TNA User Report

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Project title	Emission factors and formation of secondary aerosols related to sugar cane harvesting using field fires.
Name of the accessed chamber	ILMARI
Number of users in the project	4
Project objectives (max 100 words)	Open biomass burning is one of the largest sources of aerosols and organic gases into the atmosphere, amongst others climatic effective black carbon (BC). It has to be anticipated that agricultural workers and villagers are strongly affected by hazardous particles and gases emitted directly from the fires, but also from formation of secondary organic aerosol (SOA) causing adverse health effects. The main objective of the study is to investigate sugar cane combustion and its potential of SOA formation. Harvesting of sugar cane by burning leaves is a major source of air pollution in many countries of Africa, Asia and South America.
Description of work (max 100 words):	Emission factors and formation of secondary aerosols from sugar cane burning' including the transformation processes, that are taking place during ageing, were simulated in the aerosol physics, chemistry and toxicology research unit (ILMARI) of the University of Eastern Finland. A special designed combustion device reflecting open fire burnings was used as combustion source. The experiments were started by filling the chamber with a pre-diluted sample. After stabilization and mixing in the chamber, oxidants (O_3) were injected into the chamber. Aerosol was aged either under UV light or by dark ageing. The experiments were studied with online measurement devices as well as by collecting VOC and SVOC samples during the ageing process.

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[1] Physics; Chemistry, Earth Sciences & Environment; Engineering & Technology; Mathematics; Information & Communication Technologies; Material Sciences; Energy; Social sciences; Humanities.
[2] UNI= University and Other Higher Education Organisation;
RES= Public Research Organisation (including international research organisations and private research organisations controlled by public authority);
SME= Small and Medium Enterprise;
PRV= Other Industrial and/or Profit Private Organisation;
OTH= Other type of organization.
[3] UND= Undergraduate; PGR= Post graduate; PDOC= Post-doctoral researcher; RES= Researcher EXP= Engineer; ACA= Academic; TEC= Technician.
[4] Reproduce the table for each user who accessed the infrastructure

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New user	YES

Trans-National Access (TNA) Scientific Report

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Instructions

Please limit the report to max 5 pages, you can include tables and figures. Please make sure to address any comments made by the reviewers at the moment of the project evaluation (if applicable, in this case you were informed beforehand). Please do not alter the layout of the document and keep it in Word version. The report will be made available on the eurochamp.org website. Should any information be confidential or not be made public, please inform us accordingly (in this case it will only be accessible by the European Commission, the EUROCHAMP-2020 project partners, and the reviewers). Please include:

- Introduction and motivation
- Scientific objectives
- Reason for choosing the simulation chamber/ calibration facility
- Method and experimental set-up
- Data description
- Preliminary results and conclusions
- Outcome and future studies
- References

Name of the PI: Dr. Jürgen Orasche
Chamber name and location: ILMARI, University of Eastern Finland, Kuopio
Campaign name and period: Emission factors and formation of secondary aerosols related to sugar cane harvesting using field fires (27.05.2019 – 08.06.2019)

Introduction and motivation

Open biomass burning is one of the largest sources of aerosols and organic gases into the atmosphere. It is a large source of climatic effective black carbon (BC) and causes adverse health effects. In many developing or newly industrialized countries agricultural fires are very common for pre- or post-harvesting. The sugar industry is one of the big purchasers of agricultural products in Africa, Asia and South America. Several millions of hectares are needed to grow sugar cane worldwide – similar quantities as for oil palms. Harvesting of sugar cane is done mainly by hand. Workers burn the dry parts of the plants; the stem remains unburnt and is cut by the workers with machetes. During harvesting landscape is deeply impacted by haze events caused by the huge and harsh fires. These hazes show

