The importance of monitoring PCDD/F in the stack-gas emissions from the combustion of certain types of solid biofuels

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Outline

- ✓ Study motivation
- ✓ Legislation Framework
- ✓ Dioxins and Furans (PCDD/F)
- ✓ Main interactions between fuel components and PCDD/F emissions
- ✓ Fuels and Mixtures
- ✓ Apparatus and Experimental Work
- ✓ Experimental Results
- ✓ Conclusions

Study motivation

- Raise of energy needs → New energy sources
- Decrease of CO_2 emissions → International Commitments
- Increased waste production → Potential Loss of energy resources
  - Examples of technology promotion through European Waste Management Policies:
    - → Materials recovery processes integration with Fluidised Bed technology
    - → Co-combustion of mixtures of wastes from differents streams with conventional fuels
  - Landfill Directive - Biodegradable material deposition not allowed

Study motivation

- RES Directive → Fossil fuel replacement by renewable energy sources

  - Biomass definition includes the biodegradable fraction of municipal solid wastes and industrial wastes
  - Biomass definition very wide, including meat and bone meal and primary wates from food and beverage production

- Environment and Energy EU objectives in 2020

  - EU Energy/Climate Package 20-20-20:
    - increase Renewable Energy Sources share to 20% in EU Power production
    - increase by 20% the Energy Efficiency
    - reduce by 20% the GHG emissions (Reference year: 1990)

Legislation Framework

Dioxins and Furans Emission Limit Value
0.1 ng I-TEQ/Nm^3

Directive 2010/75/EU – IED
Industrial Emissions Directive

- Directive 2008/1/CE (IPPC)
  Integrated Polution Prevention and Control
- Directive 2001/80/CE (LCP)
  Large Combustion Plants (> 50 MW_{th})
- Directive 2000/76/CE (Wastes)
  Incineration/Co-incineration

Directive 2015/2193/EU – MCP
Medium Combustion Plant Directive

- 1 MW_{th} < rated thermal input < 50 MW_{th}
- Pollutants considered: SO_2, NO_x and dust
- 'Biomass' means any of the following:
  (a) any agriculture or forestry material
  (b) vegetable matter:
  (i) agriculture and forestry waste
  (ii) food processing industry waste
  (iii) Fibrous waste
  (iv) cork waste
  (v) wood waste

✓ ELV (PCDD/F) ≤ 0.1 ng I-TEQ/Nm^3
✓ Stack-gas: 2 seconds at T > 850°C

Dioxins and Furans (PCDD/F)

PCDD/F	WHO2005-TEF(1)	I-TEF(2)
Dioxins		
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	1	0.5
1,2,3,4,7,8-HxCDD	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01
OCDD	0.0003	0.001
Furans		
2,3,7,8-TCDF	0.1	0.1
1,2,3,7,8-PeCDF	0.03	0.05
2,3,4,7,8-PeCDF	0.3	0.5
1,2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01
OCDF	0.0003	0.001

(1) Van den Berg M. *et al*., 2006, Toxicological Sciences 93(2), 223–241.
(2) NATO/CCMS, 1988, North Atlantic Treaty Organization, Committee on the Challenges of Modern Society. Report No. 176.

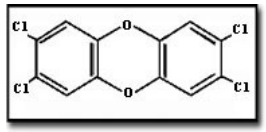
7 PCDD and 10 PCDF have different toxicities

↓

Toxicity Equivalency Factor (TEF)

2,3,7,8-tetra-chlorodibenzo-*para*-dioxin

↓



Reference: $(TEF)_{TCDD} = 1$

Conversion to I-TEQ (European Directives):

