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DIOXIN IN WASTE-TO-ENERGY
IN THE BOILER AND BOILER ASH

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APPENDICES

1. PROJECT DETAILS

Project title	Dioxin in Waste-to-Energy In the boiler and boiler ash
Project identification	PSO project 10627
Name of the programme which has funded the project (ForskVE, ForskNG or ForskEL)	ForskEL
Name and address of the enterprises/institution responsible for the project	Ramboll Hannemanns Allé 53 DK-2300 Copenhagen S Denmark
CVR (central business register)	DK REG. NO. 10160669
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2. OBJECTIVE

The original project aims were to:

1. Develop and test a method of reducing the amount of fly ash and its toxicity, especially with regard to the dioxin content.
2. Develop and test a method to increase the recycling of residues from waste incineration plants by splitting the boiler ash in a clean and contaminated fraction. Especially according to dioxin and heavy metal contamination.
3. Develop the basis for the design of boilers for waste incineration plants so that dioxin formation is minimized and the amount of residue for disposal is limited.
4. Conduct full-scale verification of CFD model for dioxin formation in waste incineration boilers in order to achieve the calculation basis for design of boiler and extract systems of ash, so that the amount of residues and their dangerousness is limited.

The focus of the project was planned to be the design phase of incinerators where design improvements can be implemented. Ideally ash fractions from the boiler that are uncontaminated by dioxin and has low heavy metal content and thus have recycling potential, should be made available for extraction. Another purpose was to investigate whether it is possible to limit the amount of residual products to be exported and disposed of as hazardous waste in German salt mines or in the Langøya waste disposal site in Norway.

Due to the problems in obtaining representative flue gas samples of dioxin the project objective 4 about CFD model verification was left and replaced by a new objective described here:

4. Obtain detailed knowledge about the dioxin contamination of the different grain sizes of the boiler ash and study the influence of operational parameters on the dioxin formation and dioxin content in the boiler ash.

3. INTRODUCTION

The project is a continuation of two previous PSO projects; PSO 5784: Residues from waste incineration and PSO 7170: Survey and modeling of dioxin formation and decomposition mechanisms in combustion units with a view to improving residual product quality.

The project is based on previous knowledge about dioxin formation resulting in PSO project 7170, where it was shown that dioxin primarily is formed in a relatively small area in the superheater section at 400-450 ° C. This is illustrated in Figure 1, where the red area in the boiler indicates dioxin. This knowledge is coupled with knowledge of ash formation and inorganic ash quality in relation to the waste as documented in PSO project 5784. The information formed an improved basis for understanding the formation of dioxins in waste boilers and also examines the possibility of selectively blocks and handling boiler ash from individual ash extract points.

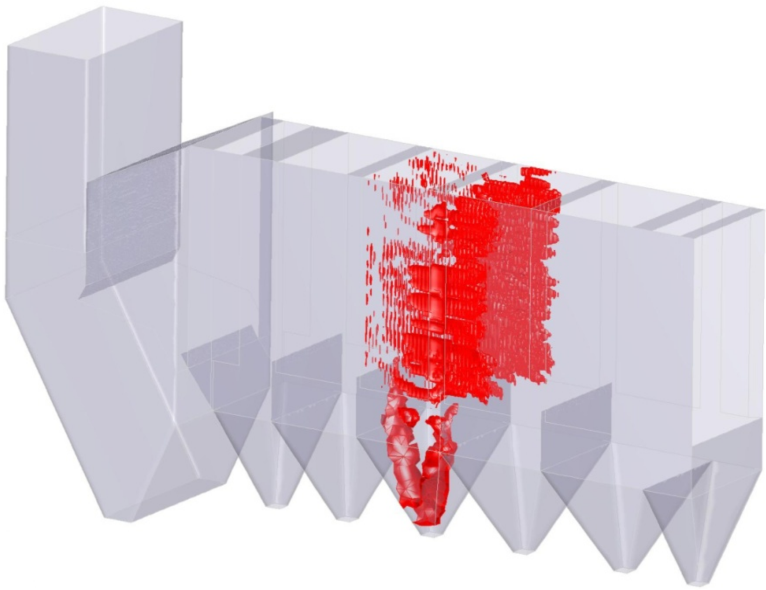

Figure 1 Dioxin formation in AffaldPlus' boiler determined from the CFD model that was developed in PSO project 7170

3.1 Project work streams

The project (2011-1-10627) is divided into two phases of full scale tests and subsequent sampling and four work streams:

<u>Sampling phase 1</u>

The main purpose is to get experience with the ash sampling since very limited experience exist. Furthermore the model results from previous work are tested in full scale.

