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Trace Compounds Analysis in Biogas and Biomethane: In Situ High Pressure Preconcentration by Adsorption Followed by Thermodesorption-GC-MS

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7th International Conference on Renewable Energy Gas Technology - Weimar, Germany, September 20-21st 2021

1 - Context organic wastes → anaerobic digestion → biogas → upgrading → biomethane → injection in natural gas grid

Contains **trace compounds (TC)** depending on organic wastes composition, seasonal effects and process conditions:

- (halogenated) volatile organic compounds
- oxygenated organic compounds
- volatile N-, S- and Si- compounds
- volatile (organo-)metal-(loid) compounds

Grid-compliant biomethane → TC must satisfy natural gas quality standards, but their **sampling and characterization can be difficult (low concentrations, complex matrices)**

2 - Objective Development of a fast and efficient field sampling set-up to directly preconcentrate the trace compounds in situ at the grid pressure (≤ 100 bar_a) + analytical method development

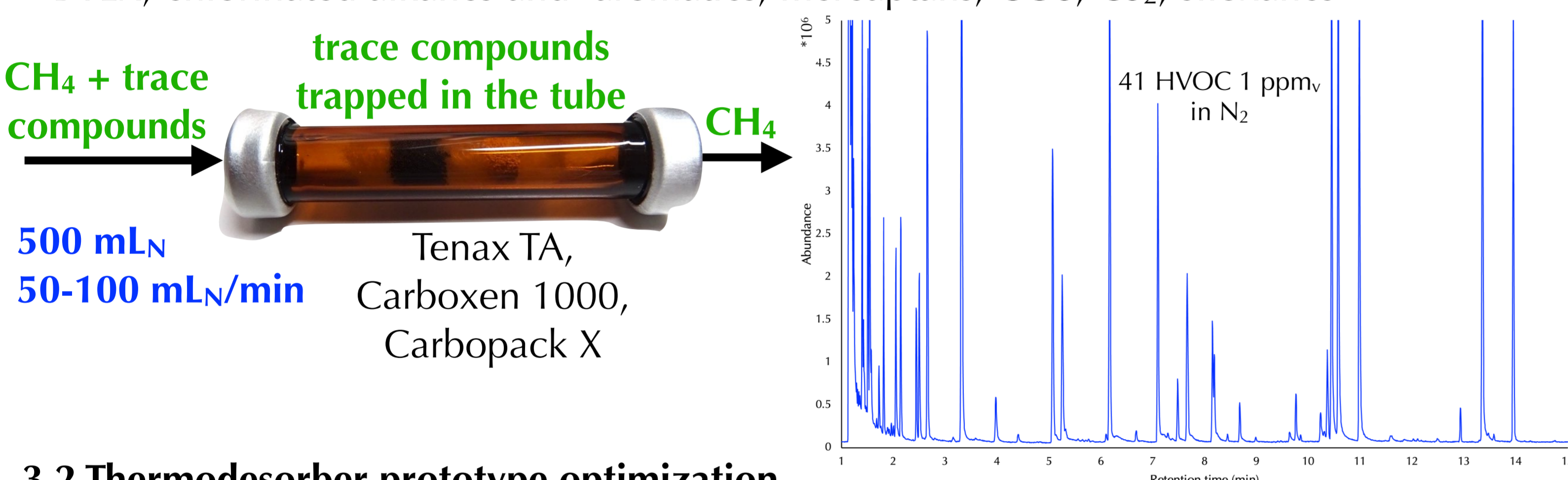
How ?