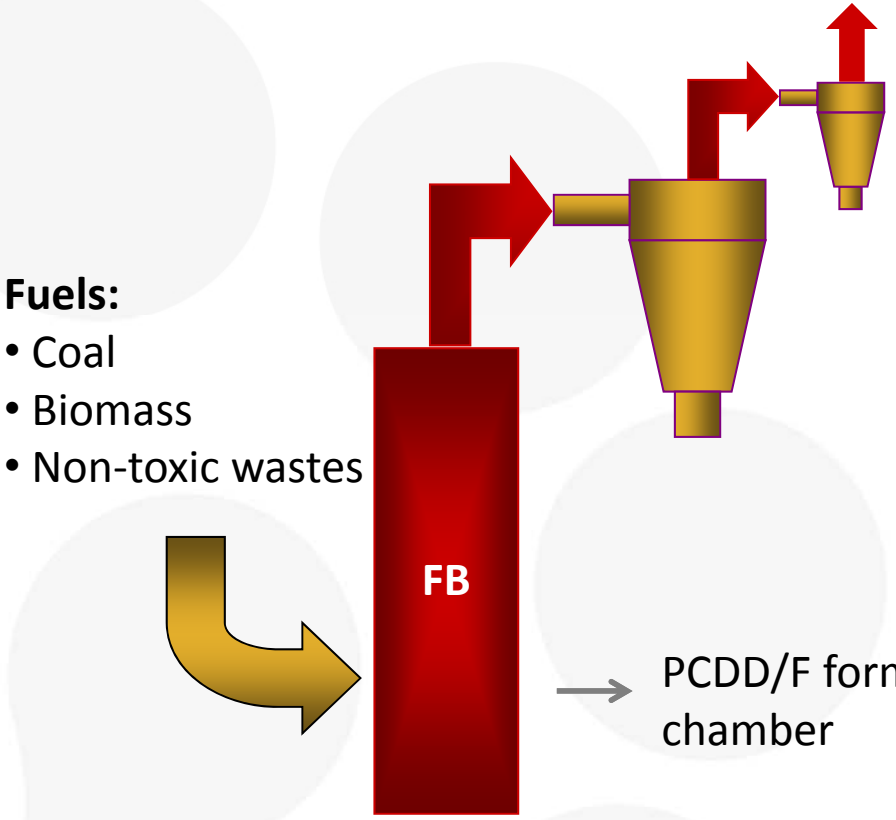
X ng $PCDD_i$ * $(I\text{-}TEF\ PCDD)_i$ = Y ng I-TEQ PCCD/F

Z ng $PCDF_j$ * $(I\text{-}TEF\ PCDF)_j$ = W ng I-TEQ PCCD/F

PCDD/F formation pathways

Dioxins and Furans

ELV = 0.1 ng I-TEQ/Nm^3



Fuels:

