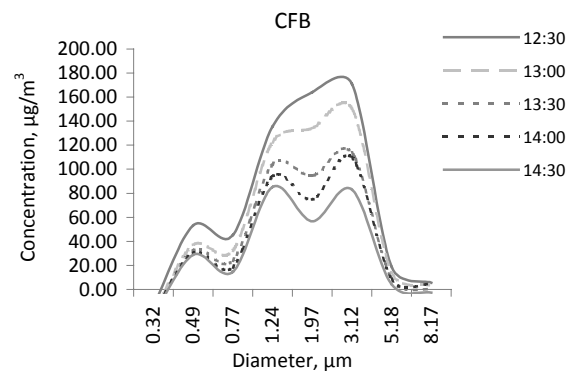


Fig. 8. Fractional distribution of CFB fly ash in 2010.

there were more particles with diameters around 0.5 µm in the results obtained in 2008. The reasons for this deviation of results could be that there had been some combustion technology adjustment during the two years and/or the oil shale combusted originated from different mines. Similar fractional distributions were found for both CFB and PF fly ash aerosols emitted, although the CFB ash formed had different compositional and morphological properties compared with PF ash [4].

One set of experiments was also made in high humidity (over 95%) conditions. The size distribution of the particles was about the same but the settling time of the aerosols was drastically shorter than in previous experiments made under normal humidity conditions. Most of the fly ash particles settled in less than 10 min (Fig. 9). This shows that weather conditions have a substantial impact on the deposition and transport of the fly ash aerosols formed.

Our results indicate that a significant amount of coarse particles settle close to the injection site (Figs 6–9). In real circumstances, the coarse fraction of fly ash emissions will be a local concern without any significant regional impact.

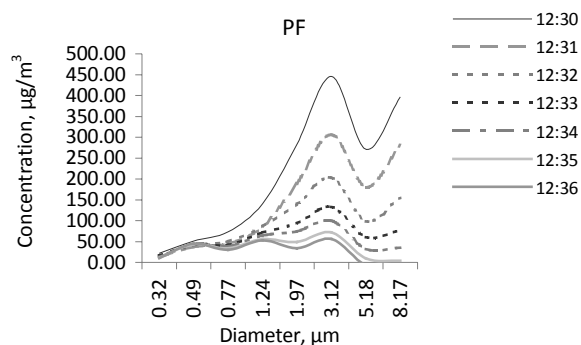


Fig. 9. Fractional distribution of PF fly ash in 2010 in high humidity conditions.

The difference in mass concentrations between the results from gravimetric analysis and automatic analysers for PF fly ash is due to the deposition of larger particles in the early stage of the experiment, which was not detected by automatic analysers. For both PF and CFB aerosols the total mass concentration was decreasing quickly due to deposition. The CFB aerosol has a higher content of finer-sized fractions than the PF aerosol. The resulting stable aerosol with a median diameter around 2 µm was formed during several hours. Therefore we can conclude that the fly ash from both combustions forms stable aerosols, which are prone to long-range transport. Evidence of long-range transport of persistent pollutants, including PAHs and heavy metals, absorbed onto fine particles has been reported in many studies [14,19]. The particulate matter with aerodynamic diameter less than 2.5 µm (PM 2.5) has been connected to the increase of cardiovascular mortality and the number of premature deaths in Estonia [20]. In Narva the decrease in life expectancy due to PM 2.5 is 0.5 years according to an earlier study [21].

Also significant amounts of ultrafine particles 0.5 µm in diameter were found. These particles could be more hazardous to human health as they can reach terminal bronchi and alveoli [22]. Studies that characterize the ultrafine aerosols from coal combustion illustrate that higher concentrations of hazardous and volatile elements occur in the ultrafine fractions than in either the coarse or fine fractions, with enrichments of up to 50 times observed for some elements [23].

Knowledge of the size distribution of fly ash particles is a useful tool for the calculation of dry deposition characteristics and modelling the dispersion of the formed aerosols.

## CONCLUSION

The properties and aging behaviour of fly ash aerosols originating from two technological processes of oil shale combustion (PF and CFB) were investigated in a

chamber study. The oil shale fly ash from the two different technological processes had similar properties and behaviour in the simulated atmospheric chamber studies.

