(Statistical) and Technical Aspects of Sampling: Focus on environmental odour sampling and IOMS

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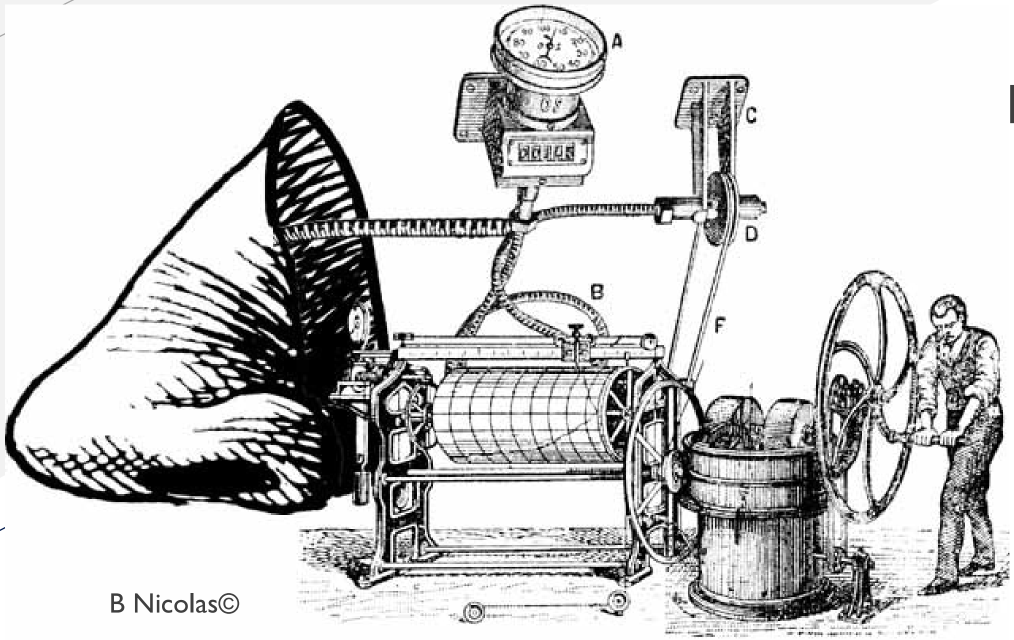

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iSOCS
International Society for Olfaction and Chemical Sensing

LIÈGE université Arlon Campus Environnement

Sensing of Atmospheres and Monitoring

Outline

From the lab to the field

Sampling

overview of some fundamentals

I. Sample/Sampling: 2 visions

Sample

for the Statistician

The **sample** "n" = a subset of the population,
The sample size = the size (or count) of the sample n
that is, the number of individuals observed in the sample

The number of individuals in the Population or the number of sampling units: N

The sampling rate = n/N

for the Scientist (chemist, biologist, …)

The **sample** is the individual sampling unit e.g.," water sample"
small portion of a larger entity,
representative
taken to be measured

1. Sample/Sampling: 2 visions

Sampling

for the Statistician

If we have to "select individuals" from a population:
→ notion of inference
→ statistics

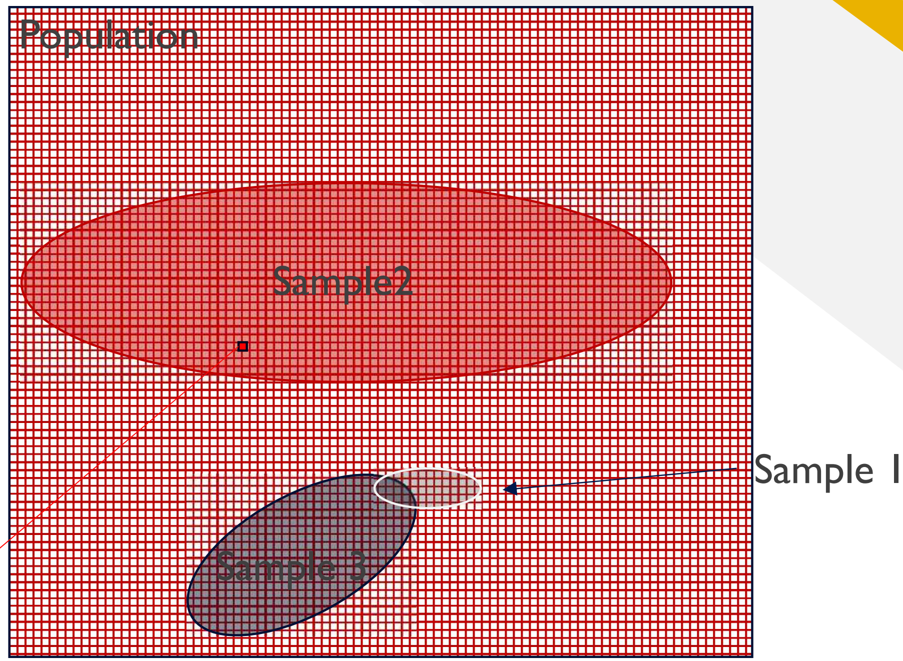
Several possible samples with different size
a sample is a subset of the population (one ellipse)

(Census : If we "take everything")

for the Scientist

"A defined procedure where a part of a substance, material or product is taken to provide for testing or calibration to give a representative sample of the whole *(ISO 17025)"*
is the way to collect one individual (technical aspect)
a sample is the individual unit (one red square)

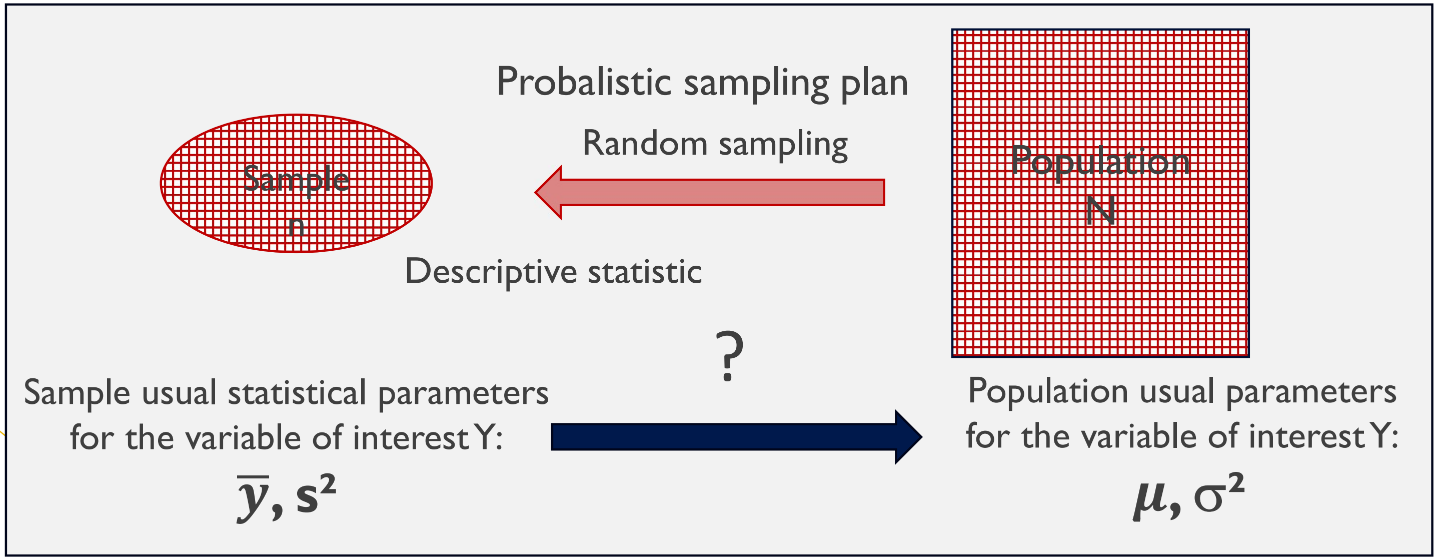
Simple random sampling



2. Fundamental Statistical concepts of sampling

Inference

to predict the behavior of a population based on one sample of n entities (individuals, units – also called samples)



*Uncertainty is the antonym of confidence

Sample parameters are (unbiased) **estimators** of the population parameters

→ Confidence* (accuracy) associated with this estimates? : expressed with a **confidence interval**

2. Fundamental Statistical concepts of sampling

Probalistic sampling plan

- Each individual/Each sample has the same chance of being selected!
  - For a simple random sampling, the probability that the ith unit of the population is selected = n/N
- Individuals are independent
- High sampling size

✓ It allows for estimation of the sampling error, and therefore enables inference about the population
✓ More expensive than non-probability sampling but allows statistical inferences about the population

In principle, each individual in the population are identifiable and labelled with numbers 1,2,…N(counted)

Finite population
or
Infinite population (very very big)

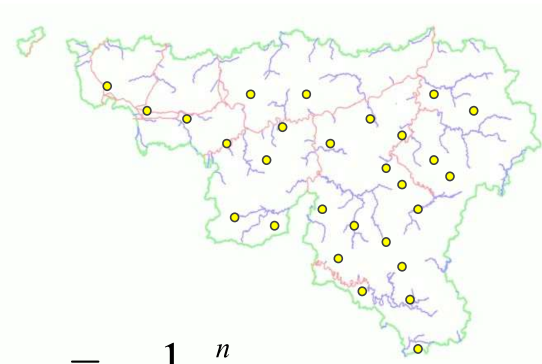
(central Limit Theorem)

Various Probalistic sampling designs:
- Simple random,
- Systematic,
  (e.g. if periodic trend, "Nyquist theorem",
  sample the signal at least twice during each cycle or period.),
- Stratified,
- Multi, …

2. Fundamental Statistical concepts of sampling

Probalistic sampling plan

Simple random sampling



$$\bar{y} = \frac{1}{n}\sum_{i=1}^{n} y_i$$

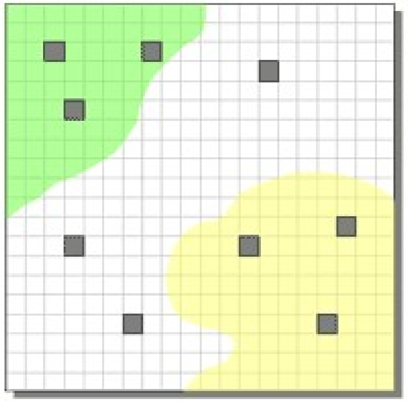
sample standard deviation = ?

$$s^2 = \frac{1}{n-1}\sum_{i=1}^{n}(y_i - \bar{y})^2$$

Unbiased estimator of the variance:

$$\widehat{var}(\bar{y}) = \left(\frac{N-n}{N}\right)\frac{s^2}{n}$$

Stratified sampling

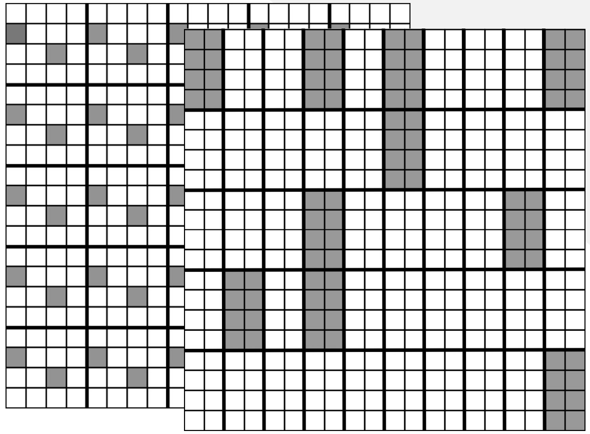


$$\bar{y} = \frac{1}{N}\sum_{h=1}^{L} N_h \bar{y}_h$$

Number of strates h = L

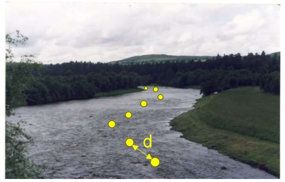
Mean of the characteristic in the strate h $\bar{y}_h$

Systematic grid sampling



$$\bar{y}_g = \frac{1}{k}\sum_{i=1}^{k} y_{gi}$$

Number of units = k



$$\bar{y} = \frac{1}{m}\sum_{g=1}^{m} \bar{y}_g$$

Number of grappes g = m

Mean of the characteristic in the grappe = $\bar{y}_g$

Recommended references

- *Sampling, Steven K, Thompson, scd edition 2002, Wiley (new edition 2024)*
- *https://www150.statcan.gc.ca/n1/edu/power-pouvoir/ch13/prob/5214899-eng.htm*
- *Fundamentals of environmental sampling and analysis, Chunlong Zhang, Wiley Blackwell, scd edition 2024*

2. Fundamental Statistical concepts of sampling

If the estimate is close to the true value for every possible sample: very little uncertainty linked to the sampling
If the estimates vary from one sample to another: uncertainty

several possible samples and several estimates of the true value (each sample will give different results)

Usually, this variability is estimated based on one single sample…

→ Construction of a confidence interval with the property that
the interval has a given high probablity to contain the true population value

If the confidence coefficient is 0,95 (1-α):
it means that for 95% of the possible samples of size n, the interval covers the true value of the population mean μ
(for a normal distribution of the mean)

(central Limit Theorem)

$$\bar{y} \pm t_{1-\alpha/2}\left(\frac{s}{\sqrt{n}}\right)$$

Recommended references, several good statistics books like

- *Handbook of Statistical Analysis AI and ML Applications, R Nisbet, G. Miner, K McCormick, 2024, Academic Press, ISBN: 9780443132735, eBook ISBN: 9780443158469*
- *Basic mathematics for students of air pollutants, Maynard R, R Atkinson, Royal society of chemistry, 2024*
- *Introduction to Probability and Statistics for Engineers and Scientists, Sheldon M. Ross, 2021, Academic Press, ISBN: 9780128177464, eBook ISBN: 9780128177471*

2. Fundamental Statistical concepts of sampling

Uncertainty

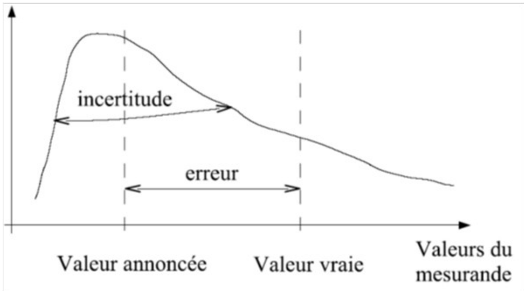
If no error in the measurement of Y (variable of interest) on every unit of the sample

→ The "Sampling Error" is simply related to the fact that only a portion of the population is considered

Just a theoretical concept, obviously they are measurement errors that will induce uncertainties on the results

Error ≈ difference between the obtained value and the true value (standard)
(2 categories: systematic and random)

Uncertainty ≈ standard deviation
(2 categories: type A and type B)



→ Recommended references:

- *JCGM 200:2012 International vocabulary of metrology – Basic and general concepts and associated terms (VIM) 3rd edition*
  https://www.bipm.org/documents/20126/2071204/JCGM_200_2012.pdf/
- *Guide to the expression of uncertainty in measurement (GUM)*

2. Fundamental Statistical concepts of sampling

Sample size (individual number)

There is a consensus that the best number is the largest possible but if the sampling design is poor, no number of samples will compensate it!
Quality before the quantity!

