Sicherheit in Technik und Chemie

20NRM04 METRIAQ - WEBINAR

Development, application and measurement uncertainty of emission reference materials

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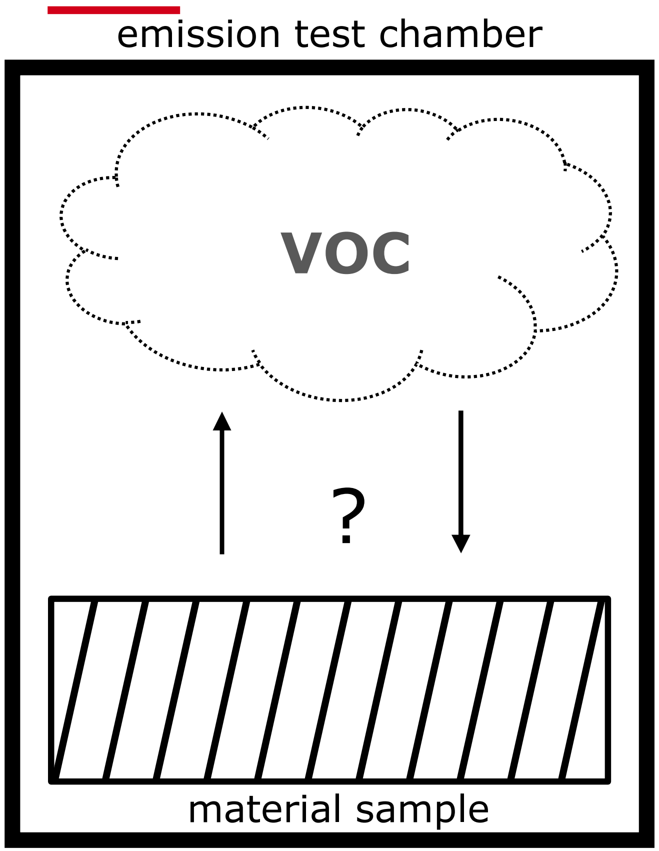
Motivation



Temperature (°C)

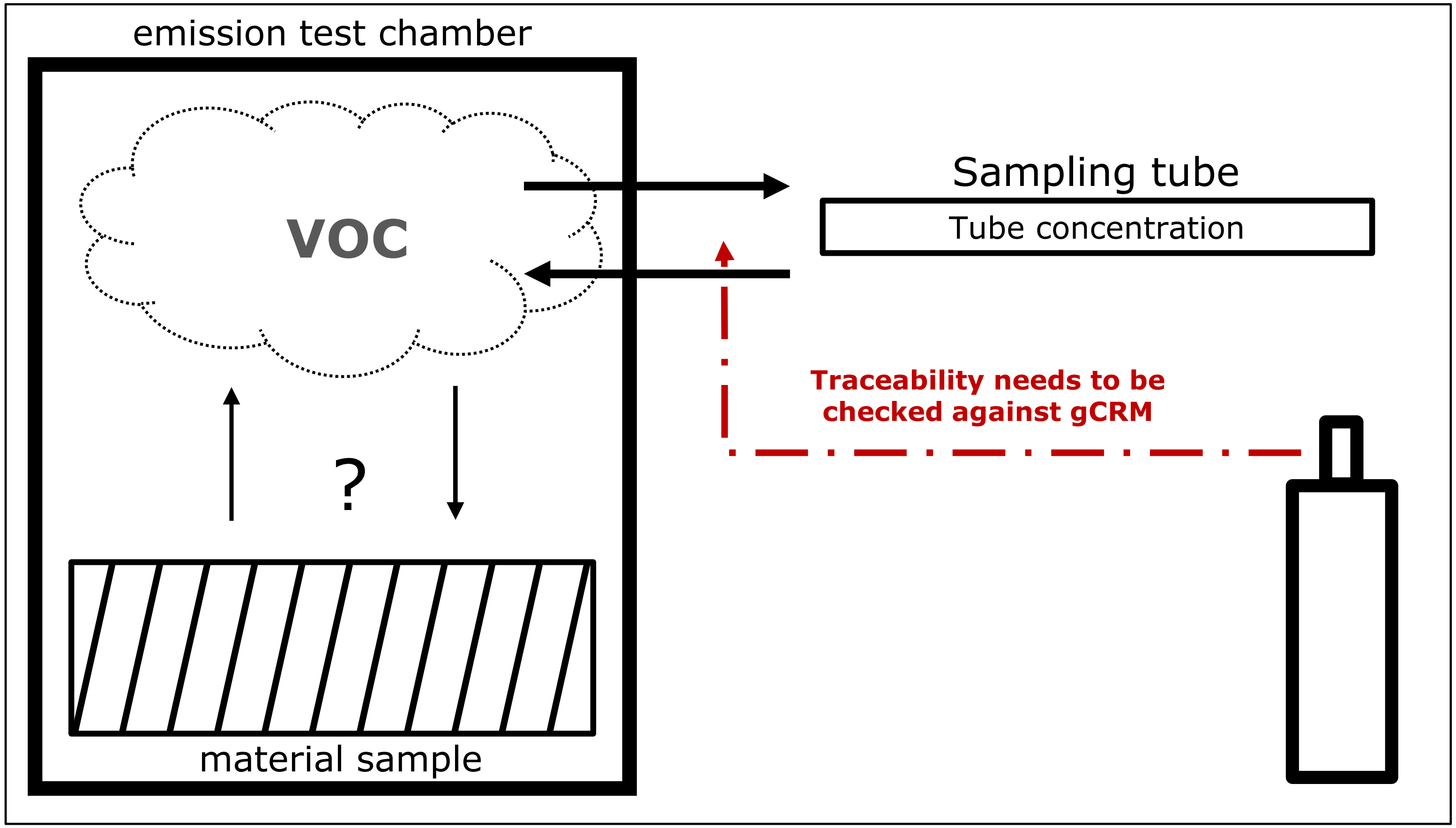
Rel. Humidity (RH [%])

Air exchange rate (AER [h^{-1}])

Great variety of VOC emissions

- **aliphatic hydrocarbons**
- **aromatic hydrocarbons**
- **aldehydes**
- **ketones**
- **aromatic alcohols**
- **glycols**
- **isothiazolinones**
- **siloxanes**
- **terpenes**
- **etc.**

