Performance evaluation of air-purifying photocatalytic commercial devices: laboratory and pilot scale tests

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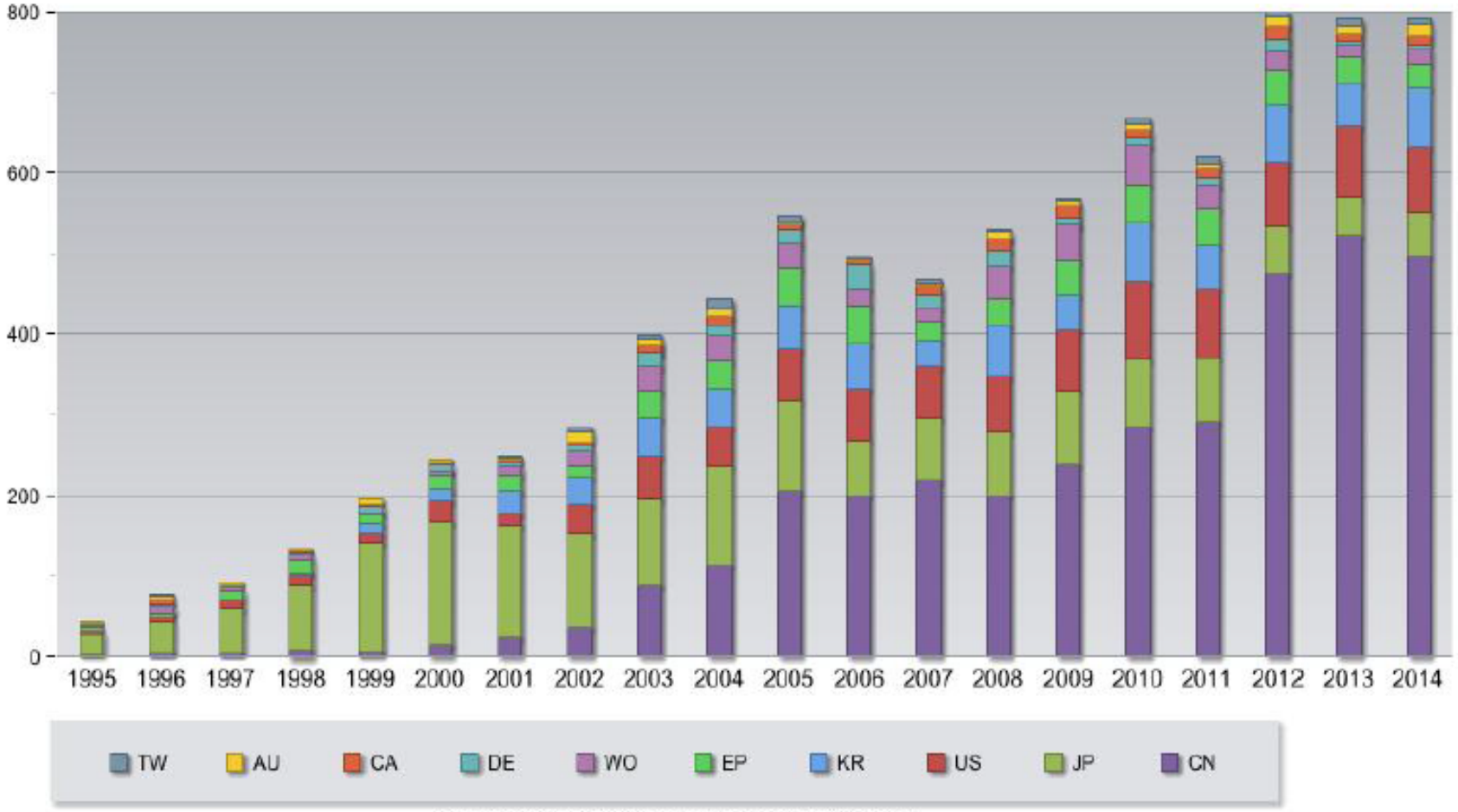
SafePHOTOCAT project

Patents analysis (1995-2015) from CTG – Italcimenti group



Source: Thomson Innovation®, www.thomsoninnovation.com

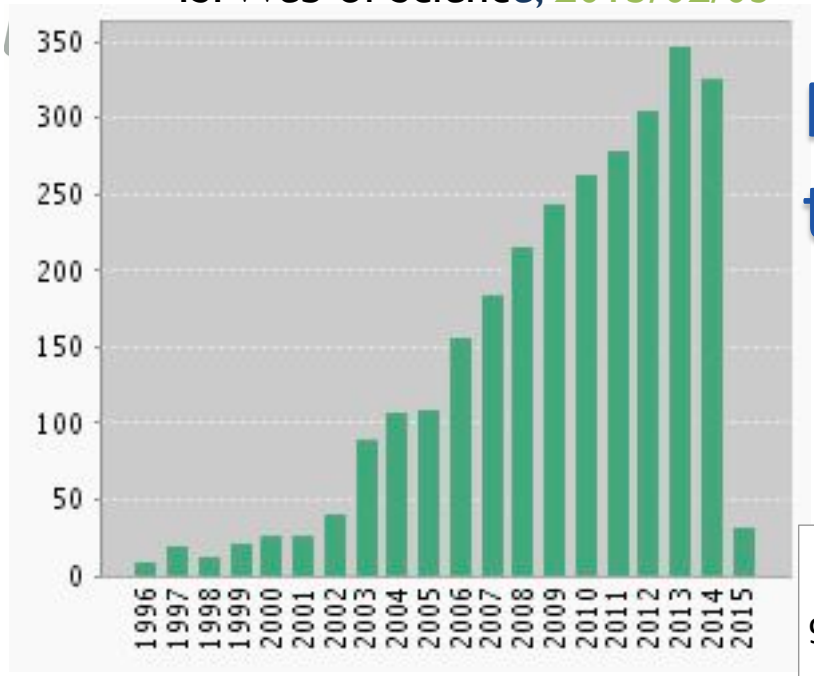
Criteria : Title /abstract /claims :photocatal* AND TiO2

Publication date :from 1995-01-01 to 2015-01-01

Results: 9018 records and 5236 DWPI families

Photocatalytic air treatment

ISI Web of Science, 2015/02/03



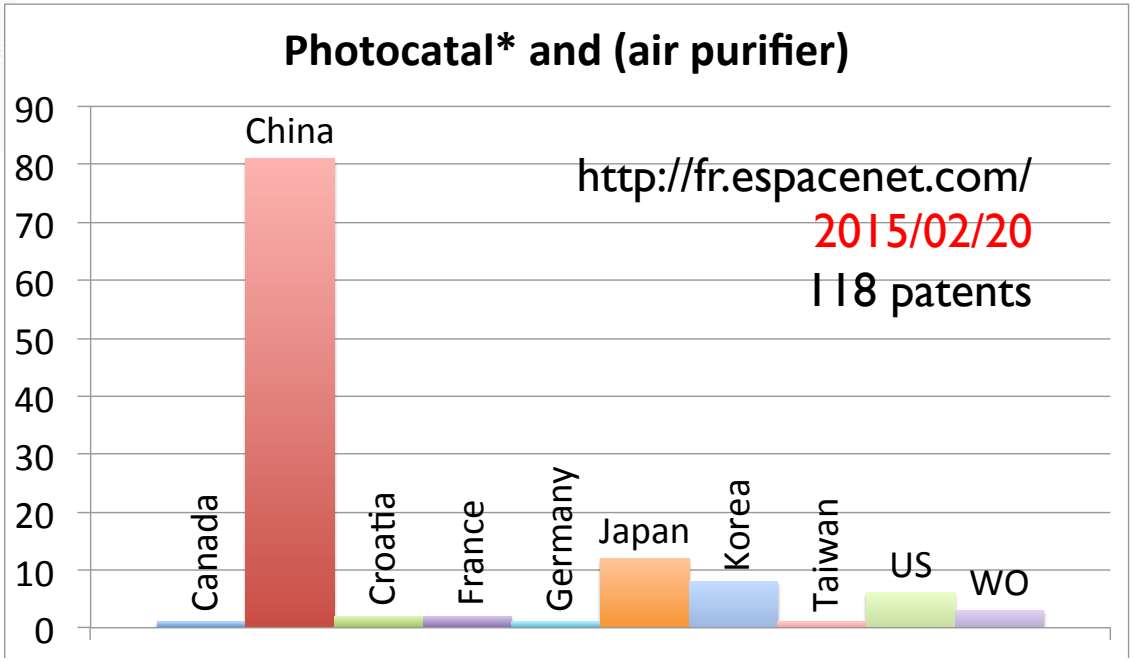
Papers on air treatment

(VOC or Volatile Organic Compound or NO_x or NO_2 or Nitrogen oxide or Nitrogen monoxide or air teatment) and **TiO_2** and **Photocatalys***

= 2 715 papers

= 108 Review papers

Patents on air purifiers only



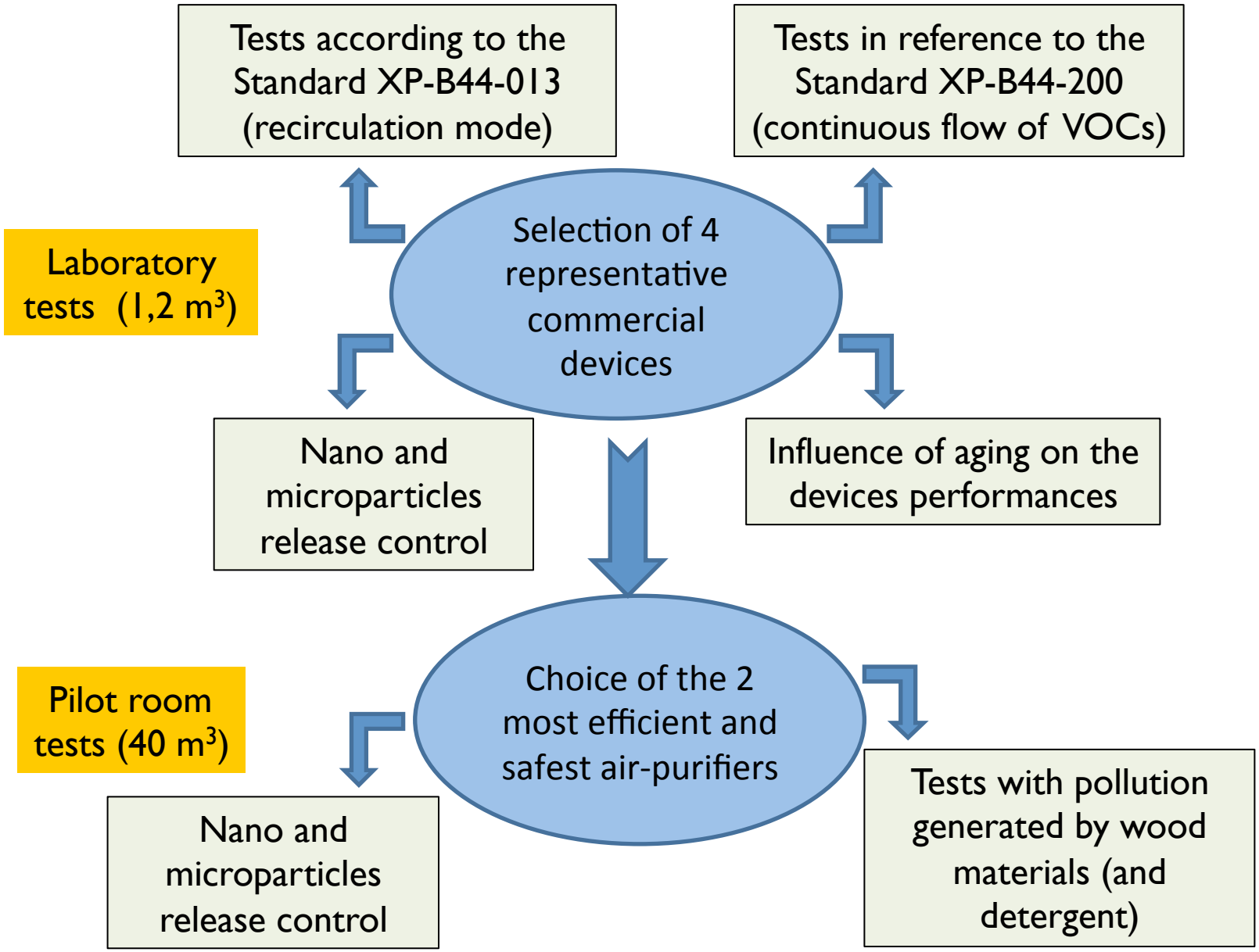
Context of the study

- A lot of air-purifying devices with photocatalytic functions are now available in the French/European Market
- Are these devices really efficient and safe ?