- ① Preconcentration on self-purpose-built **multibed adsorbent** tubes
- ② **High pressure** tube sampler (**patented**)
- ③ **Field sampling bench (ATEX, ≤100 bar_a)**
- ④ Thermal Desorption of the tubes - Gas Chromatography - Mass Spectrometry (**TD-GC-MS**)

3 - Analytical development in the lab using synthetic gases and building grid natural gas

3.1 Multibed: adsorption of non-metallic TC in a large volatility range (-30 to +215 °C)

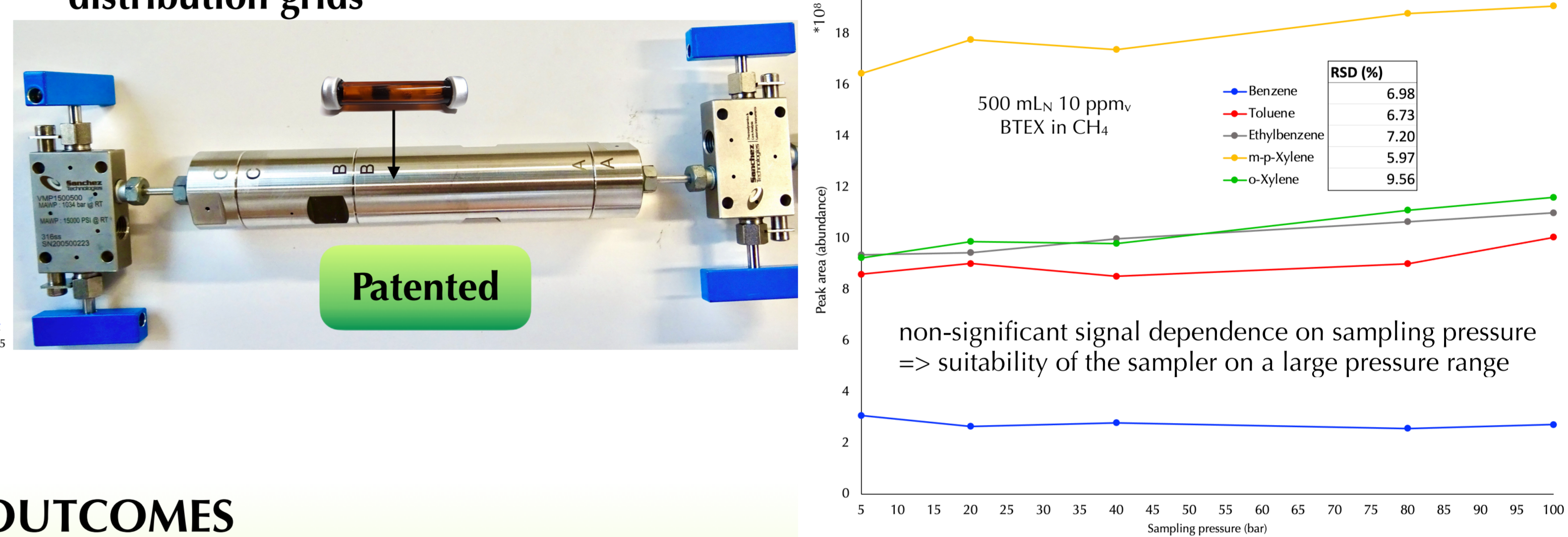
- Tested on several synthetic gases (1 ppm_v in N₂ or in CH₄): alkanes, alkenes, terpenes, BTEX, chlorinated alkanes and -aromatics, mercaptans, COS, CS₂, siloxanes