Motivation



Sampling on

- **Desorption tubes**
- **DNPH cartridges**
- **etc.**

followed by chromatographic analysis

gCRM partially available

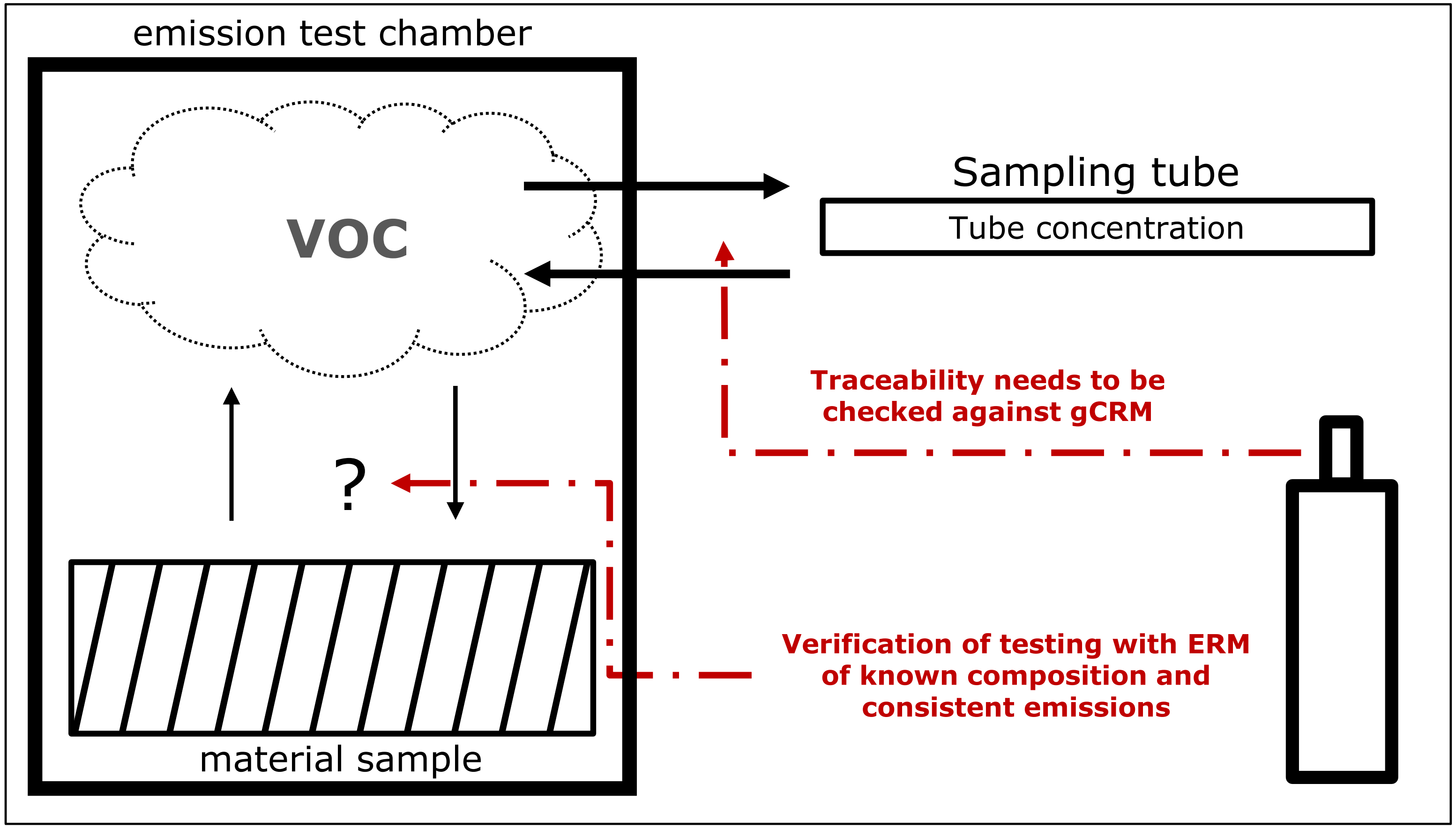
but

still needed for

- **higher boiling VOCs**
- **VOCs on EU-LCI list**

gPRM needed for certification of commercial VOC test gas mixtures

Motivation



gCRM partially available

<u>but</u>

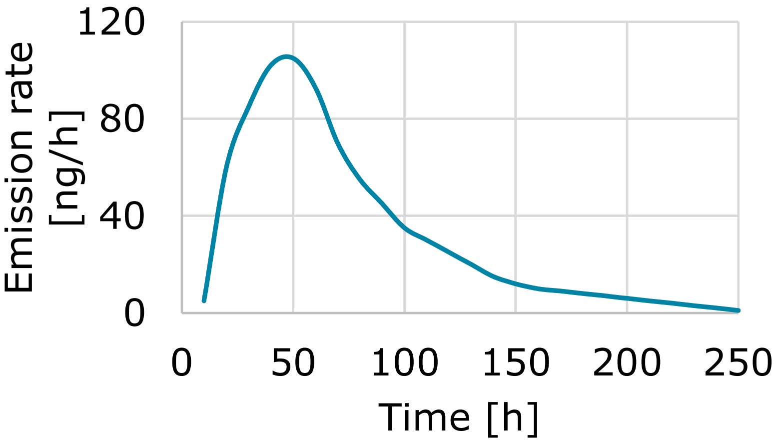
still needed for

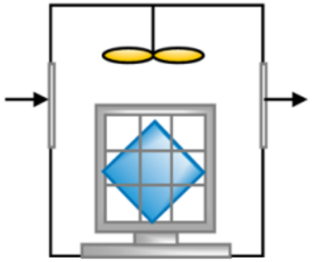
- **higher boiling VOCs**
- **VOCs on EU-LCI list**

gPRM needed for certification of commercial VOC test gas mixtures

No suitable ERM with predictable emission rates available

Motivation

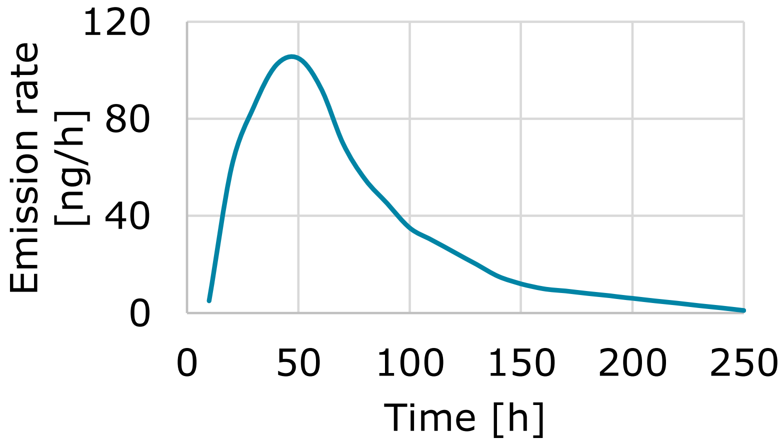




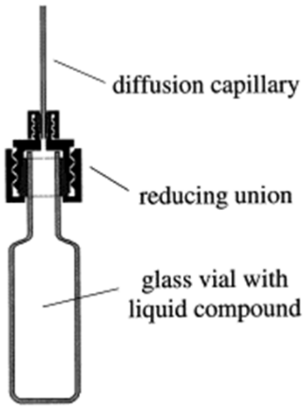
Liu et al., Environ. Sci. Technol., **2013**.

Mull et al., Air Qual. Atmos. Health, **2017**.

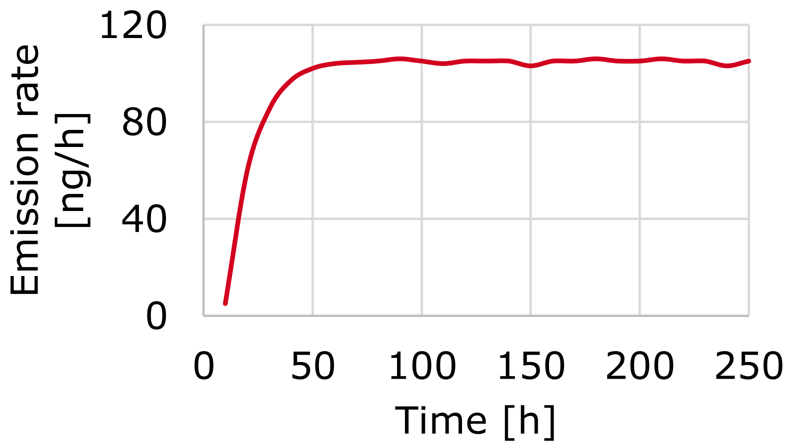
Motivation

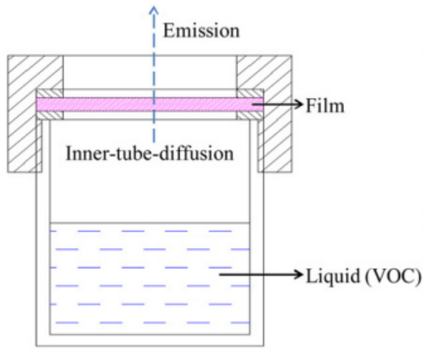


- „natural depletion curve"
- often short term or single VOC only
- not very reproducible



Gautrois et al., J. Chrom. A, **1999**.

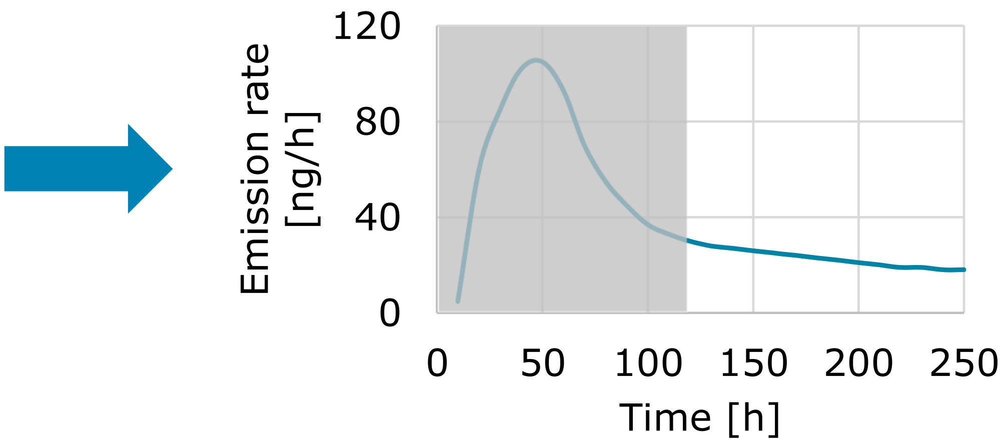




Wei et al., Atmospheric Environment, **2011**.