The sample number should be linked to

the cost, the error that you accept, the goal of your measurement, the environmental variability, the sampling design, ….

Several formulae to determine the sample size

often derived from the confidence interval :

Margin of error, e, is considered as the acceptable level of error (half of the confidence interval)

$$e = t\left(\frac{s}{\sqrt{n}}\right) \qquad \boldsymbol{n = \frac{t^2 s^2}{e^2}}$$

(Iteration process)

another exemple: Cochran formulae (for proportion)

$$n = \frac{z^2 p(1-p)}{e^2}$$

(For large population)
Z = value from the standard normal distribution corresponding to the chosen confidence level (e.g., 1.96 for 95%),
P = estimated proportion of the population that has the attribute of interest (e,g, 30%)
e= desired margin of error (e.g. 8%)
→ n=64

3. Sampling and measurement

SAMPLING is more important than the measurement itself
It is the basis of a reliable analysis/measurement
your results is strongly linked to your sampling (method)

Even if you perform very careful measurement/analysis,
if your sampling is bad, your result will be inaccurate

$$s_{total}^2 = s_{sample/ing}^2 + s_{analysis}^2$$

Unfortunately, we often try to minimize $s_{analysis}^2$
but most errors come from the sampling process rather than sample analysis

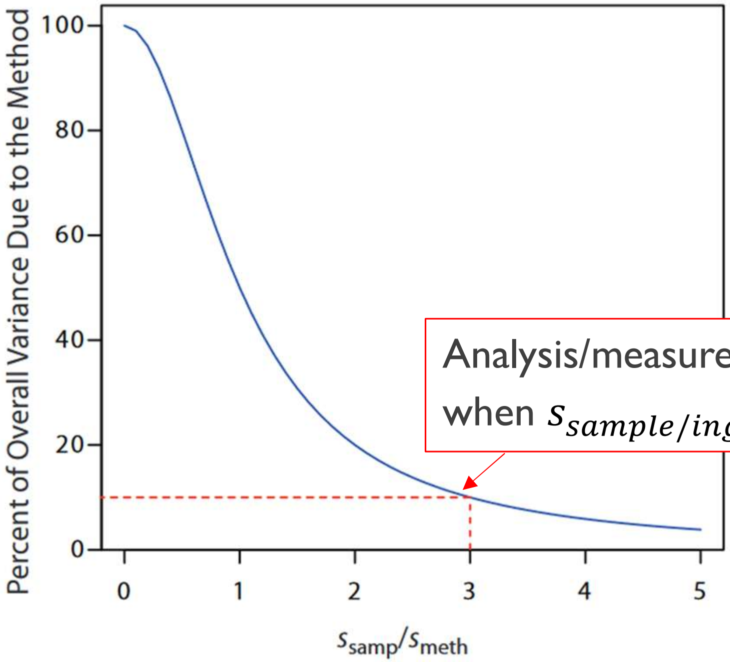
- **It is absolutely mandatory**
  - **to take care of your sampling in order to minimize the errors :**
    The results must accurately reflect the content of the sample!
  - **(for inference) that the sample is representative of your "target population"**
    Sample composition must represent accurately the population

3. Sampling and measurement

Sampling uncertainty???

$$s^2_{total} = s^2_{sample/ing} + s^2_{analysis}$$

If indeterminate (randomly) sampling errors are significant, $s^2_{analysis}$ is unhelpful!



Analysis/measurement contributes for only 10% of the overall variance when $s_{sample/ing}$ is 3 times higher than $s_{analysis}$

Ref Youden, Y. J. J. Assoc. Off. Anal. Chem. 1981, 50, 1007–1013
In https://chem.libretexts.org/Bookshelves/Analytical_Chemistry

3. Sampling and measurement

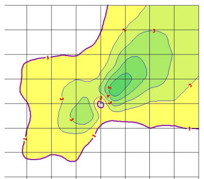
Representativeness of the sample

if the population is

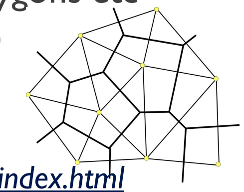
- <u>Homogeneous</u>: almost easy to collect individual samples (eg water flowing from the tap)
- **<u>Heterogeneous</u>**: Temporal/Spatial variations

  e.g. the concentration of ammonia in the ambient air is heterogenous
  due to the spreading seasons, temperature etc…

(Geostatistic* for spatial/temporal variation if usual statistics not applicable



isoplets, Thiessen polygons etc
typilcaly used for GIS)



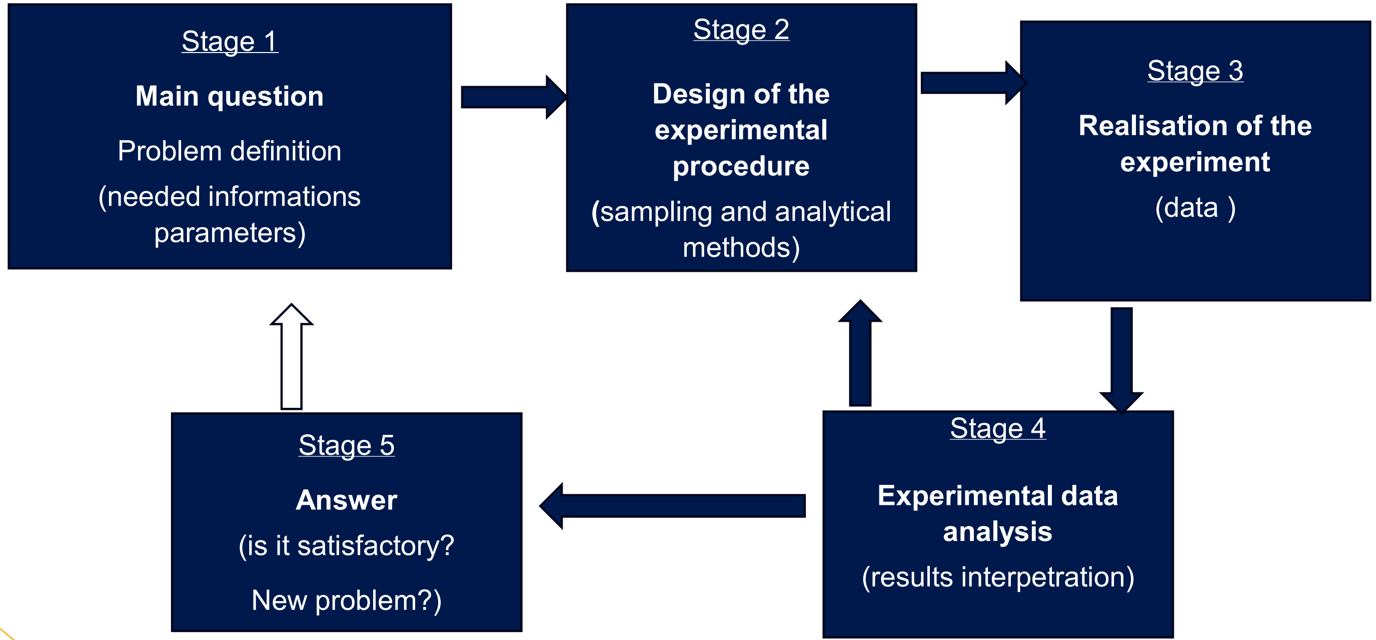
*https://spatialanalysisonline.com/HTML/index.html

➢ When and Where ? Sampling design

TO BE BUILT ACCORDING TO THE QUESTION YOU HAVE/ IN A CONTEXT OF DECISION-MAKING PROCESS

3. Sampling and measurement

Flow diagram for an experimental design



Adapted from https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Analytical_Chemistry_2.1_(Harvey)

It is not a straight-line, quite often after the data analysis, the experimental design and the sampling must be optimised

but in the field, this feedback approach is not always achievable (e.g too late, the pollution event is done, the weather/process doesn't' allow repetition/replicates, etc)

3. Sampling and measurement

The “main question” influence the sampling and the analysis effort

From the lab to the field…

real word is not as simple…

In the field: compromise between sampling cost and field constraints

“The cost of using a sampling method is a combination of the cost of collecting the measurements, and of the frame; the time taken is similarly a combination of the time spent in the field and the time spent before hand obtaining the frame and drawing the sample. It is these costs and the time limits, as well as constraints at the analysis stage, which will largely determine the sample size and the methods which are feasible » (Dixon et Leach, 1977)

Recommended reference

- *Fundamentals of environmental sampling and analysis, Chunlong Zhang, Wiley Blackwell, scd edition 2024*

From the lab to the field

I “know” the fundamentals…
let’s go to the field, it is so easy!

4. Environmental sampling

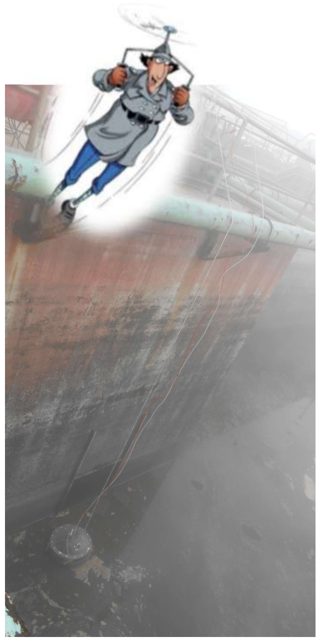
Odour/ Polluted air

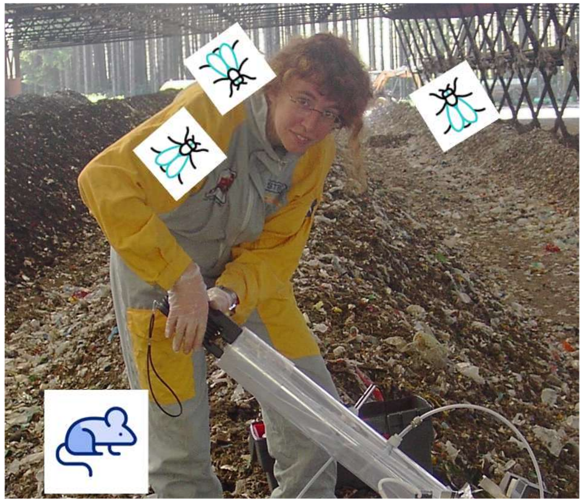
Environmental sampling is not just sampling

- Before going into the field, a planning process is highly recommended
- Sampling design and Fundamental questions: Where, When, How many

And **How, What, Who, How much (cost)**

(courtesy of F Idzack, ISSeP)





4. Environmental sampling

Odour/ Polluted air

- Always define the main **objectives**
- **Preliminary Investigation:**
  - Identify the relevant process(es) causing the pollution
  - Assess the risks of toxicity for the samplers
  - Locate the emission points
  - Prioritizing sources
  - Evaluate likely fluctuations (process, weather)
  - Locate sampling points
    (wind direction: upstream/downstream; sampling plan)

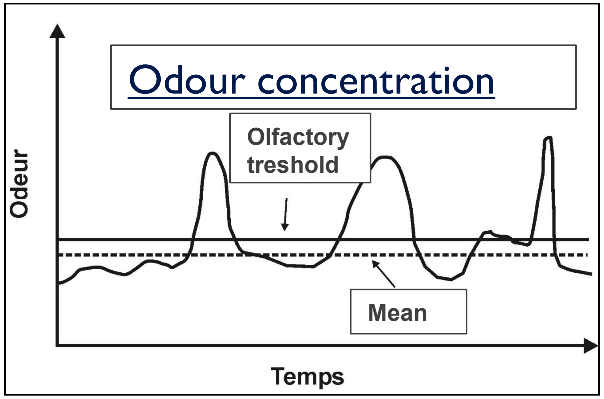
Check list

- ✓ *Check the weather*
- ✓ *Get information about the process*
- ✓ *Learn more about the accessing of the site*
- ✓ *Obtain passes*
- ✓ *Always be at least two*
- ✓ *Prepare and check your sampling equipment*
- ✓ *Bring a weather station*

- **What/Where**

Emission (source): concentration, emission rate
Exposure (fenceline, neighborhood): concentration, frequency of exposure, exposure time