<u>Sampling phase 2</u>

If phase 1 is successful phase 2 will be conducted with simultaneous boiler ash and flue gas sampling in the boiler. The results will be used in a detailed CFD model.

<u>Work stream 1: Boiler ash</u>

The main task is to conduct full-scale tests on the AffaldPlus facility line 4 with sampling of boiler ash underneath the ash hoppers in the convective parts (superheater section and economizer), and subsequently to determine the total content of heavy metals and dioxins, ash volumes and leaching characteristics in the ash in the various hoppers.

<u>Work stream 2: Dioxin in the flue gas and boiler ash</u>

Flue gas samples are taken in between the boiler tubes multiple places throughout the length of the boiler and analysed for dioxin and heavy metal content. Both ash and gas phase is sampled and analysed. Dioxins and furans are analysed and characterised in all its spices.

<u>Fase 3: Boiler ash particle size influence</u>

Dioxin analysis on different grain sizes in the solid samples and investigation on how dioxin distribute according to the grain size. The objective is to investigate the correlation between dioxin concentrations and grain size distribution in the ash samples. By selecting a few of the ash samples and sieving them to obtain subsamples with different particle size ranges and subsequently analysing for dioxin (PCDD) and furans (PCDF) this correlation can be investigated. If a simple particle size and dioxin formation correlation exists it would mean that a simple sorting of the ashes would enable an ash output with lower dioxin content. This phase was mainly conducted by the University of Umeå.

Work stream 4: Influence of operational conditions

An evaluation of the influence of operational conditions on ash production and dioxin concentration in the ash samples is carried out. The objective is to evaluate if certain operational conditions (which possibly can be controlled) lead to increased dioxin concentrations in the ash samples compared with the observed average. If such relation exists operators can be guided to minimise the dioxin "production", boilers can be designed to do the same or waste composition can be influenced. The ultimate goal is the same as the overall PSO project: To enable ash production with lower dioxin content. This phase was mainly conducted by Ramboll.

3.2 Organisation

Below an overview of the project organisation is found together with the main responsibilities of each project partner throughout the project.

Project Responsible

Ramboll Energy	Hannemanns Allé 53, 2300 Copenhagen S, Denmark
Project Manager	Christian Riber, Tlf.: +45 5161 8314, E-mail: ctr@ramboll.com
Project Participants	Dorthe Lærke Baun, Tore Hulgaard, Jens Adolphsen
Project responsibility	*Project Management and analysis of operational parameters*

Project partners

Umeå Universitet (Miljökemi)	Assistant Professor Stina Jansson
Project responsibility	*Analysis of dioxin and furans in all samples*
DTU Environment	Assistant Professor Thomas Astrup
Project responsibility	*Sampling and analysis of boiler ash (for heavy metals)*
FORCE Technology	Project Manager Ole Schleicher
Project responsibility	*Sampling of flue gas for heavy metals and dioxin*
Babcock & Wilcox Vølund:	Project Manager Kasper Lundtorp
Project responsibility	*Boiler modifications and knowledge*
AffaldPlus:	Operational Manager Tommy Fer
Project responsibility	*Plant operation and operational data*

4. SUMMARY OF EXPERIMENTS

4.1 Sampling phase 1

The sampling campaign was carried out in October 14th, 2011. Samples were taken from the bottom of the ten horizontal sections of the boiler of Line 4 of the AffaldPlus facility. Boiler ash was sampled for approximately 3 hours.