Motivation

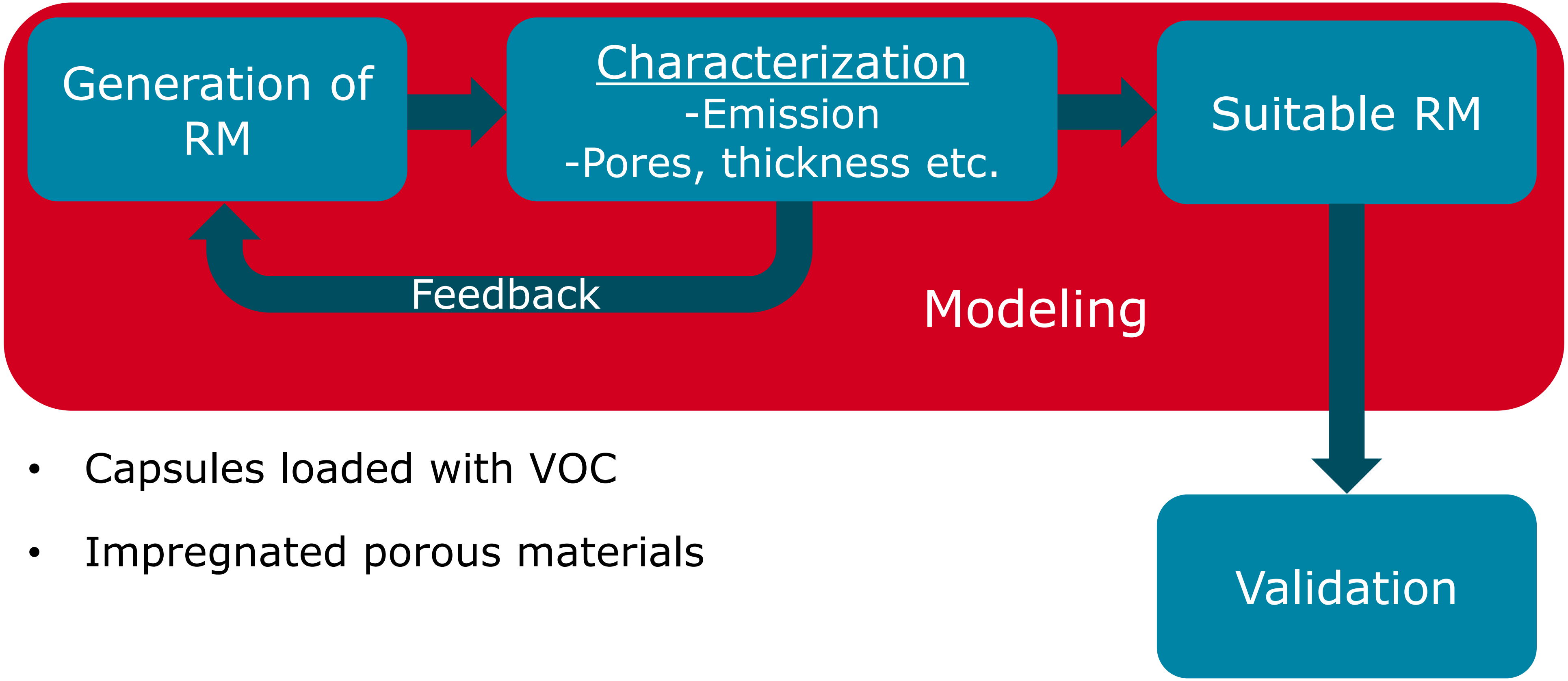
- Inherent: well defined and reliable property (emission)
- Cheap, small, easy to handle, variety of VOC etc.



(shape does not matter, as long as it is stable or reproducible)

- ➢ Project goal: reliable!
  - ➢ By constant emission with less than 10 % deviation over 14 days

Motivation



- Capsules loaded with VOC
- Impregnated porous materials

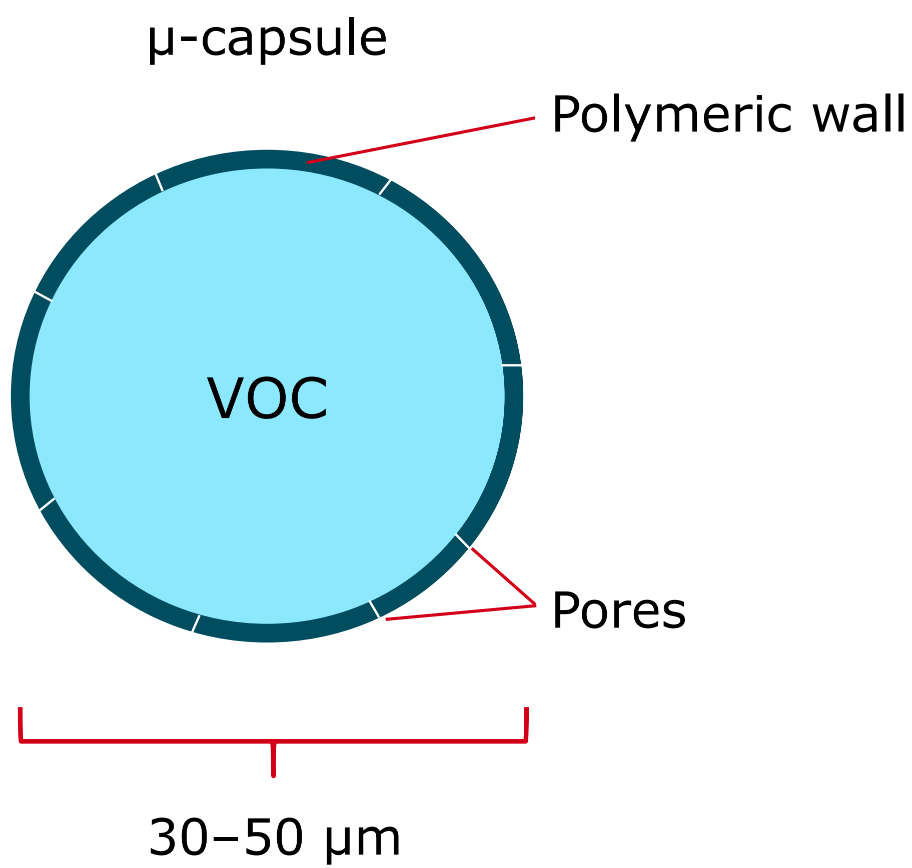
VOCs relevant for Indoor Air Quality

List based on standards, literature, experience and consultation with EU-LCI WG, stakeholder group

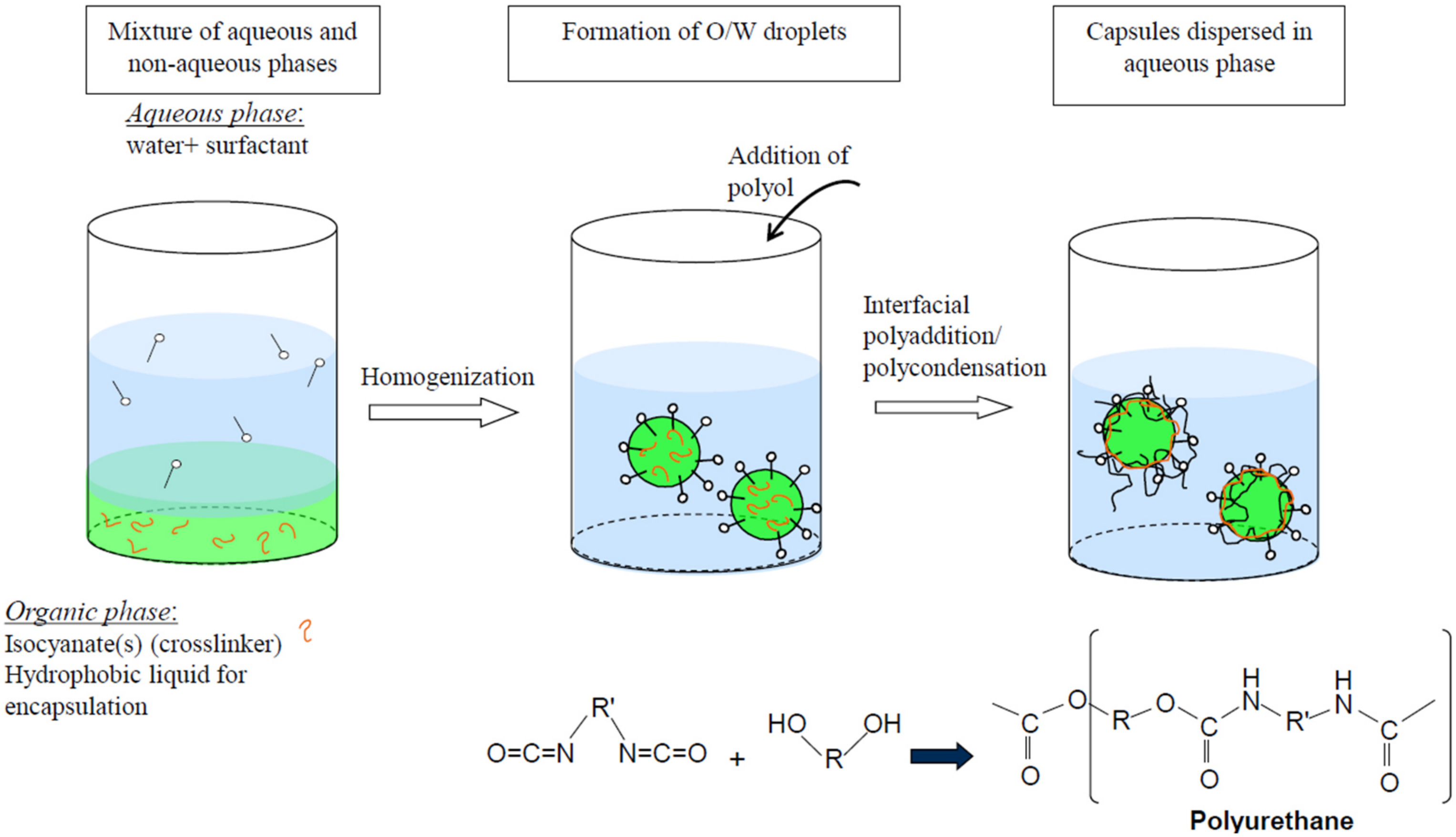
compound	capsules	impregnation
n-hexane	X	X
n-hexadecane	X	X
butyl glycol		X
propylene glycol		X
D-limonene	X	X
2-ethyl-1-hexanol		X
toluene	X	X
benzene		X
octylisothiazolinone		X
decamethylcyclo-pentasiloxane (D5)		X
methylisobutylketone		X