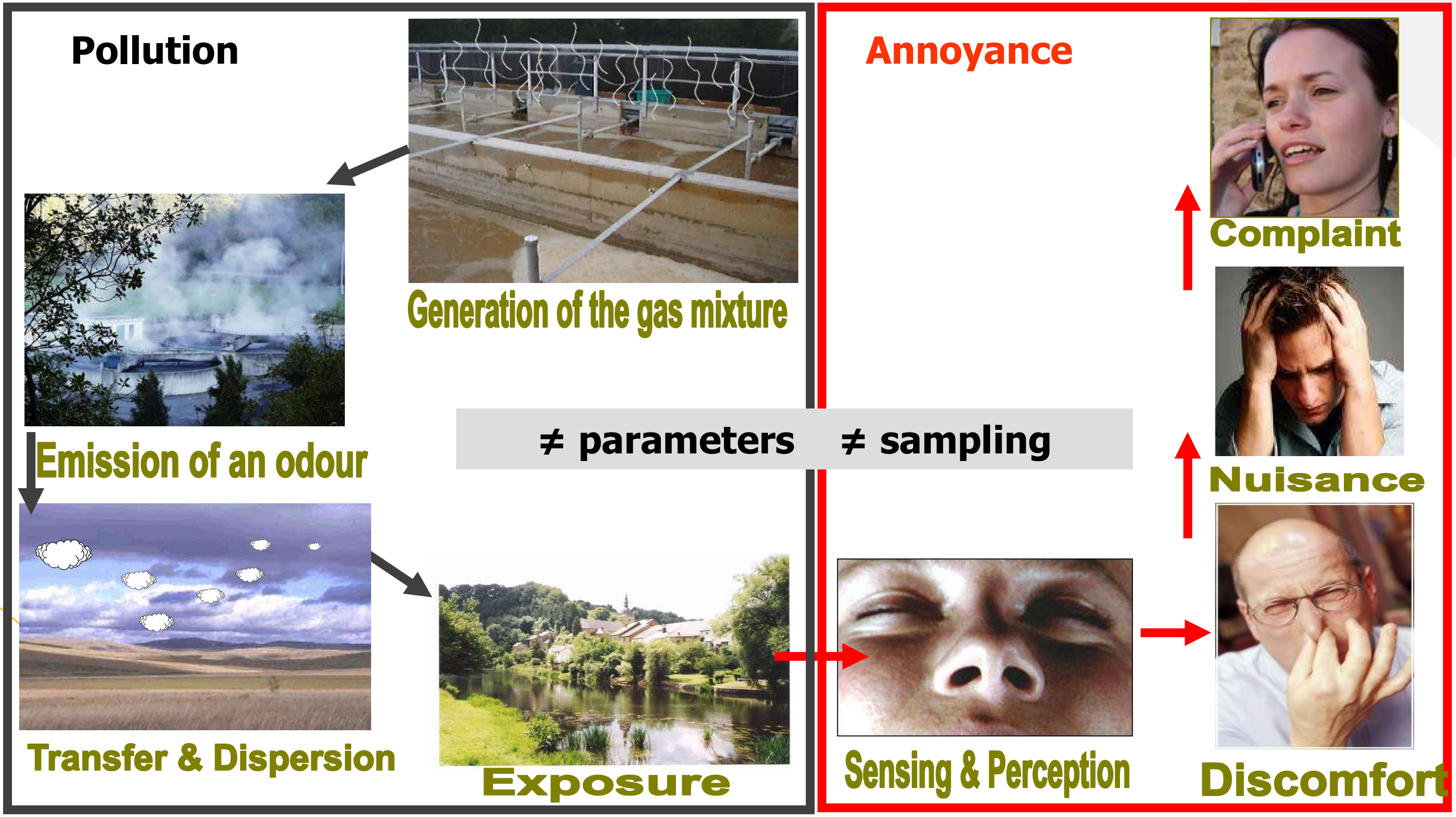
+ T, RH, Pressure, O_2, flow,



4. Environmental sampling

What?

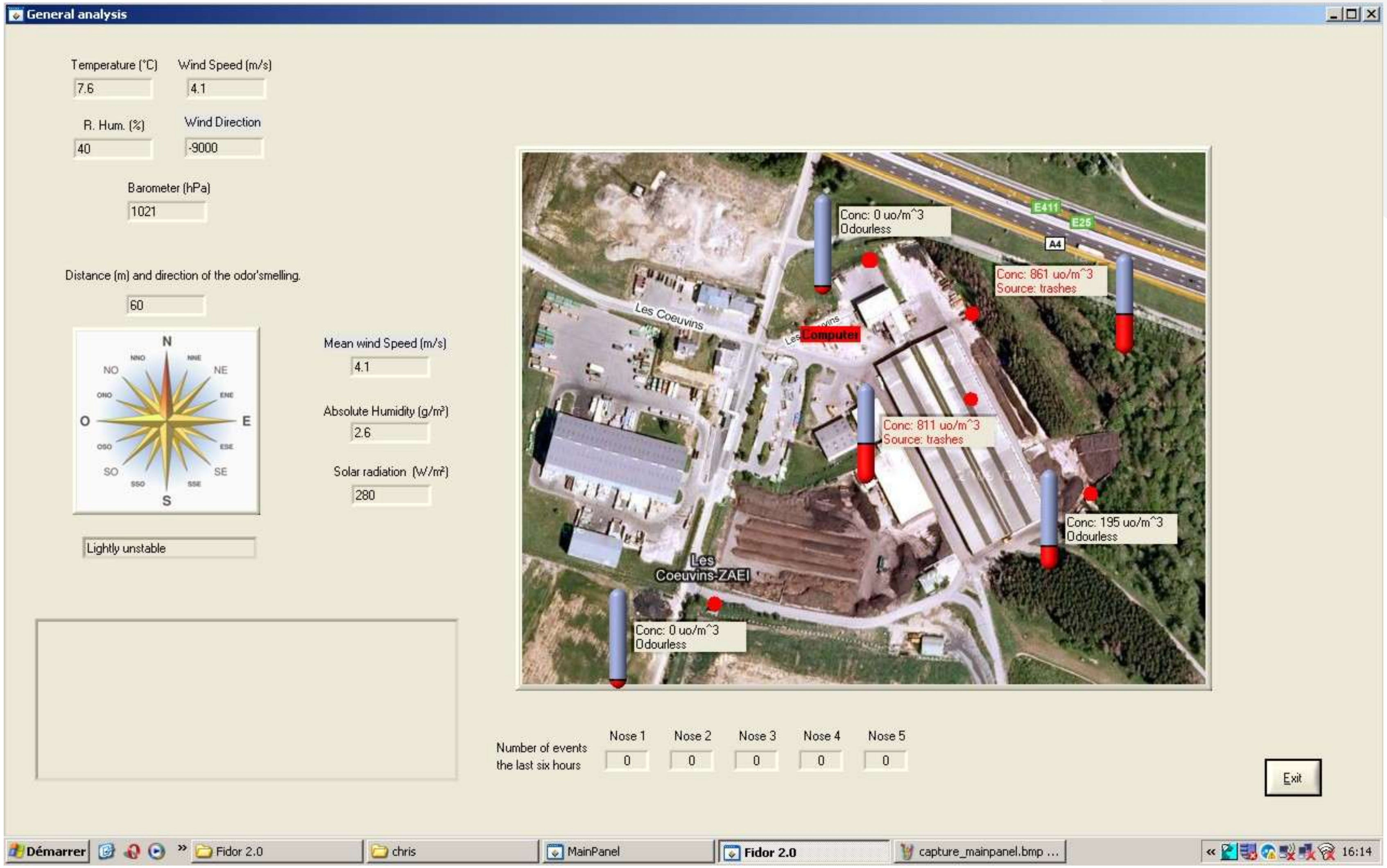
Odour



Where ?

Sampling design???

Odour



4. Environmental sampling

Environmental Odour/ Polluted air

What is a representative Air sample??

<u>What is a unit/individual?</u>

More challenging than for Solid and Water samples
Fast temporal and spatial changes

<u>Heterogeneity</u> of
environmental matrices and
environmental conditions

- high level sampling variability
  - high standard deviation

Influence of the sampling period

59 samples –
7 months (March-October 1999) –
different climatic conditions –
different emission conditions

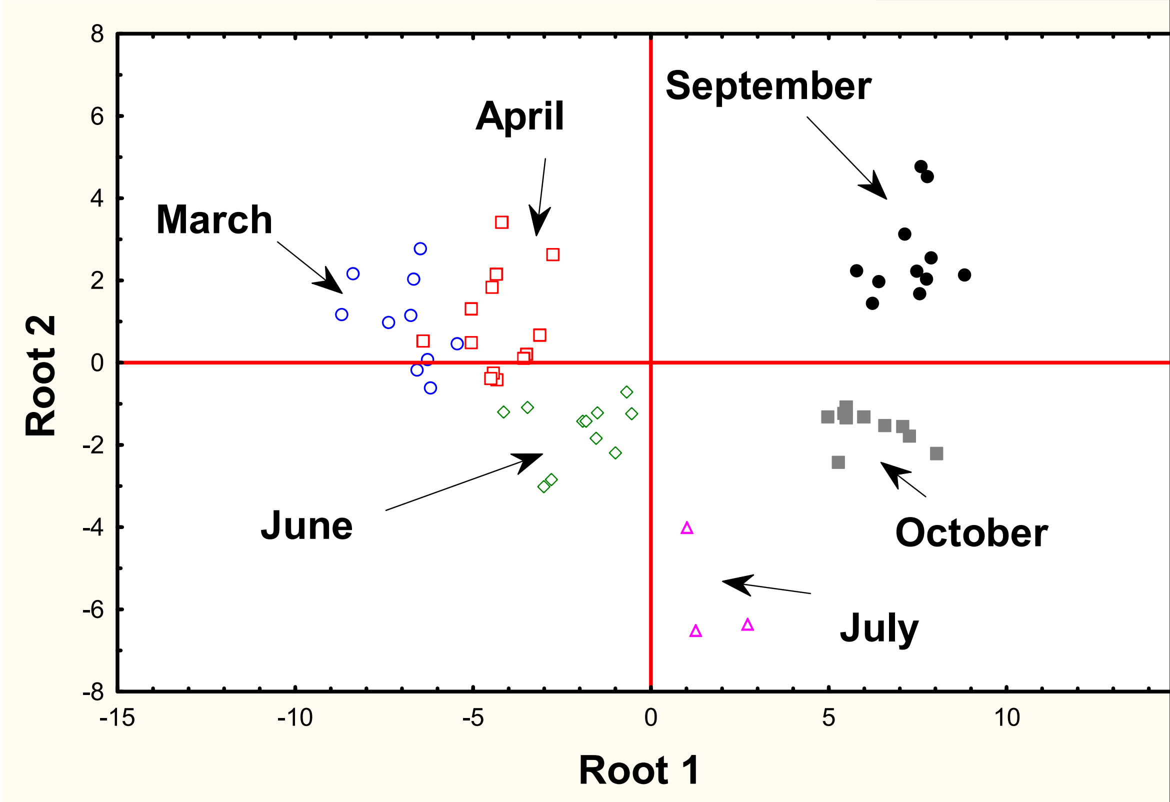
"Rendering plant"

Compost

Painting in a coachbuildig

Printing

Wastewater treatment plant



4. Environmental sampling

Environmental Odour/ Polluted air

What is a representative sample??

We never know the **true value** of an environmental samples like an odour??

(What is a reference sample for an odour linked to composting emission?)

No perfect solutions, we have to deal with and share tips

Except for sample in which the single analytes are measurable with specificity, regardless the sample matrix

Is an e-nose/chemical sensor specific to an analyte regardless the sample matrix ???

Odour (smell) of complex gaseous mixture

≠

sum of individual chemical components

(non-odorous components also contribute to the final smell)

Predict smell based on chemical composition???

Synergy and Inhibition between molecules

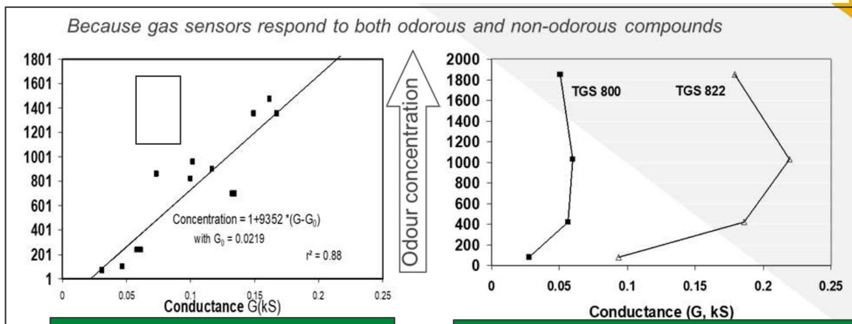
For the perception of odours,

1+2 ≠ 3

1 + 2 = 4

1 + 2 = 2

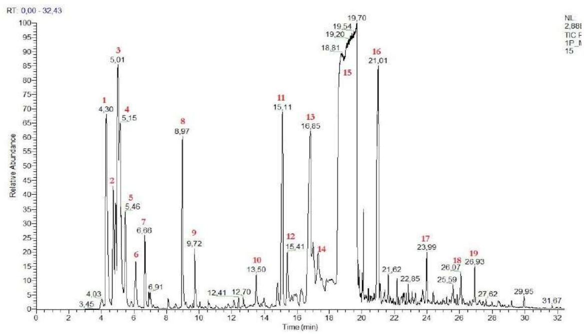
if the output of your sensor array (e-nose) is an indicator of the "smell" and that the "chemical" concentration is not correlated with the odour concentration: FORGET!

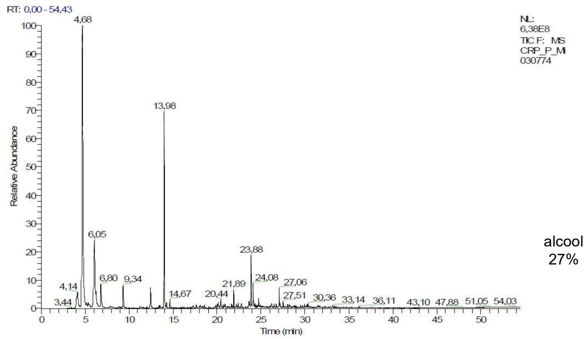


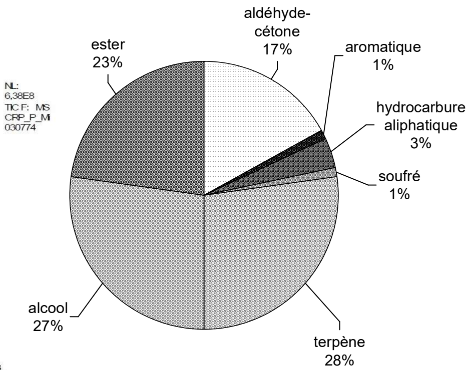
OK for compost

Not for a printing press

High variability for the same « type » of environmental odours:
chemical composition of an odour from composting plant is never constant







4. Environmental sampling

In our scientific community, sampling is closely linked to measurement

In-line
measurement device integrated into the process line and performs instant and continuous analysis.

