# Investigation of polycyclic aromatic hydrocarbons and soot formation in swirled flames of *n*-butanol and conventional diesel fuel

L. D. Ngo[1,2], C. Irimiea[1,2,3], A. Faccinetto[1], N. Nuns[4], Y. Carpentier[1], C. Focsa[1], E. Therssen[2]

[1] Univ. Lille, CNRS, UMR 8522 – PC2A – Physicochimie des Processus de Combustion et de l'Atmosphère, F-59000 Lille, France
[2] Univ. Lille, CNRS, UMR 8523 – PhLAM – Laboratoire de Physique des Lasers Atomes et Molécules, F-59000 Lille, France
[3] ONERA – The French Aerospace Laboratory, F-91123 Palaiseau, 91120, France
[4] Univ. Lille, CNRS, INRA, Centrale Lille, ENSCL, Univ. Artois, FR 2638 – IMEC – Institut Michel-Eugène Chevreul, F-59000 Lille, France

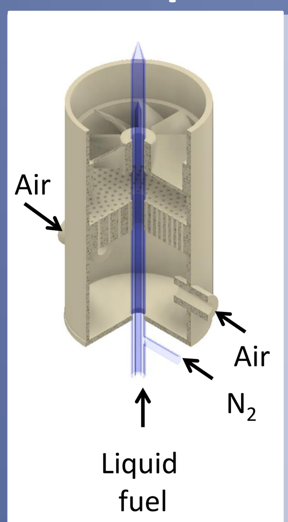
## Context

With the explosion of the worldwide population, the increase of average living standards and the development of technologies, the demand on energy, especially on fossil fuels, has increased day by day. Hazardous effects of particulate matter emitted by transportation using fossil fuels are not only linked to human health, but also to the whole ecosystem and global climate. Huge effort has made to reduce not only soot particles but also polycyclic aromatic hydrocarbons (PAHs), greenhouse gases, NOx, etc. One promising solution consists in replacing partly or entirely conventional fossil fuels by biofuels. However, the impacts of biofuels on soot surface chemical composition and PAH formation have been only scarcely studied.

## Objectives

In this study, we compare the influence of the fuel nature - conventional diesel vs. *n*-butanol - on soot formation and soot surface chemical composition in a laboratory jet flame.

## Sampling procedure




*Burner setup*

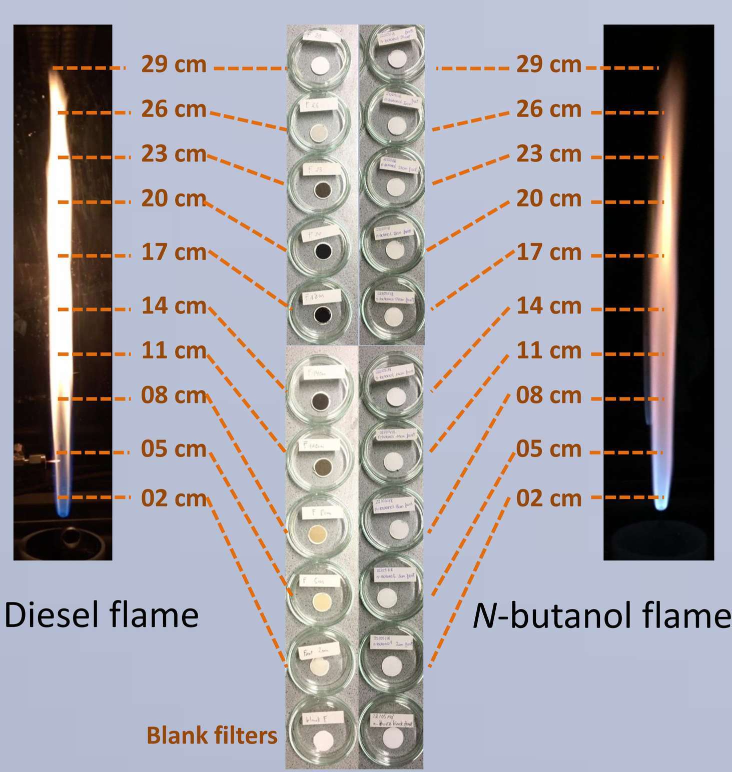
Burner setup:

- Direct Injection High Efficiency Nebulizer (DIHEN): to atomize the liquid fuel with a flow of nitrogen.
- Honeycomb: to homogenize the air flow
- Swirler: to stabilize the flame