3.3 Application to grid natural gas (1.03 bar_a)

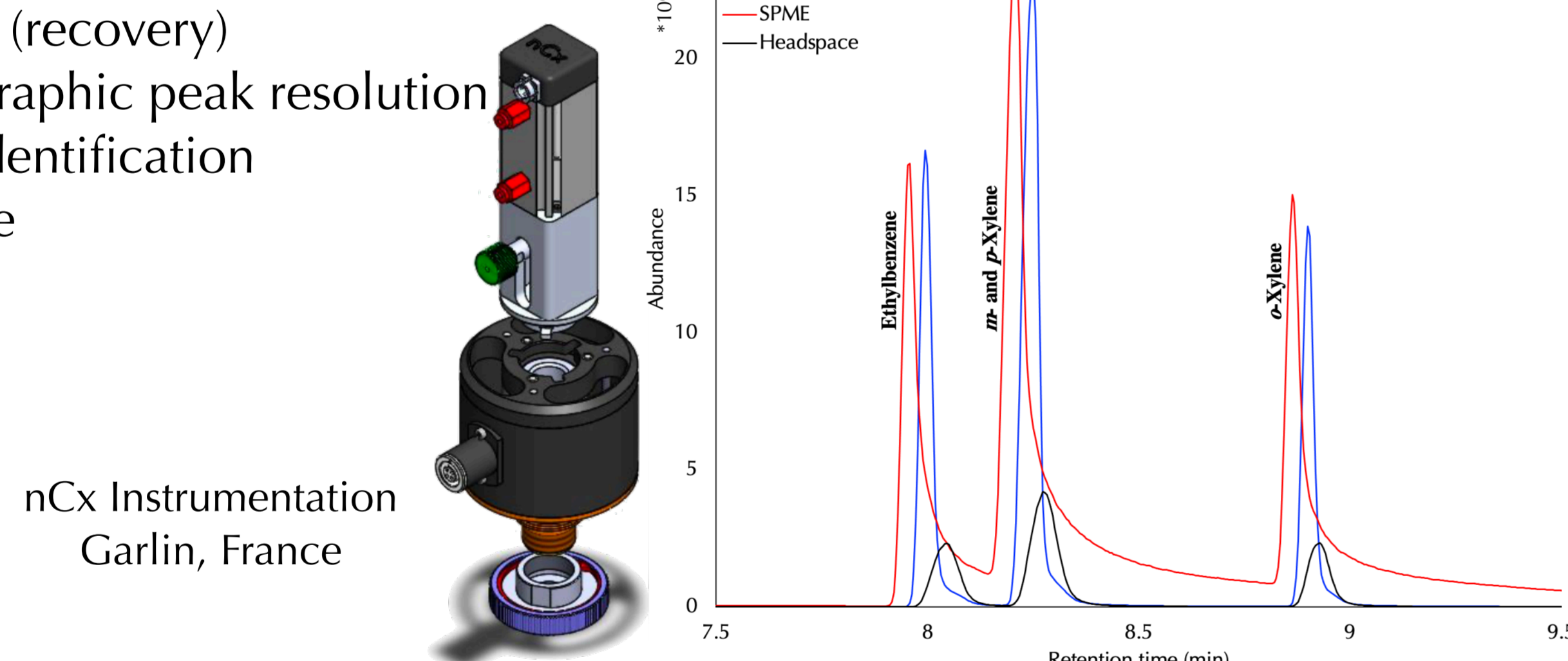
- 50 trace compounds detected: aliphatic and cyclic alkanes up to C₉, BTEX, thiophene, 2,3-dihydrothiophene, THT

3.4 High pressure tube sampler tested at pressures representative for transport and distribution grids



3.2 Thermodesorber prototype optimization

- efficient thermal desorption of multibed adsorbent tubes (recovery)
- high chromatographic peak resolution → compound identification
- Field-deployable