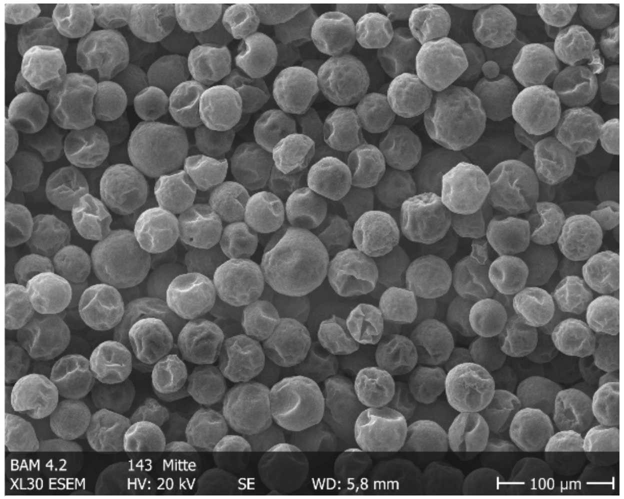
1. Approach: μ-Capsules

- Polymeric capsules filled with VOC
- Diameter, wall thickness, porosity, material etc. can be altered by adjusting synthesis route
- Emission through pores in the shell



1. Approach: µ-Capsules

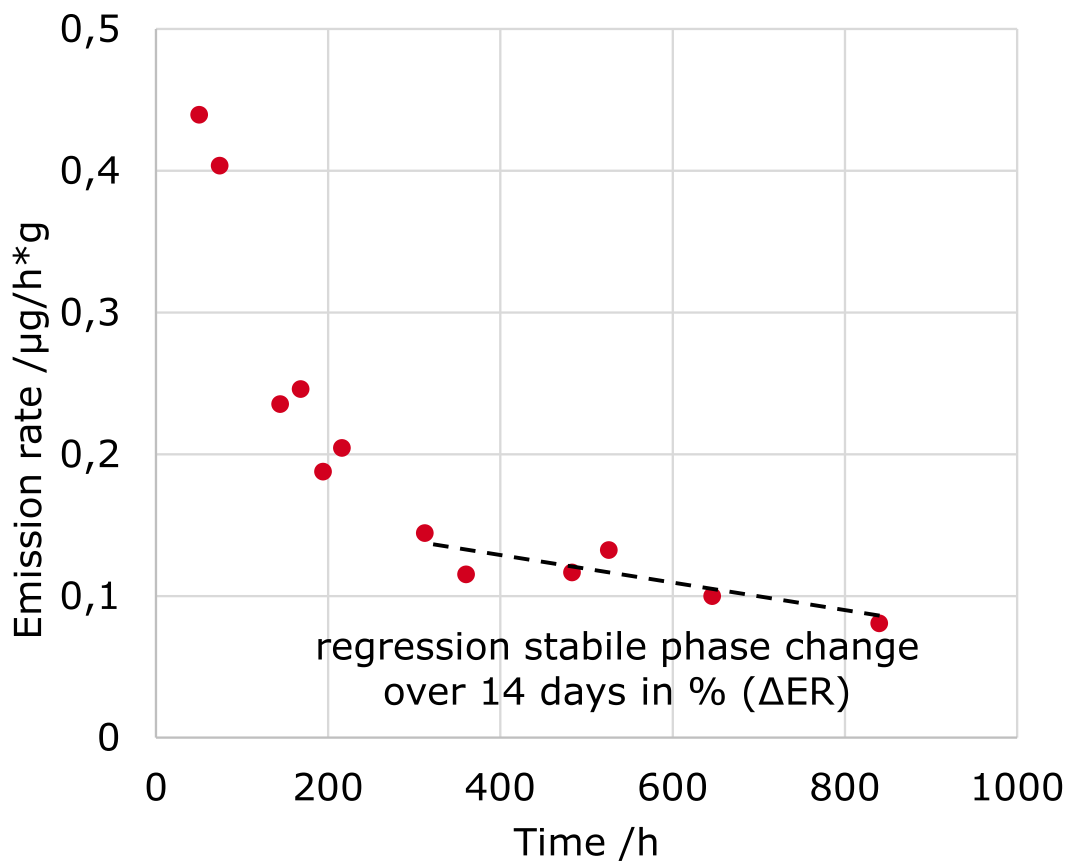




1. Approach: µ-Capsules

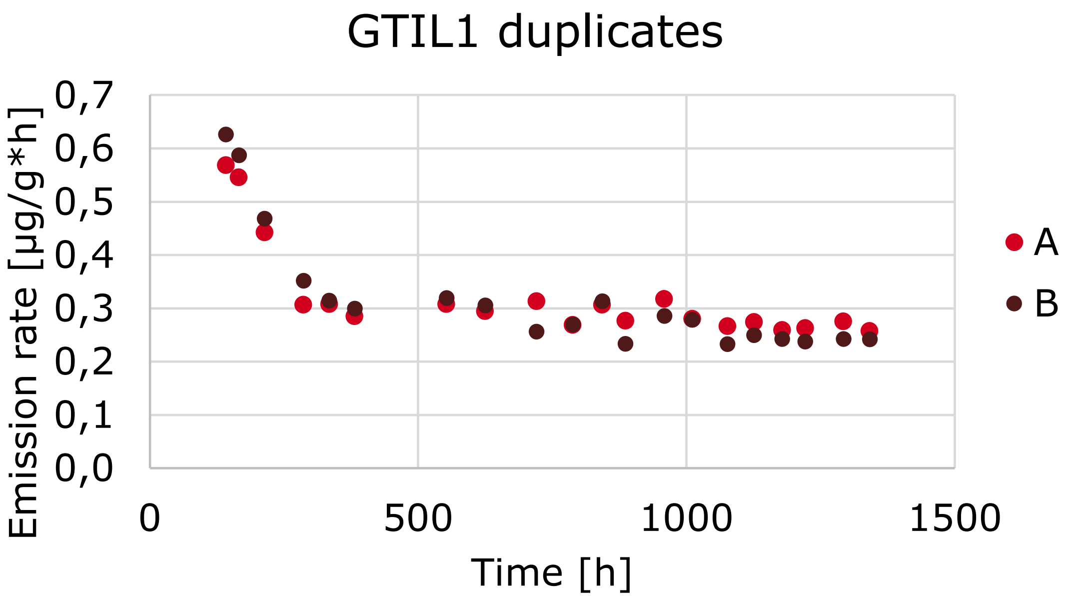
Example / interpretation:

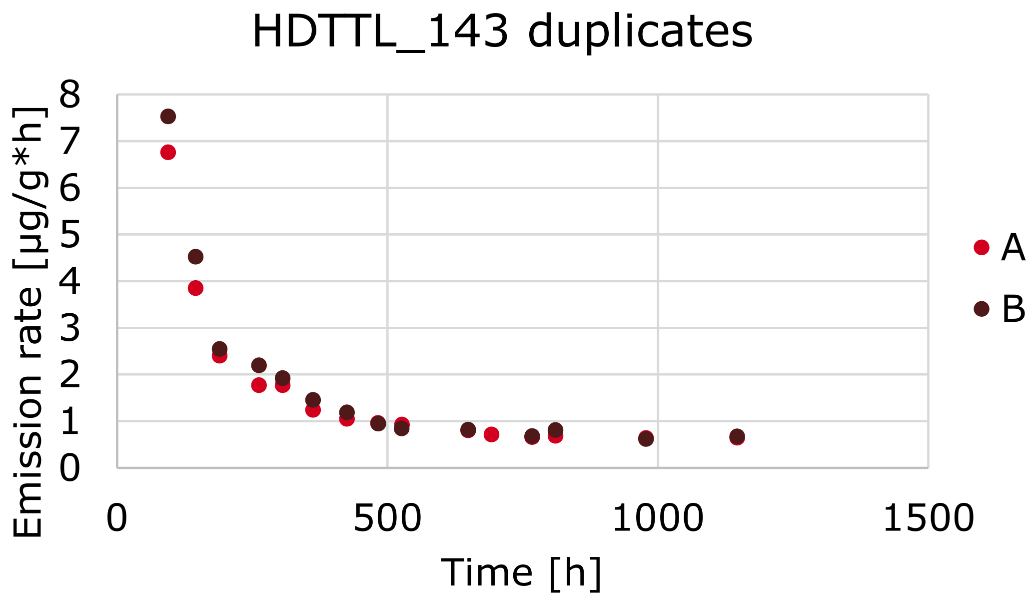
- Capsules (as suspension with H_2O) were pipetted into a petri dish and put into an emission chamber
- Focus on D-limonene as VOC