4.2 Sampling phase 2

The sampling campaign was carried out during three consecutive days: August 21st, 22nd and 23rd, 2012. Boiler ash samples were taken in the same locations as in phase 1 for approximately 5½ hours during DAY1 and DAY2, and 3 hours during DAY3. Flue gas samples were taken simultaneously with the boiler ash but in between the boiler tubes for a continues period between one and two hours in length.

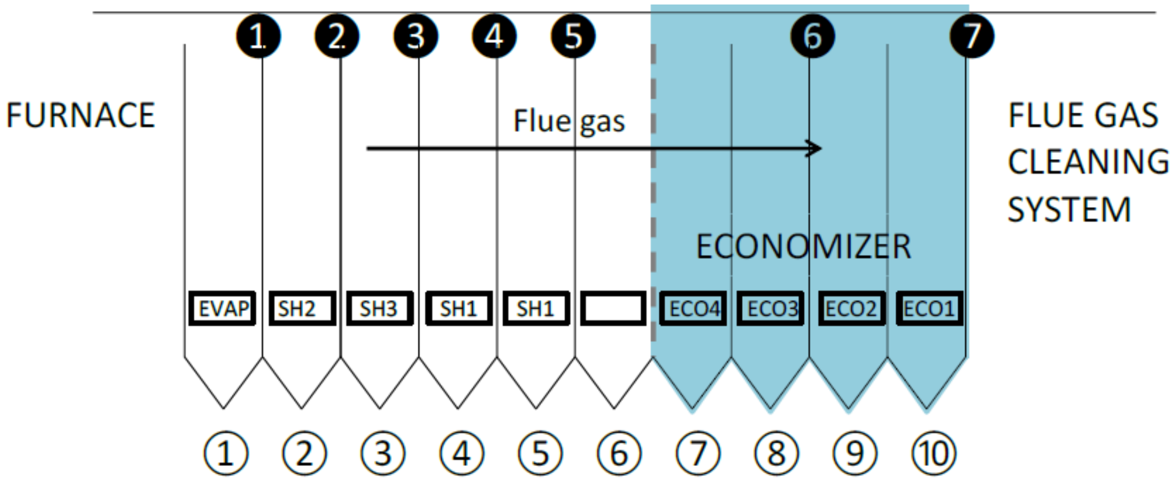

Figure 2 Scheme of the horizontal section of the boiler with flue gas (full black circles) and boiler ash sampling points (white circles). /From DTU Phase 1 report/

5. SUMMARY OF WORK DTU ENVIRONMENT

Participants: **Allegrini, Elisa; Boldrin, Alessio; Kruse, Susanne; Fruergaard Astrup, Thomas.**

DTU Environments task in the project included sampling and characterization of boiler ash produced at Line 4 of Næstved incineration plant. The overall aim of the work was to characterise the individual fractions of boiler ash produced at ten individual sections of the boiler in order to identify possible differences in terms of physical, chemical characteristics and leaching behaviour. The results of the study were meant as basis for possible optimisation of the boiler ash management, following a different classification of the material originating at different sections of the boiler.

DTU Environments employees were directly involved in the planning phase, in the sampling campaign and in the analytical activities. Two sampling campaigns were carried out for Phase 1 (one day sampling) and Phase 2 (three days sampling) of the project, where the production of ash along the boiler was quantified, and the collected samples were representatively mass reduced for the subsequent laboratory analyses. Samples from Phase 1 and 2 were additionally mass reduced and prepared in grain size fractions for Phase 3.

Samples were analysed for moisture content, grain size distribution, total content of inorganic elements and leaching behaviour. The leaching behaviour was assessed using a compliance leaching test for simple comparison with existing limit values and a characterisation leaching test in which the release of contaminants was observed at varying pH conditions. The samples were also provided to Umeå University for analysis of PCDD and PCDF. The results of all chemical analyses (including PCDD and PCDF) were elaborated through Pearson's correlation analysis together with key operations plant parameters.