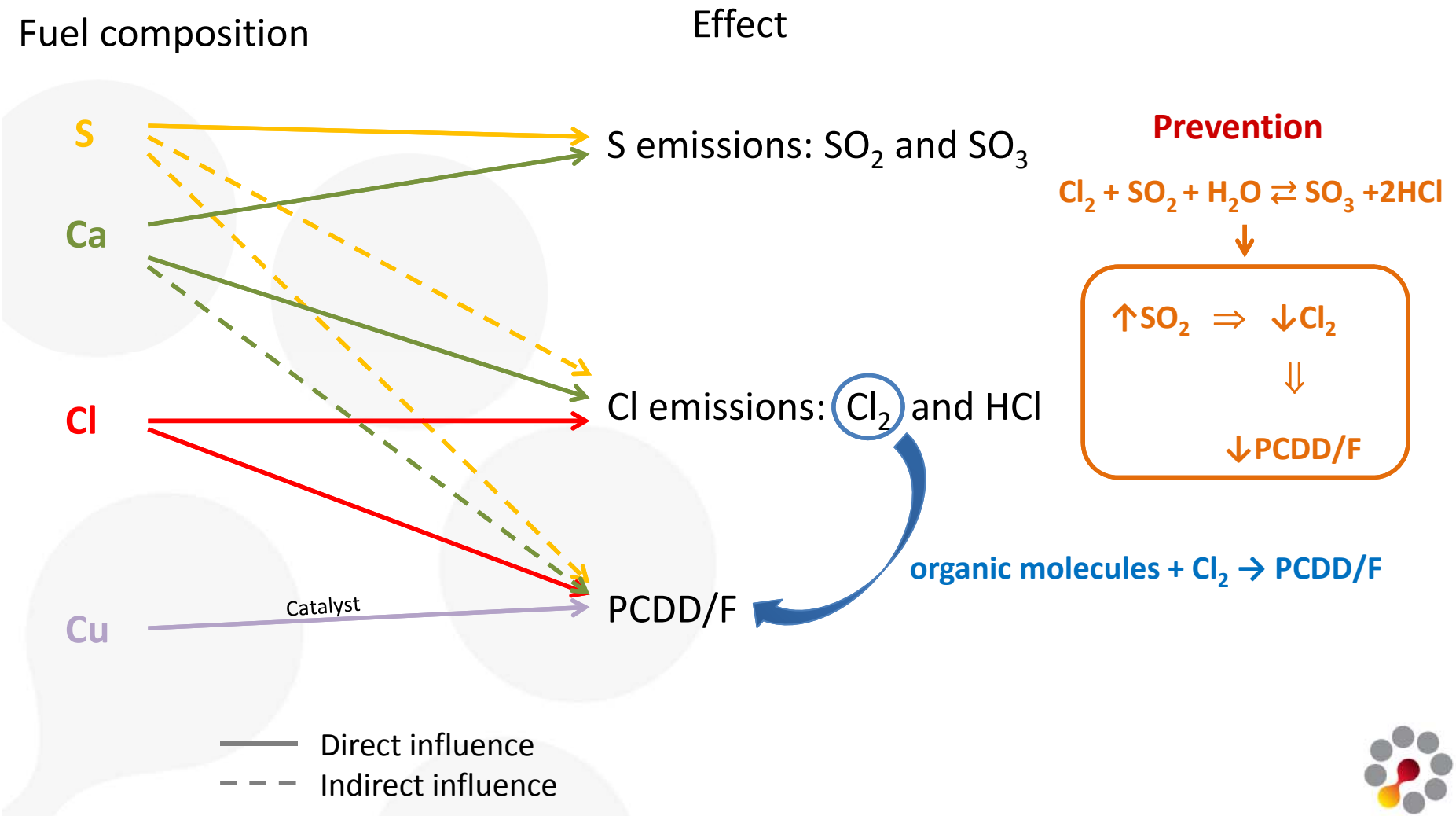
- Coal
- Biomass
- Non-toxic wastes

PCDD/F formed through catalytic synthesis in the gas cleaning system

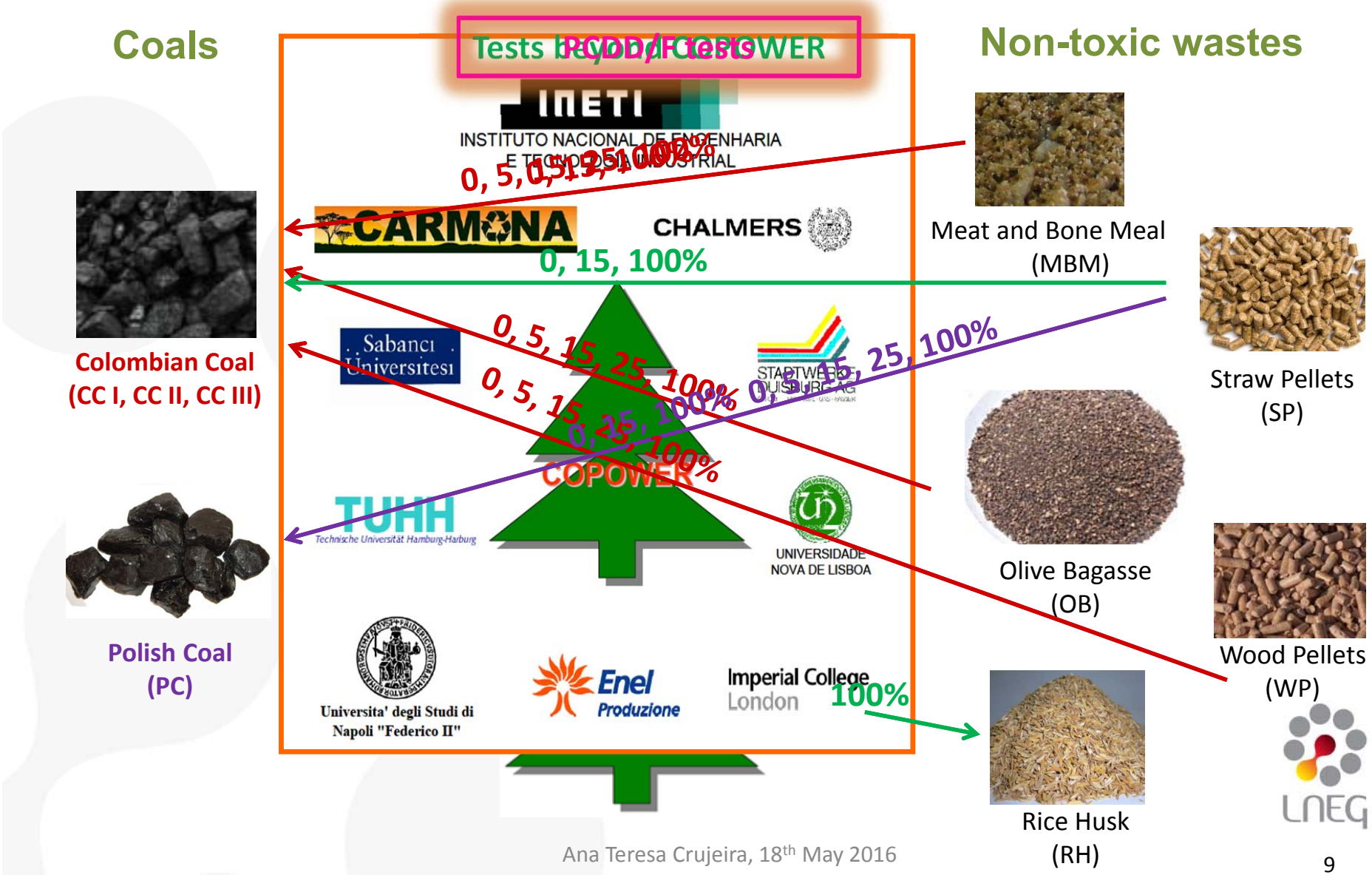
- ***de novo* mechanism**
- **Precursor mechanism**