The particle count data obtained from the aerosol sizing instruments showed that the CFB aerosol had a relatively higher content of finer fractions than the PF aerosol. The total settling time for fly ash particles with diameters less than 10 µm from both combustion technologies was several hours. It was also noted that particles larger than 4 µm in diameter deposited within a 2-h period, but particles of about 2 µm were still hovering after 4 h, although their concentration had decreased by a factor of 5.

The initial fly ash aerosol had a trimodal fractional distribution with aerodynamic diameters of 0.1–0.4 µm, 1.5 µm, and 4 µm. The highest concentration was measured for the particles with diameters around 4 µm, and high concentrations were determined also for particles with 2 and 3 µm diameters.

In high humidity (over 95%) conditions the size distribution of the particles was about the same, but the settling times of the particles were drastically shorter than in experiments made in normal humidity conditions.

Based on the experimental results, we can conclude that both the new CFB and the old PF technology can produce fine and stable aerosols when emitted into the atmosphere. Therefore they can pose a threat to human health within a long distance. Humid atmospheric conditions have a strong impact on the particle growth rate and increase the settling velocity of the whole aerosol.

## ACKNOWLEDGEMENTS

The authors are thankful to the authorities of Narva PP, Mr Arvo Tordik and Mr Aleksandr Pototski, who provided the representative fly ash samples needed for the experiment. Erik Teinmaa and Uuve Kirso gratefully acknowledge the support from the Estonian Science Foundation Programme INTROP (Exchange Grants 2558 and 2559). Gary Urb has been granted the Estonian Kristjan Jaak mobility grant.

## REFERENCES

1. Narva Power Plants, <https://www.energia.ee/en/power/oilshale/start> (visited 20-05-2011).
2. Savest, N., Oja, V., Kaevand, T., and Lille, Ü. Interaction of Estonian kukersite with organic solvents: a volumetric swelling and molecular simulation study. *Fuel*, 2007, **86**, 17–21.
3. Bauert, H. and Kattai, V. Kukersite oil shale. In *Geology and Mineral Resources of Estonia* (Raukas, A. and Teedumäe, A., eds). Estonian Academy Publishers, Tallinn, 1997, 313–326.