1. Approach: µ-Capsules

- Long-duration measurements (up to 60 days)





ΔER = 5 % (14 days)

averaged

ΔER = 10 % (14 days)

averaged

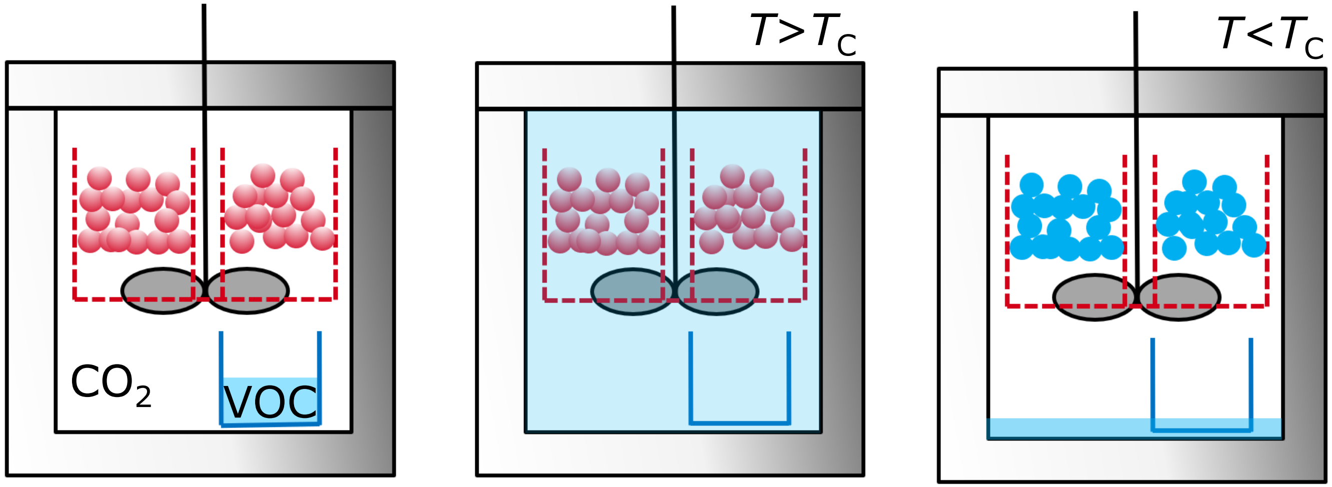
2. Approach: impregnated porous materials

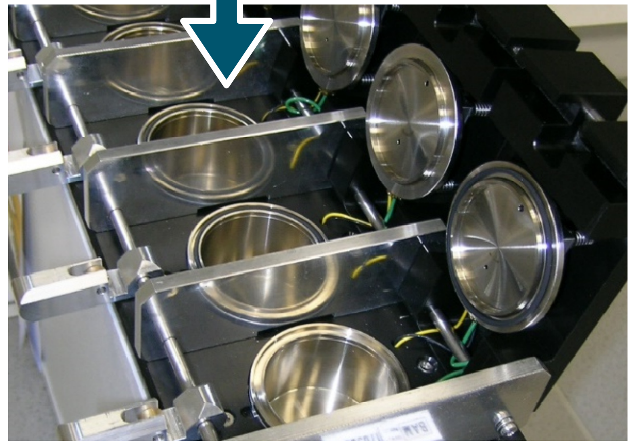
Preparation

Impregnation (supercritical)

Pressure release

Transfer into chamber





- Regular sampling on thermodesorption tubes
- Analysis by TD-GC-MS

Impregnated porous materials

- Initial conditions:
  - Zeolite = faujasit (FD-107)
  - *T* = 31 °C
  - *p* = 74 bar
  - CO_2 atmosphere (supercritical)
  - VOC = heptane

- Variation of impregnation parameters (*p*, *T*, *t*)

  …VOCs, materials, types, dry/humid air…

BEA (tablet)

FD-107 (granulate)

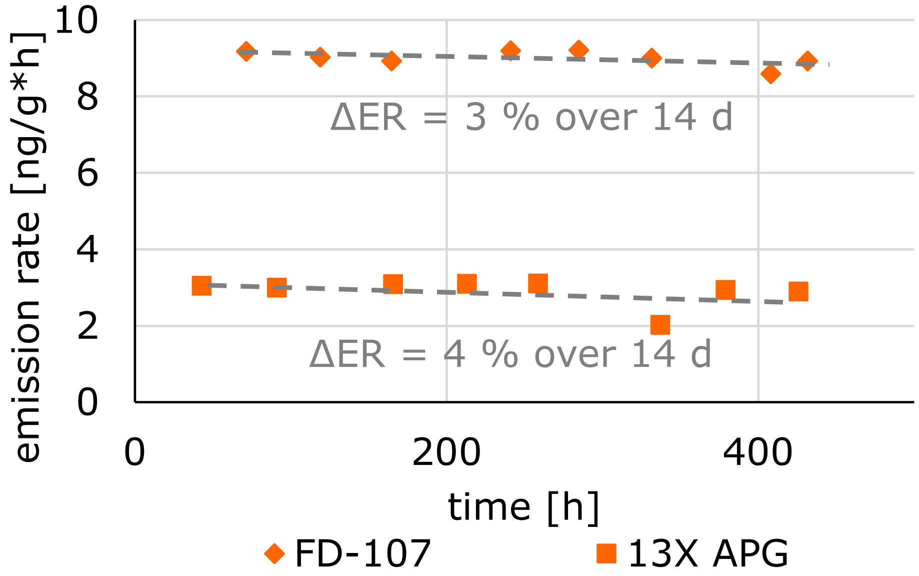
BEA (powder)

40/4 (powder)

40/4 (granulate)

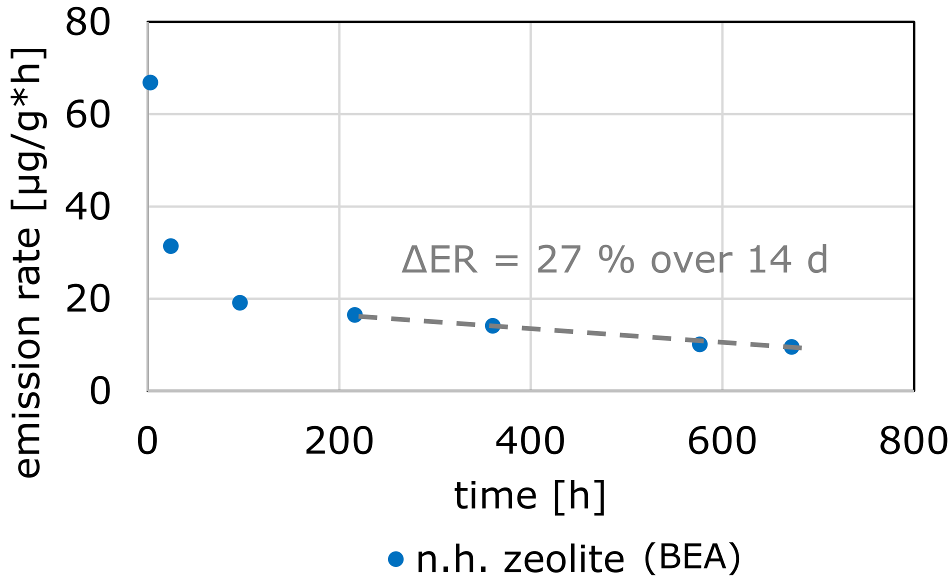
Impregnated porous materials

Hygroscopic zeolite; dry; *n*-hexane



- „Standard zeolites" (hygroscopic)
- Very high stability
- Only in dry air – no emission in humid air!