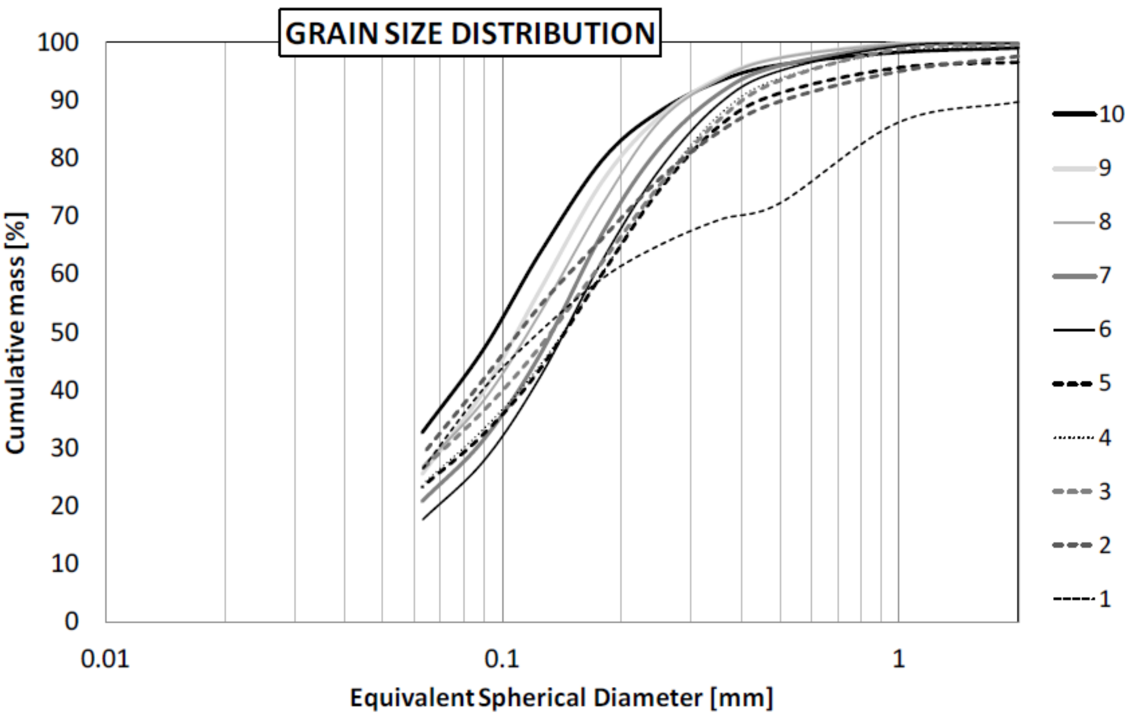

Figure 3 Grain Size Distribution of the ashes produced at different sections. Average of the results from the analysis of the samples from phase 2 DAY1, DAY2 and DAY3.

The results of the analyses did show some differences between samples in terms of total physical characteristics, chemical composition and leaching behaviour. However, overall differences were not significant and a different classification and subsequent management of the individual fractions of the boiler ash could not be supported.

The results of the study were published in the Journal of Hazardous Materials, in the proceedings to the 4th International Symposium on Energy from Biomass and Waste (VENICE 2012), and in two internal reports where detailed procedures and results were reported for Phase 1 and Phase 2 of the project. Part of the results was included in the PhD Thesis of Allegrini Elisa at DTU Environment. All documents are included in appendix.

6. SUMMARY OF WORK BY UMEÅ UNIVERSITY

Participants: **Stina Jansson**, Department of Chemistry

Phase 1 only included ash samples. These were collected from the ten sections of the boiler. The concentrations in the different sections were quite similar for polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF). The concentrations in the first sections (closest to the boiler) were notably low and in some cases close to blank levels. The highest concentrations of PCDDs and PCDFs were found in the last sections, peaking in section 8. The concentrations then decreased somewhat downstream of this section, and for the PCDDs this decrease was particularly notable. Possible explanations for this observation may be adsorption to surfaces in the duct and/or funnels, dechlorination reactions, or substitution reactions occurring at these temperatures which alter the chemical structures of the dioxins and furans (PCDD/F), e.g. by bromine or other substituent addition.

The temperatures in the boiler were, from a dioxin formation perspective, high over several sections and not until section 9 the flue gas reached temperatures below 300°C, which may be considered as a lower temperature limit of PCDD and PCDF formation. Therefore almost the entire investigated range, (i.e. the sampled sections) may be considered to be within the active window of PCDD and PCDF formation, and the risk of sampling artifacts affecting mainly the flue gas samples and to a lesser degree also the ash samples could not be neglected.

