



Laboratoire  Institut de Science des Matériaux de Mulhouse

CEM 2011 5th - 7th October 2011
Prague, Czech Republic
Emissions Monitoring Conference & Exhibition




New operating mode for on-line analysis of dioxin emission from stationary sources

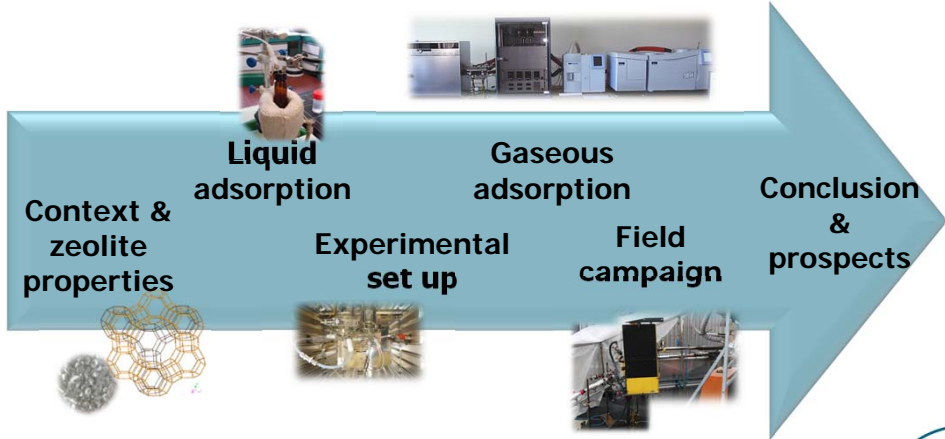
M. Mercury, L. Bonvalot, J. Llorens, M. Carette, Y. Zerega, A. Janulyte, C. Reynard, A. Simon-Masseron, J. Patarin, M. Soulard

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Outline

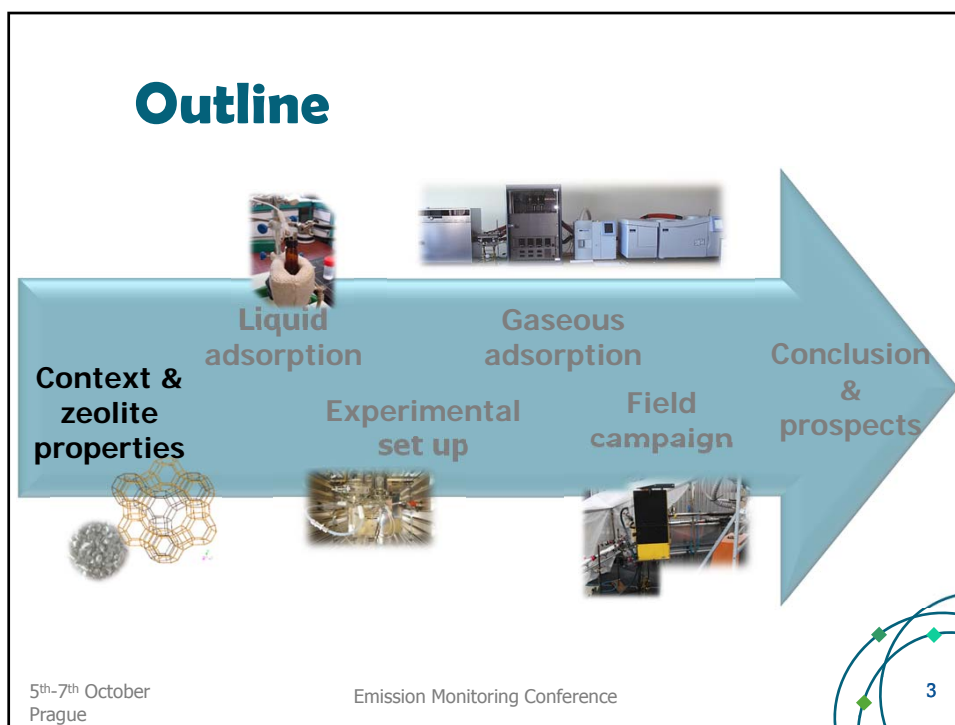


Context & zeolite properties **Liquid adsorption** **Gaseous adsorption** **Conclusion & prospects**