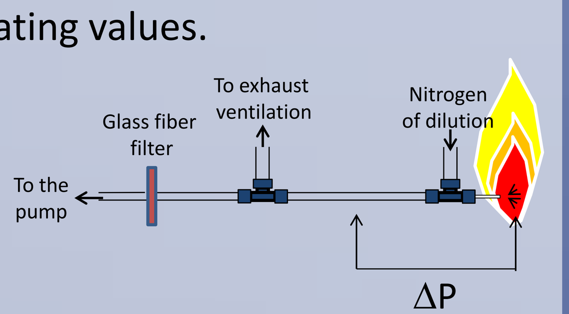
Flame conditions:

| Flame | Fuel flow rate (g/h) | Air flow rate (sLm) | $N_2$ flow rate (sLm) | Lower heating value (MJ/kg) |
|---|---|---|---|---|
| Diesel | 130 | 26.5 | 0.264 | 43 |
| N-butanol | 142 | 21.9 | 0.264 | 33 |

The flow rate of diesel and *n*-butanol were chosen with the ratio of their lower heating values.



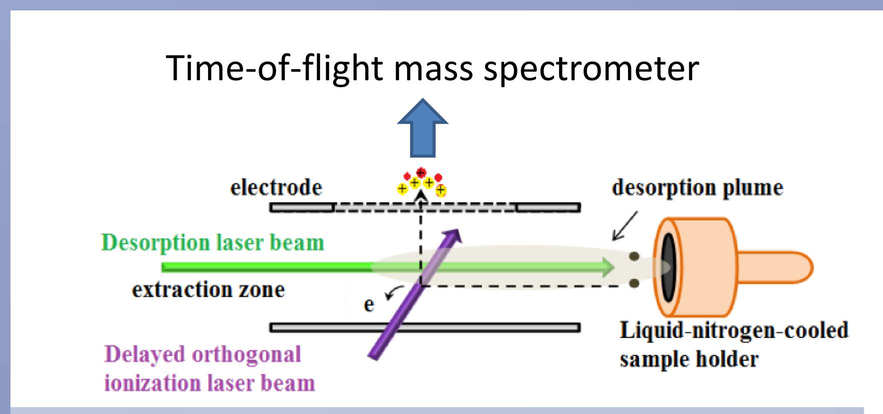

Diesel flame N-butanol flame




Sampling time: 2 mins
$N_2$ flow rate: 4 sLm
Differential pressure (ΔP): 10 mbar

→ *N*-butanol flame produces less soot particles compared to conventional diesel flame