- How are these systems tested ?
- Information are not very clear in the advertisements
- In some cases, reference to tests carried out in various laboratories, but not **standardized**

Need for standard tests for photocatalytic air purifiers
Need for data in real conditions use

Aim of the study

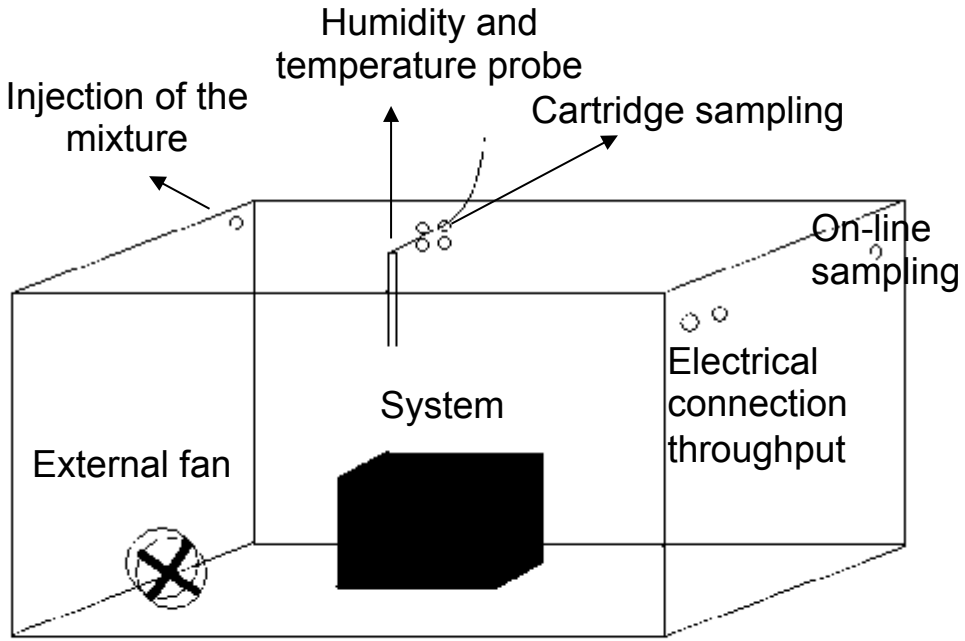


Principle of the standard closed chamber test (AFNOR XP B44-013 – French standard)

This protocol applies solely **to photocatalytic systems alone or to combined systems that include a photocatalytic function.**

Conditions

- Pollutants : acetaldehyde, acetone, n-heptane, toluene (formaldehyde in project for CEN)
- Indoor air at two concentrations
  1 : 250 ppbv/pollutants
  (check for by-products)
  2 : 1000 ppbv/pollutant
  (check for CO_2)
- Industrial issue : concentration depends on the application.
- Starting humidity and temperature : 50 ± 5 % RH and 22 ± 2 °C (may be varied)
- Total sampling volume : < 5% of the total chamber volume (50 L/m³)



Closed chamber : **V >1 m³**
System : flow max **1000 m³/h**
Vsystem/Vchamber ≤ 0.25
(< 0.1 in project for CEN)

Principle of the standard chamber test (AFNOR XP B44-200 – French standard)

This protocol applies **to all kind of autonomous air purifier**. Mesurement of device efficiency with various contaminants : Gas : mixture of VOCs → only contaminants in relation with our project.

Conditions

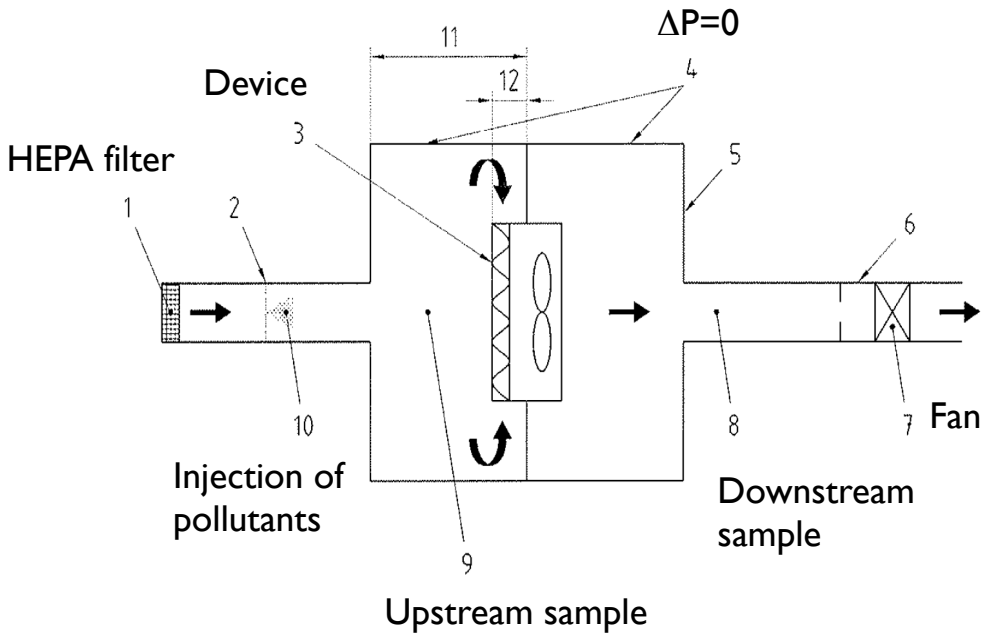
- Pollutants : acetaldehyde, acetone, n-heptane, toluene

  (generated continuously)

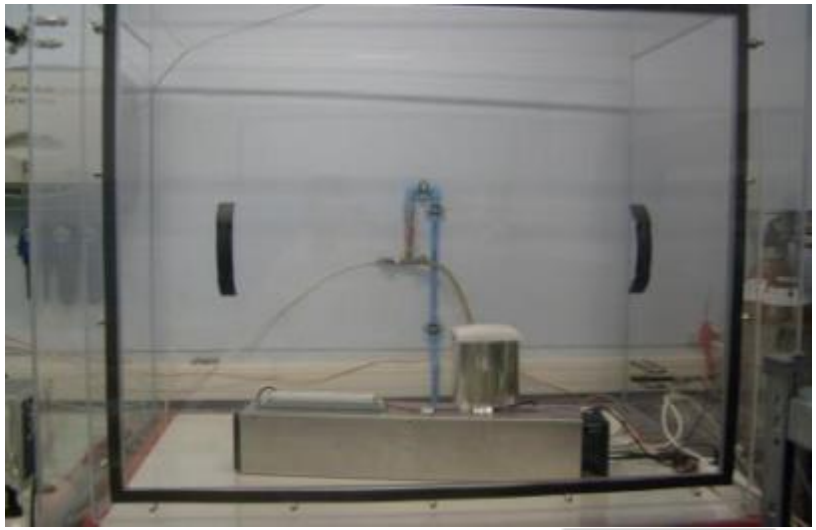
- Concentrations : 250 to 500 ppbv/pollutants (check for by-products : O_3, HCHO, CO, NO, NO_2)

- Humidity and temperature : 50 ± 5 % RH and 22 ± 2 °C

- Test air filtration : HEPA filter (NF EN 1822-1 and CA filter)



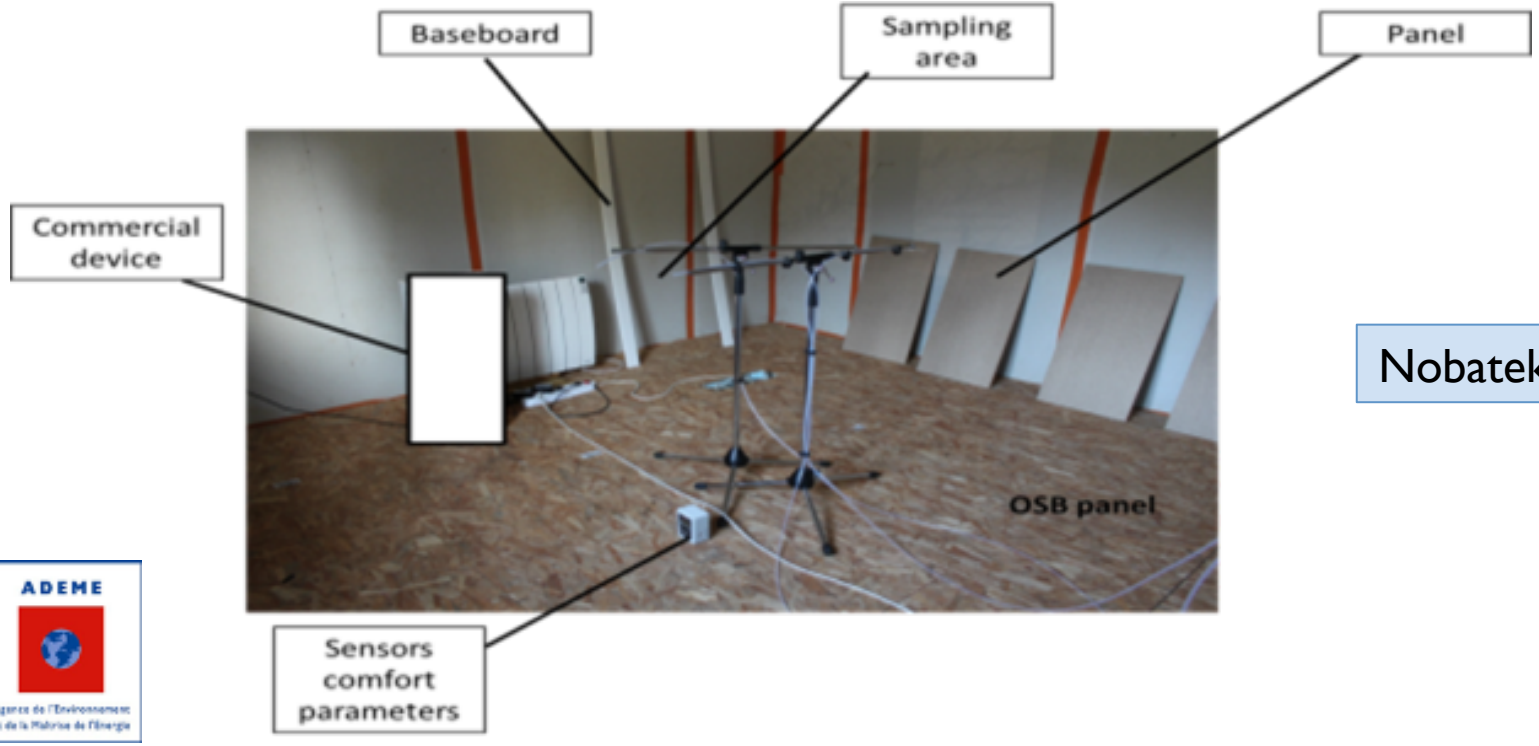
Chamber test IPREM and pilot room NOBATEK