PCDD/F formed through synthesis in the combustion chamber

Main interactions between fuel components and PCDD/F emissions



Fuels and Mixtures



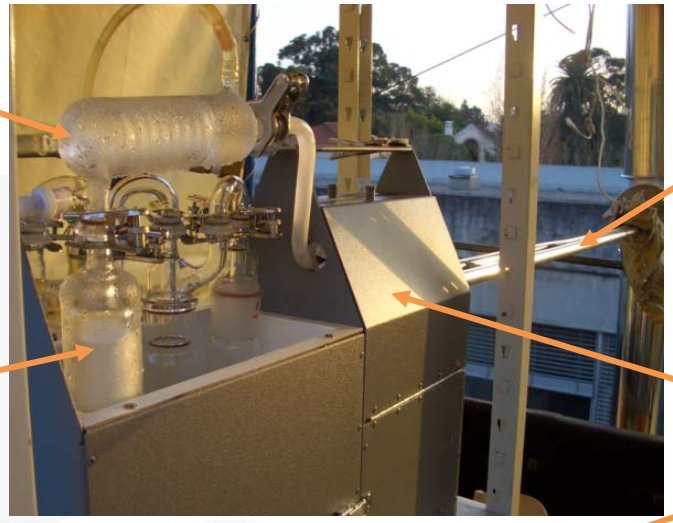
Apparatus and Experimental Work

Fluidized Bed Pilots

- ✓ Stainless Steel
- ✓ Height (H): 5m (Old); 6m (New)
- ✓ Side (L): 0.3m (Old); 0.35m (New)
- ✓ External insulation
- ✓ Water coil refrigeration
- ✓ Bed material-Sand
- ✓ Air Staging between bed and freeboard
- ✓ 2 Cyclones for fly ash separation
- ✓ Sampling Probes along the Reactor for gas measurements
- ✓ Sampling Probes in the stack for particles, metals, HCl and PCDD/F
- ✓ Computerized Control (T, P, air and Fuel flow)