In **Phase 2**, a clear domination of furan formation over dioxin formation was observed in the flue gas samples, which is generally said to be an indication of de novo-type formation, i.e. formation mainly involving carbonaceous materials in the ash matrix. Overall, the PCDD congeners contributed to a much higher degree to the TEQ concentrations; 53-72% from PCDD compared to 28-47% from PCDF congeners. This was to some extent related to the TEF values which are for several congeners higher for the PCDDs than for PCDFs.

The homologue profiles of PCDDs displayed a shift from the high temperature sampling locations and downstream, and the last sampling locations were mainly composed of the higher chlorinated homologues (Hx- to OCDD). This increase in chlorination degree might be the result of chlorination reactions transforming the existing CDDs into higher chlorinated ones, or alternatively specific formation of higher chlorinated CDDs from e.g. highly chlorinated precursors such as phenols and/or benzenes. This shift in chlorination degree was not observed for the PCDFs, at least not to the same extent.

In **Phase 3** we analysed sieved ash samples collected in Phase 1 and Phase 2. The samples were prepared by sieving the samples into three grain size fractions; >0.355 mm (fraction A); 0.355-0.09 mm (fraction B) and <0.09 mm (fraction C). The mid-size fraction was the largest fraction and constituted 50-60% of the total sample, followed by the smallest fraction (35-41%). The coarse fraction was the smallest, representing only 5-10% of the sample. For a selection of the samples the ashes from specific sections were combined in pairs (sections 1-2, 3-4, 5-6, 7-8, and 9-10). Interesting to note is that the TEQ concentrations in the coarse fraction (>0,355 mm) of sections 1-6 were very low, both in ng/g of ash and normalized to daily ash production. In general, the highest TEQ concentrations were found in the finest fraction. The low concentrations of TEQs, PCDFs and PCDDs in the coarse particles may be related to their weight since they would descend quicker than the smaller particles in the hoppers. Possibly a rapid descend in the hoppers might make the coarse particles enter a temperature range below the temperature range in which PCDFs and PCDDs are formed, which would result in the low or non-detectable levels.

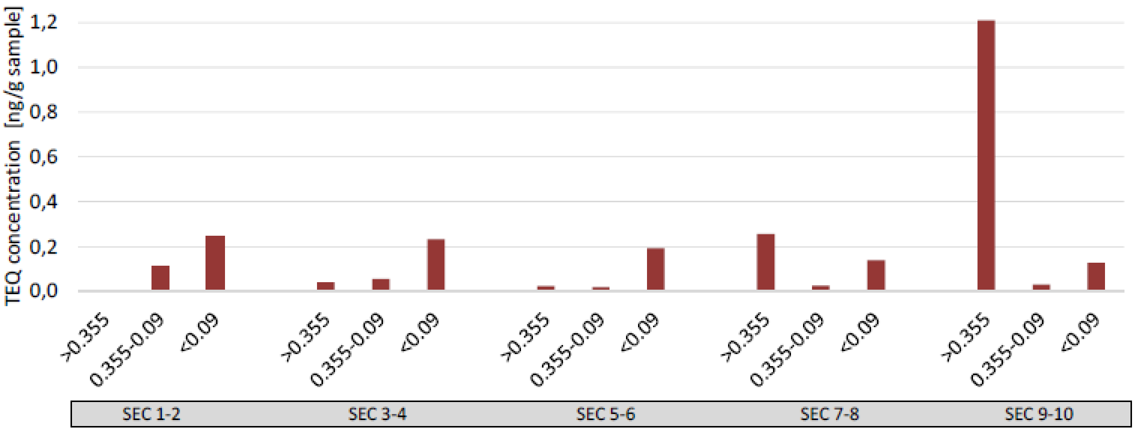

Figure 4 TEQ (toxic equivalent) concentrations (based on the 2005 WHO-TEFs) in the sieved ashes from Phase 2. Concentrations are expressed as ng TEQ / g of ash.