IPREM : 1.17 m^3

Chambers validation :

- No VOCs release : <5 ppbv on 24 h
- Good airtightness : <10% COV leak on 24 h



Nobatek : 40 m^3

Analytical equipment used

PARAMETERS	ANALYTICAL EQUIPEMENT
Primary VOC (acetaldehyde, acetone, n-heptane, toluene)	**GC-PID /on line** (LD = 2 to 17 ppbv)
CO-CO_2 : VOC mineralisation	**GC-methanizer-FID / on line** (LD=1ppmv)
Secondary species and VOC in the pilot room	**Formaldehyde :** **adsorption on cartridges +HPLC-UV** (LD=4ppbv) **adsorption on SPME fibers+GC-MS or GC-FID** (LD<4ppbv) **VOC:** adsorption on cartridges +ATD-GC-MS (LD=1ppbv) **Ozone :** adsorption on cartridges +HPLC-UV (LD O3<0,5 µg/m^3)
Nano and microparticles	**ELPI (Electric Low Pressure Impactor) :** **13 stages : 7nm to 10 µm** (detection threshold: 0.5 part. cm^{-3} for 380 nm class, 7 part. cm^{-3} for 100 nm class)

Standardized tests (AFNOR XP B44-013) with the 4 selected commercial devices

Device	Irradiation source	Photocatalysis only	Control test without VOC		Photocatalytic test with 4 VOC (24 hours maximum)		
			VOC release	CO_2 produced	VOC removal	Mineralization	End by-product
D1	**UVA**	**Yes**	No	**Yes**	> 99%	complete	No
D2	**UVC**	**No** (ionization, filtration/activated carbon)	**Yes**	No	<20%	<5%	HCHO
D3	**UVC**	**No** (filtration/ activated carbon)	No	**Yes**	> 99%	not determined	No
D4	**unspecified**	**No** (ionization, filtration)	**Yes**	No	48 to 99%	<5%	HCHO

The devices could be ranked in two classes:

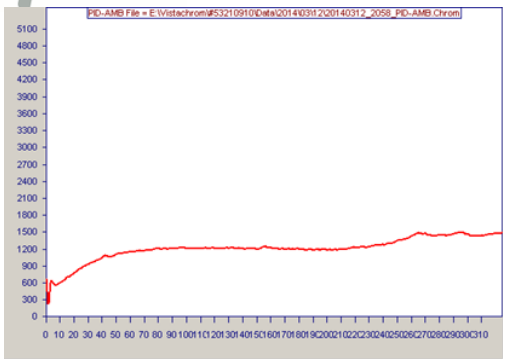
- **class 1 for efficient devices** : high VOCs elimination, extended mineralization, no by-product
- **class 2 for inefficient and unsafe ones** : by-product release even in the absence of VOCs, low VOCs removal and mineralization

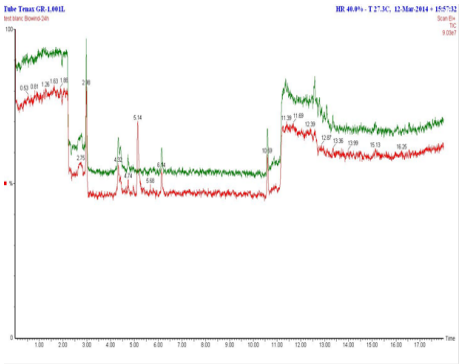
Determination of the Clean Air Delivery Rate (CADR, $m^3\ h^{-1}$)

Costarramone N., Kartheuser B., Pécheyran C., Pigot T., Lacombe S., *Catal. Today, 252, 35-40* (2015).

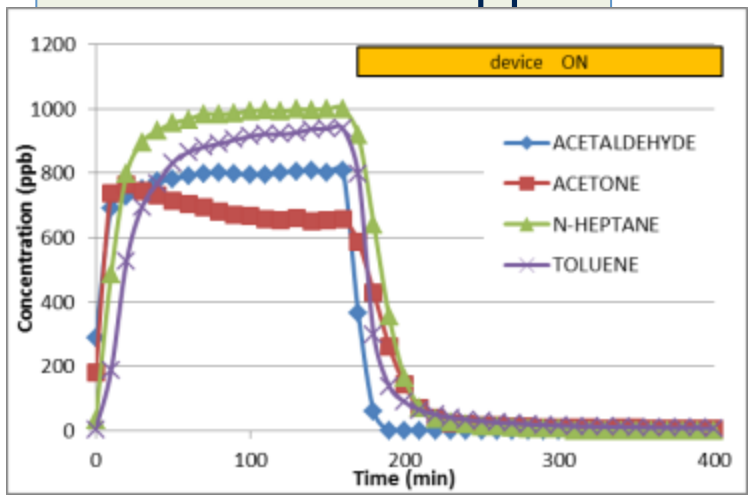
Example of photocatalytic device D1

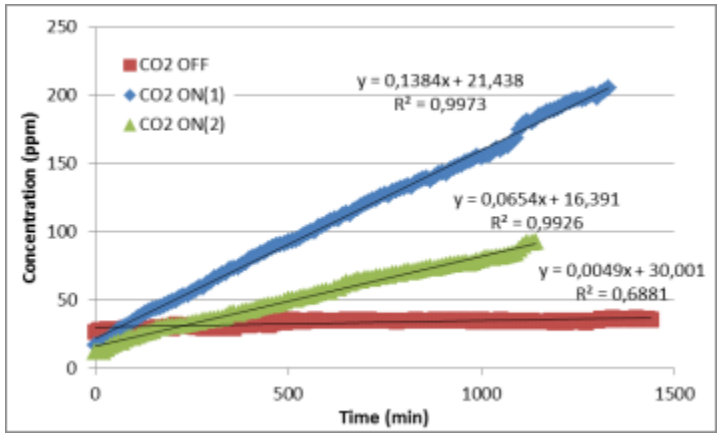
Without VOC added

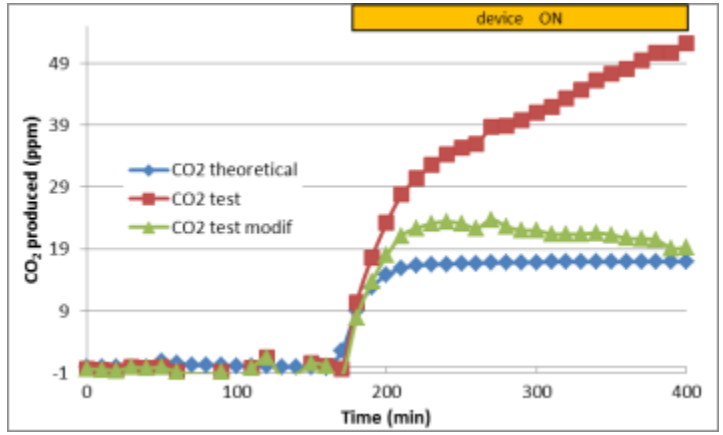




With 4 VOC ≈1 ppm





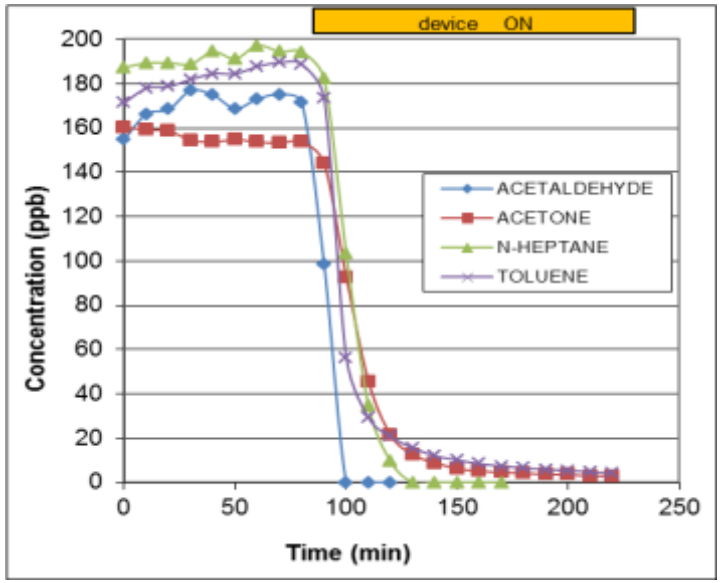


No VOC release but
CO_2 produced by the device
(decrease with time):
interfere with CO_2 from mineralisation

Complete 4 VOC elimination with device ON – Total mineralisation

Example of photocatalytic device D1

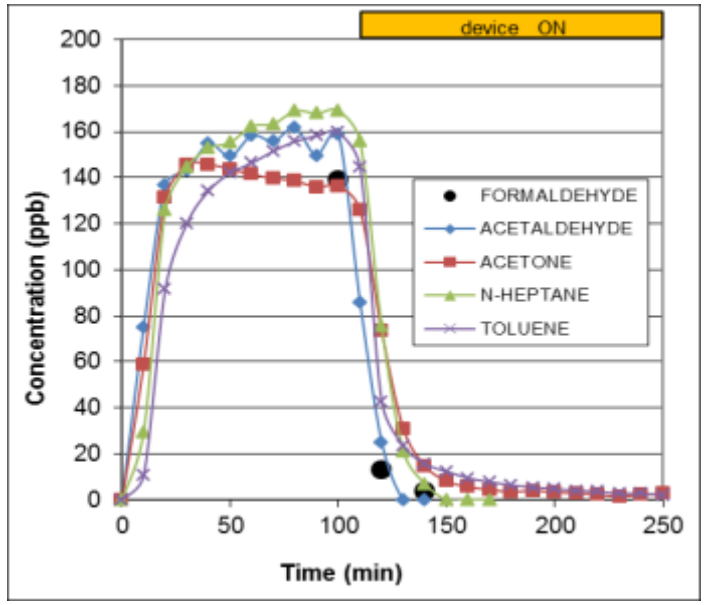
4 VOC ≈ 250 ppb



Sampling time (after start)	Formaldehyde test 1	Formaldehyde test 2
T 5-20 min	----------	14 ppb
T 15-30 min	8 ppb	----------
T 30-45 min	----------	5 ppb
T 45 min-1h	<DL	----------

Formaldehyde : only transient by-product detected in low amount

5 VOC ≈ 250 ppb



Complete elimination of 5 VOCs with device ON

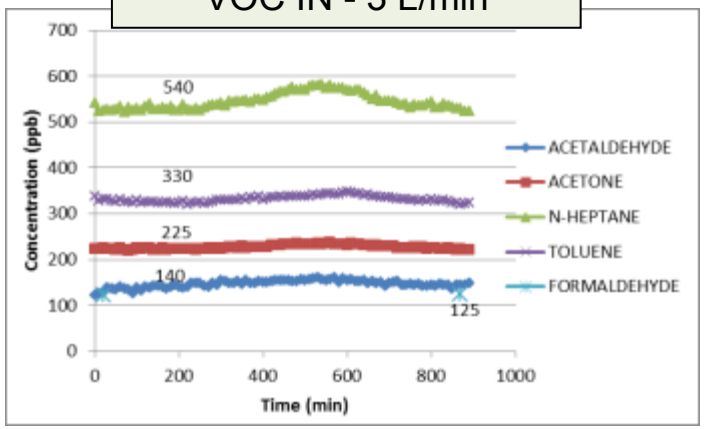
Tests according to the AFNOR XP-B44-200 standard