similarities to "Beijing haze" events, even on rural areas. The biomass combustion plumes spread widely through the areas. Studies about the effects of such massive agricultural fires are very rare. It has to be anticipated that workers and villagers are not only affected by hazardous particles and gases, but also from a high potential of secondary organic aerosol (SOA) formation by precursors. Expected precursors are e.g. huge quantities of cresols (e.g. Schauer et al. 2001), but also other mono-aromatics, almost exclusively in the gas phase. Those aromatics have a high SOA formation potential. Studies from wood combustion (Heringa et al. 2011) showed that SOA formation can more than triple the amount of organic aerosols. It is not known yet how high the impact of pollution due to sugar cane burning has to be assigned. This is the main objective of the study next to identification and quantification of key compounds.
First, the determination of emission factors of sugar cane burning in realistic but controlled lab experiments was aimed. Second, the formation potential of SOA was investigated by introducing emissions into the ILMARI smog chamber. Third, the chemical and physical characterization of primary and secondary organic aerosol as well as their inorganic composition will be determined from samples collected during the campaign. Beside polycyclic aromatic hydrocarbons (PAH), alkylated and oxygenated PAH, phenols, polyphenols and many other compound classes will be investigated. Subsequently, general health relevant factors, e.g. TEQ values can be calculated for PAHs. Identification of unknown substances will be done e.g. with GCxGC-High Resolution-Time of Flight-Mass Spectrometry.

Scientific Objectives

1. Determination of emission factors of sugar cane burning (POA).
2. A comprehensive characterization of sugar cane combustion aerosols.
3. Determination of the SOA formation potential.
4. Determination of the emission factors related to POA and SOA.
5. Study the changes in the profile of chemical species and sugar cane combustion aerosol properties during aging.
6. Study the influence of ageing on key properties of combustion emissions.
7. Identification of important ageing products and their linkage to respective precursors.

Reason for choosing the simulation chamber

The ILMARI facility at the UEF has a unique infrastructure which enables us to

- assess all parameters of the combustion process at the same time - a complete physicochemical analysis of the emissions both online and offline
- assess all parameters of the ageing process - a complete physicochemical analysis

This multidisciplinary scientific research project needed multiple approach methods (e.g. combustion unit, dilution of emissions, aging, comprehensive physical and chemical analysis) to take full advantage of the research results. Those resources were completely available at the ILMARI Research Unit. The project needs expertise in preparing and running the combustion experiments reflecting open fire burnings of sugar cane as well as running the chamber experiments, and specific instruments (gas monitors, particle sizing units, aethalometers), as well as the combustion sources.

Method and experimental set-up

We used an open combustion device to reflect open fire burnings. The sugar cane leaves came from two different sites from South Africa, one from coastal site from Kearsney (tropical climate) and the other one from the Midlands (subtropical climate). Sugar cane leaves were burned batch wise 5 times 30 grams within 15 minutes. The leaves were packed very loose within a special designed cage and lighted with a lighter. With a low dilution ratio of 1:6, aerosol was cooled and semi-volatile products were allowed to condense on particles.

Transformation of emissions which are taking place during aging, was simulated in the aerosol physics, chemistry and toxicology research unit (ILMARI) of the University of Eastern Finland (https://www.eurochamp.org/Facilities/SimulationChambers/ILMARI.aspx). It includes a 29 m3, air-conditioned FEP Teflon chamber with UV lights, humidification systems and ozone generators.

Five minutes after chamber feeding d9-Butanol was injected and after 10 min of mixing of aerosol in the chamber filter and gas phase sampling was started to collect aerosol from primary emissions – in parallel primary emission were measured online with Aerosol Mass Spectrometer (AMS), Aethalometer, FTIR and gas monitors (NOx, CO, O_3). Particle mass (TEOM) and size distribution (SMPS) were measured as well. The primary emissions (filter and gas phase samples) will be analysed by GC-MS and elemental composition will be done by ICP-MS and/or ICP-OES.