Experimental set up **Field campaign**

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Context

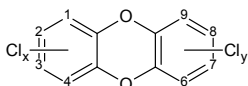
- Dioxins and furans are produced by an incomplete combustion of organic and chlorinated compounds
- Generated by stationary sources such as waste incinerators, cement/metalworking industry...
- Dispersal in the environment as aerosols, accumulation in the food chain

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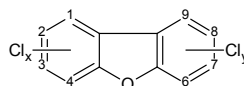
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Context

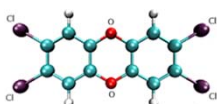


Polychlorodibenzo-p-dioxin (PCDD)



Polychlorodibenzo-furan (PCDF)

- 75 PCDDs and 135 PCDFs
 - Toxicity is due to the chlorine atoms located in the 2,3,7,8 positions
 - Only 17 congeners of PCDD/Fs are toxic at various levels
 - « I-TEQ » = « International Toxic Equivalent Quantity »



The most toxic dioxin is 2,3,7,8-TCDD (Seveso dioxin) TEF=1

$$I\text{-TEQ} = \sum_i \text{TEF}_i \times C_i$$

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Context

- Directive 2000/76/EC of the European Parliament on the incineration of waste. Emission threshold set at 0.1 ng.m⁻³
- Standard methods NF EN 1948 for emission measurement
 - Part 1: Field sampling (6-8h), with adsorption on resin or activated carbon
 - Part 2&3: Extraction/purification and identification/quantification in an accredited laboratory

⇒ Up to 1 month to get the analysis result

- Semi-continuous measurement techniques (14-28 day sampling period) : AMESA, DECS and DMS
- On-line analysis system : currently not competitive (REMPI-MS)

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Aims of the research programme

- Conception of a new analytic device for **on line** and **real time** dioxin analysis
 - Reduce the extraction/purification time
 - Carry out analysis with standard GC/MS

New Adsorbent

- Selective adsorption
- Thermally stable : extraction/purification by thermodesorption

➔ Zeolite

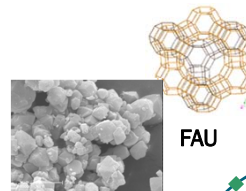
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Zeolites : properties