Device	Control test without VOC		Test with 4 VOCs added continuously (24 hours maximum)		
	NO_x produced	O_3 generated	VOC removal	Mineralization	By-products
D1	YES	NO	> 99%	Yes	NOx
D3	NO	NO	> 99%	Yes	None
D4	YES	NO	residual acetone and toluene (≈20 ppb)	No	Formaldehyde NOx

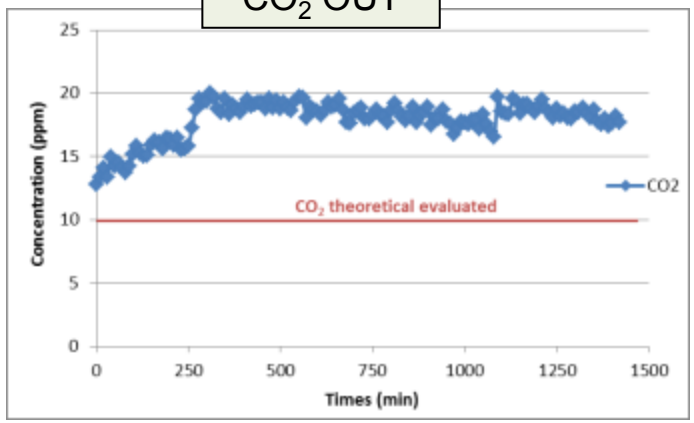
2 devices/3 seem efficient for mineralization
Only 1 device release neither VOC nor NO_x (D3)

Test according to the AFNOR XP-B44-200 standard : exemple of device D1

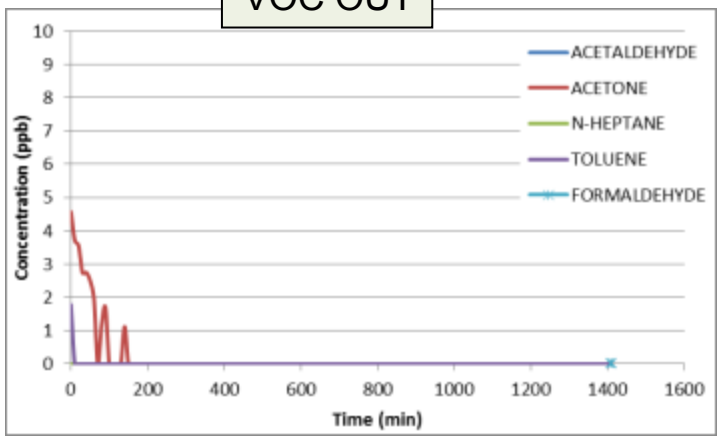
VOC IN - 3 L/min



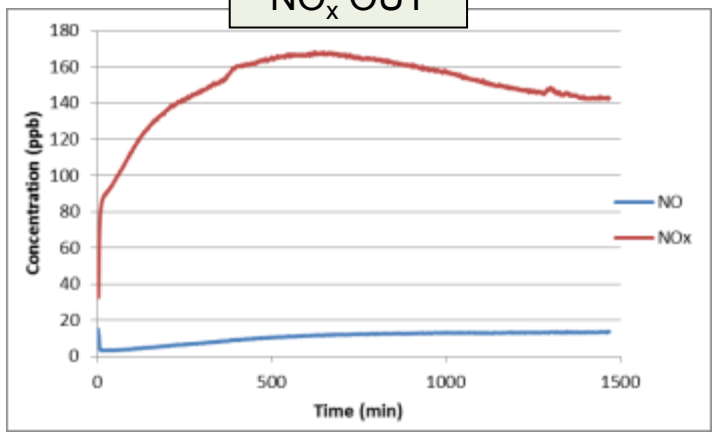
CO_2 OUT



VOC OUT



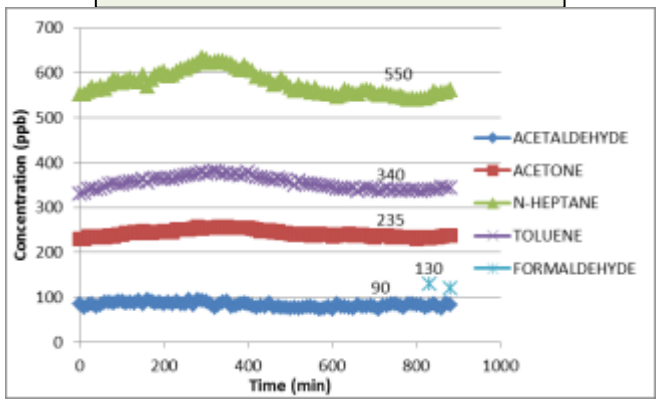
NO_x OUT



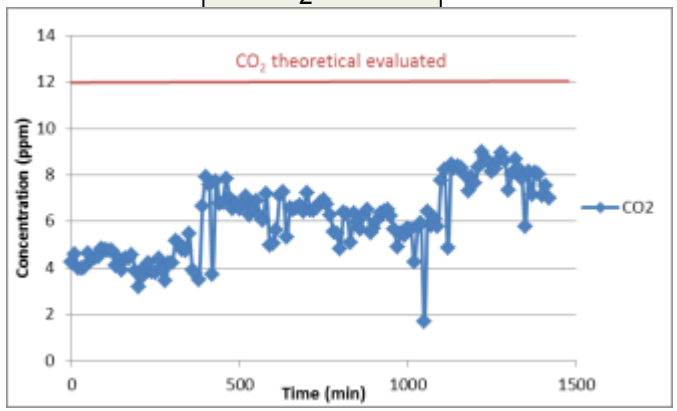
No residual VOC
Good VOC mineralization
BUT : NO_x release by the device (due to the particles filter)

Test according to the AFNOR XP-B44-200 standard : exemple of device D4

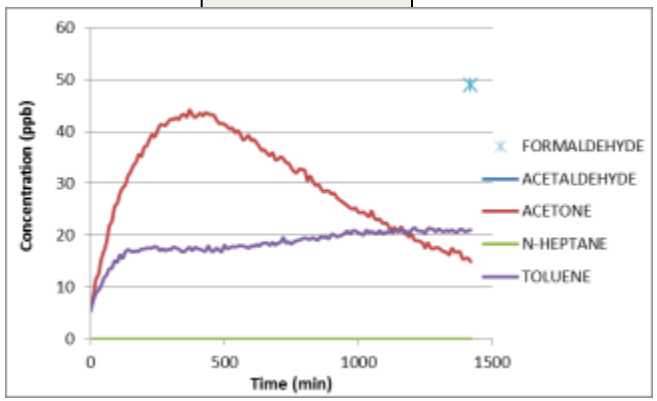
VOC IN - 3 L/min



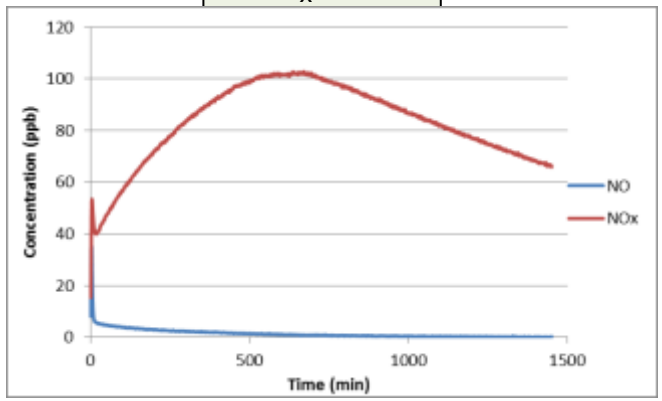
CO_2 OUT



VOC OUT



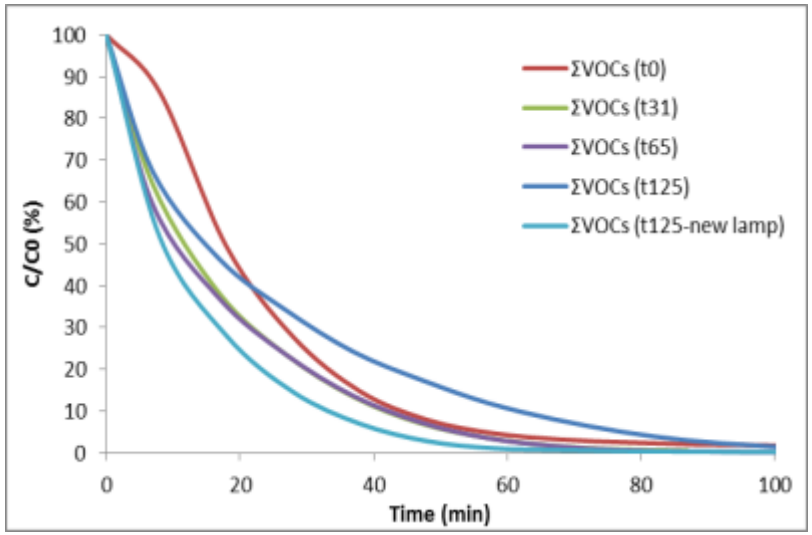
NO_x OUT



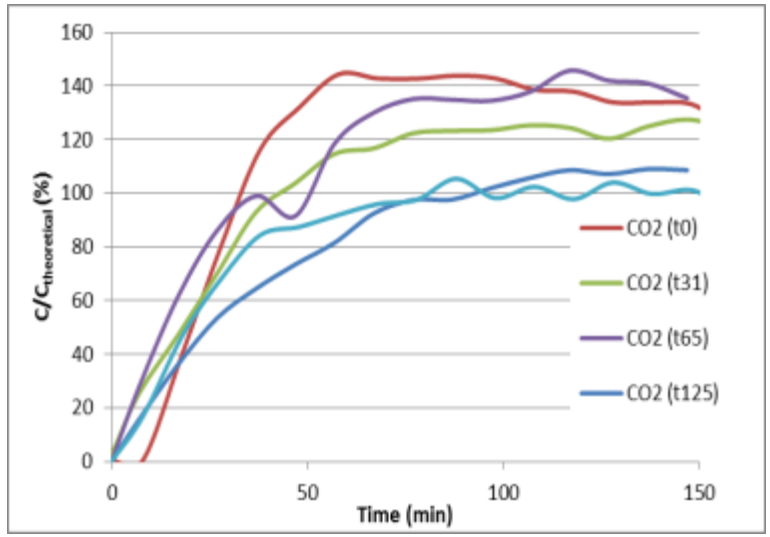
Residual VOC : few ppbv
No VOC mineralization
NO_x release by the device

Results about system aging - device D1- XP B44-013

VOC DECREASE (1 ppmV)



Mineralisation



CADR

Clean Air Delivery Rate

($m^3\ h^{-1}$)

CADR	Acetaldehyde	Acetone	n-heptane	Toluene	Σ COV
t 4 months (new lamp)	10.30±0.94	2.85±0.16	4.26±0.17	13.18±0.58	5.42±0.36
t 4 months	5.18±0.28	1.44±0.04	1.85±0.03	8.29±0.01	2.64±0.04
t 2 months	9.49	2.51	2.76	11.81	3.88
T 1 month	10.03±0.70	2.84±0.15	2.89±0.27	8.31±0.26	4.14±0.25
t_0 (new device)	9.10±0.90	2.79±0.25	2.71±0.18	4.39±0.10	3.65±0.16