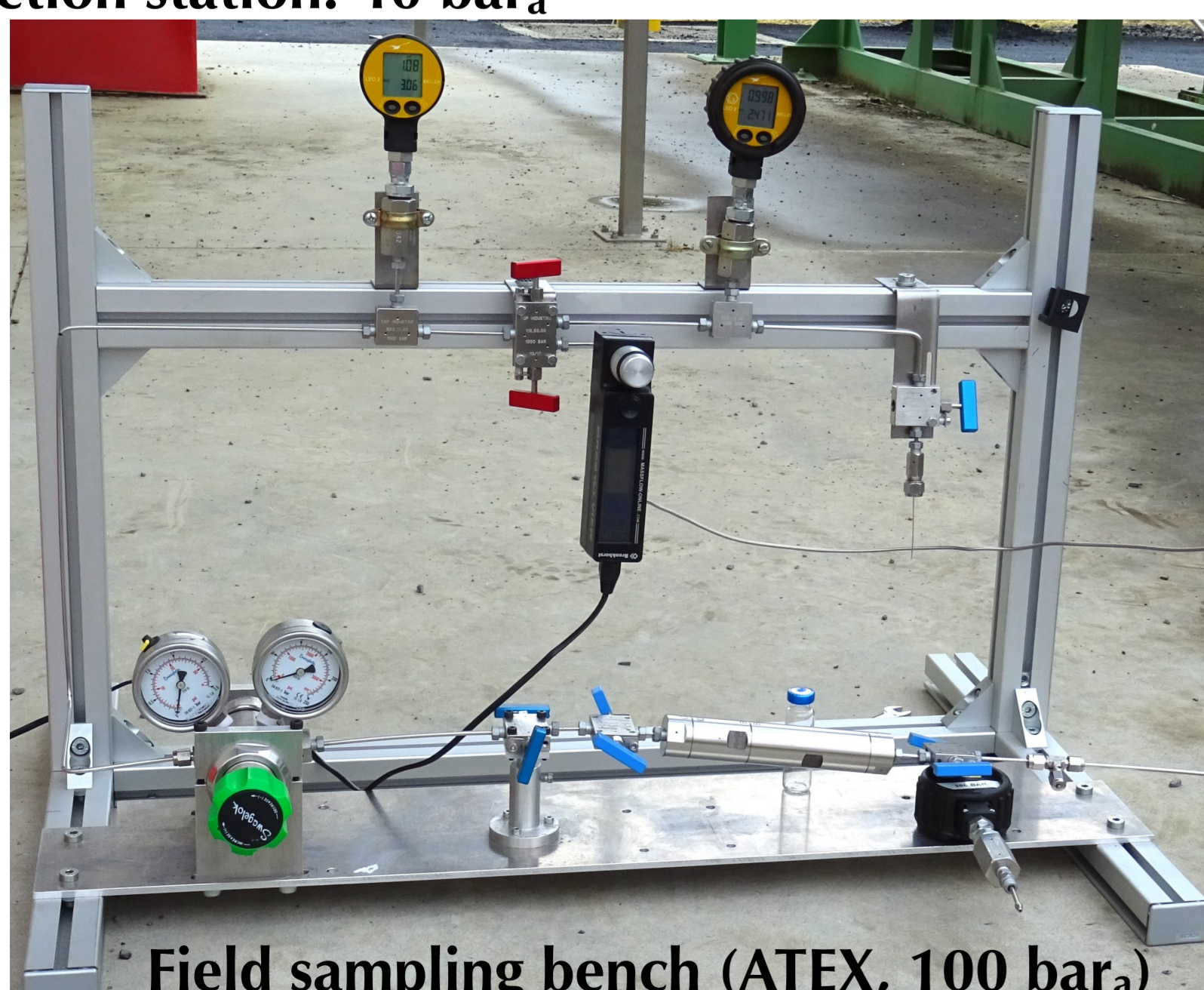
OUTCOMES

- ✓ **High affinities and capacities** of the adsorbents for TC:
 - **strong preconcentration** of a wide range of TC
 - **low gas volumes** needed: 500 mL_N => **less pollution**
- ✓ **Pressurized sampling**: more preconcentration (no TC dilution by depressurization) + **shorter sampling times**
- ✓ **TD-GC-MS**: efficient to **recover and identify broad range of TC** from many different chemical families