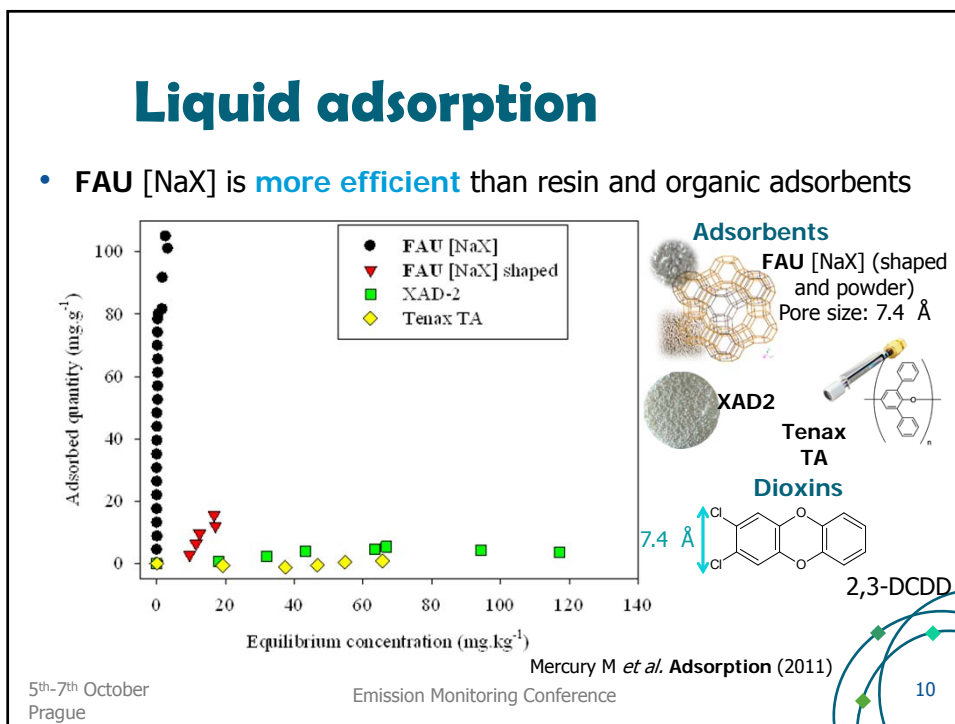
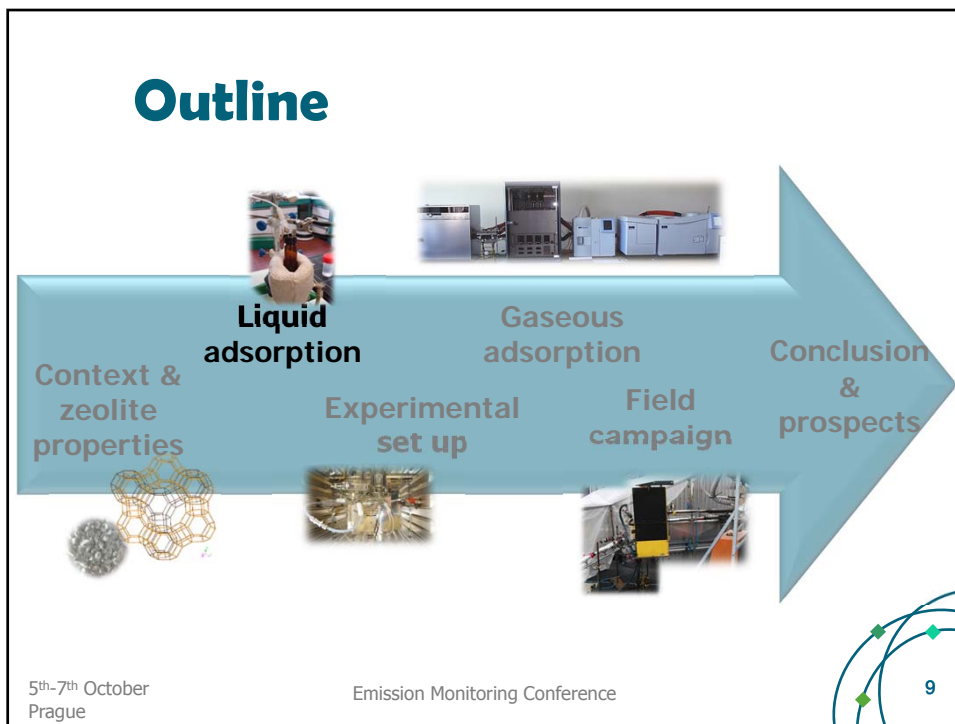
- Microporous crystallised solid, 196 structural types
- Three dimensional structure made up of TO_4 (T = Si or Al) tetrahedrons bonded by bridging oxygens
- Choice of the compensating cations to get a neutral structure
- Controlled porosity (pore size)



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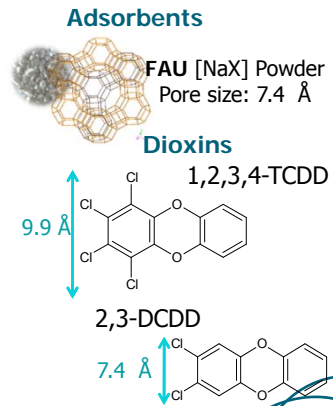
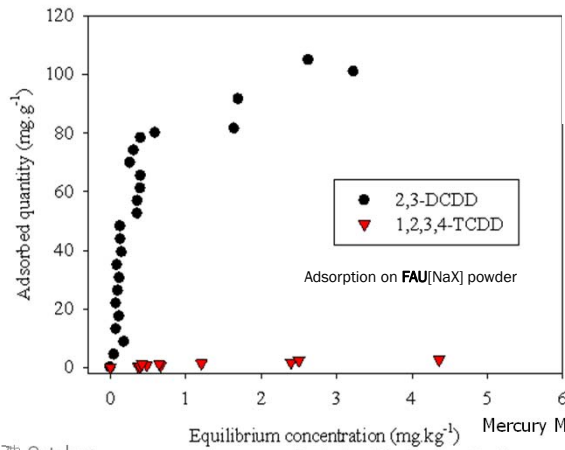
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Liquid adsorption