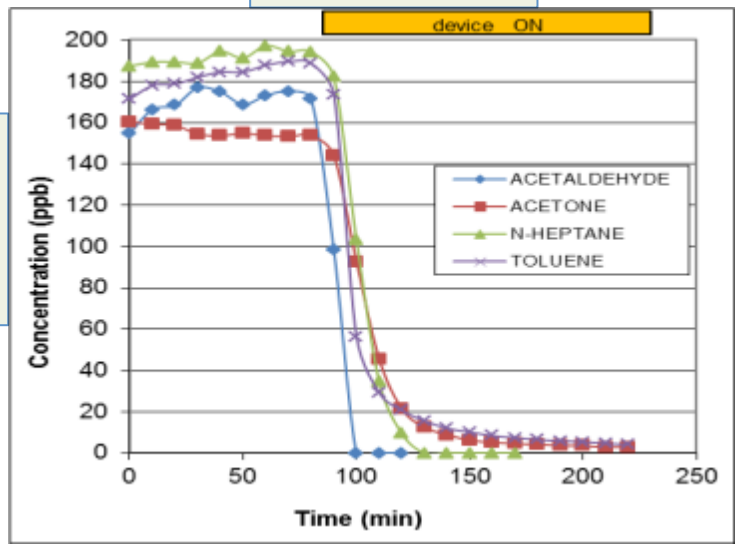
Irradiance

Wavelength range	300-550 nm Lamp 1- up	300-550 nm Lamp 2 - down
New device	5.7 mW/cm²	5.8 mW/cm²
4 months old device	2.2 mW/cm²	2.3 mW/cm²

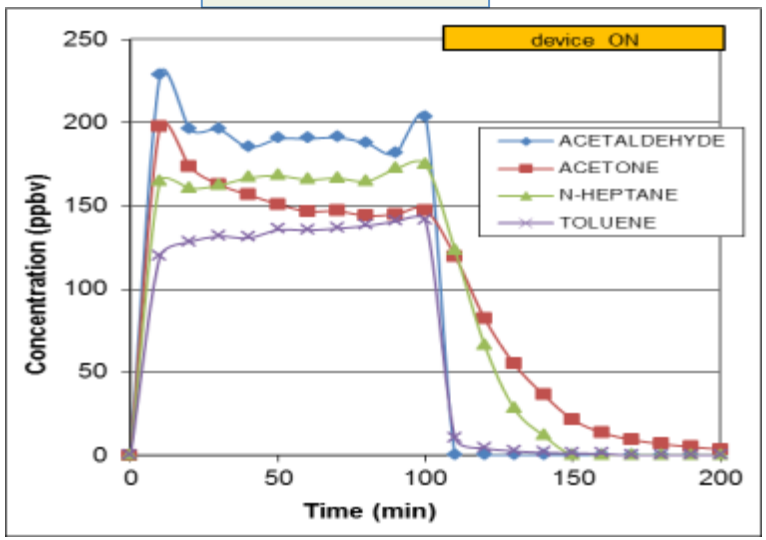
Results about system aging - device D1

4 VOC
≈ 250 ppb

t_0



$T_{4\ months}$



Sampling time (after start)	Formaldehyde test 1 - t_0	Formaldehyde test 2 – t_0
T 5-20 min	----------	14 ppb
T 15-30 min	8 ppb	----------
T 30-45 min	----------	5 ppb
T 45 min-1h	ND	----------

Sampling time (after start)	Formaldehyde test 1 – $t_{4\ months}$
T 5-20 min	19 ppb
T 30-45 min	5 ppb

Formaldehyde : only transient by-product detected in low amount

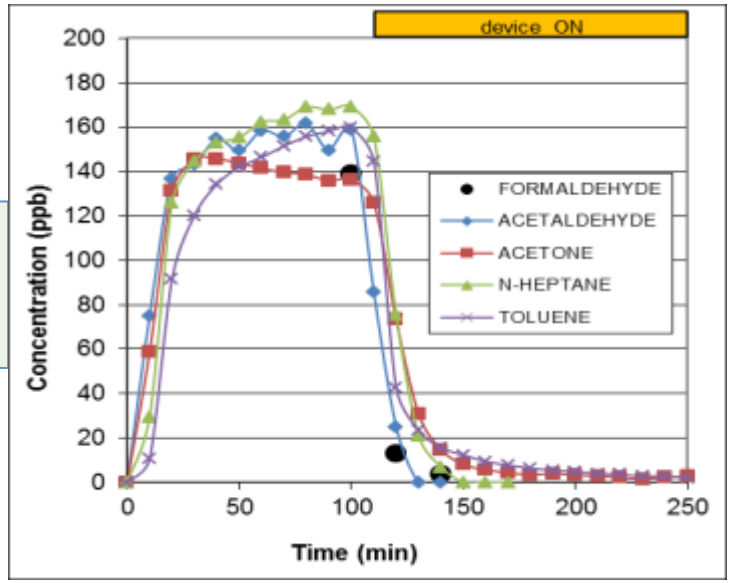
CADR
($m^3\ h^{-1}$)

CADR	Σ COV
Device 4 month	5.67
Device 2 month	8.41
Device 1 month	8.35±0.09
New device	5.01±0.06

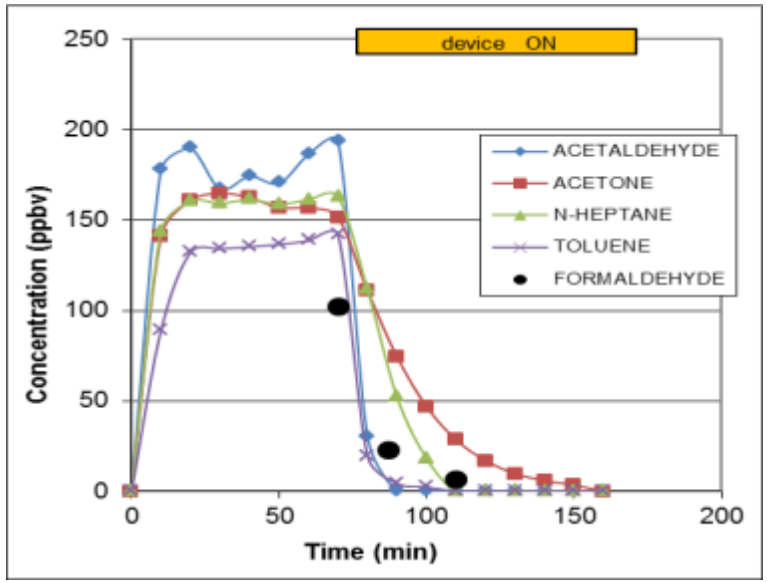
Results about system aging - device D1

5 VOC
≈ 250 ppb

t_0



$t_{4\ months}$

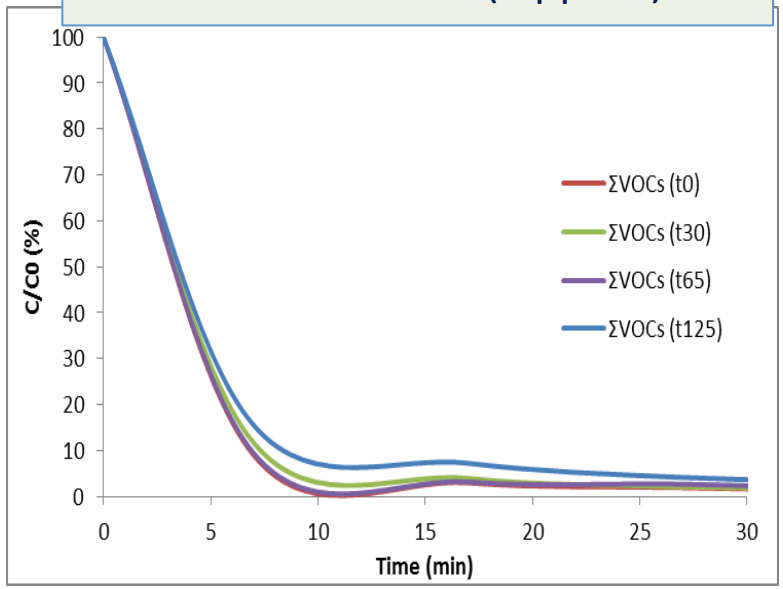


CADR ($m^3\ h^{-1}$)	Σ COV
t 4 months	6.50
t 1 month	7.53
T_0 (new device)	5.53±0.15

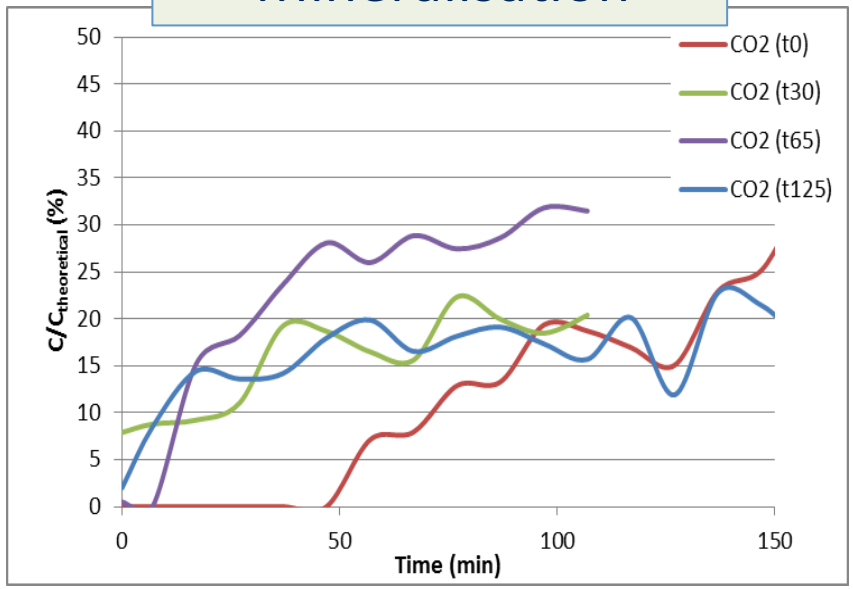
Complete elimination of 5 VOCs with device ON
Low variation of efficiency between 0 and 4 months

Results about system aging - device D3

VOC DECREASE (1 ppmV)



Mineralisation



CADR ($m^3\ h^{-1}$)

CADR	Acetaldehyde	Acetone	n-heptane	Toluene	Σ COV
t 4 months	10.5±0,4	11.6±2.1	23.4±0.4	18.3±1.9	15.6±1.4
t 2 months	10.9±1.8	17.2±1.2	28.6±2.2	25.6±0.5	22.3±1.4
t 1 month	11.8±0.6	23.7±4.0	31.4±3.7	29.7±2.9	26.8±3.4
t_0 (new device)	12.8	23.2	29.4	24.5	34.4