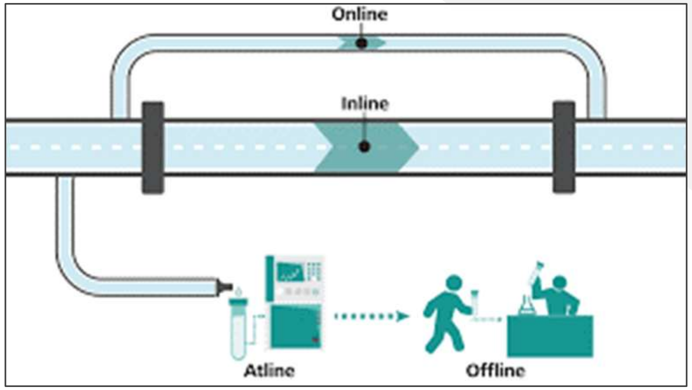
On line

measurement device close to the process line and perform real time measurement but is not in the process

often with an automated sampling (pump) and bypass system; continuous or periodic

At line
samples are taken and analysed outside the running process in another measuring room or laboratory very closed

Off line
Samples are taken, send to a laboratory at a significant distance, for analysis,
higher time delay than at line
higher accuracy of the measurement



https://metrohm.blog/on-in-at-offline/

4. Environmental sampling

Odour/ Polluted air

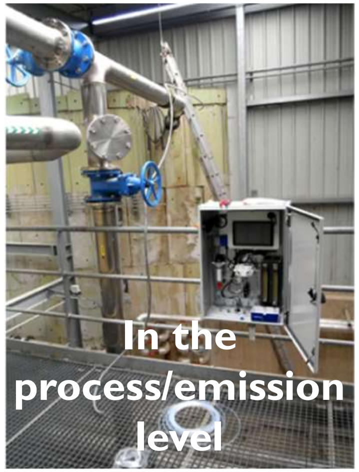
OFF line





ON line





4. Environmental sampling

OFF line

Odour/ Polluted air

<u>Sampling for what?</u>
(what dimensions, units?)

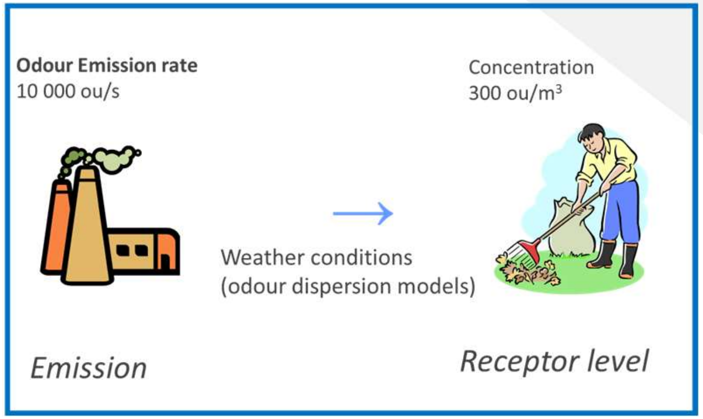
<u>How is the source?</u>

Source Geometry

<u>Punctual-channeled</u>
Air flow **measurement** in m^3/h

<u>Surface</u>
Air flow **estimation** (flow chamber)

<u>Fugitive</u>
Air flow **evaluation** field inspection team modelling



Odor (pollutant) emission rate

=

OER = C x Q, ou/s

C: Concentration, ou/m^3

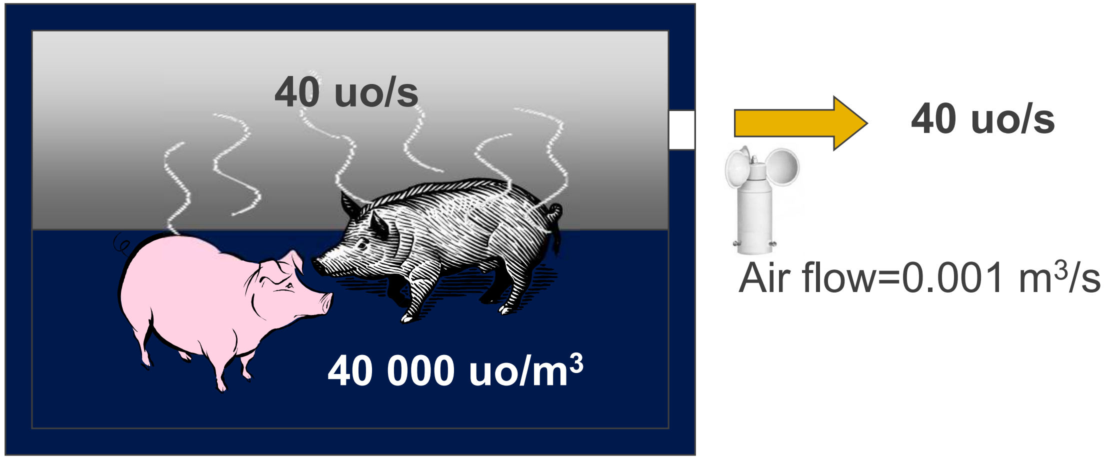
Q: Air flow, m^3/s

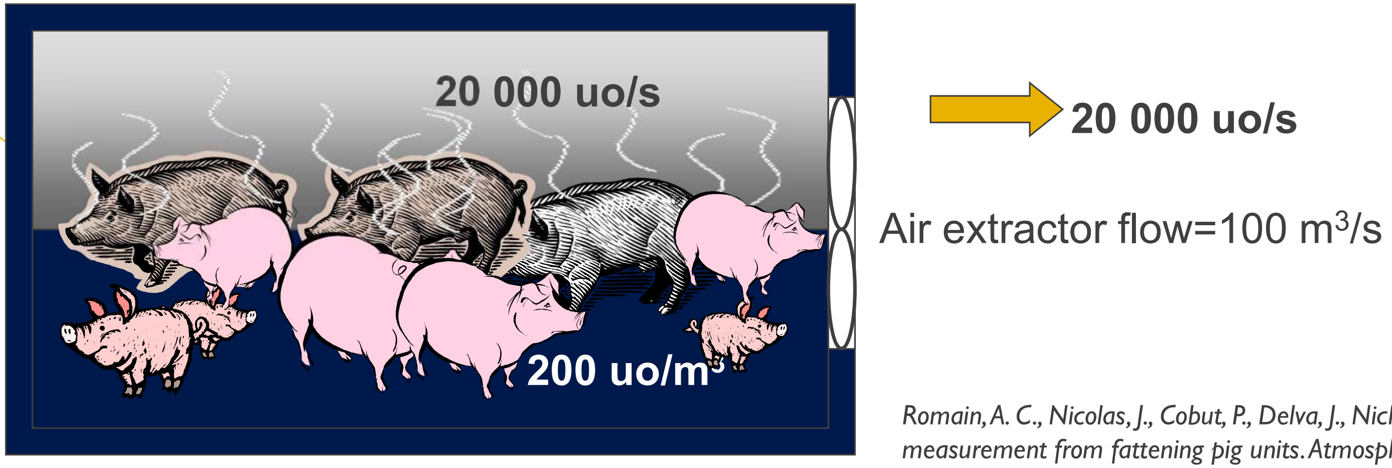
At the emission level, pollutants concentration is not useful

Collecting an odour sample is not enough

4. Environmental sampling

Odour/ Polluted air





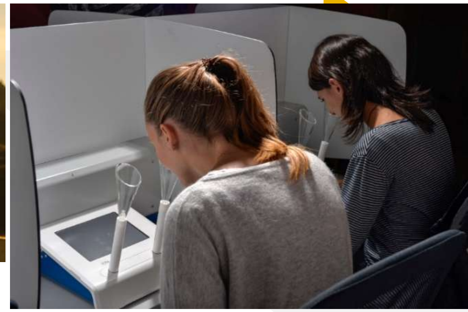
Odour emission rate (OER)

Romain, A. C., Nicolas, J., Cobut, P., Delva, J., Nicks, B., & Philippe, F. X. (2013). Continuous odour measurement from fattening pig units. Atmospheric Environment, 77, 935-942.

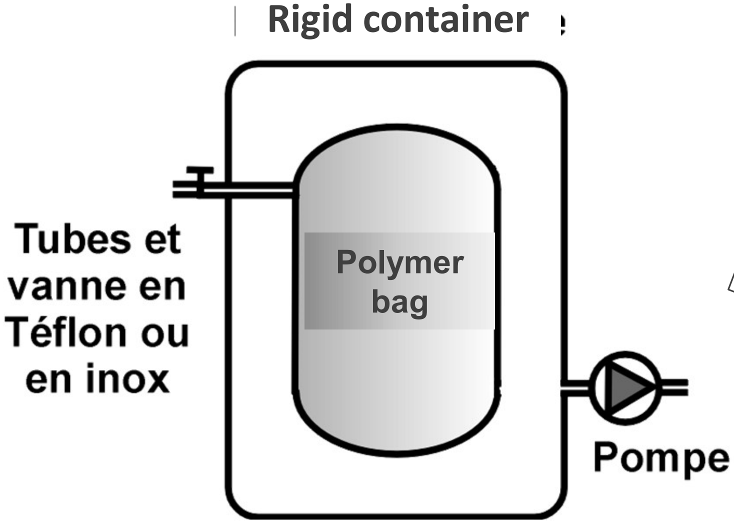
5. Odor sampling in the field: Technical considerations (how)

A. <u>A global air sample in a bag is needed for</u>

- Olfactometric measurement in lab (EN 13 725)
- E-nose development (calibration, recognition/quantification model, test)



Lung technique



Expensive « commercial » equipment not necessary
Easy to build yourself

No contact with the pump!! Passive lung inflation method

Sampling time: as short as possible to avoid the dilution effect (representative)

5. Odor sampling: Technical considerations (how)

A. A global air sample in a bag is needed for

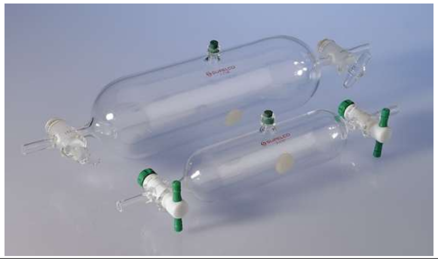
Sampling materials

- Odorles, no emissions
- Chemical inertness
- Negligible adsorption of the substances studied
- Low gas permeability
- Sufficient mechanical strength

- Type of materials:
  - PTFE (Polytetrafluoroethylene): Teflon
  - **FEP (Fluorinated ethylene propylene): Teflon FEP – close to Teflon**
  - PFA (Perfluoroalkoxy)
  - PET (polyethylenerephthalate) NalophanTM
  - PVDF; polyvinyldifluoride (
  - "Passivated" stainless steel
  - Glass

Plastic bag (up to 80 l) with septum, in teflon, nalophan, multifoild,

Canister in inox (the best) passivated for sulfurous compounds)
Expensive, + depressure device



Glass bulb (50 ml to 1 l)
With septum

5. Odor sampling: Technical considerations (how)

A. A global air sample in a bag is needed for

Bags (compliance with EN 13 725)

- **Cleaning**

  3 bags with neutral gas for 30h, olfacto test (< LOD or < Fs4 factor of the sample)
  Reuse not recommended unless in accordance with above

- **Leak test**

  place the entire sampling system in negative pressure by closing the inlet of the bag, the bag must not fill

- **Filling the bag**

  filling-evacuation with the sample, at least once, 10 to 20% of its volume or by flushing with the sample before sampling

- **Filling technique**
  - Lung
  - Direct if source with positive pressure
  - (Direct with an open bag (mostly for indoors))
  - (Direct with pump if no contamination by pump etc (field blank must be measured))

5. Odor sampling: Technical considerations (how)

A. A global air sample in a bag is needed for

- **Pre-dilution**
  - Avoid condensation
  - Limit diffusion
  - Reduce hazardousness by reducing the concentration of toxic compounds
  - Decrease the temperature of the sample
  - (add a filter if high dust content and heat if necessary)

Technique

- Pre-filling of a known volume of dry air:
  - if dilution greater than 3, prefer dynamic pre-dilution
- Dynamic pre-dilution in stack: under flow with dilution probe
- **Uncertainty calculation**
- Dilution check:
  - Example:

    if the gas is prediluted with N_2 and this gas contains O_2 21% or other known value, measuring the oxygen of the prediluted mixture will indicate the dilution factor

5. Odor sampling: Technical considerations (how)

A. A global air sample in a bag is needed for

Transport and storage of the sample

- **Risks**

  adsorption
  diffusion
  chemical transformation (reduced if prediluted with N2)
  popping of the bag…

- Analysed within 30 hours (EN 13725 standard)

  the shorter the better! in the SAM lab: max 24 hours
  increasing the thickness of the material and working in double bags can help

- Storage Temperature >Dew Point Temperature (< Lab T)
- Sample humidity similar to or less than RH ext to avoid diffusion of water and water-soluble molecules
- Protected from light
- Protected from shocks (be careful with transport)

5. Odor sampling: Technical considerations (how)

A. A global air sample in a bag

Bag sampling is recommended for quite high concentrations (usually at the emission):

➢ If dynamic olfactometry is the measurement:

- Detection limit≈ 50 ou_E/m^3
- "Odourless" sample sometimes ≈ 200 ou_E/m^3

➢ If sampling at the receptor level:

- Uncontrolled dilution between source and point of sampling
- No possible link with the source
- Possibly for verification of a maximum concentration never to be exceeded

The only information is a concentration at a time t,
no idea of the frequency and duration of odour exposure

➢ Interest in making a blank with a twin bag and upstream of the presumed source

➢ Not allowing a local resident to sample!