- **Selectivity** between 2,3-DCDD and 1,2,3,4-TCDD is obtained with FAU [NaX]



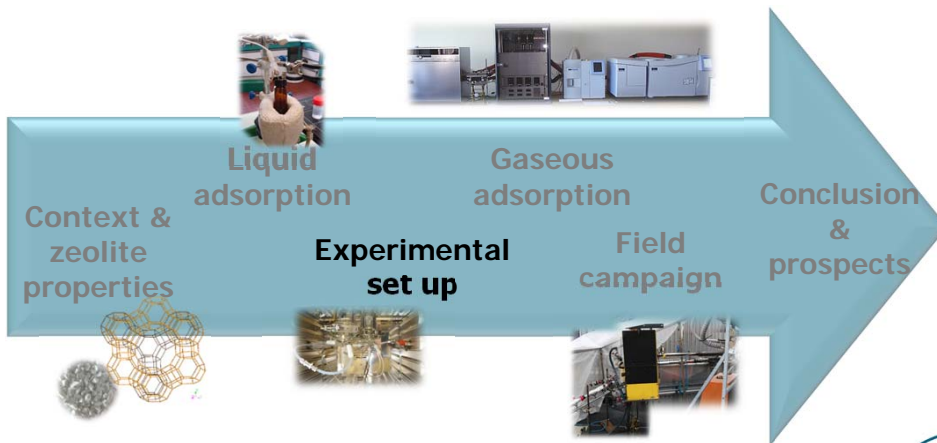
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Mercury M *et al.* Adsorption (2011)

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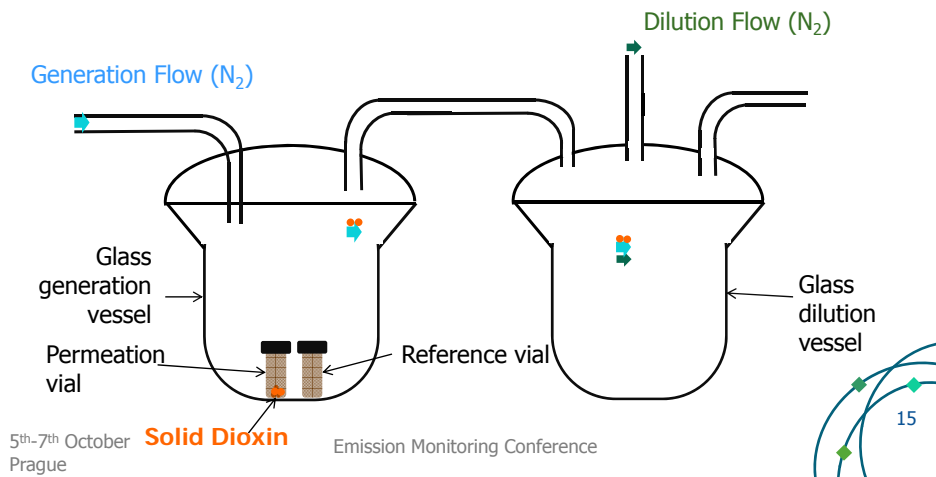
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Experimental set-up Dioxin (2,3-DCDD) generation

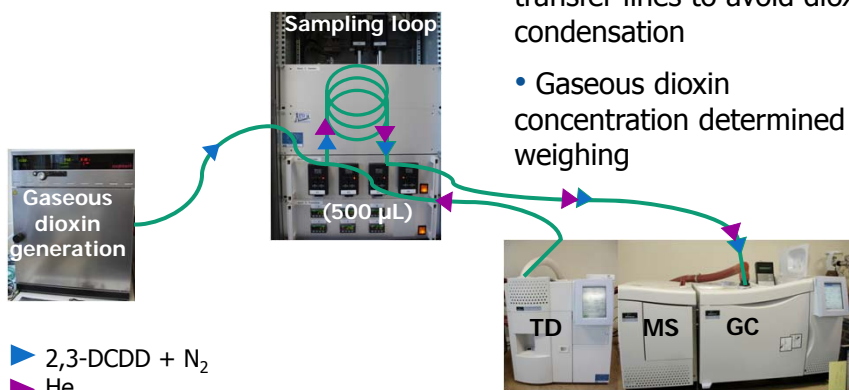
Glass vessels inserted in oven at controlled high temperature