## Methodology

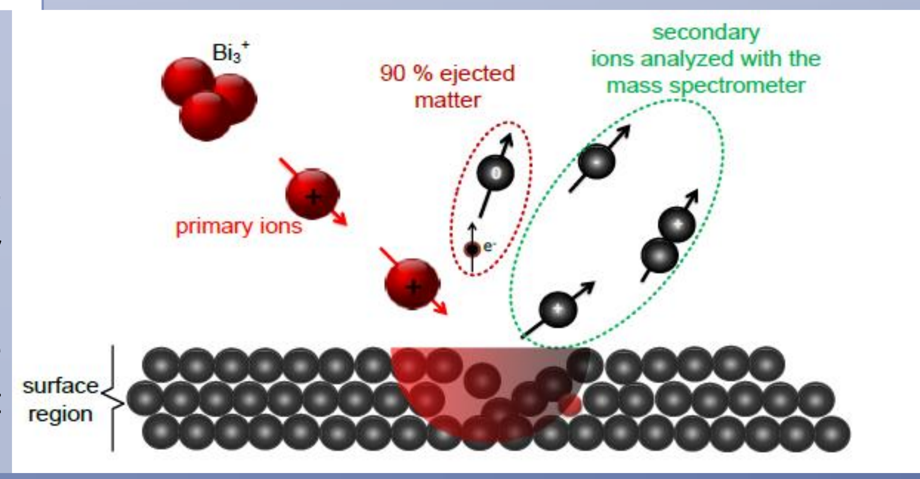



**Two-step Laser Mass Spectrometry (L2MS)**

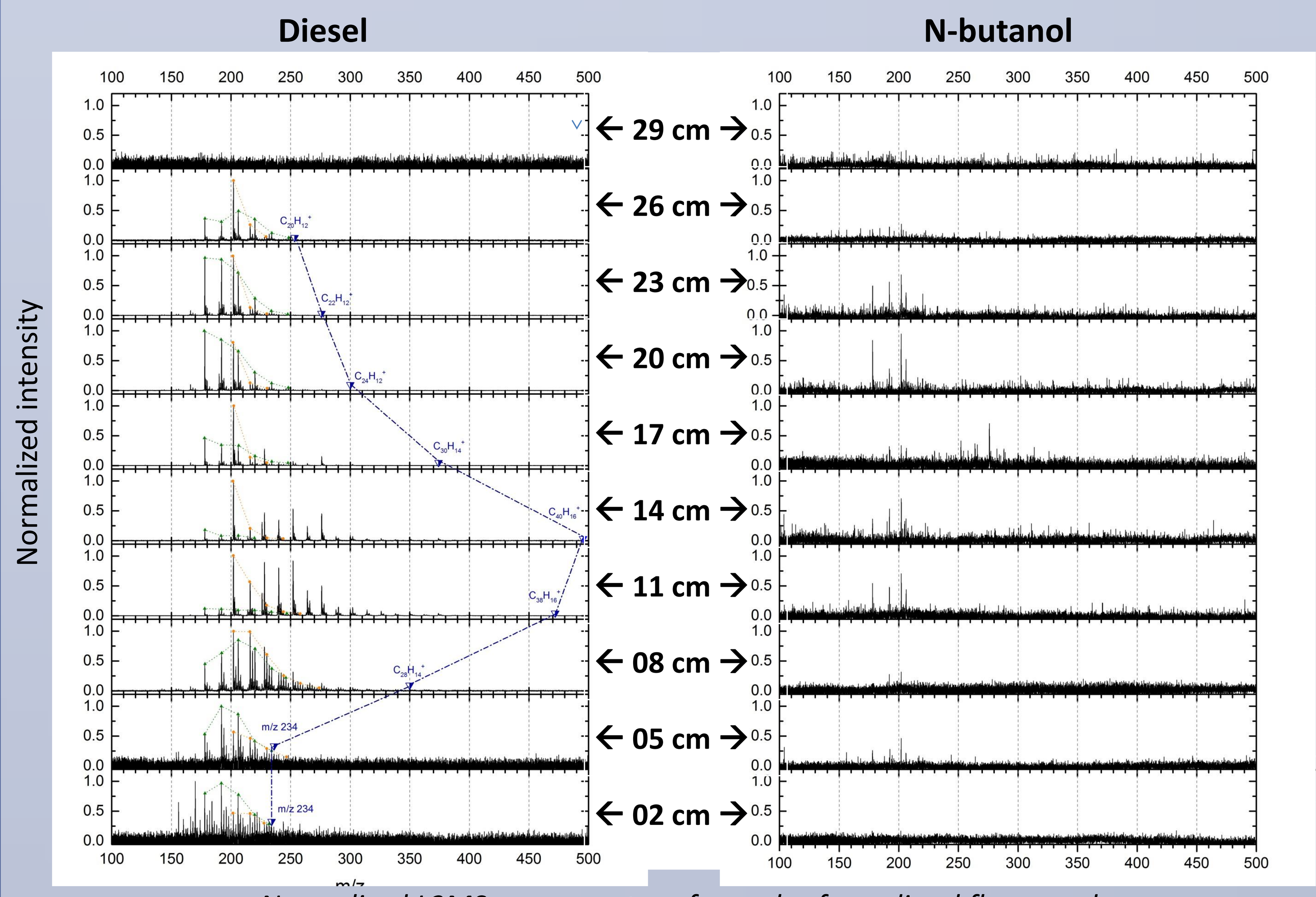
- Samples are cooled down to less than -100°C.
- Laser desorption: Nd:YAG 532 nm.
- Laser ionization: Nd:YAG 266 nm.
- Mass resolution (m/Δm) ≈ 800

**Secondary Ion Mass Spectrometry (SIMS)**

- Primary ion source: $Bi_3^+$, 25 keV, 0.3 pA.
- A cascade of collisions occurs between the atoms in the solid → emission of secondary atoms and molecules via sputtering.
- Few percentage of them is in ionized state and is then mass-analyzed by a time-of-flight mass spectrometer.