N.h. zeolite; humid; *n*-hexane



- Non-hygroscopic (n.h.) zeolites work well
- Less stable over time

Impregnated porous materials

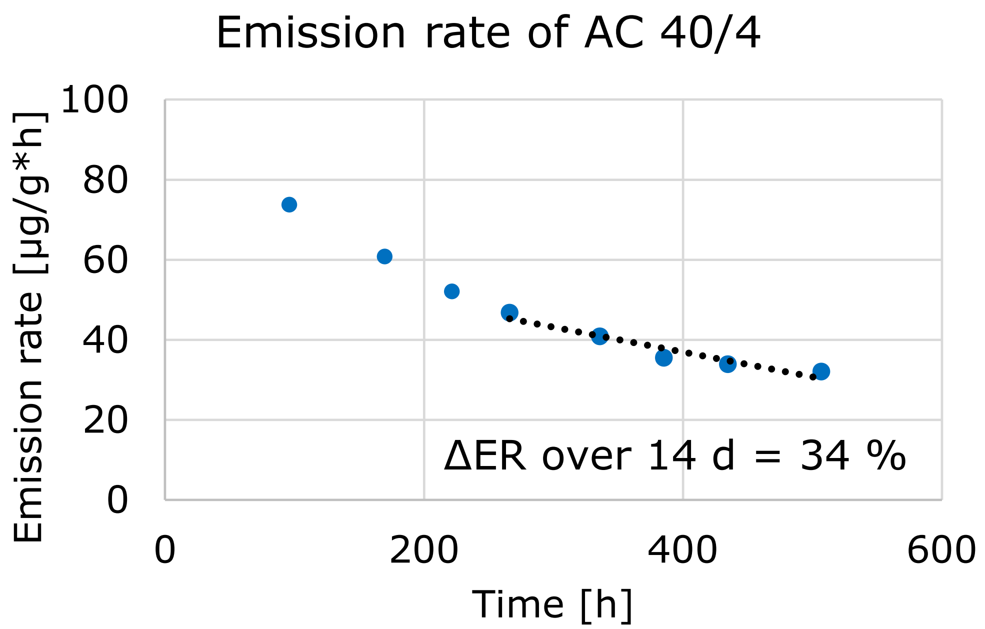
BAM

- Testing of different materials and material properties
- Focus on VOCs tested so far: *n*-hexane, toluene and 2-ethyl-1-hexanol

Material	pore volume [cm³/g]	pore size [nm]	Surface area [m²/g]	
FD-107	0.217	0.86	610	Zeolites
13X APG	0.245	0.8	686	Zeolites
3A EPG		< 0.4	15	Zeolites
n.h. BEA		0.7	> 500	Zeolites
n.h. MFI		0.6	> 300	Zeolites
A8x30	1.538 (total)	distribution	1250	Carbons
MC14x35	1.909 (total)	distribution	1200	Carbons
40_4		distribution	1250	Carbons
45_4		distribution	1000	Carbons
47_4		distribution	900	Carbons
Merck		1–25		Carbons
ZIF-8	0.663	1.16	686	MOF
Aerogel		> 10		Aerogel

Impregnated porous materials

Activated Carbons (AC); humid; *n*-hexane



AC	ΔER [%] over 14 d	SD	n
40/4	31	6.1	6
45/4	38	-	1
47/4	37	6.6	3

4X-4 behave similar; A 8x30 slightly worse, but within uncertainty

Impregnated porous materials

Material	ΔER [%] over 14 d	VOC
BEA	35–53	heptane
	20–42	toluol
	32	ethylhexanol
A8x30	39–42	hexane
40_4	19–44	hexane
	27–46	toluene
	39–47	ethylhexanol
45_4	36–50	hexane
	34–52	toluene
47_4	26–43	hexane
	24–44	toluene
	40–47	ethylhexanol
ZIF-8	33–59	heptane

ΔER = 20–50 %

Stable emission with ≤ 10 % deviation over 14 days could not be achieved

Maybe not necessary, if reproducible enough!

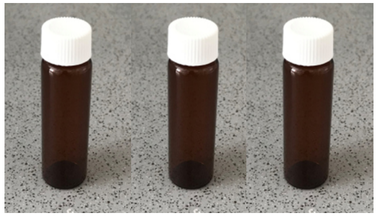
-> Reject goal of constant emission?

Application

Air-tight package

Before loading: let it reach RT, then open

Inweight based on chamber size!



+

open and pour into 3 different petri dishes

open

+

Polymer petri dish (found inside the package)

Glass petri dish with capsules (ready to use)

Transfer without lids

Emission test chamber

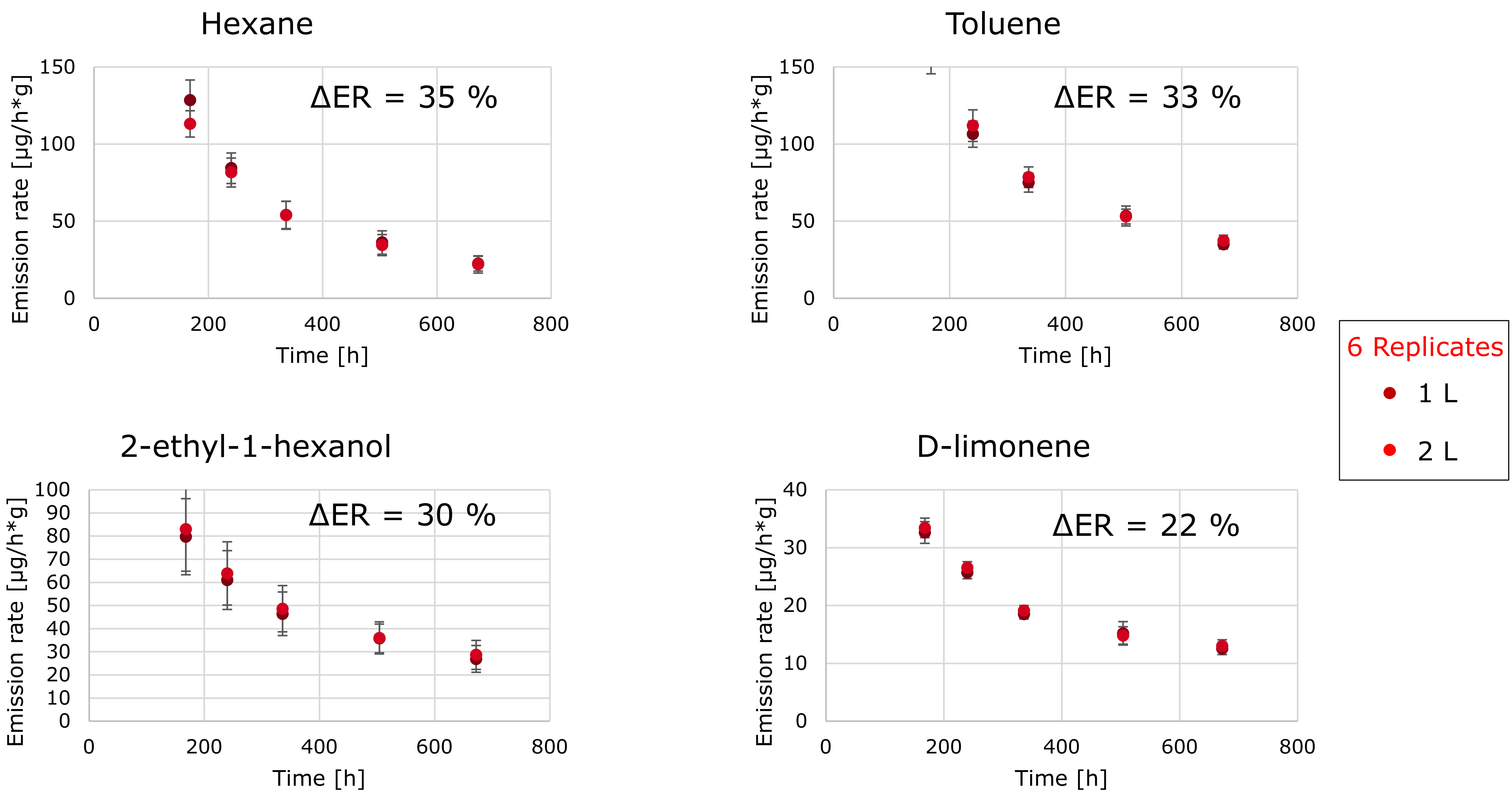
Protocol/Guideline with instructions and hints soon available!

Uncertainty

Typical uncertainty parameters taken from:

- ✓ Repeatability test (in-batch)
- ✓ Short and long term stability test
- ✓ Reproducibility test (in-batch)
- ✓ Interlaboratory comparison (ILC) part 2
- ○ Development (e.g., batch-to-batch repeatability)

Estimation of MU is currently ongoing task in our project! (preliminary results)



Hexane
ΔER = 35 %
Emission rate [µg/h*g]
0
50
100
150
0
200
400
600
800
Time [h]
Toluene
ΔER = 33 %
Emission rate [µg/h*g]
0
50
100
150
0
200
400
600
800
Time [h]
2-ethyl-1-hexanol
ΔER = 30 %
Emission rate [µg/h*g]
0
10
20
30
40
50
60
70
80
90
100
0
200
400
600
800
Time [h]
D-limonene
ΔER = 22 %
Emission rate [µg/h*g]
0
10
20
30
40
0
200
400
600
800
Time [h]
6 Replicates
1 L
2 L