The coarse particles in the first six sections of the boiler appeared to be non-toxic with regard to dioxin-induced toxic responses (indicated by TEQ concentrations), but also almost free from PCDFs and PCDDs when considering the full homologue concentrations. Even though the total mass of the coarse fraction (>0.355 mm) in this boiler is relatively small, this is still a very important finding which might allow separation and alternative handling of such a “clean” fraction. Furthermore, since the mid-size fraction is this study covers a quite wide range (0.355-0.09 mm) a continuation of this research could be to divide the mid-size fraction into sub-fractions to determine whether the coarse, non-toxic fraction could be handled separately and potentially be mixed with the bottom ash.

7. SUMMARY OF WORK BY B&W VØLUND

Participant: **Kasper Lundtorp**

The following sampling points were produced and installed by B&W Vølund for use in the flue gas sampling campaign:

1. Between Evaporator and Super Heater 2 (SH2)
2. Between Super Heater 2 (SH2) and Super Heater 3 (SH3)
3. Between Super Heater 3 (SH3) and Super Heater 1A (SH1A)
4. Between Super Heater 1A (SH1A) and Super Heater 1B (SH1B)
5. Between Super Heater 1B (SH1B) and the Economiser
6. In the middle of the Economiser
7. After the Economiser at boiler exit

8. SUMMARY OF WORK BY FORCE TECHNOLOGY

Participant: **Ole Schleicher**

During **Phase 2** flue gas samples were taken from the boiler ports made by B&W Vølund. Dioxin sampling was performed isokinetic according to CEN standard EN 1948 Part 1 on sampling. Particle bound dioxin was collected on a filter and gaseous dioxins accumulated in an adsorbent (XAD). All the components of the sampling device which come into contact with the flue gases were made of glass. The sample was mixed prior to analyses hence it was not possible to distinguish between particle bound dioxins and gaseous dioxins.

It was concluded based on the analytical results that some dioxin formation probably took place in the sampling equipment. Hence measured flue gas dioxin concentrations were overestimated and thereby not representative to the flue gas. In the future actively cooled equipment should be developed to allow dioxin sampling in very hot flue gases.

9. SUMMARY OF WORK BY RAMBOLL

Participants: **Dorthe Lærke, Tore Hulgaard, Jens Adolphsen** and **Christian Riber**

The main objective of work by Ramboll was to investigate how the formation of dioxins, collected in boiler ash and flue gas samples correlates with different operating parameters of the facility. The activities include investigation of:

- Distribution and mass flow of PCDD/Fs in each of the boiler ash hoppers compared to the distribution and mass flow of the boiler ash.
- Possible correlations between mass flow of PCDD/F in the boiler ash with the flue gas flow and the respective mass flows of SO_2 and HCl in the flue gas.
- The effect of combustion conditions (CO-level) on the content of PCDD/F in boiler ash and flue gas, respectively.
- Possible correlations between PCDD/F flow in the flue gas samples with the flue gas flow and the respective mass flows of SO_2 and HCl in the flue gas.
- Possible correlations between PCDD/F flow in the flue gas and the dioxin content in boiler ash.

Boiler ash production rates vary in the AffaldPlus facility line 4 from 410-590 kg/day and the distribution throughout the boiler is documented with the highest production rate in the hopper just before the economiser (section 7) with an average production rate of 90 kg/day during the tested conditions.

Sampling of boiler ash from each of 10 boiler sections of the horizontal pass on three separate days reveals:

The mass flow of boiler ash from each hopper varies between 5 and 18% of the total mass flow with boiler ash of the economiser of section 7 and 10 being highest as shown in Figure 5. The mass flow of dioxin (TEQ) in each boiler section varies between 5 and 20% of the total dioxin mass flow with boiler ash, being lowest in section 3-6. Whereas the mass flow is relatively high all days in section 7, section 1, 2, 8, 9 and 10 has remarkable differences between the three test days.