5. Odor sampling: Technical considerations (how)

B. Source geometry

- **Channelled source (chimney):** the best situation

Odour

sample in a bag
Olfactometric measurement (EN 13725)
Concentration in uo_E/m^3

Flow rate

Speed profile in the chimney (m/s)
(ISO 10780, ISO 9096)

Flow rate(m^3/s) = speed * diameter

Odour flow rate (uo/s) = concentration* flow rate

+Pressure, Temperature, O2 level, RH

Recommended ref: AMIGO & Olores.org (2023) International Handbook on the Assessment of Odour Exposure using Dispersion Modelling
DOI: 10.5281/zenodo.8367724

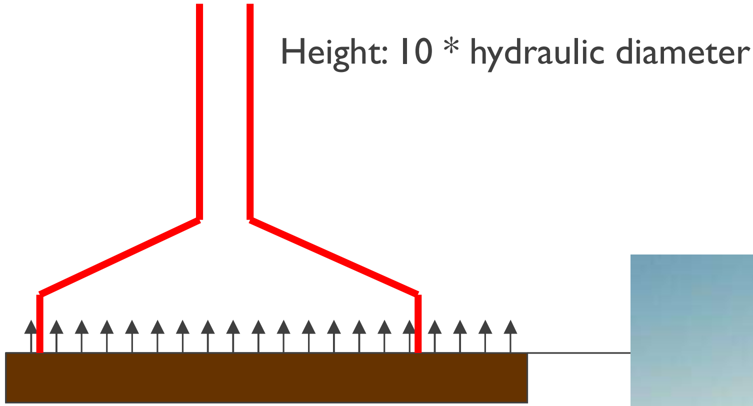
Channelled

5. Odor sampling: Technical considerations (how)

- **Surface/area source (active)**

- Sampling hood

For active source, the flow is generated by the source itself (no estimation with a carrier gas)



Surface area: 1 – 4 m²

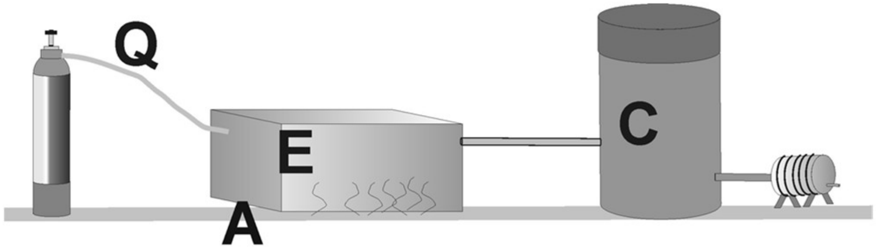
Speed: not higher than 3m/s

Recommended readings F.-B. Frechen, 2014, Considerations on Sampling and measurement of odours (VDI 3880 & VDI 3885/1) and eNoses, 1st International Seminar of Odours in the Environment, Santiago, Chile, www.olores.org

5. Odor sampling: Technical considerations (how)

- **Surface/area source (passive)**

- Flow chambers and Wind tunnels



SOER (specific odour emission rate) **ou/m².s**

E: emission flow of the isolated surface (ou/m²s)
Q: flow rate of the carrier air (m³/s)
A: isolated surface area (m²)
C: odour concentration (ou_E/m^3) canister to collect odour sample
T: time to collect the sample

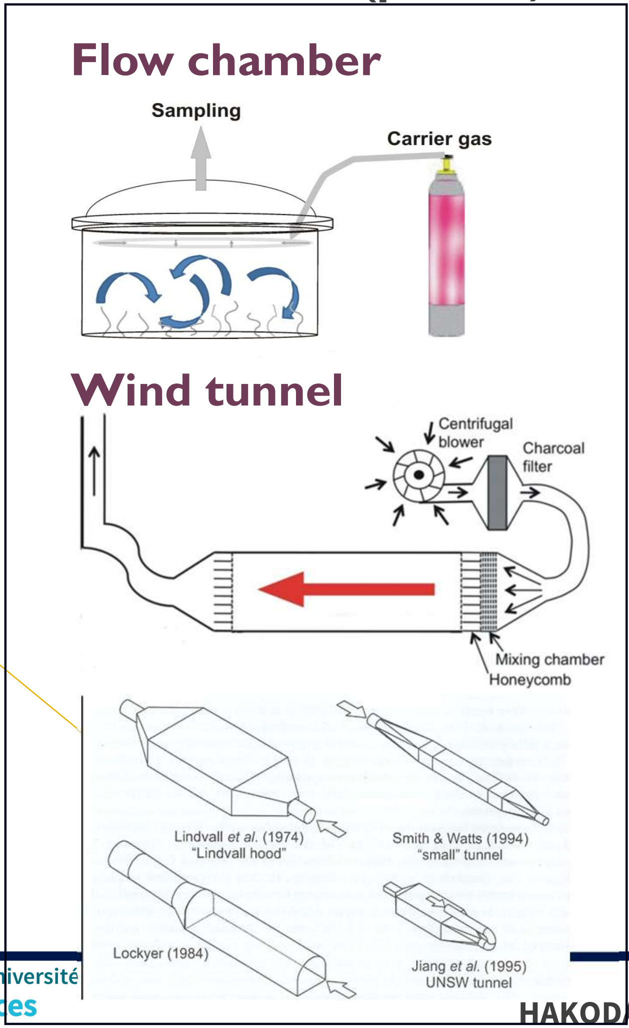
OER (odour emission rate) ou/s

- K: total area of the source/isolated area
- OER= K X SOER (**big assumptions of homogeneity!!!**)

A-C Romain, J Delva, J Nicolas, Complementary approaches to measure environmental odours emitted by landfill areas, Sensors and Actuators B: Chemical, Volume 131, Issue 1, 2008,

5. Odor sampling: Technical considerations (how)

- **Surface/area source (passive)**



Wide variability in odour concentration and flow depending on the "chamber" used

Interlab Testing

No harmonisation yet (probably never)

Always associate the measurement result with the method used, whether sampling or measurement!

The true value is never known.

Always compare the results obtained with the same methodology

5. Odor sampling: Technical considerations (how)

- « Fugitive » source and for « unsampled » source

No defined volume flow
Odour sample?

For VOC
- Emission factors (Modelling)–
- Specific techniques as DIAL (Differential Absorption Lidar) see EN 17628:2022

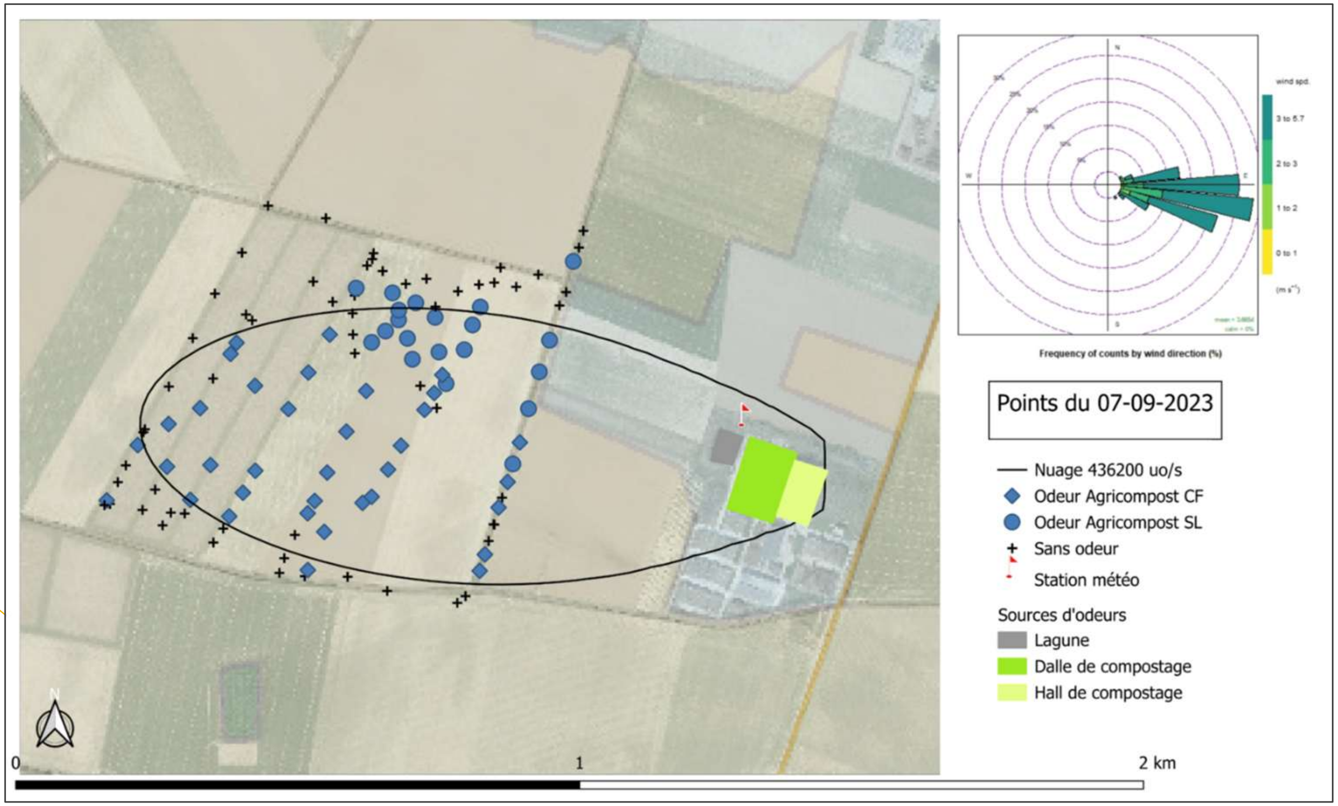
For odour, there is another way using the expert sense of smell + air dispersion models:
The field inspection method (EN 16841-2 –plum- or 1 –grid-)

Nicolas, J., Delva, J., Cobut, P., & Romain, A. C. (2008). Development and validating procedure of a formula to calculate a minimum separation distance from piggeries and poultry facilities to sensitive receptors. Atmospheric Environment, 42(30), 7087-7095.

5. Odor sampling: Technical considerations (how)

- « Fugitive » source and for unsampled source

e.g. of a field inspection (EN 16841-2 –plum) + odour dispersion modelling



5. Gas sampling in the field: Technical considerations (how)

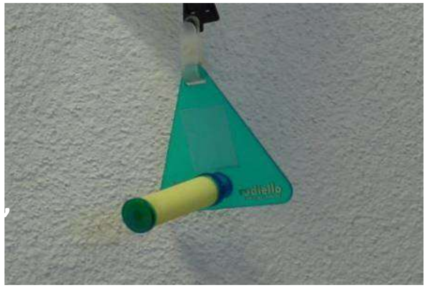
C. Specific sampling

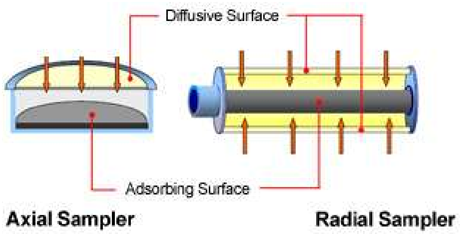
- ~~Olfactometric measurement in lab (EN 13 725)~~
- ~~E-nose development (calibration, recognition/quantification model, test)~~
- Chemical analysis (TD-GC-MS, HPLC, …)

Sorbent tubes

Active

Passive



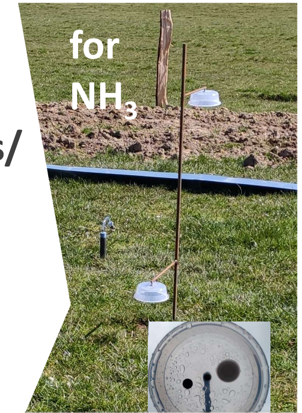


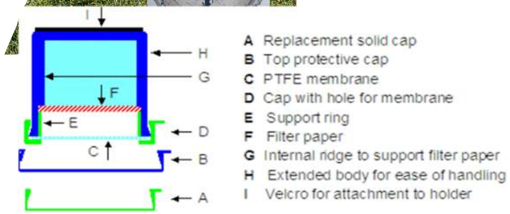
Chemical reactions sampling

DNPH cartridges

for aldehydes/ ketones

Badge alpha





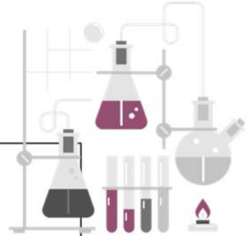
Impringers

Colorimetric tubes

6. Lab sample for gas sensor systems

Even for environmental applications of e-nose (IOMS), a lot of work needs to be conducted **in the laboratory** for :

*calibration, gas sensor test bench, metrological performance evaluation, validation, (algorithms) model development **

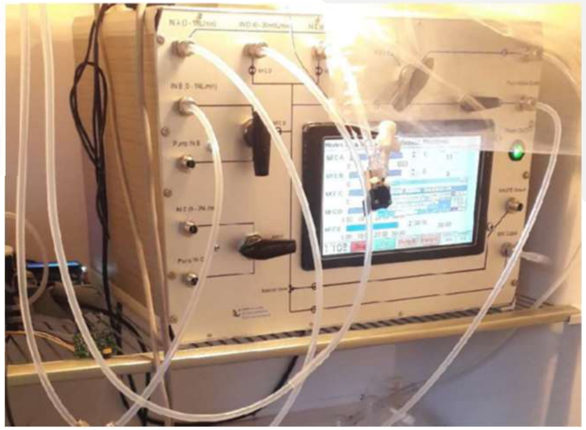


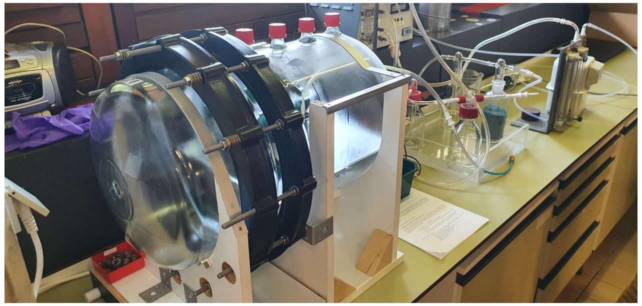
A- Preparation of a gaseous sample in the lab (gaseous standard mixtures)
or
B- (Aliquot of) a field sample + several preparation steps
(preconcentration, filtration, dilution)

- Under controlled conditions
- Design of experiments (DOE) is possible:
  optimization of the condition while minimizing the number of trials
- Matrix usually constant (for instance : synthetic air –N_2+O_2+Humidity-(CO_2))
  for sample created in the lab

Mixtures having matrix composition and analyte concentrations close to those of real samples result in more reliable measurement results
“tests under realistic operating conditions”

✓ *gas sensor test bench, metrological performance evaluation*





**JRC Technicla report, Protocol of evaluation and calibration of low-cost gas sensors for the monitoring of air pollution, Aleixandre, M ; Gerboles, M ; Spinelle, L, 2013 https://op.europa.eu/en/publication-detail/-/publication/bf86f3fe-c036-42cd-a347-f777230238a6/language-en*