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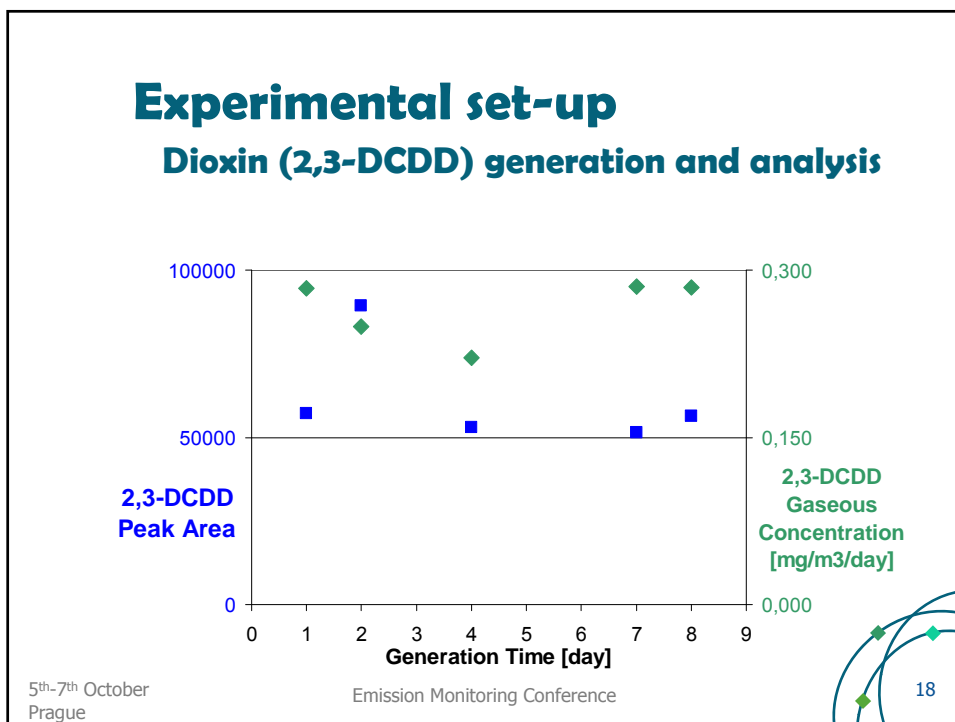
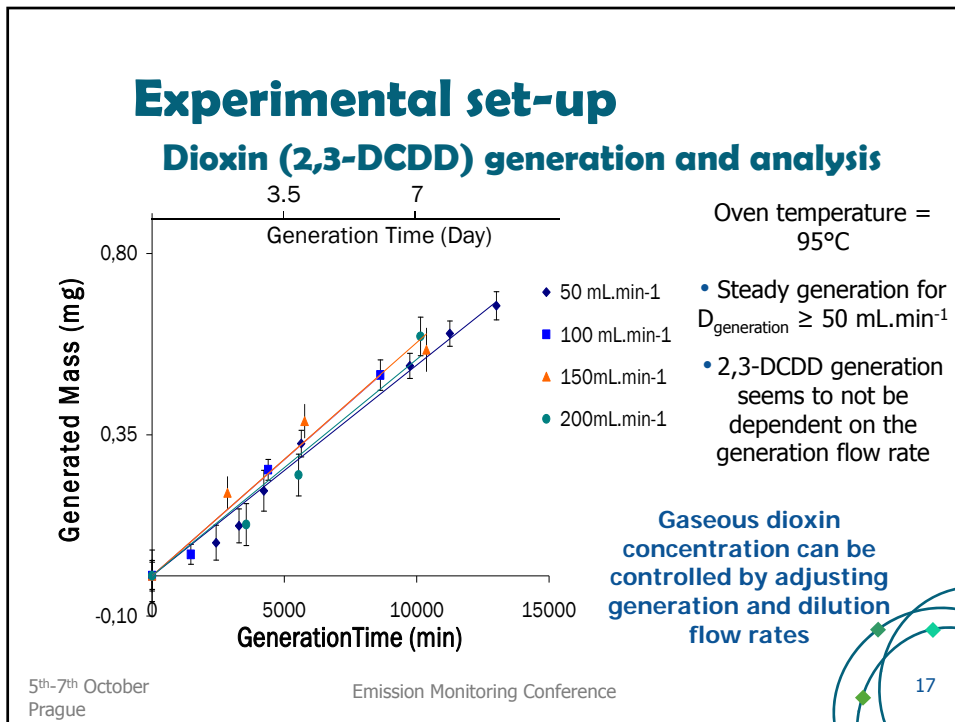
Experimental set-up Dioxin (2,3-DCDD) generation and analysis