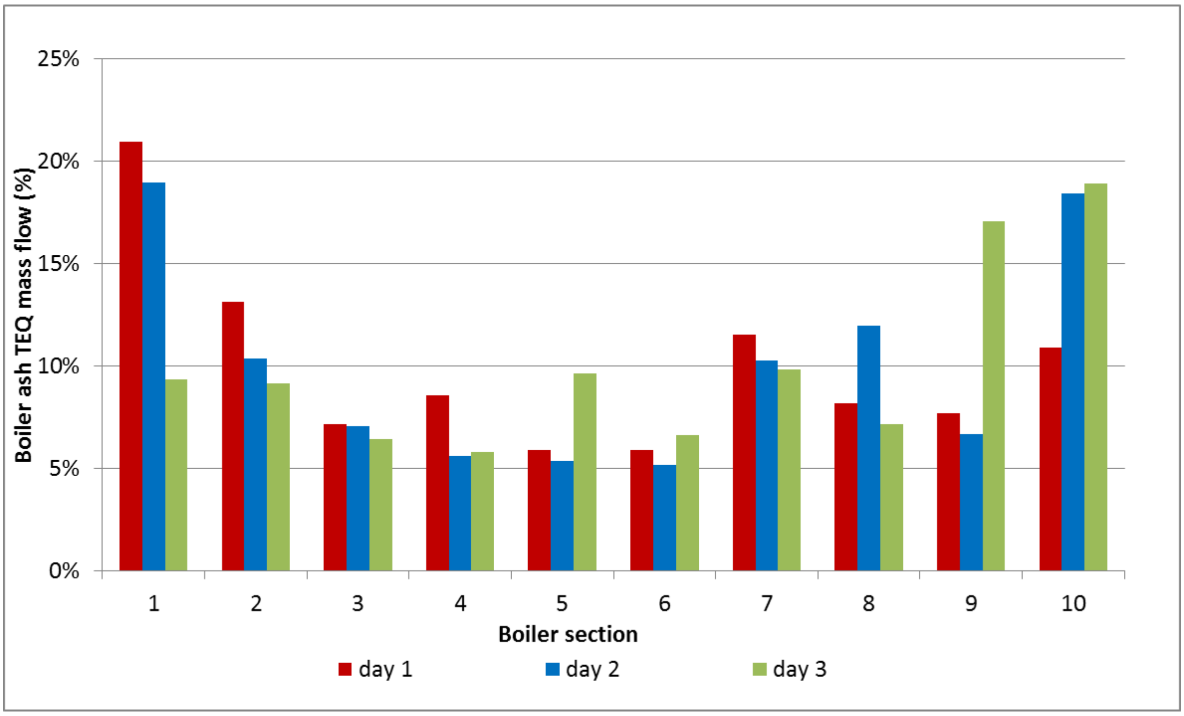

Figure 5 Relative distribution of TEQ mass flow in the boiler ash along the horizontal sections of the boiler.

No correlation is found between the dioxin mass flow in the boiler ash and the flue gas flow rate, the mass flow of HCl or the mass flow of SO_2. The variation has probably been too small.

No significant effect of combustion conditions (CO level) on the content of PCDD/F in boiler ash and flue gas was found, probably because of generally a low CO level with few and small CO peaks all three test days.