6. Lab sample for gas sensor systems

Few words on the Generation of gaseous standard mixtures

- More than complex than for solid and liquid matrices numerous manipulation problems and low stability
  - Standard mixture with a composition like the analized real samples
  - Adsorption/desorption
  - Leaks
  - Wall memory (interferents from the containers)
  - Numerous analytes are not available in commercial gas cylinder
  - **Need of expertise in chemical analysis techniques and good laboratory practice**
- Several techniques of preparation *
  - Static : introduction of a specific amount of analyte into a known volume of the diluent gas under defined conditions
  - Dynamic : stream of analytes into a stream of the diluent gas
  - Mixed
- Principal approaches
  - Commercial gas cylinder
  - Headspace from solid or liquid phase
  - Gas sampling "plastic" bags (spike of liquid)
  - Stainless steel – canisters (spike of liquid)
  - Permeation tube/diffusion

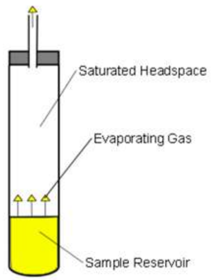


Image credit: owlstone

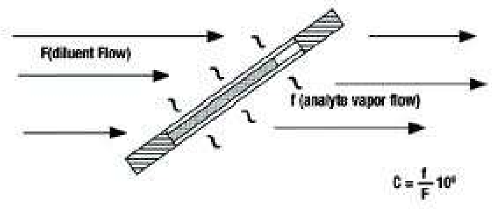


Figure 2. Schematic of an effective permeation tube blending system

*Ref : Anna Naganowska-Nowak, Piotr Konieczka, Andrzej Przyjazny & Jacek Namieśnik (2005) Development of Techniques of Generation of Gaseous Standard Mixtures, Critical Reviews in Analytical Chemistry, 35:1, 31-55, DOI: 10.1080/10408340590947916

6. Lab sample for gas sensor systems

*« **A gas mixture called Standard** (or reference material)*

- constant concentration of the analyte;
- knowledge of concentration of the analyte in a mixture with
an accuracy greater by a factor of 2.5–3 than the accuracy of a device being calibrated;
- ready availability because of many determination during the device calibration step;
*- **knowledge of all sources of error** » **

**Ref :Anna Naganowska Analytical Chemistry, 35:1, 31-55, DOI: 10.1080/10408340590947916*

Good practices

- Even if you made good calculation for the dilution and for determination of the analytes concentrations, a check with an analytical equipment like GC-MS is highly recommended

  The calibration of the analytical device must also be carried out correctly, and the **uncertainty of its calibration** model must also be known
- A concentration is never 5µg/m³ but always: 5µg/m³ +/-80 µg/m³ (1 atm, 20°C)
  - Consider the temperature and pressure on the final concentration

    see International Union of Pure and Applied Chemistry (IUPAC)
  - You must master the calculations of concentrations and the conversion: 1 ppmv is not 1 mg/m³
- Memory effects of the material: even PTFE tubing (porous material) can adsorb molecules
- …

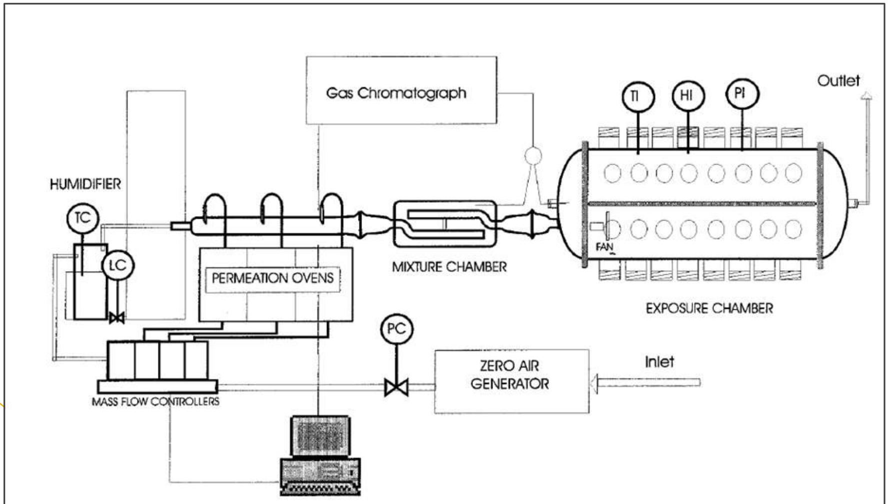
Interlaboratory tests

6. Lab sample for gas sensor systems

- Never pass the gas mixture through the humidifier

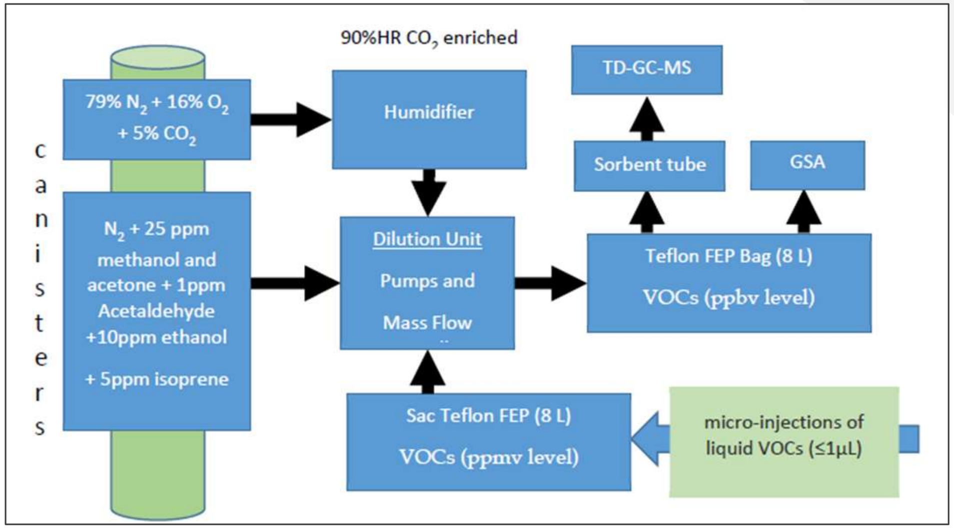
always have at least two gas lines:

- one with synthetic air that can be humidified by passing through a bubbler containing water (after the MFC)
- one with gas (or several) and mixing (therefore dilution) with humid air



ure 1. Standard atmosphere generation system.

Ref P. Perez Ballesta, A. Baldan, and J. Cancelinha Analytical Chemistry, Vol. 71, No. 11, June 1, 1999 (ISPRA)*



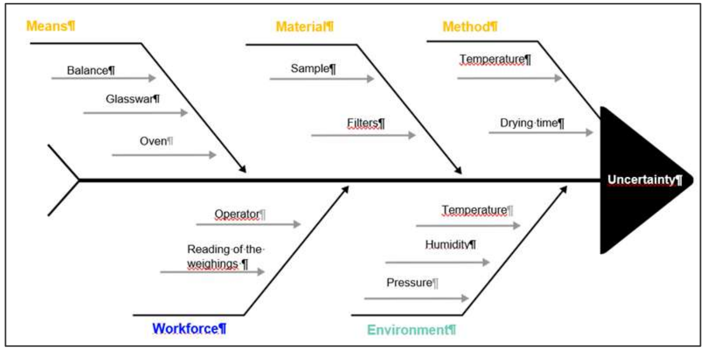
Ref J Martin thesis, ULiège, SAM, AC Romain (2024)

6. Lab sample for gas sensor systems

In the lab, calculating **UNCERTAINTY** is more feasible than in the field

$$u(G) = \sqrt{u_A{}^2(G) + u^2{}_B(G)}$$

Identification of sources of uncertainty : the fish bone diagram or Ishikawa diagram



Determine the uncertainty of each of the sources

data sheet of the mass flow controller/meter; balance's calibration certificate, reading errors of the syringe etc

e.g. u_A :instrument's certificate indicates +/- 0.01 µl for a 10 µl syringe

$$\boldsymbol{u(V) = \frac{0{,}01\ \mu l}{\sqrt{6}} = \pm 0.004}$$

Identify the most important contributions to the total uncertainty

Uncertainty propagation

$$u(G) = \sqrt{\boldsymbol{u(V)^2} + u(?)^2 + \dots}$$

several errors are not possible to quantify (operator,…)

Exercises and solution in Fundamentals of environmental sampling and analysis, Chunlong Zhang,

From the lab to the field

Taking the path to the real world
but the road is long and with several traps…

7. Calibration of IOMS for field application

A. In the laboratory

With "standard" gas mixtures ?

Only to test the metrological performance of sensors (LOD, sensitivity, selectivity, drift…) and hardware

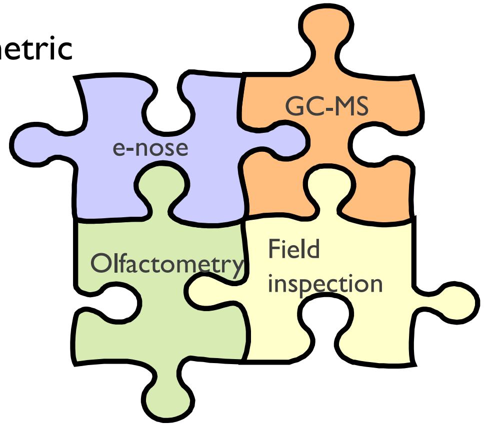
→ Even if the results are good, it does not guarantee that it will work well in the field
In the field: Concentration range, humidity, matrices, …differ

With field sample: the best calibration gas

→To develop a model (calibration function) between the response of the sensors and the odour metric for the odour under study and under specific conditions

The chemical composition of the sample in a bag can change,
The specific conditions are almost never the same

Higher uncertainty than for a standard but more representative



need to characterise your sample

7. Calibration of IOMS for field application

Standards (reference materials) for e-nose ???

"More than a big challenge… (see slide 24)

Several difficult discussions within the odour community for more than 20 years,
Heated and difficult discussions are a bit like a struggle between the pros and cons" AC Romain

CEN/TC 264/WG 41 "Emissions and ambient air – Instrumental odour monitoring"

Instrumental Odour Monitoring Systems (IOMS). Part 1: Definitions and general aspects
Instrumental Odour Monitoring Systems (IOMS). Part 2: Technical specifications and QA/QC requirements
Instrumental Odour Monitoring Systems (IOMS). Part 3: Field validation

IEEE standard association

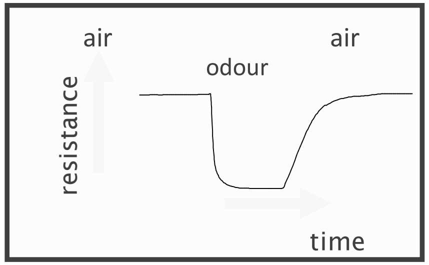
(see Laura and Yanxia talks)

The Heart of The big story: From the lab to the field…

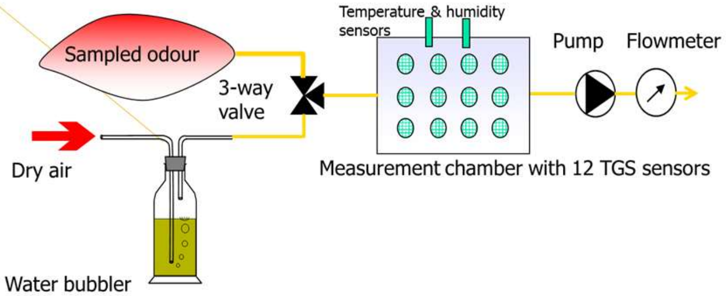
7. Calibration of IOMS for field application

A. In the laboratory

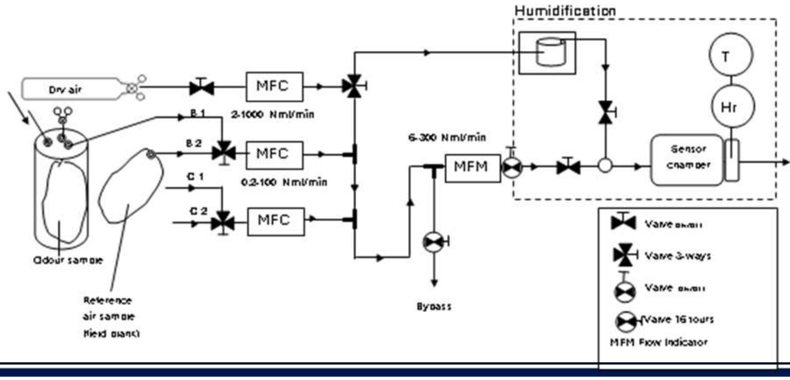
Generally: sample introduction is cyclic
Reference air (odourless/without analytes) – Sample - Reference



sample (usually a bag) connected to the gas sensor system

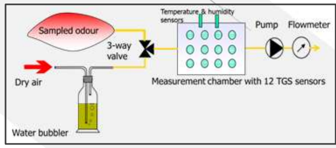


online sampling delivery system



7. Calibration of IOMS for field application

A. In the laboratory



Good practices with gas sensor systems

- The best reference air is not synthetic air but

  a bag collected upstream of the source according to the wind direction (a blank sample) as the same time as the sample

- Keep the same conditions between the ref air and the sample

  if the humidity of your air is not the same as that of the sample,
  if the temperature changes between the sample and the reference
  you will get a sensor answer!

- Do multiple repetitions (at least 3)
- Always start with the least concentrated samples
- Be careful as the cycles progress, the sensors take longer and longer to return to their initial state
- Representativeness: have samples that represent the conditions of the field as much as possible

  different matrix compositions, different concentrations, different humidities,…

- Under pression if gas cylinder: not possible in the field!
- Under depression with a pump after the sensor chamber to avoid contamination/adsorption

Gas leakages (check under fumes)

Pay special attention to sample preparation and the gas flow introduction system

pneumatic pump, flow meters, pipes, filters, concentration unit, headspace generator, sample changer, etc.

7. Calibration of IOMS for field application

B. In the field

Performances of the sensors in the field will be never as good as in the lab!