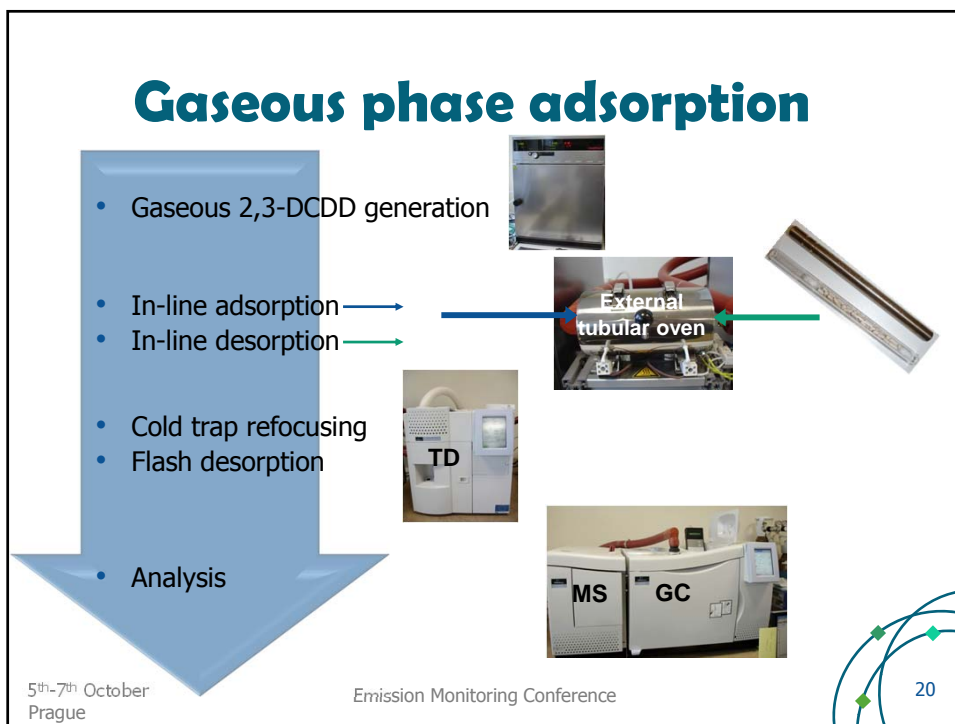
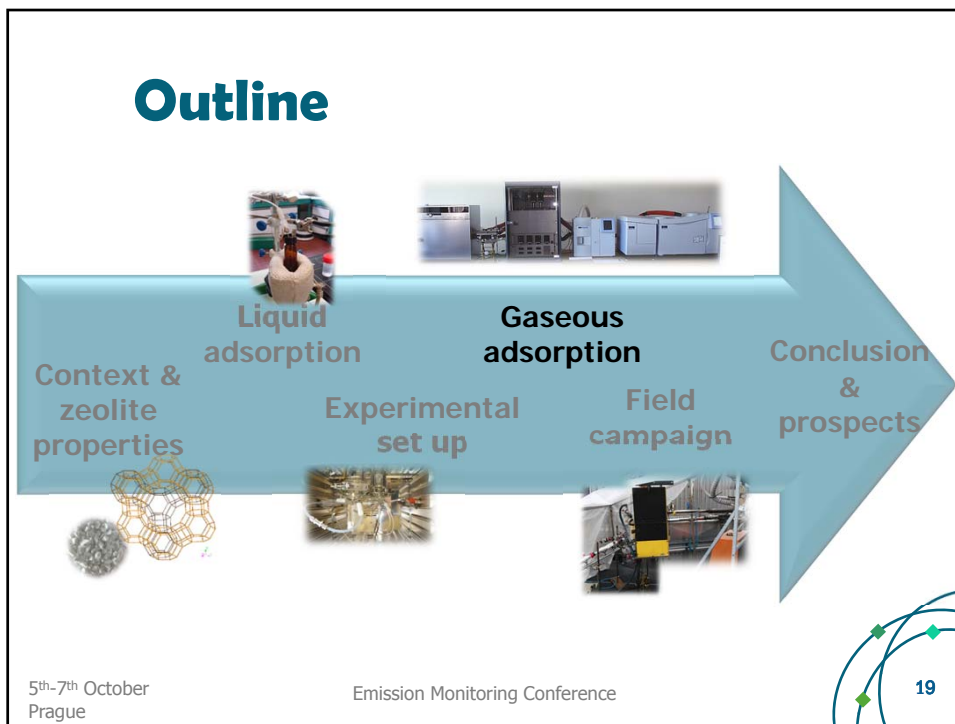
- Heated sampling loop and transfer lines to avoid dioxin condensation
- Gaseous dioxin concentration determined by weighing