Apparatus and Experimental Work

Isokinetic sampling of PCCD/F

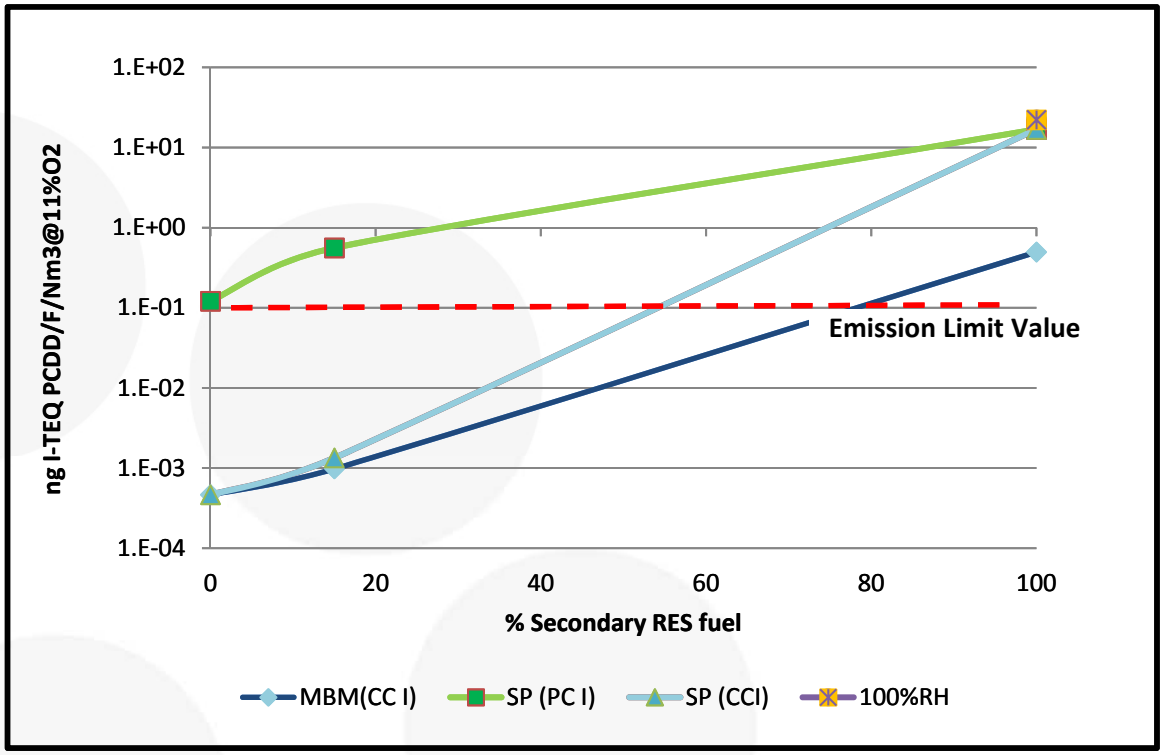


Methodology EN 1948-1

- ✓ Filter/Condensation
- ✓ Sampling time: 6 hours
- ✓ Resin: XAD-2
- ✓ Spiking: Filter
- ✓ Analysis: HRGC/HRMS
- ✓ Preparation+analysis: Portuguese Environmental Reference Laboratory
- ✓ Sampling validation:
  - ✓ % Spiking recovery >50%
  - ✓ Blanks < Detection Limit

Table 6.1 - Freeboard residence time of the gases for the PCDD/F tests.

Experimental Results



- Emissions higher than the ELV for all solid biofuels 100% tests;