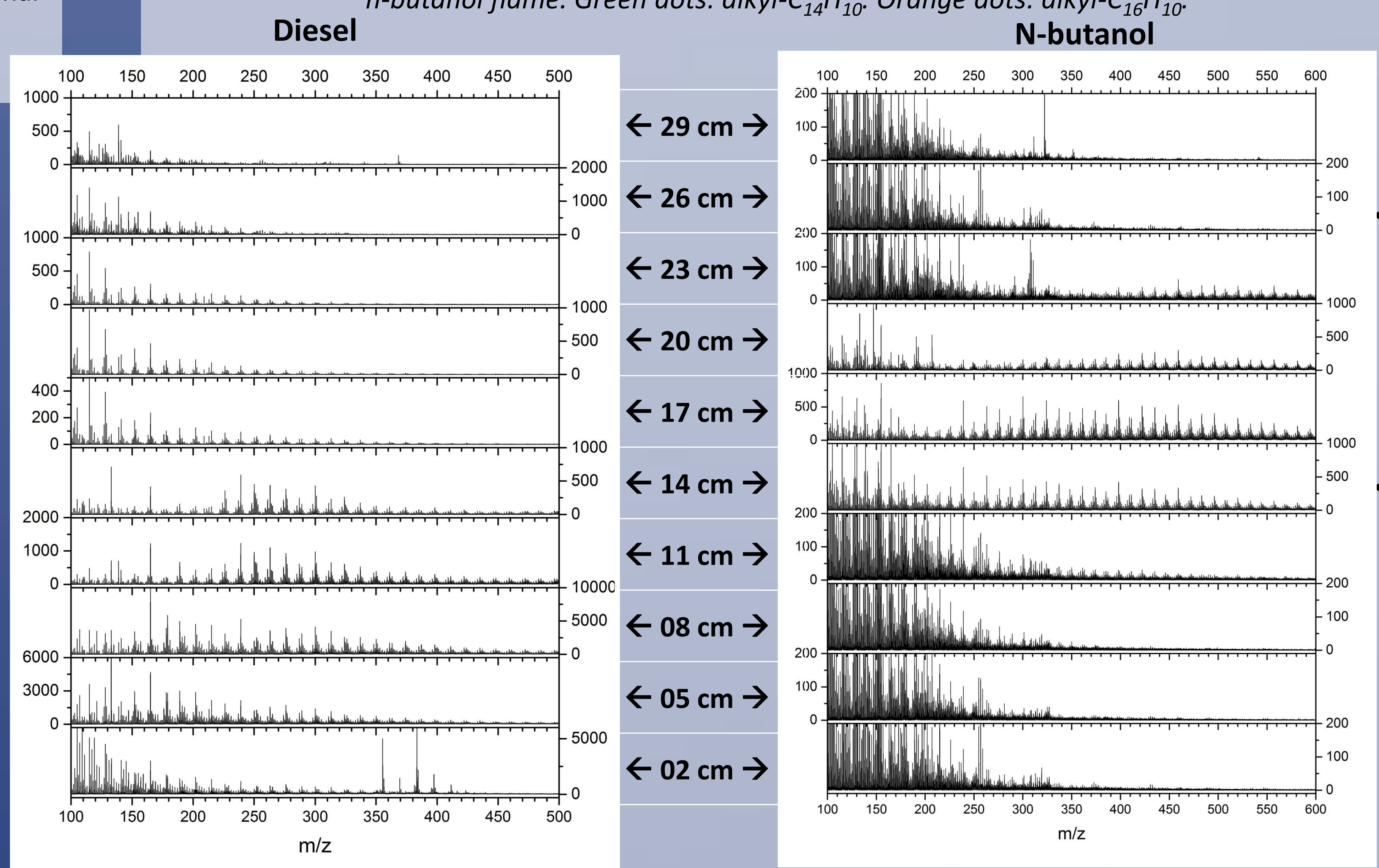

## Results and discussion




*Normalized L2MS mass spectra of samples from diesel flame and n-butanol flame. Green dots: alkyl-$C_{14}H_{10}$. Orange dots: alkyl-$C_{16}H_{10}$.*

**L2MS**

- N-butanol samples have low loading → few signal in their mass spectra with low signal to noise ratio.
- Diesel samples show PAH-rich mass spectra.
- Alkylated PAHs are present in mass spectra of Diesel samples. The bell-shape curve [1,2] of a family of alkylated PAHs indicates the present of petrogenic PAHs.