Irradiance

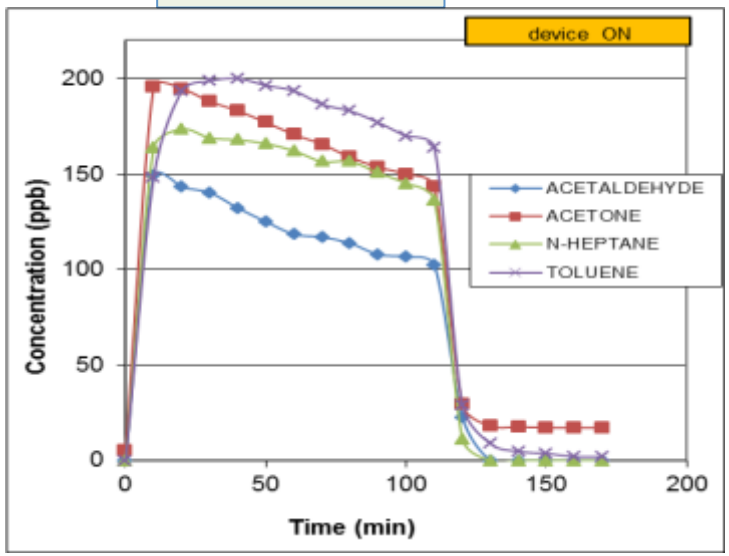
Wavelength range	200-300 nm	200-800 nm
New device	7.7 mW/cm²	10.8 mW/cm²
4 months old device	9.4 mW/cm²	11.5 mW/cm²

Mineralisation cannot be quantified : AC present
Low variation of efficiency between 0 and 4 months

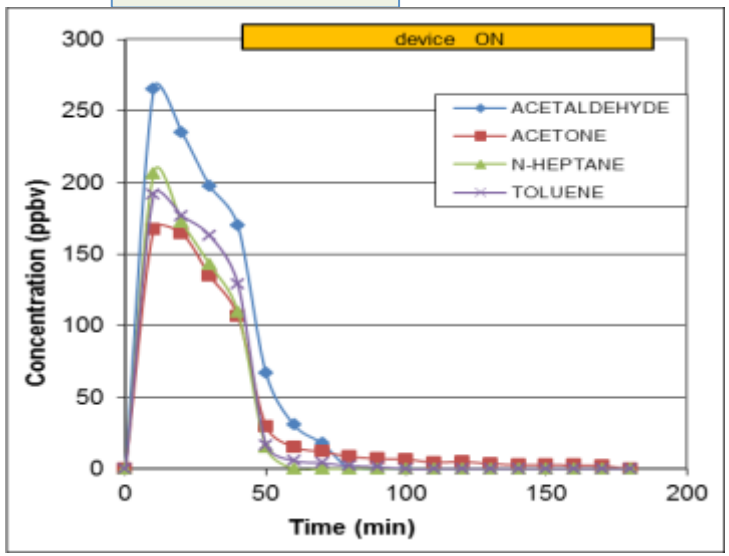
Results about system aging - device D3

4 VOC
≈ 250 ppb

t_0



$T_{4\ months}$



Sampling time (after start)	Formaldehyde test t_0
t 5-20 min	13 ppb
t 30-45 min	10 ppb

Sampling time (after start)	Formaldehyde test $t_{4\ months}$
t 5-20 min	7 ppb
t 30-45 min	<5 ppb
t 2h15-2h30	<5 ppb

Formaldehyde : only transient by-product detected in low amount

CADR
($m^3\ h^{-1}$)

CADR	Σ COV
t 4 months	23.2
t 2 months	31.8
t 1 month	25.8±6.1
t_0 (new device)	38.5±0.1

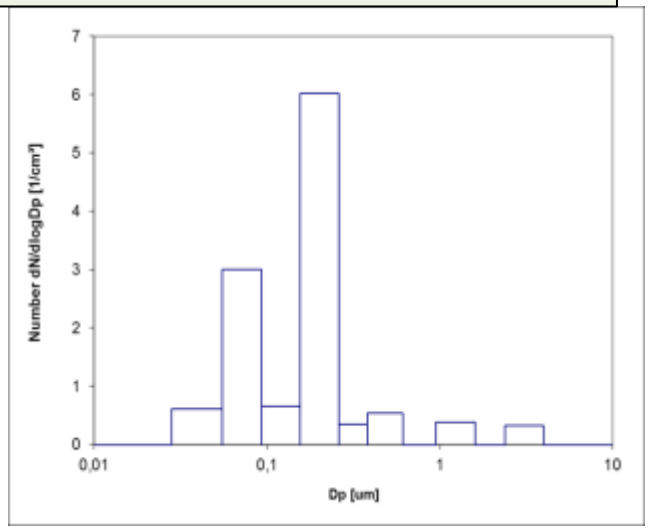
VOC adsorption, device OFF
Fast VOC elimination, device ON

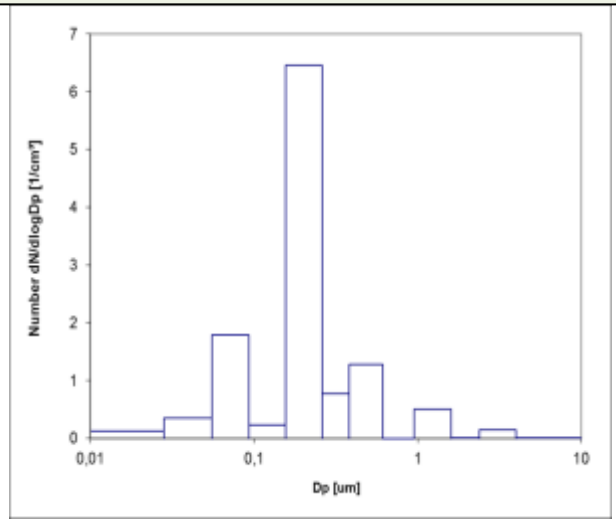
First results of nanoparticles release

Average distribution of the background of the chamber flushed with clean air

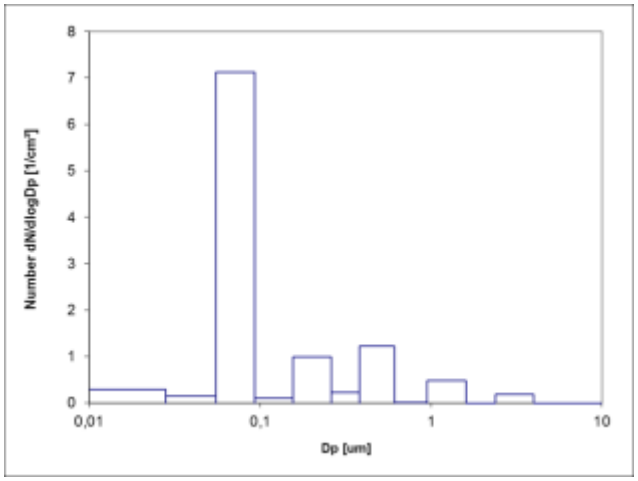
Average distribution with system ON during 3h30 (D1) and 4h30 (D3)

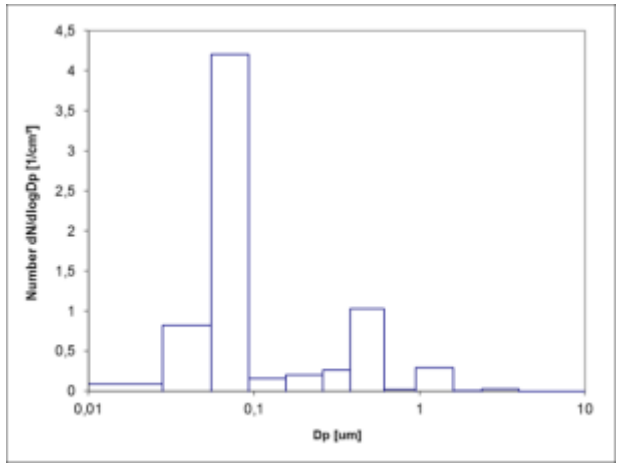
Test D1





Test D3





No nanoparticles emitted by 4 devices (either new or old) D1/D2/D3/D4

PILOT SCALE TESTS (EVALIS) - STUDY WITH DEVICE D3

Tests conditions and organisation

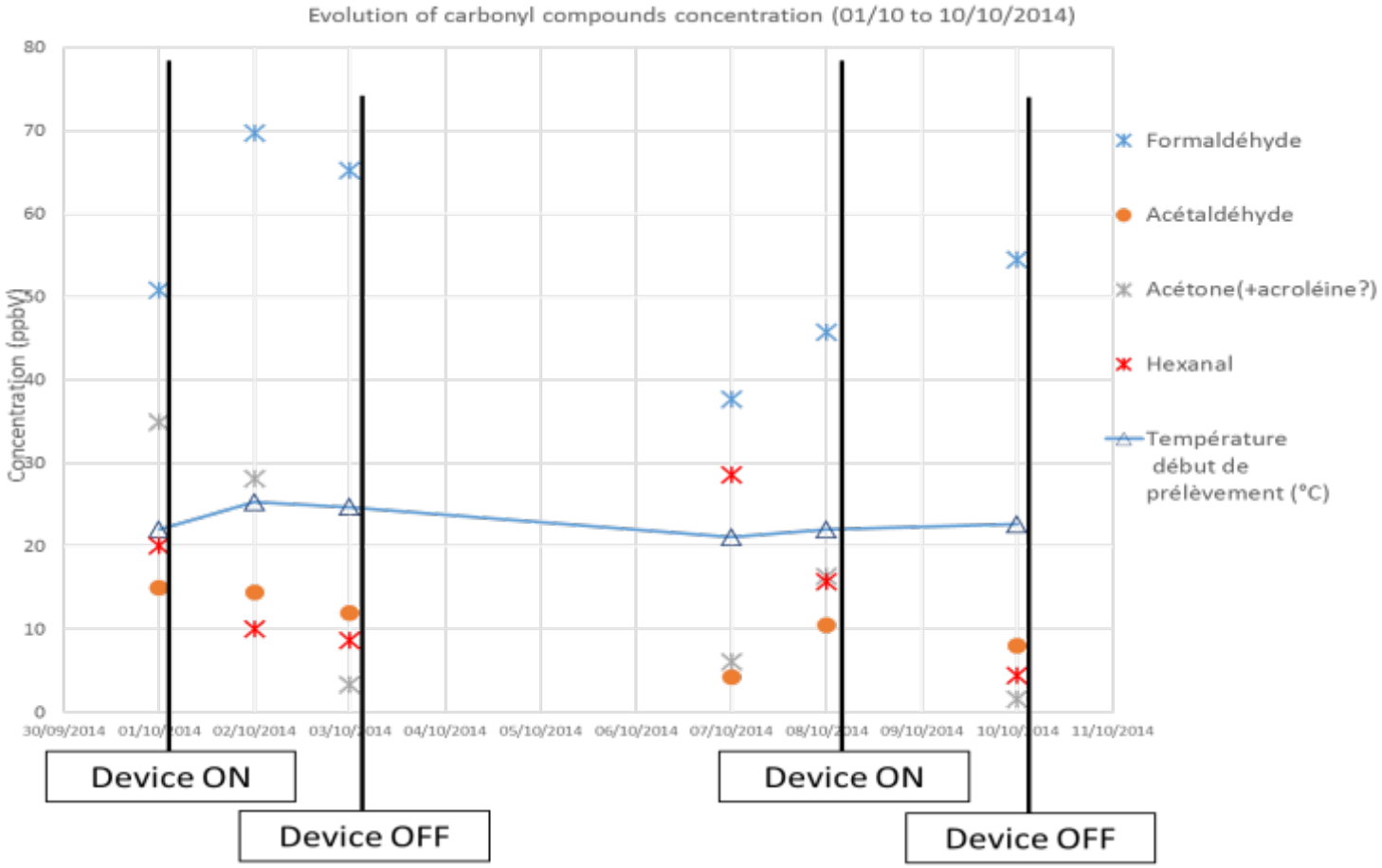
Temperature	**21 °C ± 5°C**
Air exchange	0,02 vol/h ± 0.01 vol/h
Air pollution simulation	Panel and baseboard introduction