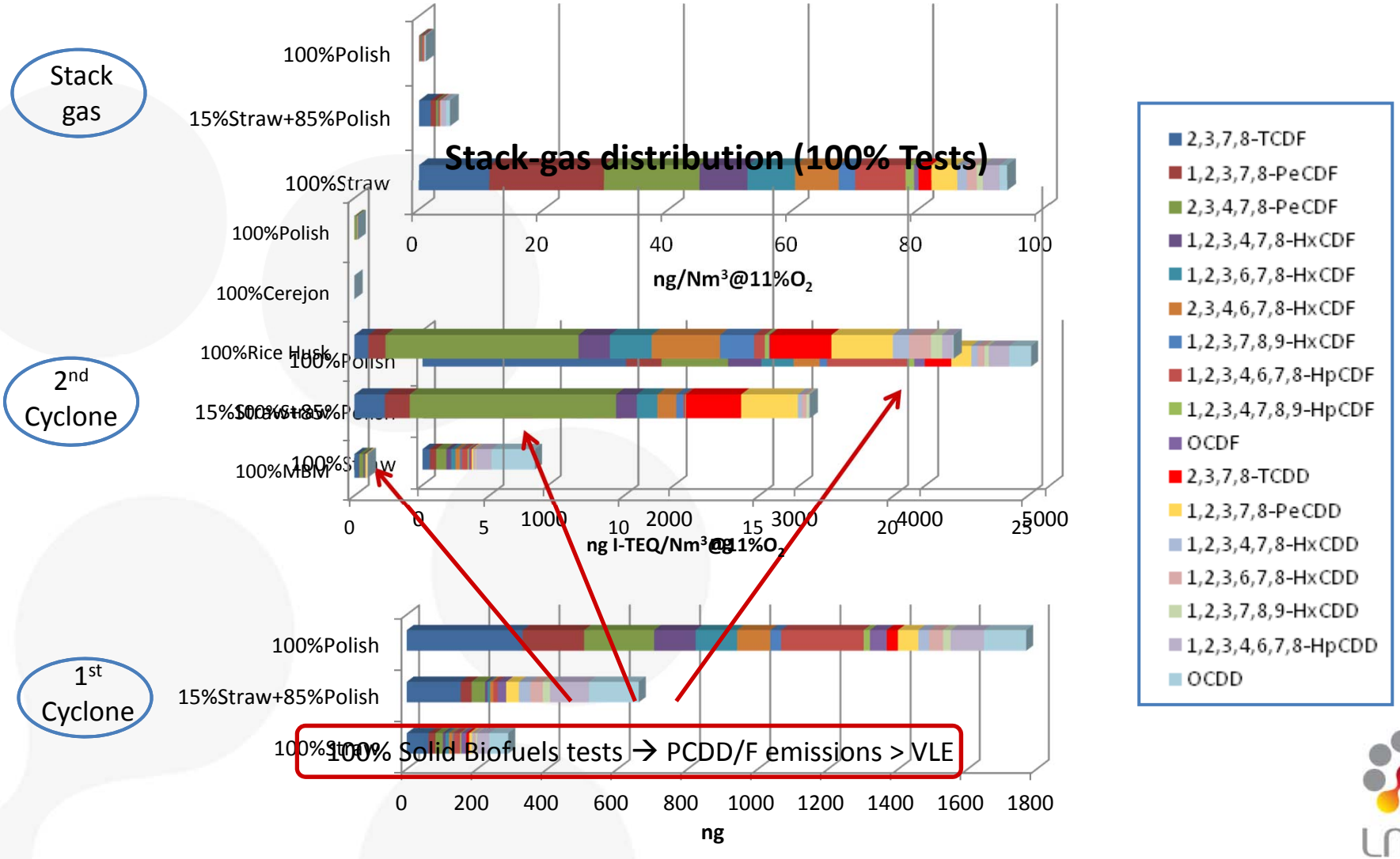
-Significant reduction of the PCDD/F emitted for co-combustion with coal

Residence time of stack-gas in the freeboard at T>750°C

$\tau_{freeboard}$ (s)	100%PC	15%SP(PC)	100%SP	100%CC	15%MBM(CC)	100%MBM	15%SP(CC)	100%RH
T>750°C	1.5	2.4	1.9	1.7	1.3	1.8	3.0	4.0

Experimental Results

Pollutant Emissions in a pilot fluidized bed: PCDD/F in the SP/PC tests



Conclusions

- Dioxins and Furans (PCDD/F) may occur from the combustion of fossil fuels and from certain types of solid biofuels, such as straw or rice husk.
- The PCDD/F stack-gas emission was higher for the renewable energy sources.
- When the solids biofuels were burnt in a co-combustion fluidised bed system with coal, a significant (>70%) reduction of the PCCD/F emissions was observed, when compared with the combustion of renewable energy sources materials.
- Under the LCP Directive, PCDD/F should only be monitored in incineration and co-incineration processes, whereas other solid biofuels used in LCP are exempted of being controlled.
- The new MCP Directive, mainly focused in the use of renewable energy sources doesn't predict the monitoring of PCDD/F.

The results presented show the importance of including PCDD/F monitoring and control in a broader range of materials and fuels, with a particular focus in renewable energy sources such as the solid biofuels, in the installations covered by LCP and MCP Directives.

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Thank you for your attention!

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