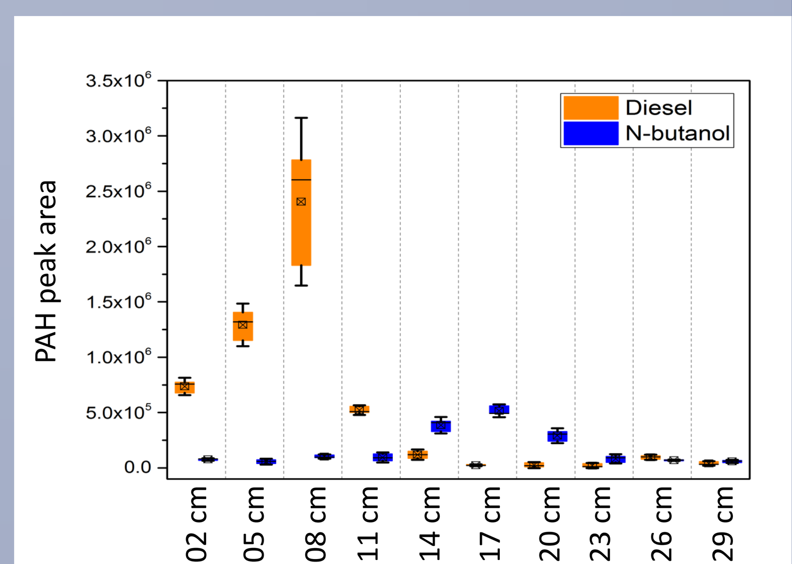



*SIMS mass spectra of samples from diesel flame and n-butanol flame.*

**SIMS**

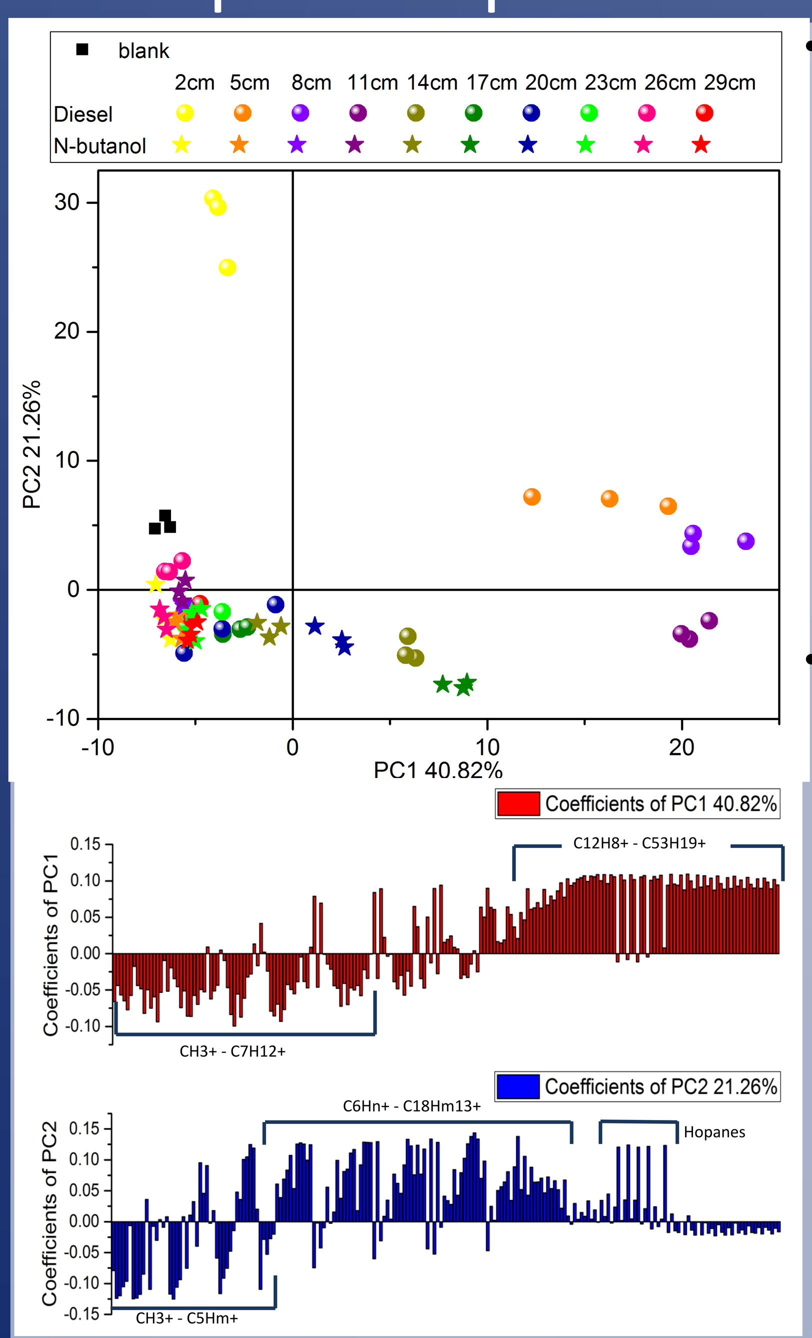
- PAHs are present in diesel flame from 2 cm HAB. Most of them are petrogenic PAHs. This is confirmed by the bell-shape curve of alkylated-aromatic family in L2MS mass spectra.
- For diesel samples, the PAH peak area increases gradually and reached the maximum at 8 cm HAB. Then it decreases strongly until 17 cm to 29 cm.
- In the case of n-butanol samples, the rise of PAH peak area is delayed compared to diesel samples. It starts increasing at 11 cm HAB until reach the peak at 17 cm and then decrease gradually until 26 cm HAB.