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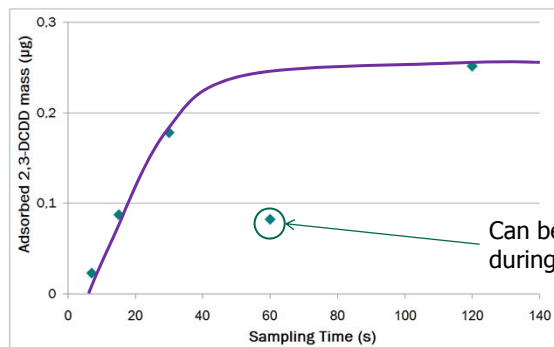
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Gaseous phase adsorption

- Breakthrough curve for 0.65 g of zeolite



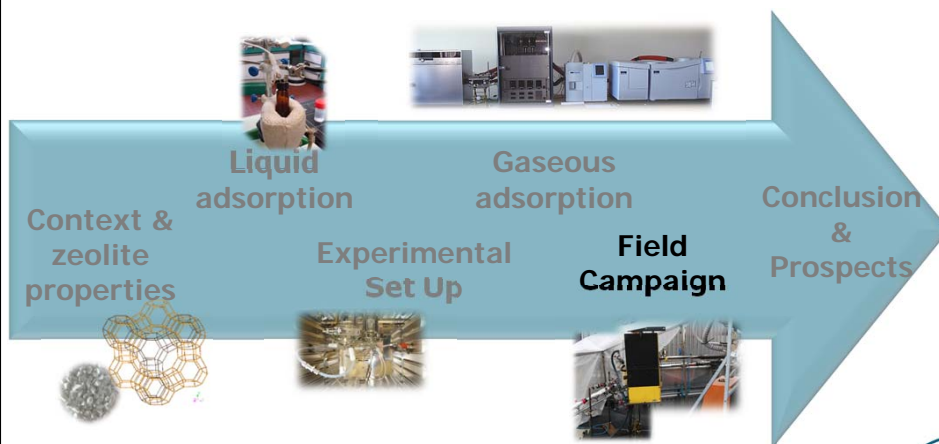
- Gaseous dioxin adsorption is **controlled** and **characterised** by the experimental set-up

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Outline



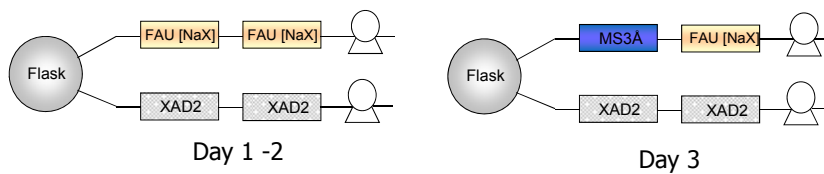
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Field campaign