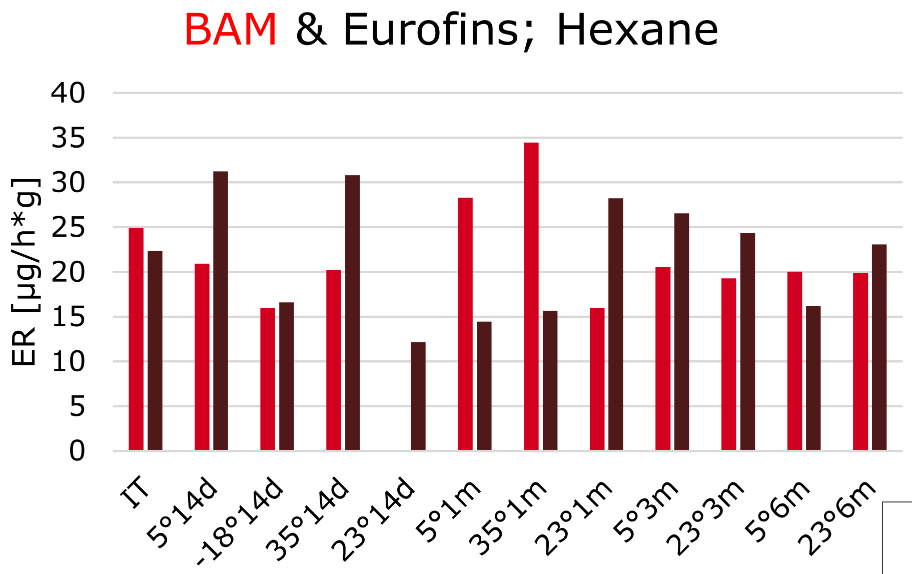
Uncertainty: in-batch repeatability

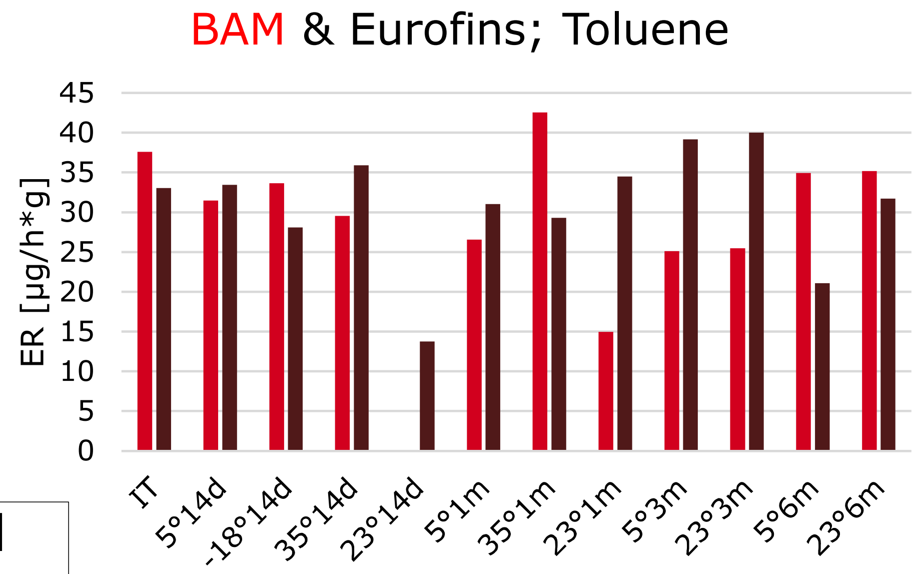
(Values at day 28)	AC 40/4 Hexane	AC 45/4 Toluene	AC 40/4 Ethylhexanol	HDTTL_143 Limonene
Mean ER Rep1-6 [µg/h*g]	23,99	36,24	28,24	13,12
SD Rep1-6 [µg/h*g]	3,48	1,09	5,26	0,88
rel. SD Rep1-6 [%]	14,49	3,01	18,64	6,73

Repeatability within one batch very good, especially of toluene and limonene

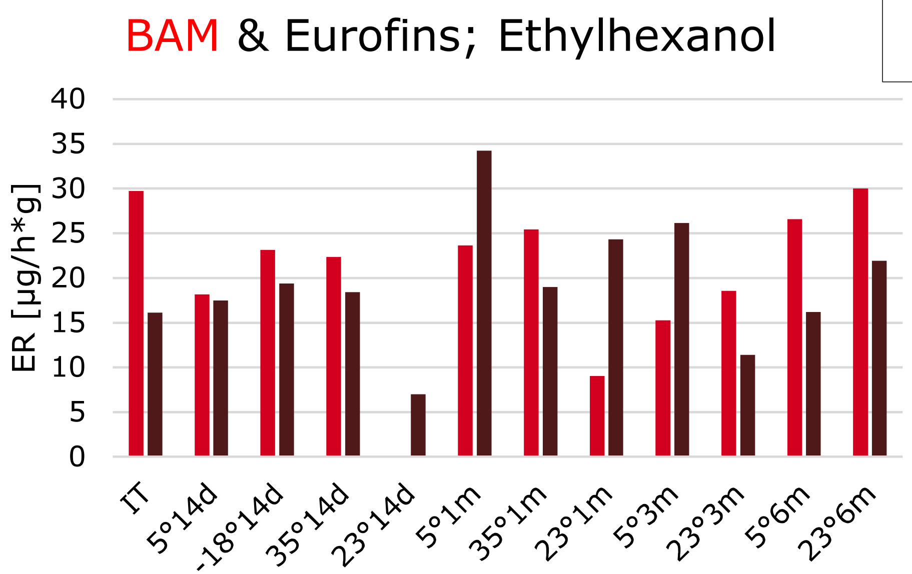
➢ Good homogeneity of these materials

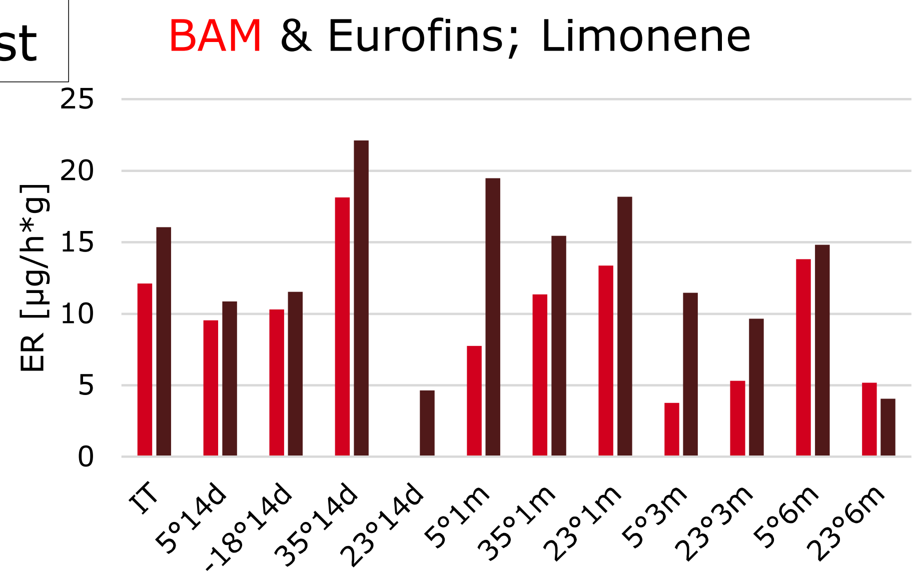
(all ACs were granulates)





Short and long term stability test





Uncertainty: in-batch reproducibility

(Values at day 28)	AC 40/4 Hexane	AC 45/4 Toluene	AC 40/4 Ethylhexanol	HDTTL_143 Limonene
Mean ER BAM	21,9	30,6	22,0	10,1
Mean ER E	21,8	30,9	19,3	13,2
SD BAM	5,5	7,5	6,3	4,3
SD E	6,6	7,4	7,0	5,6
rel. SD BAM	25,0	24,4	28,8	43,1
rel. SD E	30,5	23,9	36,3	42,1

In good agreement!

Good reproducibility!

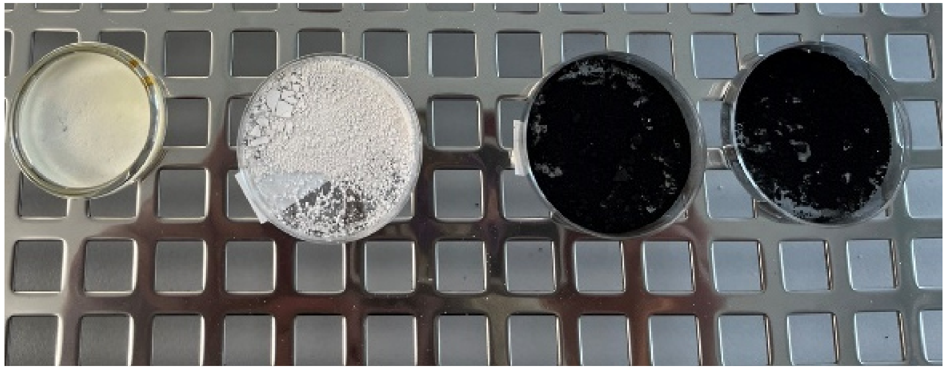
… higher than repeatability

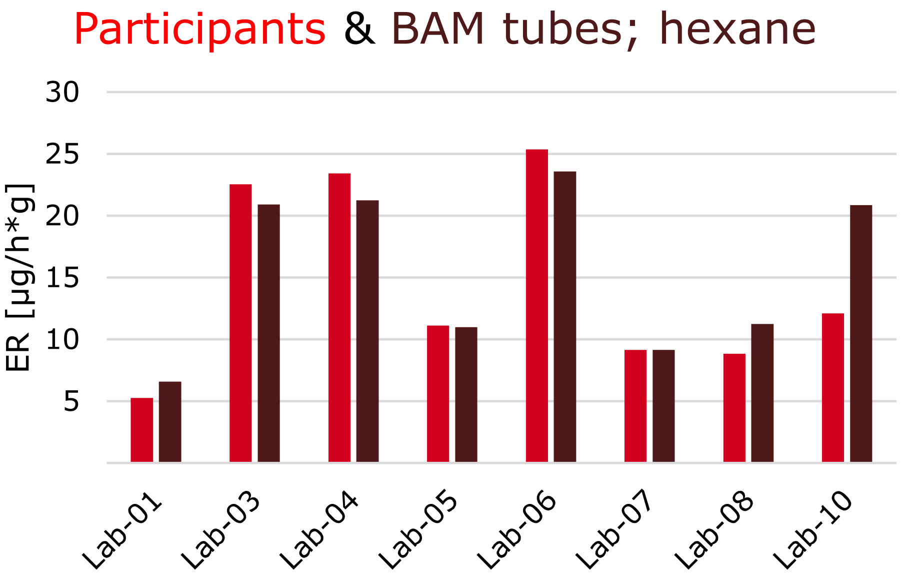
(all ACs were granulates)