N° phase	Description	Date – number of days
Phase 1	The room is empty, this is the reference.	18/09-20/09/2014 – 2 d
Phase 2	Device introduction in the room. The device is OFF.	22/09-24/09/2014 – 2 d
Phase 3	Device ON	24/09-26/09/2014 – 2 d
Phase 4	**Device OFF, Panel and baseboard introduction**	29/09-01/10/2014 – 3 d
Phase 5	**Device ON**	01/10-03/10/2014 – 2 d 08/10-10/10/2014 – 2 d 21/10-21/11/2014 – 31 d
Phase 6	**Supplementary pollution added (detergent)**	12/11-21/11/2014 – 9 d

PILOT SCALE TESTS (EVALIS) - STUDY WITH DEVICE D3

Formaldehyde and others carbonyl compounds with pollution introduced, device ON/OFF

Results PHASES 4-5-6

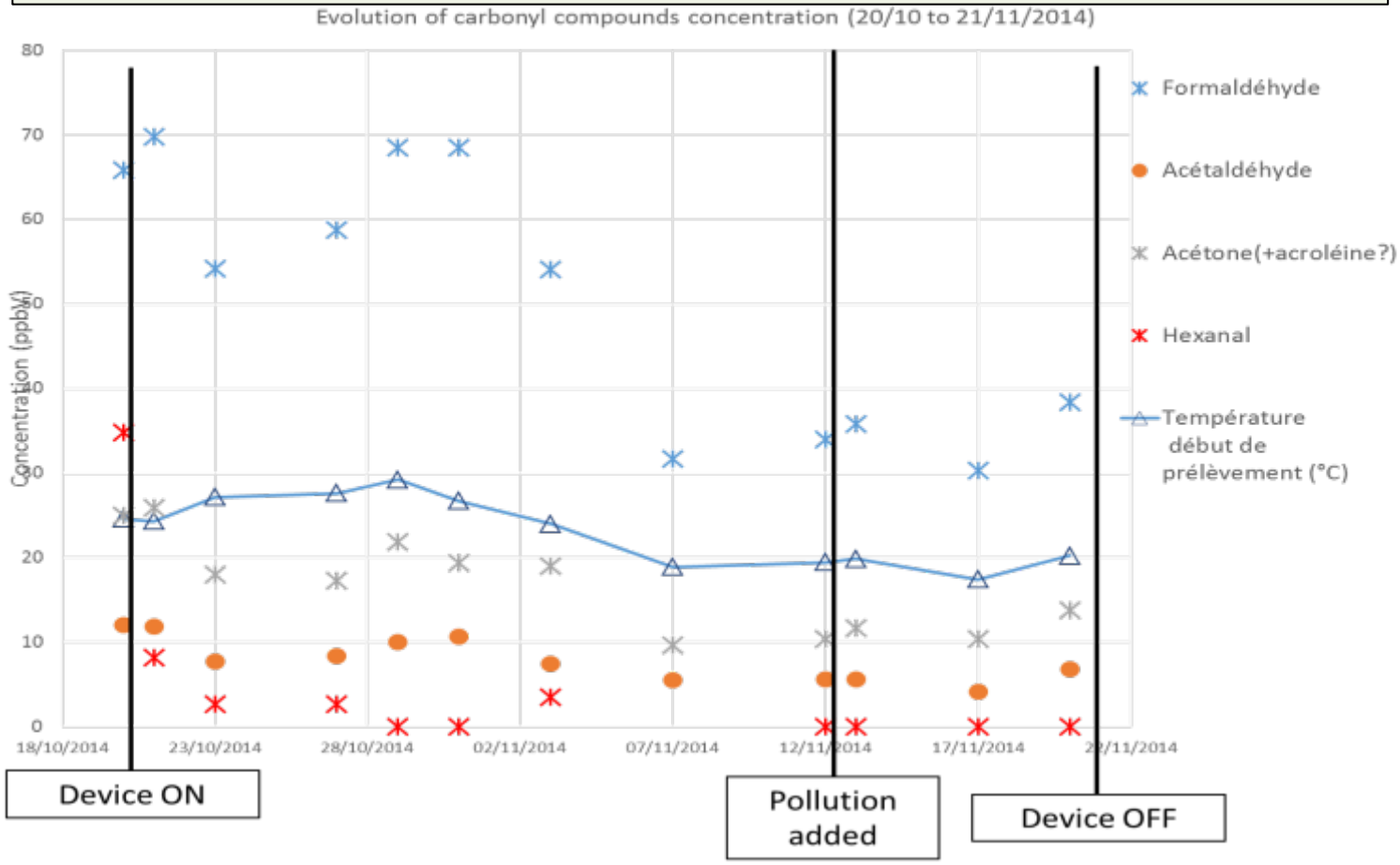


With device ON : effect on carbonyl compounds except formaldehyde continuously released in high amount from the wooden material

PILOT SCALE TESTS (EVALIS) - STUDY WITH DEVICE D3

Formaldehyde and others carbonyl compounds with pollution introduced, device ON during 1 month

Results PHASES 4-5-6

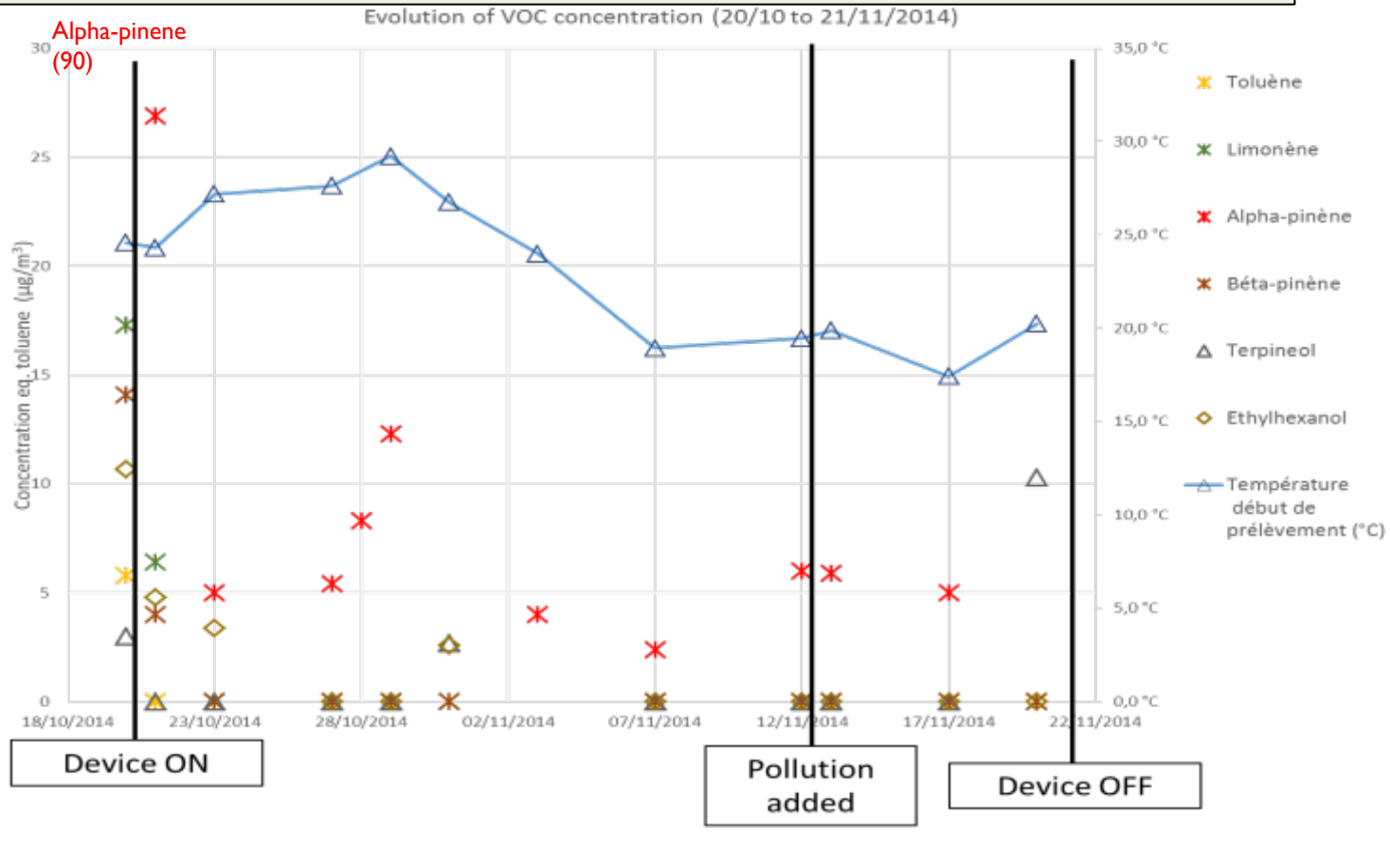


Stabilisation of the concentrations after 3 days : formaldehyde concentration remains high.
The equilibrium is sensitive to T.

PILOT SCALE TESTS (EVALIS) - STUDY WITH DEVICE D3

Others VOC (TENAX+ATD-GC-MS) with pollution introduced, device ON during 1 month

Results PHASES 4-5-6

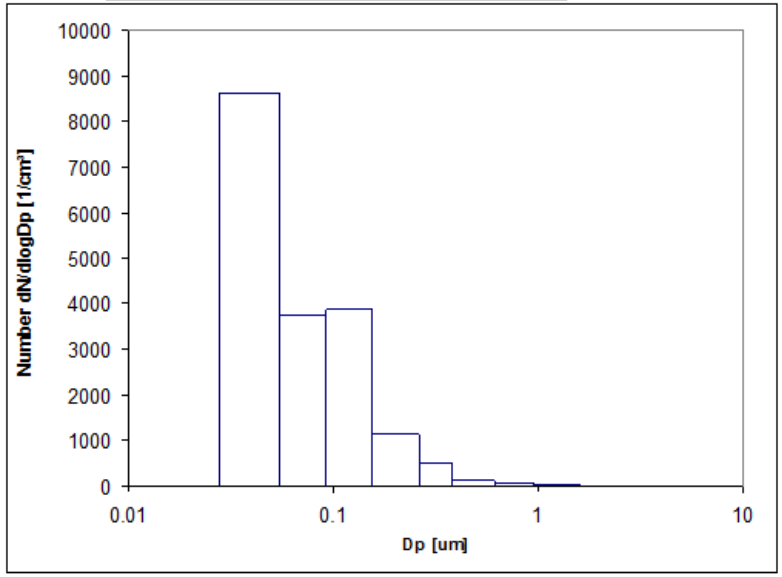


Stabilisation of the concentrations after 3 days with device ON.
Alpha-pinene decreases from 90 to 27 µg/m^3 eq. toluene in only 1 day. The others pollutants show a high elimination rate too. The equilibrium is sensitive to T.