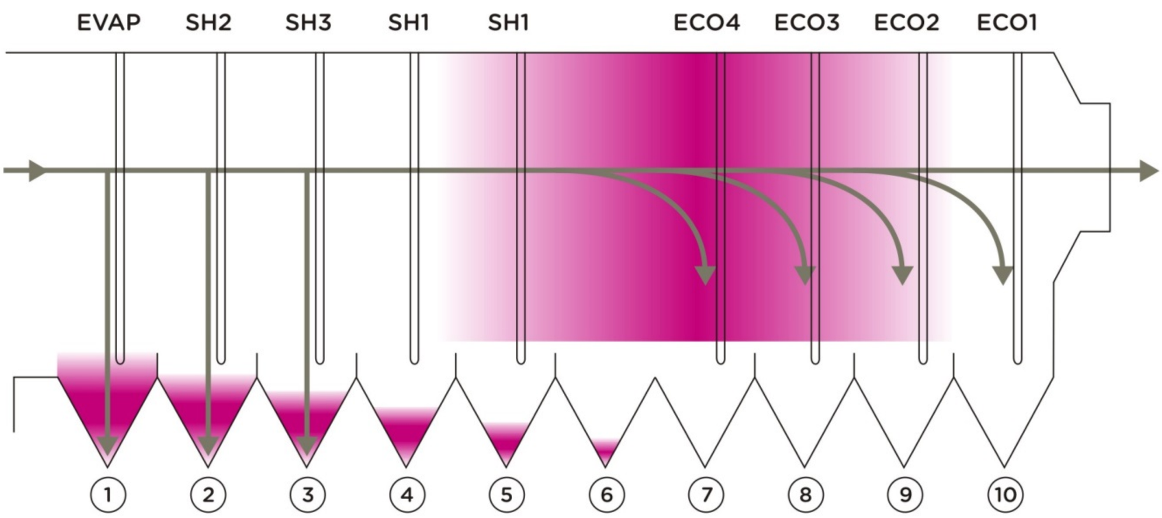

Figure 6 Dioxin formation zones in the boiler (red) and recognised particle paths (gray) for the AffaldPlus boiler line 4 under the tested conditions.

No correlation was found between PCDD/F flow in the flue gas samples and the flue gas flow or the respective mass flows of SO_2 and HCl in the flue gas.

Two dioxin/furan production zones are believed to exist in the boiler; 1) at cold surfaces in the bottom part of the first boiler sections, 2) in the flue gas at the end of the superheater and in the beginning of the economizer. The two zones are indicated in Figure 6 above. From the results it looks like that the first zone produces predominantly furans and the second predominantly dioxins however in toxicity terms they are equal in terms of both concentrations and mass flow. This corresponds very well with the findings in the CFD modelling in the first PSO project shown in Figure 1 and hence the two studies mutually supports the findings.

Approximately 90 % of the mass flow of PCDD/F (TEQ) leaves the boiler with the flue gas and roughly 10 % leaves as boiler ash, most of which is expected to be adsorbed/condensed on the surfaces of the fly ash particles entrained within the flue gas. The dioxin concentrations of the three test days varying between 0.3 and 0.43 ng/Nm^3 at the boiler exit represent relatively low levels.

It appears that the dioxin mass flow with the flue gas at the boiler exit is inversely correlated to the mass flow in the last boiler sections. The flue gas mass flow is highest on the test days where the mass flow is relatively low in boiler section 9 and 10, and vice versa.

10. UTILIZATION OF PROJECT RESULTS

The project conclusions will be used in future boiler design considerations when designing for low dioxin toxicity production and further research into the mechanisms of dioxin and furan production in full scale waste to energy boilers.

The project results have been presented at:

- Elisa Allegrini, Resource recovery from waste incineration residues, Fourth International Symposium on Energy from Biomass and Waste, Venice Oct. 2012.
- Baun, D.L., Dioxin Generation and Regeneration in Modern Energy Recovery Plants, ISWA 6th Beacon Conference on Waste-to-Energy , Malmö Nov. 2009

Further project presentation is planned for:

- 14th International Congress on Combustion By-Products and Their Health Effects, (PIC2015) which is held here in Umeå in June 14-17th 2015
  and/or
- 35th International Symposium on Halogenated Persistent Organic Pollutants, (Dioxin 2015) in Sao Paolo, Brazil, August 23-28th 2015
  and/or
- ISWA 9th Beacon Conference on Waste-to-Energy , Malmö, November 2015

11. PROJECT PUBLICATIONS

The project has been published in the following scientific journals and other technical literature:

- Elisa Allegrini et al. / Journal of Hazardous Materials 270 (2014) 127–136

- Elisa Allegrini, PhD Thesis, Resource recovery from waste incineration residues, November 2014, DTU Environment

Further publication has been planned for:

- Waste Management, http://www.journals.elsevier.com/waste-management
  And/or
- Environmental Science & Pollution Research, http://www.springer.com/environment/journal/11356
  And/or
- Biopress http://www.biopress.dk/forside
  And/or
- Teknik & Miljø, Stads - og havningeniøren, http://www.ktc.dk/teknik-miljoe/om-teknik-miljoe/