After stabilization and mixing in the chamber, oxidants (O_3) were injected into the chamber. Three different scenarios were studied:

1. The UV lights were switched on and the aerosol was aged under UV light for 4 h representing approx. 1 day of atmospheric ageing after sugar cane harvesting after dawn.
2. The UV lights were switched on and the aerosol was aged under UV light for 3 h, two further batches of fresh exhaust aerosol (2 times 30 grams leaves were burned) were introduced to the chamber. After 25 minutes lights were turned off and three hours of dark ageing followed. Those experiments should represent sugar cane harvesting in the morning and evening hours.
3. The UV lights were switched on for 30 minutes before dark ageing was started. Those experiments should represent sugar cane harvesting before dusk.

Chemical and physical properties of the aerosols during the ageing process were measured using on-line measurements of aerosol concentration and size distribution (SMPS), black carbon (Aethalometer), NO_x, CO, O_3, chamber RH, and T measurements. Offline molecular speciation with comprehensive mass spectrometry based techniques as well as quantification of important target compounds will be done from collected samples with IDTD-GC-MS (e.g. PAH, phenols, carbonyls, multifunctional acids, etc.). Identification of unknown compounds will be done with High Resolution-TOF-MS or FTICR-MS.

The offline samples which were collected during the experiments are not analysed so far. Therefore the following description of data and preliminary results is just related to online instruments which were operated as described before.

Data description

A soot particle aerosol mass spectrometer (SP-HR-ToF-AMS ; Aerodyne Research Inc.) measured changes in mass concentrations, chemical compositions and size of submicron species during the aging process in the simulation chamber. Two vaporizer configurations, i.e., dual laser and tungsten vaporizers and tungsten vaporizer only modes, were alternated every 120 s; particle time-of-flight (PTOF) modes were operated for 20 s/min. The primary emissions (filter and gas phase samples) will be analysed by GC-MS and elemental composition will be done by ICP-MS and/or ICP-OES. The aged aerosols will also be analysed by GC-MS. Therefore two different approaches will be applied. Gas samples were collected on graphitized carbon black adsorber which will be thermally extracted with a Thermal-Desorption-GC-MS (TD-GC-MS). Filter samples will be analysed using IDTD-GC(xGC)-MS. With this unique method polar and non-polar compounds can be analysed within one measurement due to in-situ derivatization with MSTFA [Orasche et al. 2011]. This will allow us to identify and quantify specific sugar cane combustion tracers – in particular due to the expected high fraction of polar organic combustion products. It will also allow the observation of formation of secondary organic aerosols (identity and quantity). Additional measurements will be done with IDTD-GCxGC-MS for the automated profiling of two-dimensional gas chromatography-time-of-flight mass spectrometry data of SOA.