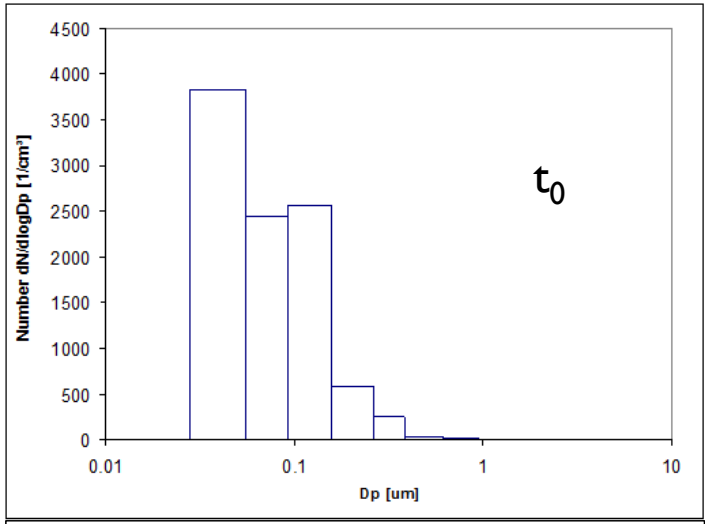
PILOT SCALE TESTS (EVALIS) - STUDY WITH DEVICE D3

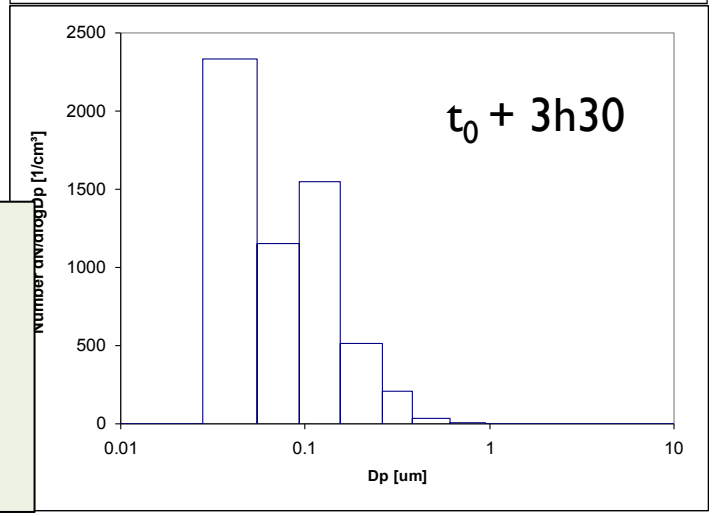
Measurements after 6 days with device continuously ON (27-10)

Outdoor air EVALIS



Indoor air EVALIS with device ON



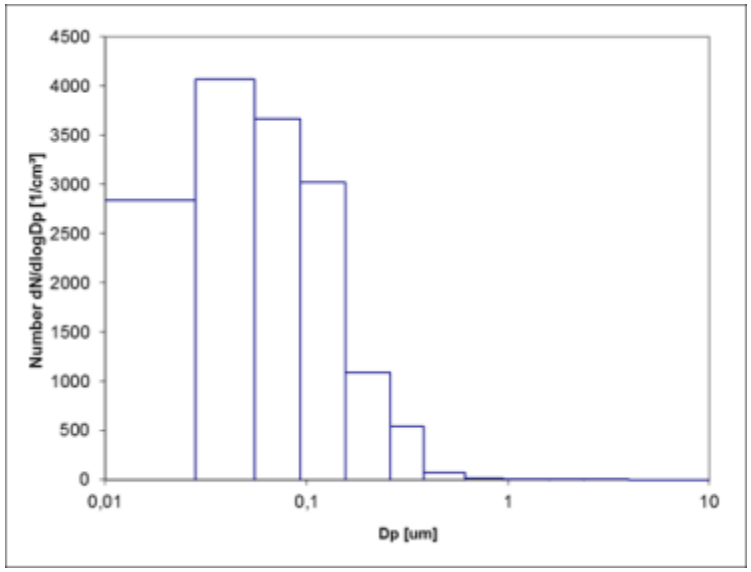


- Nano and microparticles measured outdoor upper than indoor.
- Downward trend of the nano and microparticles inside the platform with the device ON between the beginning and the end of experiments.

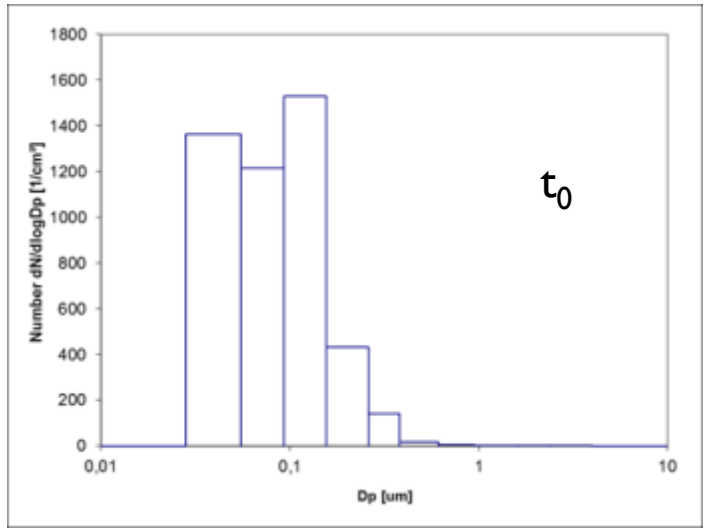
PILOT SCALE TESTS (EVALIS) - STUDY WITH DEVICE D3

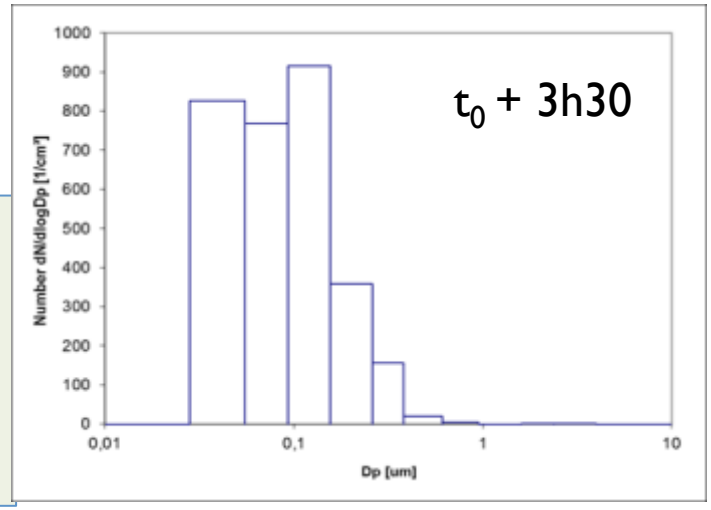
Measures after 30 days continuous device working (20-11)

Outdoor air EVALIS



Indoor air EVALIS with device ON



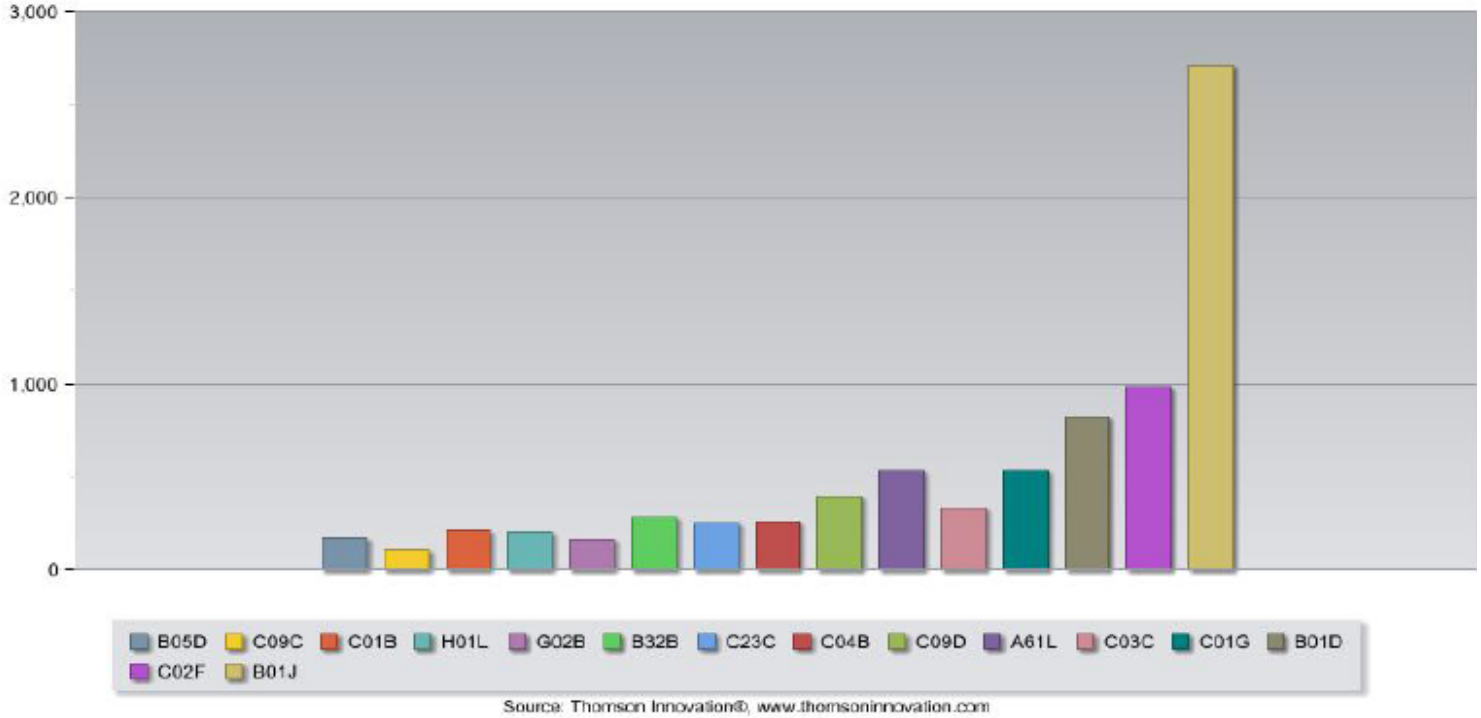


- Nano and microparticles measured outdoor upper than indoor.
- Downward trend of the nano and microparticles inside the platform with the device ON between the beginning and the end of experiments.

Conclusion

- Possible laboratory-scale comparison of photocatalytic commercial and innovative devices and materials using standardized tests.
- Standardised tests useful to guarantee that devices found in the market are safe and efficient.
- Certification needed for these commercial products.
- Analysis of systems and media aging as well as nanoparticles release useful to determine the evolution of efficiency with time.
- First tests in real conditions with an efficient device (previously tested in laboratory) show that VOC concentrations are reduced except for formaldehyde. No nano and microparticles were released by the device.
- In progress : tests in real conditions with a second efficient device.

Thank you for your attention



1Catalysis,2 Treatment of water,3 Separation,4 Coating compositions,4 Treatment of air,5 Glass,6 concrete and ceramics

B05D: PROCESSES FOR APPLYING LIQUIDS OR OTHER FLUENT MATERIALS TO SURFACES
C09C: TREATMENT OF INORGANIC MATERIALS, OTHER THAN FIBROUS FILLERS
C01B: NON-METALLIC ELEMENTS
H01L: SEMICONDUCTOR DEVICES
G02B: OPTICAL ELEMENTS, SYSTEMS, OR APPARATUS
B32B:LAYERED PRODUCTS
C23C: COATING METALLIC MATERIAL
C04B: LIME, MAGNESIA; SLAG; CEMENTS; COMPOSITIONS THEREOF, e.g. MORTARS, CONCRETE
C09D: COATING COMPOSITIONS
A61L: METHODS OR APPARATUS FOR STERILISING MATERIALS OR OBJECTS
C03C: CHEMICAL COMPOSITION OF GLASSES, GLAZES, OR VITREOUS ENAMELS; SURFACE TREAT
C01G: COMPOUNDS CONTAINING METALS
B01D: SEPARATION
C02F: TREATMENT OF WATER, WASTE WATER, SEWAGE, OR SLUDGE
BO1J: CHEMICAL OR PHYSICAL PROCESSES