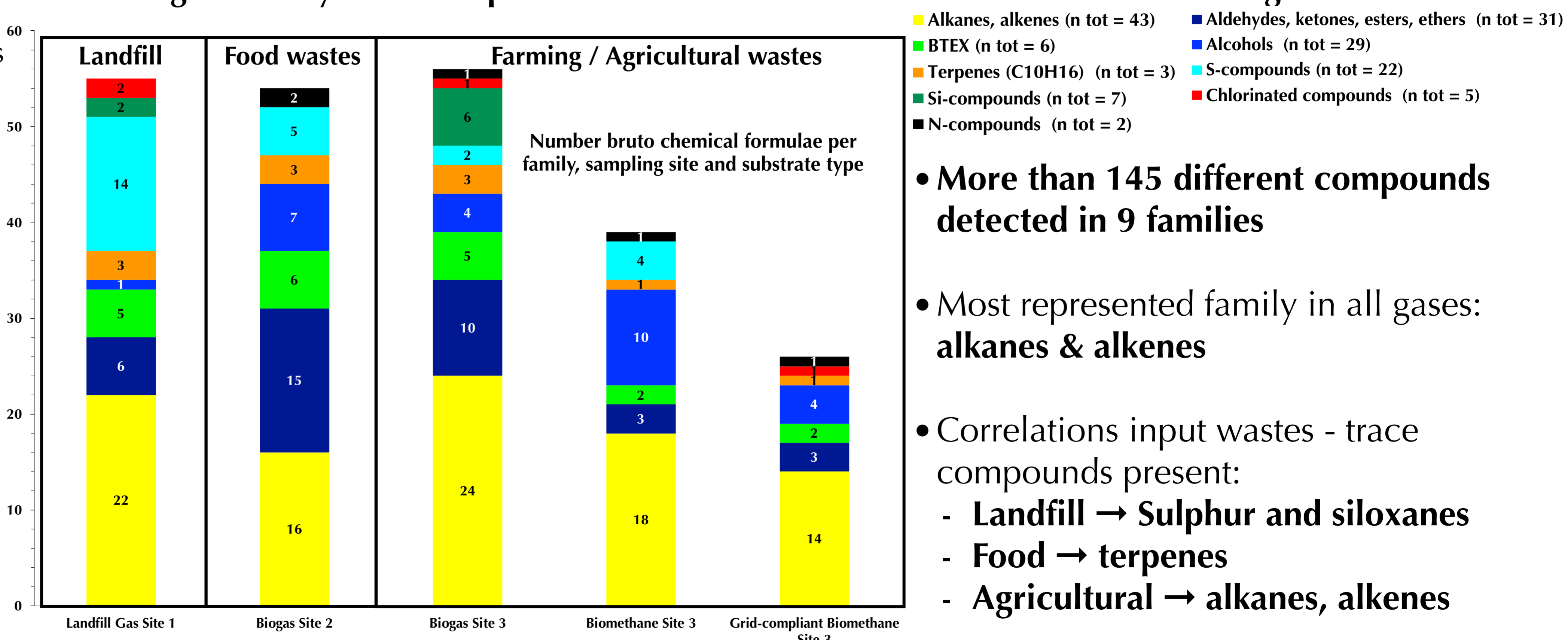
4 - Field sampling campaigns: biogas and biomethane at production and injection stations

Sampled gases:

- Raw landfill biogas
- Raw and purified (activated carbon) biogas from food wastes
- Raw biogas from farming/agricultural wastes
- Biomethane from farming/agricultural wastes **at grid injection station: 40 bar_a**



Results: huge diversity trace compounds from diverse chemical families detected in biogas and biomethane



• **More than 145 different compounds detected in 9 families**

• Most represented family in all gases: **alkanes & alkenes**

- Correlations input wastes - trace compounds present:
 - **Landfill** → Sulphur and siloxanes
 - **Food** → terpenes
 - **Agricultural** → alkanes, alkenes

5 - Conclusions - Perspectives: Analytical chain validated !

- **High pressure preconcentration on multibeds: wide range volatile compounds** detected on a **large pressure range**
- **Low detection limits**
- **Direct in situ preconcentration: SAFEST way !**
 - ✓ **no contamination, no loss (avoid sample transfers)**
 - ✓ **no dangerous transport**
- Evidence of TC composition differences across biogases / biomethanes
- Evidence of correlations substrates - TC composition
- Perspectives: quantification and 2D-GC