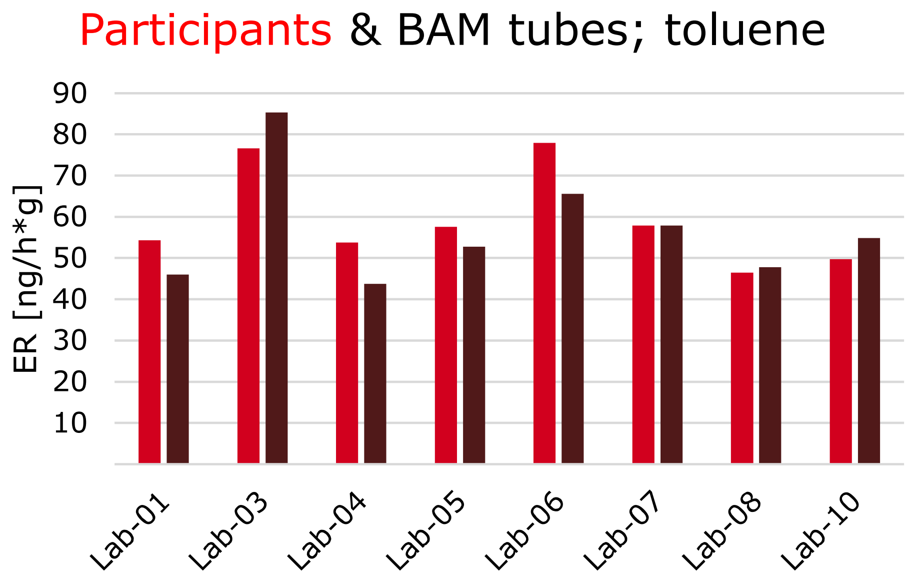
Uncertainty: ILC part 2 (ERM)

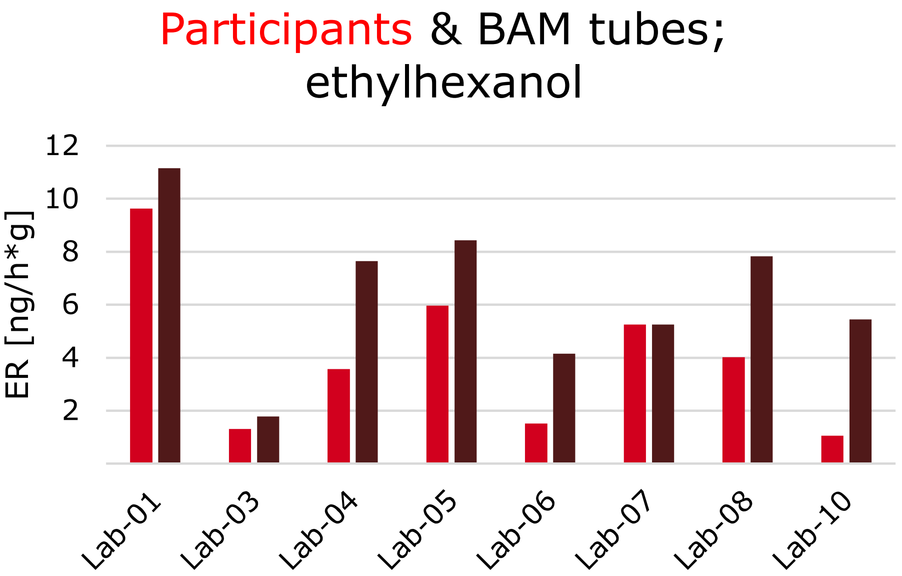
Similar to application & storage stability test, but partly other materials:

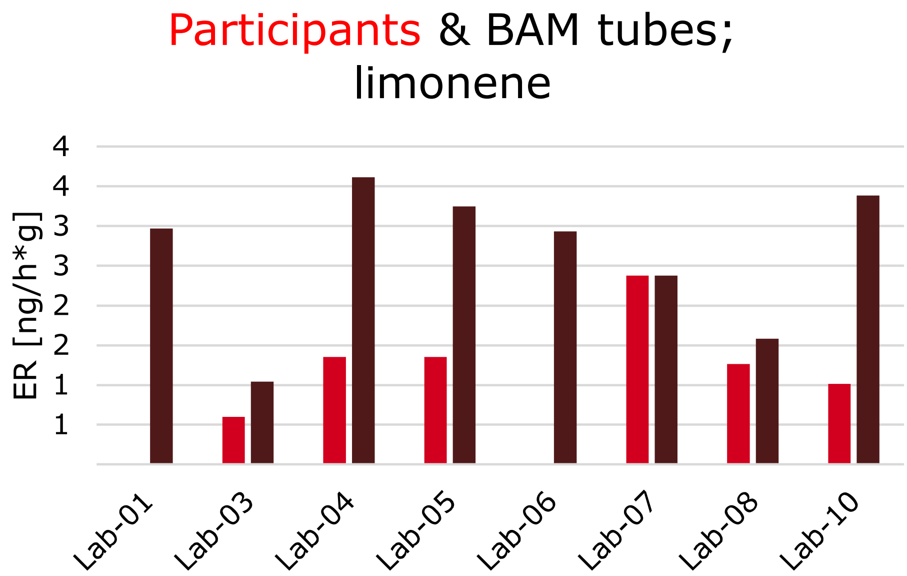
AC 40/4 (granulate) [hexane]	→	**BEA** (**powder**) [hexane]
AC 45/4 (granulate) [toluene]	→	AC **40/4** (**powder**) [toluene]
AC 40/4 (granulate) [ethylhexanol]	→	AC 40/4 (**powder**) [ethylhexanol]
µ-capsules (HDTTL143) [limonene]	→	same batch (but longer stored)




Participants & BAM tubes; hexane
ER [µg/h*g]
30
25
20
15
10
5
Lab-01
Lab-03
Lab-04
Lab-05
Lab-06
Lab-07
Lab-08
Lab-10


Participants & BAM tubes; toluene
ER [ng/h*g]
90
80
70
60
50
40
30
20
10
Lab-01
Lab-03
Lab-04
Lab-05
Lab-06
Lab-07
Lab-08
Lab-10


Participants & BAM tubes; ethylhexanol
ER [ng/h*g]
12
10
8
6
4
2
Lab-01
Lab-03
Lab-04
Lab-05
Lab-06
Lab-07
Lab-08
Lab-10


Participants & BAM tubes; limonene
ER [ng/h*g]
4
4
3
3
2
2
1
1
Lab-01
Lab-03
Lab-04
Lab-05
Lab-06
Lab-07
Lab-08
Lab-10

ILC part 2 (ERM)

(Values at day 14)	BEA Hexane	AC 40/4 Toluene	AC 40/4 Ethylhexanol	HDTTL_143 Limonene
mean ER [µg/h*g] participants	13.61	56.79	4.43	1.47
SD [µg/h*g] participants	7.70	10.17	2.92	0.52
rel. SD [%] participants	56.57	17.90	65.89	35.63

Good results for toluene impregnated AC C 40/4 (powder)

Result of the µ-capsules (limonene) was a negative surprise (very low ER)

Hexane and ethylhexanol impregnated materials performed worse

Uncertainty:

Best materials (based on uncertainty parameters):

- AC C 40/4 (powder) & AC C 45/4 (granulate) impregnated with toluene
  - Very good performance
- AC C 40/4 (granulate) impregnated with hexane & ethylhexanol
  - Good performance (good enough?)

- µ-capsules (HDTTL_143) filled with limonene
  - Good performance and stable, at least when pre-aged

Conclusion:

- Proof of principle found:
  - Stable emission: under dry air (FD-107) impregnated with hexane
  - Stable emission: µ-capsules (HDTTL_143) filled with limonene
  - Very reproducible: AC 4X/4 impregnated with toluene

- Promising, but not perfect yet → improvement likely possible
  - ➢ More matches (material <-> VOC) must be found to improve scope

Then one day soon: commercially available ERMs?! ☺

Thanks for your attention

BAM

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https://metriaq.eu/

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The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

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