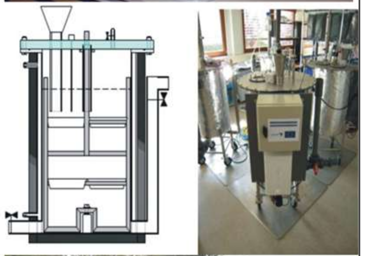
Matrix, Interences, Lower or higher concentration, Fluctuation, **cycle not easy in the field usually online without ref air**, harsh conditions

Objective of this work:
Early detection of process disturbances from the monitoring of the gas phase by an electronic nose

Multi-method monitoring of odor emissions in agricultural biogas facilities, J.Nicolas, G.Adam, Y.Ubeda, A.C.Romain, 5th IWA conference odour and air emisisons, 2013

Lab-scale → 12 anaerobic semi-continuous reactors

Pilot-scale → 4 digestors fed with sugar beet pulp



Real-size → 4 facilities in the 4 countries involved in the project

Adam, G., Lemaigre, S., Romain, A.-C., Nicolas, J., & Delfosse, P. (2013). Evaluation of an electronic nose for the early detection of organic overload of anaerobic digesters. Bioprocess and Biosystems Engineering, 36 (1). doi:10.1007/s00449-012-0757-6

7. Calibration of IOMS for field application

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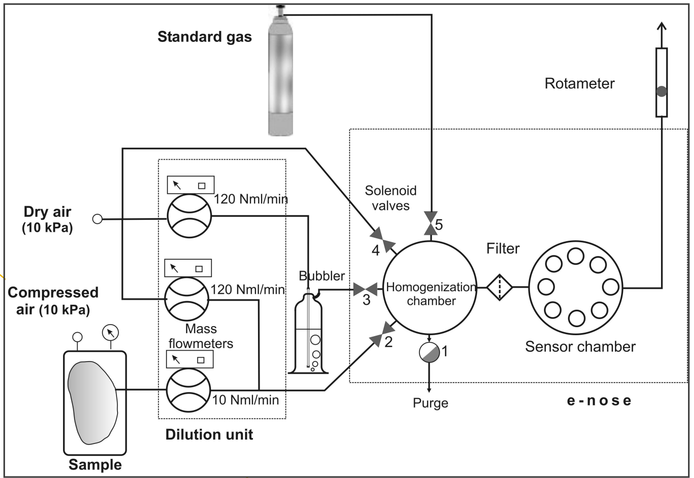
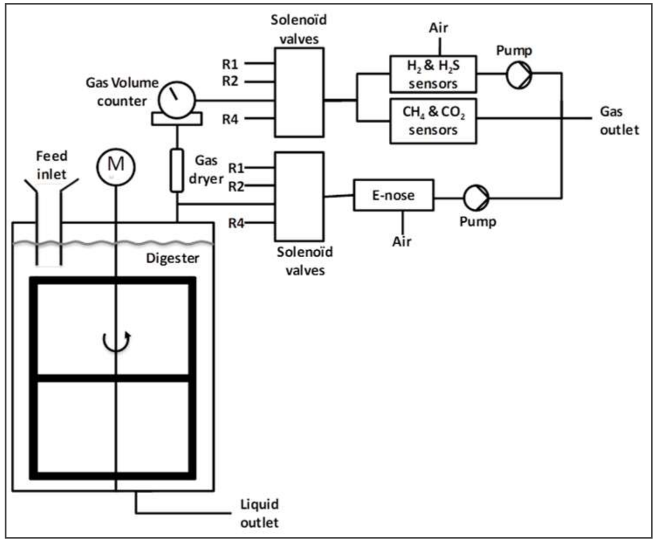
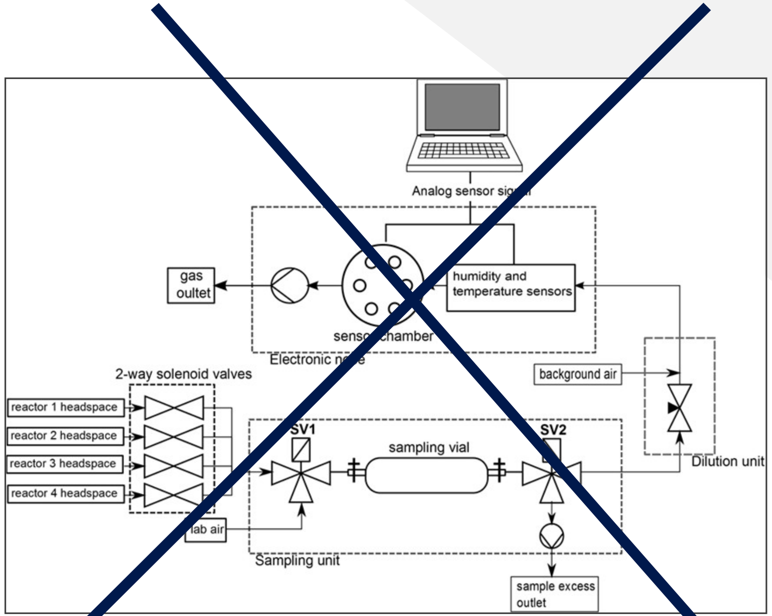


In the lab schematic representation of the ***biogas dilution*** *and sensing with an electronic nose device.*

G Adam Thesis, Uliege, 2013



Schematic representation of the pilot-scale anaerobic digesters (100L) and gas phase monitoring system.



Schematic representation of the e-nose system employed for the real-time online monitoring of two anaerobic reactors

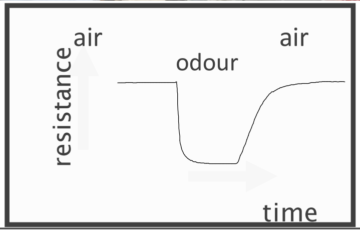
From the lab to the field

Different approaches to "calibrate" (to train) the nose

Usually, sampling of odour **bags**
analyses in the **laboratory with air-odour cycle**

Field sampling "bag approach"

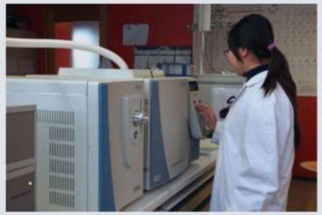
E-nose training



Identification/Quantification

Sensorial

Analytical

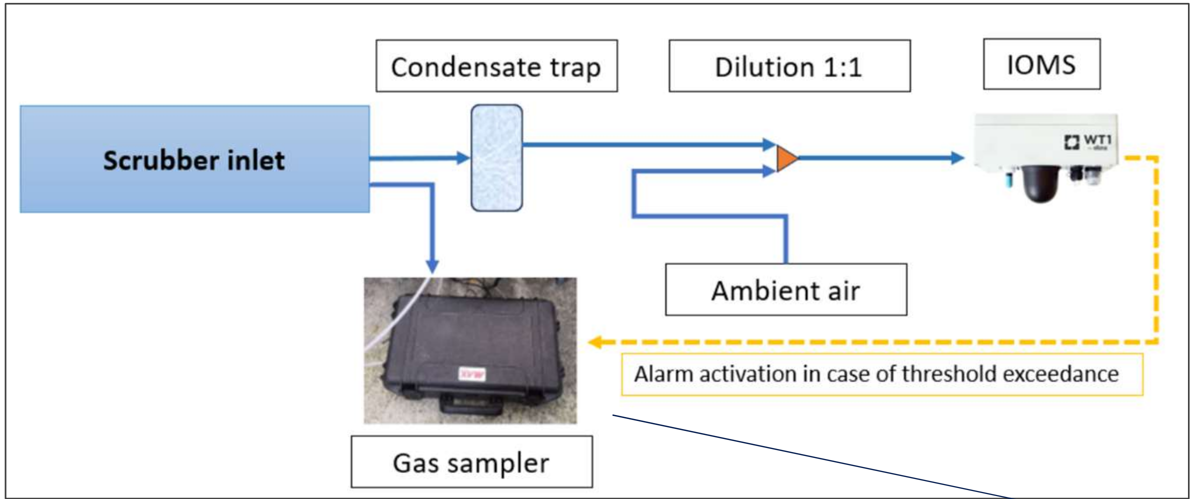


Alternative:
odour **bags** connected to the e-noses
already installed in the field
no more lab measurements with e-nose

AN ALTERNATIVE APPROACH OF THE E-NOSE TRAINING PHASE IN ODOUR IMPACT ASSESSMENT, Giuliani, Stefano; Zarra, T; Nicolas, Jacques, AC Romain.
2012 • In Del Rosso, Renato (Ed.) Chemical engineering transactions : NOSE2012 International Conference on Environmental Odour

7. Calibration of IOMS for field application

B. In the field



ref: S Prudenza, C Bax and L CapelliReal-time monitoring of odour concentration at emission sources by IOMS: comparison of different regression models, ISOEN 2024

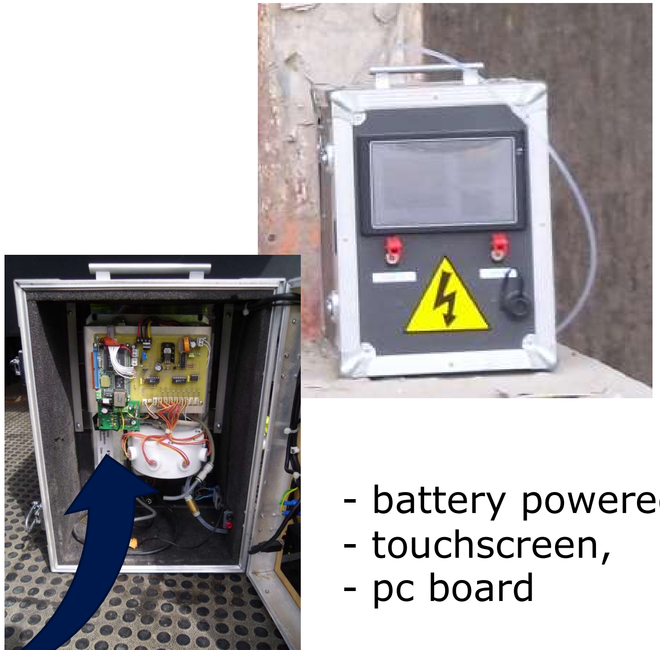
Lab of olfactometry

Is it possible to avoid bag sampling?

The e-nose « 5 » has been removed and positioned in a portable box:

e-nose 5: Static

“same”e-nose 5: Portable

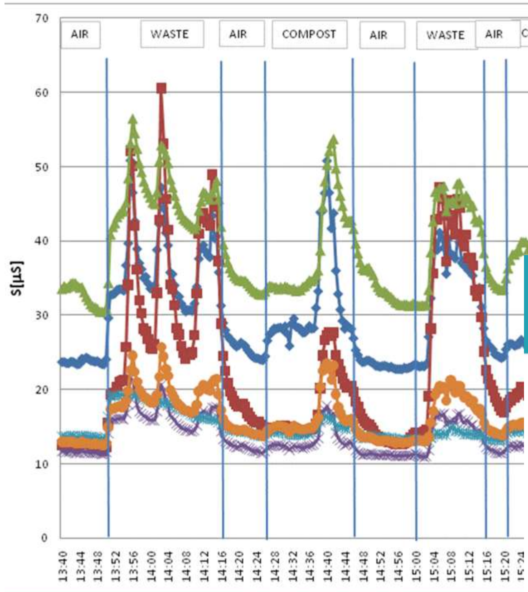


- battery powered,
- touchscreen,
- pc board

AN ALTERNATIVE APPROACH OF THE E-NOSE TRAINING PHASE IN ODOUR IMPACT ASSESSMENT, Giuliani, Stefano; Zarra, T; Nicolas, Jacques, AC Romain. 2012 • In Del Rosso, Renato (Ed.) Chemical engineering transactions : NOSE2012 International Conference on Environmental Odour

e-nose sensor signals in field: Example

Duration time: 3 hours

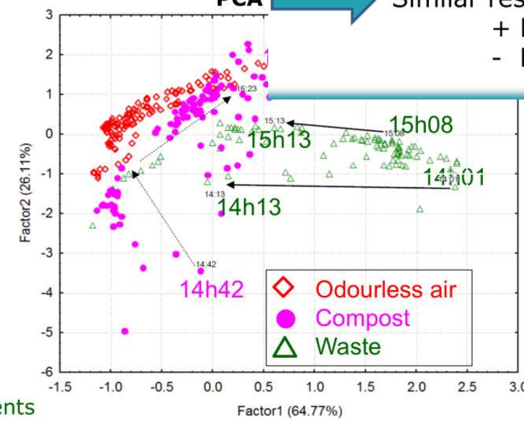


Signal evolution/movem

instrument information related to
the movement and the observation of the o

- Day measurement: 1th May
- 301 observations (Gnor)
- Time interval: 30 s
- Measurement duration: 3 h

PCA



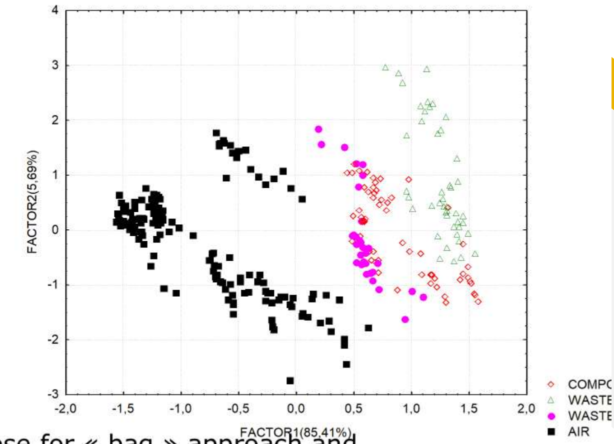
→ Time evolution of waste odour events
--→ Time evolution of compost odour events

First results

5 odour field campaigns (5 differents days)
From May toJune 2011

- 366 observations
  - 154"non odorous background air"
  - **87 "waste –high-"**
  - 46 "waste-low-"
  - 79 "compost"

PCA score plot



Similar results to those for « bag » approach and
+ better separation for low concentration values (compost);
- higher dispersion

AN ALTERNATIVE APPROACH OF THE E-NOSE TRAINING PHASE IN ODOUR IMPACT ASSESSMENT, Giuliani, Stefano; Zarra, T; Nicolas, Jacques, AC Romain.
2012 • In Del Rosso, Renato (Ed.) *Chemical engineering transactions : NOSE2012 International Conference on Environmental Odour*

1- Context : a) Methodology of our research department

Department of Environmental Monitoring : our researches incited by environmental problems

specificity : **malodour pollution in the field** and indoor emissions

e-nose has the best **potentialities** to answer to the **expectations of the actors** in the olfactive pollution problematic

Continuous monitoring in the field

Application

Why an e-nose ?