- This difference might be associated to the fuel composition. The presence of aromatic compounds in diesel fuel causes a faster formation of PAHs in the flame, and then at a certain concentration, PAHs are consumed to form soot, leads to the decrease of PAHs In the flame. Whereas in the n-butanol case, it might take more time to form the first aromatic compounds, leading to the delay of PAHs peak area in their mass spectra. The concentration of PAHs in n-butanol might not be enough to form soot, but they are oxidized quickly in the oxidation zone of the flame




*Box plot of PAHs integrated peak area from SIMS mass spectra of diesel samples and n-butanol samples.*

## Principle Component Analysis

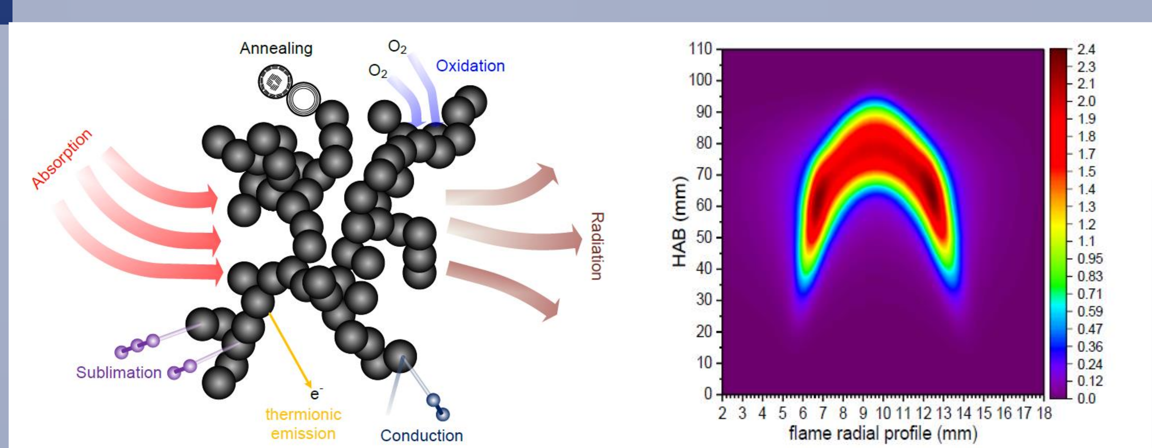



- Diesel samples at 5 to 11 cm with the highest PAHs peak area are in the far positive side of PC1, following by n-butanol samples at 17cm and 20cm HABs and diesel samples at 14cm HABs.
- PC2 discriminates samples containing petrogenic PAHs as diesel samples near the burner: 2 to 8 cm. Samples with non-petrogenic products is in the negative side of PC2

*Score plot and loadings plot for SIMS mass spectra*

## Conclusion and Perspectives

- N-butanol produces significantly less soot particles than conventional diesel fuel.
- In the flame of n-butanol, the formation of PAHs is delayed compared to diesel flame due to their non-aromatic composition.
- Petrogenic PAHs and hopanes are detected in the diesel flame at the region close to the burner.
- In-situ techniques as Laser Induced Incandescence (LII) and Laser Induced Fluorescence (LIF) will be conducted to map soot particles and PAHs in the flames respectively.
- Different biofuels as Dimethyl Tetrahydrofuran, Iso-butanol, etc.




Soot aggregate illustrating the process influencing the collection of the LII signal and an example of LII signal from methane flame [4]

**[1] Stogiannidis et Laane,** *Reviews of Environmental Contamination and Toxicology Volume 234, 2015*
[2] Wang et al., *International Oil Spill Conference*, 2008
[3] Nollet, Chromatographic Analysis of Environment
[4] PhD thesis Cornelia Imrimiea