Preliminary results and conclusions

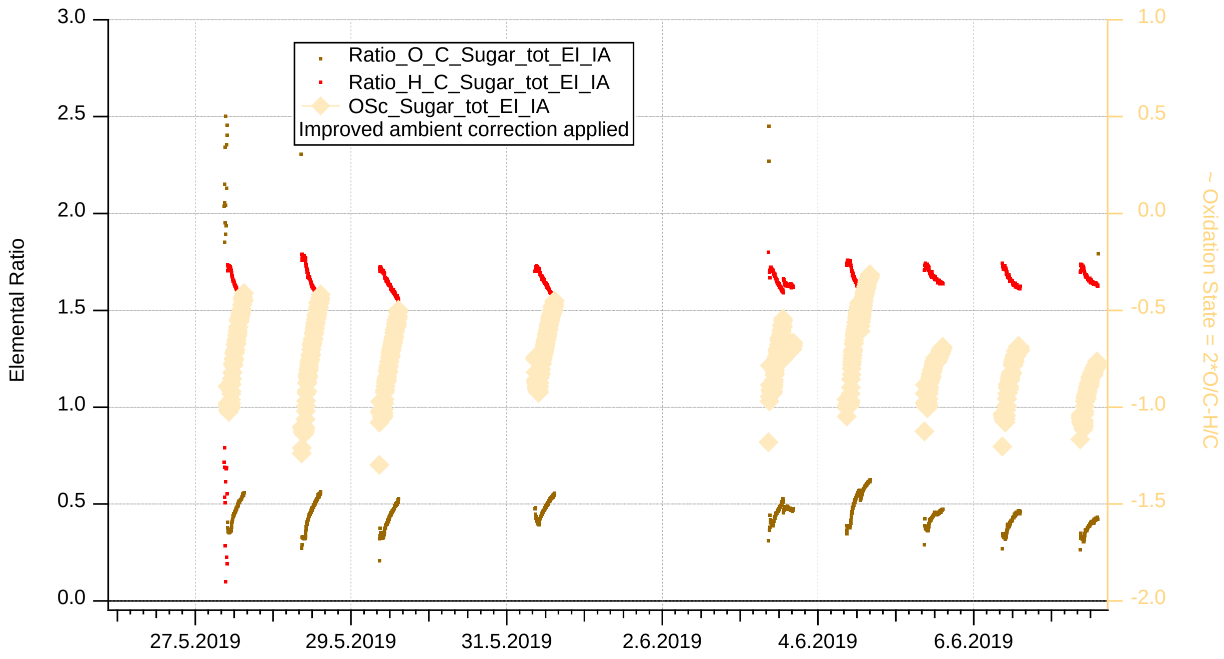

Figure 1 a): OA elemental composition shown for all experiments.

Figure 1a shows the increasing O/C-values and Carbon Oxidation States (OSc) as measures of oxidative ageing for all experiments which were done in the frame of this EUROCHAMP study.
Van Krevelen diagrams are used to show H/C ratio as a function of O/C ratio. They have been used to deduce oxidation reaction mechanisms for organic aerosols (Fig. 1b).

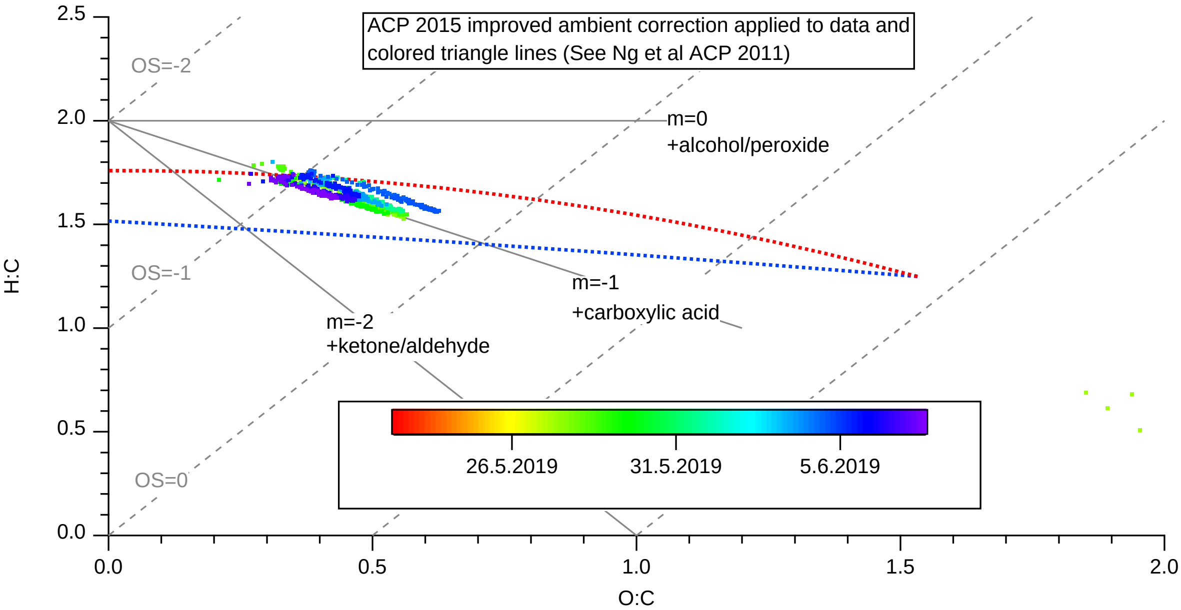

Figure 1 b): van Krevelen diagram throughout sugar cane measurement campaign 2019. The improved-ambient method was applied for the elemental analysis.