- 3 days of field sampling campaign
- Comparative sampling at Novergie waste incinerator
- Modified filter/condenser sampling train



- MS3Å used as water filter

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Field campaign

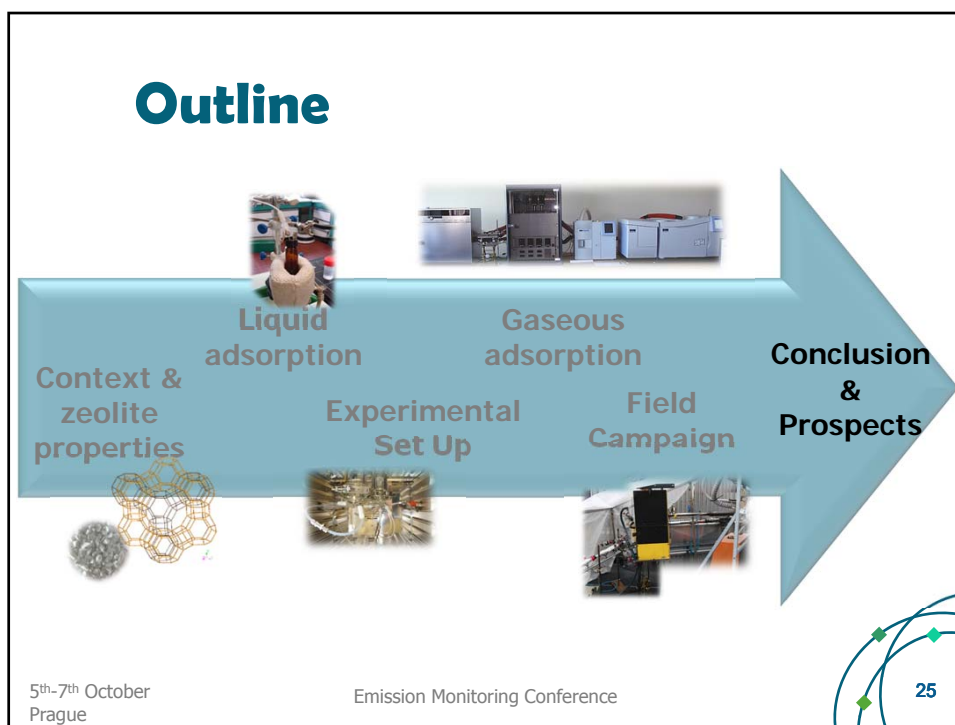
Total I-TEQ (ng/extract) lower bound	FAU Day 1	XAD2 Day 1	FAU Day 2	XAD2 Day 2	Zeolite Day3	XAD2 Day 3
1 st cartridge	0.0008	0.0001	0.022	0.077	0.020 (MS3Å)	0.041
2 nd cartridge	0.0008	0.00001	0.022	0.0023	0.00025 (FAU)	0.00069

- Standard sampling method used
- Non regular breakthrough
- FAU/XAD2 → same adsorbent quantities
- MS3Å → weaker adsorption

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Conclusion

- Selective and more **efficient** dioxin adsorption on **FAU[NaX]**
 ⇒ **New adsorbent for dioxin sampling**
- Gaseous dioxin standard generated, controlled and quantified by the experimental analytical device
- Thermodesorption and **analytic** part carried out **in a few hours**
 ⇒ **Efficient experimental device for dioxin analysis and generation**

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Prospects

- Optimisation of gaseous dioxin phase adsorption:
 - Unshaped **FAU**[NaX]
 - Adsorption at different flow rates
 - Temperature of adsorption
- Adapt laboratory techniques for field procedures

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Acknowledgements

- Field campaign
 - Novergie 
 - Cetiat 
ensemble, innover et valider
 - Groupe CARSO 
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French Agency for Environment and Energy Management
 - ANR Precodd 
French National Research Agency

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Thank you for your attention!