4. Bitjukova, L., Mõtlep, R., and Kirsimäe, K. Composition of oil shale ashes from pulverized firing and circulating fluidized-bed boiler in Narva thermal power plants, Estonia. *Oil Shale*, 2010, **27**, 339–353.
5. Ots, A. *Oil Shale Fuel Combustion*. Tallinna Raamatu-trükikoda, Tallinn, 2006.
6. Hotta, A., Parkkonen, R., Hiltunen, M., Arro, H., Loo-saar, J., Parve, T., Pihu, T., Prikk, A., and Tiikma, T. Experience of Estonian oil shale combustion based on CFB technology at Narva Power Plants. *Oil Shale*, 2005, **22**(4S), 381–397.
7. Teinemaa, E. The environmental fate of the particulate matter and organic pollutants from an oil shale power plant. PhD Thesis, University of Tartu, 2003.
8. Teinemaa, E., Kirso, U., Strommen, M. R., and Kamens, R. M. Deposition flux and atmospheric behavior of oil shale combustion aerosols. *Oil Shale*, 2003, **20**(3S), 429–440.
9. Teinemaa, E., Kirso, U., Strommen, M. R., and Kamens, R. M. Atmospheric behavior of oil shale combustion fly ash in a chamber study. *Atmos. Environ.*, 2002, **36**(5), 813–814.
10. Kirso, U., Laja, M., and Urb, G. Polycyclic aromatic hydrocarbons (PAH) in ash fractions of oil shale combustion: fluidized bed *vers* pulverized firing. *Oil Shale*, 2005, **22**(4S), 537–545.
11. Laja, M., Urb, G., Irha, N., Reinik, J., and Kirso, U. Leaching behavior of ash fractions from oil shale combustion by fluidized bed and pulverized firing processes. *Oil Shale*, 2005, **22**, 453–465.
12. Luan, J., Li, A., Su, T., and Li, X. Translocation and toxicity assessment of heavy metals from circulated fluidized-bed combustion of oil shale in Huadian, China. *J. Hazard. Mater.*, 2009, **166**, 1109–1114.
13. Realo, E., Realo, K., and Jõgi, J. Releases of natural radionuclides from oil-shale-fired power plants in Estonia. *J. Environ Radioactiv.*, 1996, **33**(1), 77–89.
14. Jalkanen, L., Mäkinen, A., Häsänen, E., and Juhanoja, J. The effect of large anthropogenic particulate emissions on atmospheric aerosols, deposition and bioindicators in the eastern Gulf of Finland region. *Sci. Total Environ.*, 2000, **262**, 123–136.
15. Querol, X., Alastuey, A., Lopez-Soler, A., Plana, F., Mantilla, E., Juan, R., Ruiz, C. R., and La Orden, A. Characterisation of atmospheric particulates around a coal-fired power station. *Int. J. Coal Geol.*, 1999, **40**(2–3), 175–188.
16. Plamus, K., Soosaar, S., Ots, A., and Neshumayev, D. Firing Estonian oil shale of higher quality CFB boilers – environmental and economic impact. *Oil Shale*, 2011, **28**(1S), 113–126.
17. Rattanavaraha, W., Rosen, E., Zhang, H., Li, Q., Patong, K., and Kamens, R. M. The reactive oxidant potential of different types of aged atmospheric particles: an outdoor chamber study. *Atmos. Environ.*, 2011, **23**, 3848–3855.
18. Lee, S., Jang, M., & Kamens, R. M. SOA formation from the photooxidation of [alpha]-pinene in the presence of freshly emitted diesel soot exhaust. *Atmos. Environ.*, 2004, **38**(16), 2597–2605.
19. Beyer, A., Mackay, D., Matthies, M., Wania, F., and Webster, E. Assessing long-range transport potential of persistent organic pollutants. *Environ. Sci. Technol.*, 2000, **34**, 699–703.
20. Orru, H., Teinemaa, E., Lai, T., Tamm, T., Kaasik, M., Kimmel, V., Kangur, K., Merisalu, E., and Forsberg, B. Health impact assessment of particulate pollution in Tallinn using fine spatial resolution and modelling techniques. *Environmental Health*, 2009, **8**, 7.
21. Orru, H., Maasikmets, M., Lai, T., Tamm, T., Kaasik, M., Kimmel, V., Orru, K., Merisalu, E., and Forsberg, B. Health impacts of particulate matter in five major Estonian towns: main sources of exposure and local differences. *Air Quality, Atmosphere & Health*, 2011, **4**(3–4), 247–258.
22. Siegmann, K., Scherrer, L., and Siegmann, H. C. Physical and chemical properties of airborne nanoscale particles and how to measure the impact on human health. *J. Mol. Struct. Theochem.*, 1998, **458**(1–2), 191–201.
23. Linak, W. P., Yoo, J. I., Wasson, S. J., Zhu, W., Wendt, J. O., Huggins, F. E., Chen, Y., Shah, N., Huffman, G. P., and Gilmour, M. I. Ultrafine ash aerosols from coal combustion: characterization and health effects. *P. Combust. Inst.*, 2007, **31**(2), 1929–1937.

## Põlevkivi põletamisel keevkiht- ja tolmpõletustehnoloogial tekkivate tahkete jäätmete kamberuuringud

Gary Urb, Erik Teinemaa, Richard M. Kamens, Uuve Kirso ja Toomas Tenno

Käesolevas töös uuriti põlevkivi põletamisel elektritootmiseks tekkiva lendtuha fraktsioonilist jaotumist ja käitumist ajas. Uuringud viidi läbi suurtes atmosfääriosakeste uuringute kambrites nii USA-s kui ka Eestis. Tuhaproovid pärinesid AS-i Narva Elektri jaamad kahel erineval tehnoloogial põhineva põletamisprotsessi viimastest elektrifiltritest. Katsetulemustena oli selgelt näha, et keevkihtpõletustehnoloogiast pärinevas lendtuhas on väiksemaid osakesi rohkem kui tolmpõletustehnoloogiast pärinevas lendtuhas. Uuritud tuhade fraktsioonilised jaotusomadused ja käitumine ajas olid suhteliselt sarnased. Mitmemodaalse jaotusega tuhaosakeste suurused olid enamasti vahemikus diameetriga 1–5 µm, hilisematel katsetel leiti märkimisväärne kogus neid ka diameetriga 0,5 µm. Enamik osakesi settis väga kiiresti, mõne tunniga, väiksemad olid aga stabiilsemad. Võib eeldada, et nendel osakestel on potentsiaal lenduda tuulega kaugemale. Eksperimendi tulemustest lähtudes võib väita, et osakeste lenduvuse ja jaotuse poolest ei ole keevkihttehnoloogia keskkonna seisukohalt parem kui tolmpõletustehnoloogia.