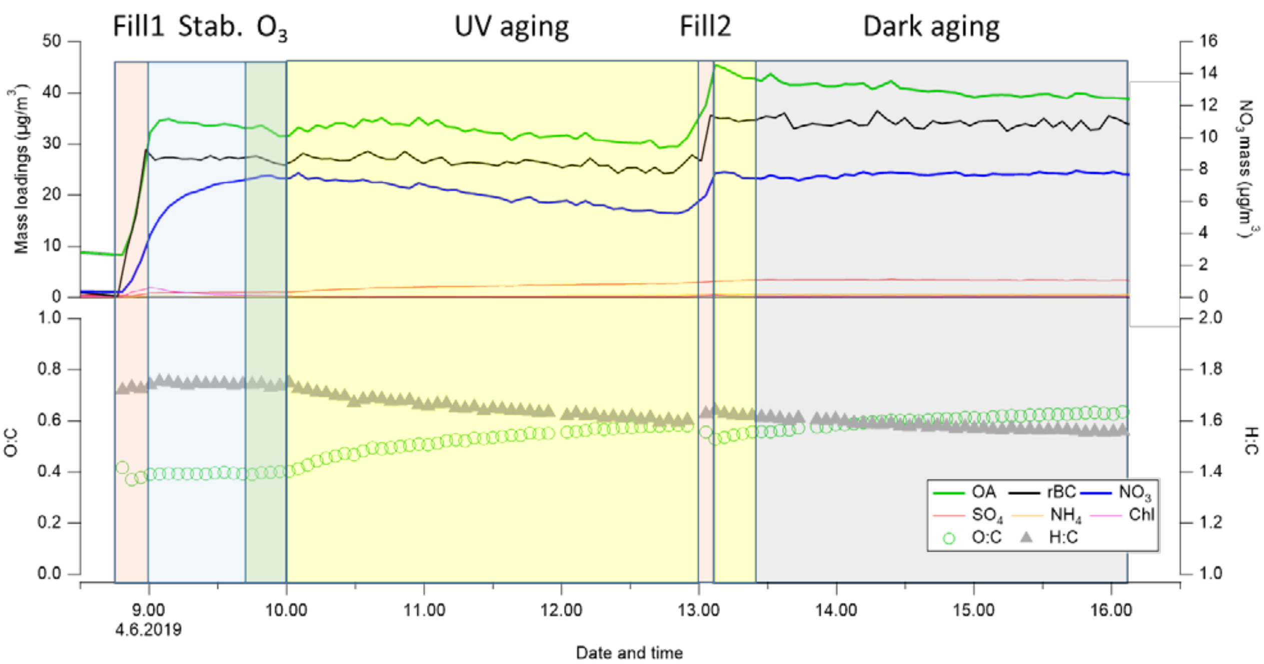

Figure 2 a): Evolution of aerosol composition during UV and dark aging in the ILMARI chamber (Exp.6: 4.6.2019) measured by AMS. No wall loss corrections were applied so far.

In figure 2 the complete time plot for one experiment (UV light ageing 3 h (5 x 30 g sugar cane leaves from Kearsney) + dark ageing 3 h (added fresh aerosols 2 x 30 g sugar cane leaves from Kearsney)), is shown by AMS data (Fig. 2a) and Aethalometer data (Fig. 2b). Both instruments indicate the formation of SOA during UV ageing and dark ageing, too. AMS measurements showed also the formation of sulfates during UV ageing.

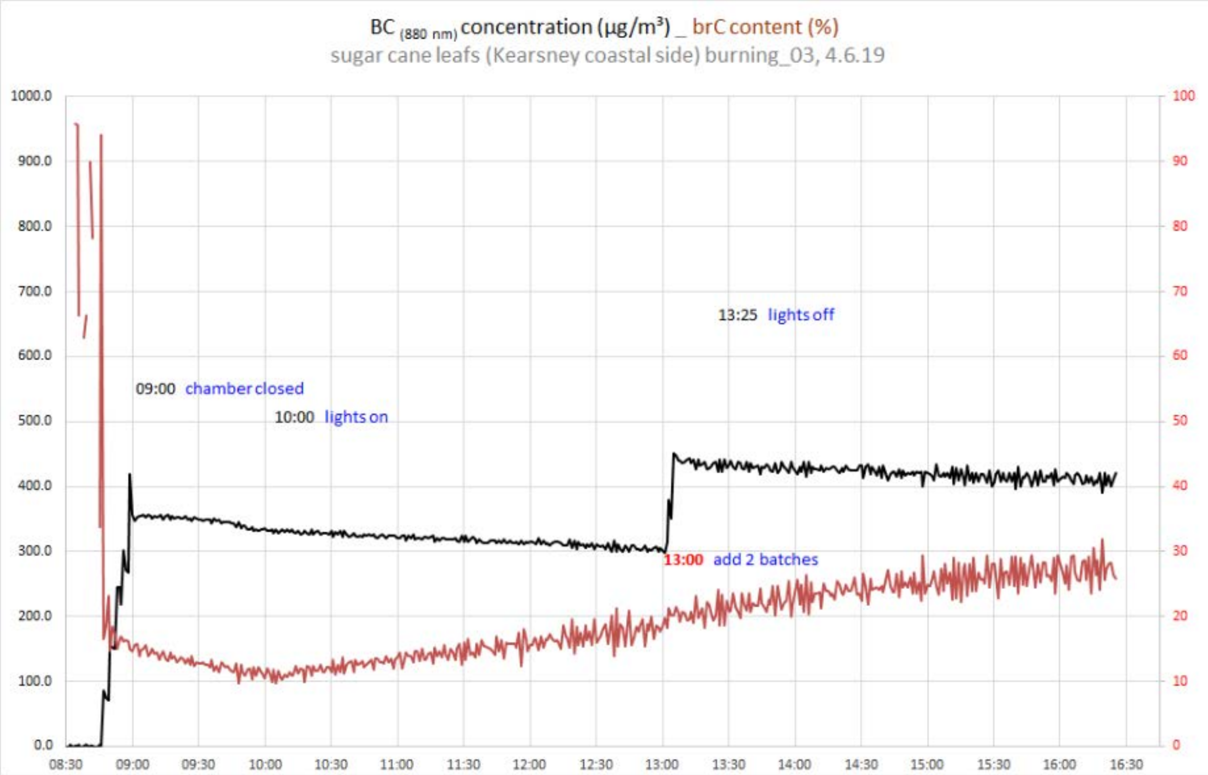

Figure 2 b): BC and brC measured by Aethalometer for the same experiment. No wall loss corrections were applied

Outcome and future studies

Transformation of sugar cane emissions during aging was investigated simulating diurnal emissions profile changes in Southern Africa including dark aging (night-time). Clear differences could be detected between fresh and aged emissions. The first results from online measurements are very promising in regard of chemical ageing. Thus data from these measurements will be compared with more detailed chemical analyses from filter sampling. The measurements in the laboratories will be done soon to prepare a scientific publication from the results of this study.

References

Heringa, M. F., et al. (2011). "Investigations of primary and secondary particulate matter of different wood combustion appliances with a high-resolution time-of-flight aerosol mass spectrometer." Atmos. Chem. Phys. **11**(12): 5945-5957.

Orasche, J., et al. (2011). "Technical Note: In-situ derivatization thermal desorption GC-TOFMS for direct analysis of particle-bound non-polar and polar organic species." Atmospheric Chemistry and Physics **11**: 8977-8993.

Schauer, J. J., et al. (2001). "Measurement of Emissions from Air Pollution Sources. 3. C_1-C_{29} Organic Compounds from Fireplace Combustion of Wood." Environmental Science & Technology **35**(9): 1716-1728.