In the field (in real life)

1. Investigation of the problem
3. Test - Measurement

In the lab

2. Development of measurement system

(instrumentation, experimentation, data treatment)

Bioinspired signal processing workshop
A-C Romain,
Barcelona, january 2007

Book: Biologically Inspired Signal Processing for Chemical Sensing, A. Gutiérrez, S.Marco, Studies in Computational Intelligence, Springer Berlin, 2009

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Department of environmental monitoring : our researches incited by environmental problems

specificity : **malodour pollution in the field** and indoor emissions

e-nose has the best **potentialities** to answer to the **expectations of the actors** in the olfactive pollution problematic

Continuous monitoring in the field

Application

Why an e-nose ?

In the field (in real life)

1. Investigation of the problem
3. Test - Measurement
5. Learning phase
7. **validation**

In the lab

2. Development of measurement system (instrumentation, experimentation, data treatment)
4. Improvement-Optimisation
6. Verification

Bioinspired signal processing workshop
A-C Romain,
Barcelona, january 2007

1- Context : a) Methodology of our research department

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In the field (in real life)

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Application

Why an e-nose ?

8. Functioning : best possible answer to the expectations

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Barcelona, january 2007

e-nose is not universal:
to dedicate each instrument with it's final utilisation guarantees the best results

A dedicated signal processing is one of the key of the e-nose success

1 – Context : b) Operating conditions

NEVER REPRODUCIBLES

VARIATIONS :

- Various activities
- Raw materials composition variations
- Process variations

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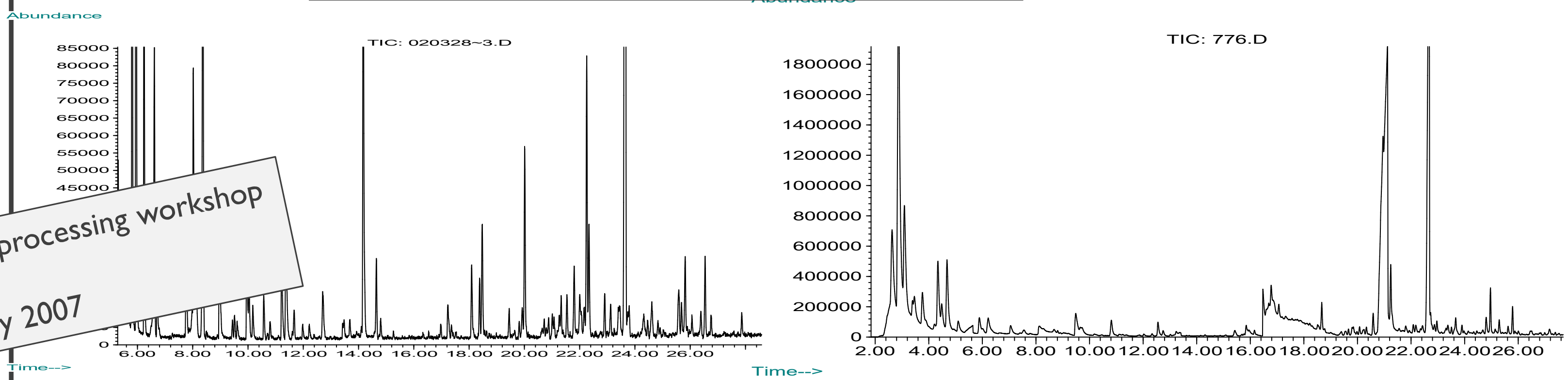
For one odour source (1 class in PARC): variable complex compounds mixtures

Different chromatographic profiles for the same odour



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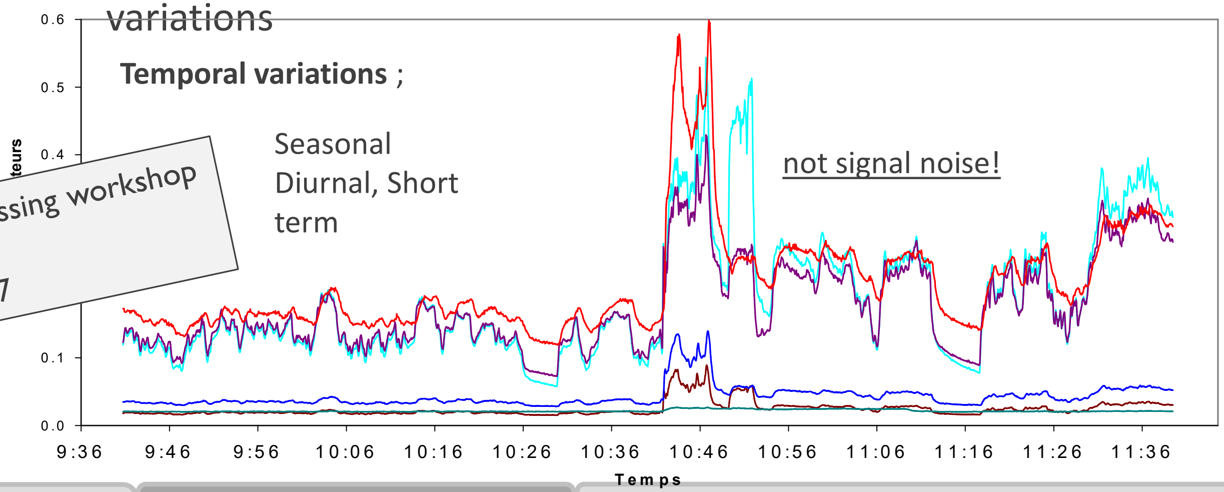
For one odour source (1 class in PARC): variable complex compounds mixture

- Influence of meteorological parameters: ex. humidity variations



Temporal variations ;

Seasonal
Diurnal, Short term

not signal noise!

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1 – Context : b) Operating conditions

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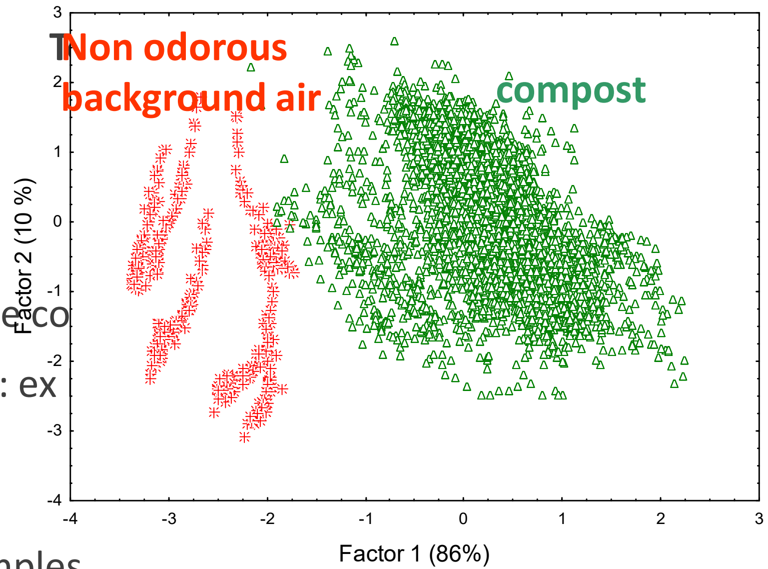

Signal processing

- Need a great number of samples to consider all the conditions and chemical compositions
- High dispersion of the data of a same class and/or of the same concentration

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1 – Context : b) Operating conditions

NEVER REPRODUCIBLES

VARIATIONS :

- Various activities
- Raw materials composition variations
- Process variations

Fo… ur source (1 class in PARC):variable

…ce of meteorological parameters:e…

variations

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Temporal variations ;

Seasonal, Diurnal, Short term

(not signal noise!)

Signal processing

- Need a great number of samp… to consider all th… ositions
- High dispersion of the data of … concentration

HARSH conditions for the materials

ODOUR DIMENSION (not evaluation of chemicals)

CONTINUOUS FUNCTIONING with maintenance as low as possible

1 – Context

With the environmental conditions and with the e-nose hardware limitations and imperfections,

odour monitoring with an e-nose is a real challenge:

If these problems cannot be solved by an hardware optimisation or correction

signal processing has to cope with them

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2 – Some « real examples » of signal processing/data treatment

No standards of « compost odour» or « printshop odour »,…!

<u>Our criteria of selection are:</u>

Simple mixture

Reproducible

Time stable

Well known compounds

Easy to obtain

Intensity of the sensor response similar to the concerned odours

b) Quantification = Correlation with sensory data

Still the standard question…

1. **Standards = real** samples with variable composition

   1 odour source = several chemicals mixtures in a variable background

2. concentration = **sensory dimensions (large errors!)**

   usual european odour concentration : ou_E/m^3

Forget the perfect regression model!

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Conclusions/Requirements

- **Common classical and simple techniques**
- The **ideal** signal processing recommendations are **rarely applicable**
- **Consider the specific environmental odour problem :**

variations, number of different odour category, lot of samples, sensory dimensions, no standard

- **keys of success** for signal processing

field investigation, application dedicated

even if

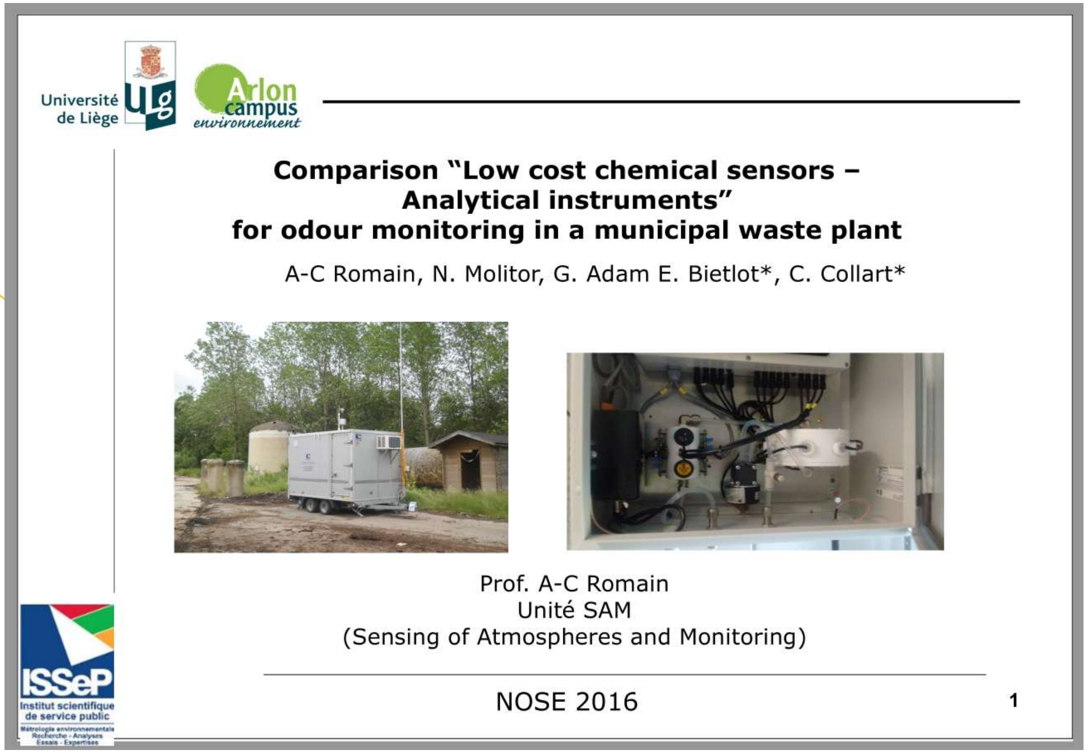
- time consuming
- validation in the field is not easy

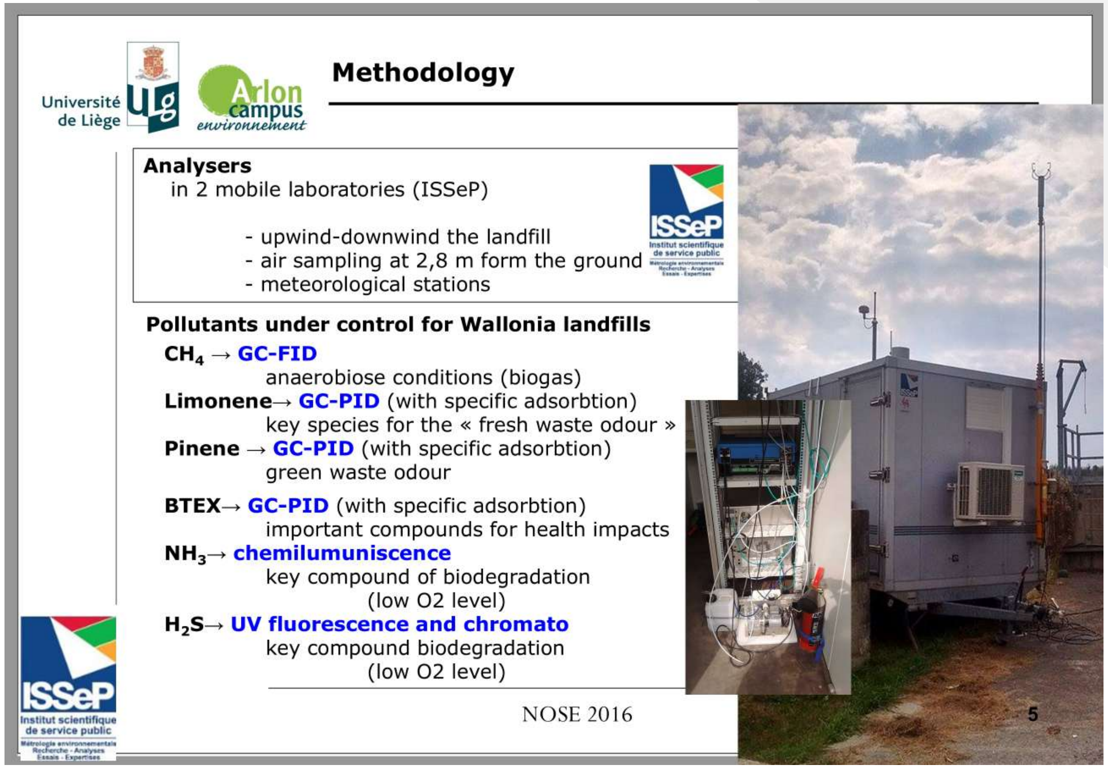
…ction **in continuous** for monitoring

7. Calibration of IOMS for field application

B. In the field

If no reference materials,
calibration by comparison with a reference method,
preferably in the field

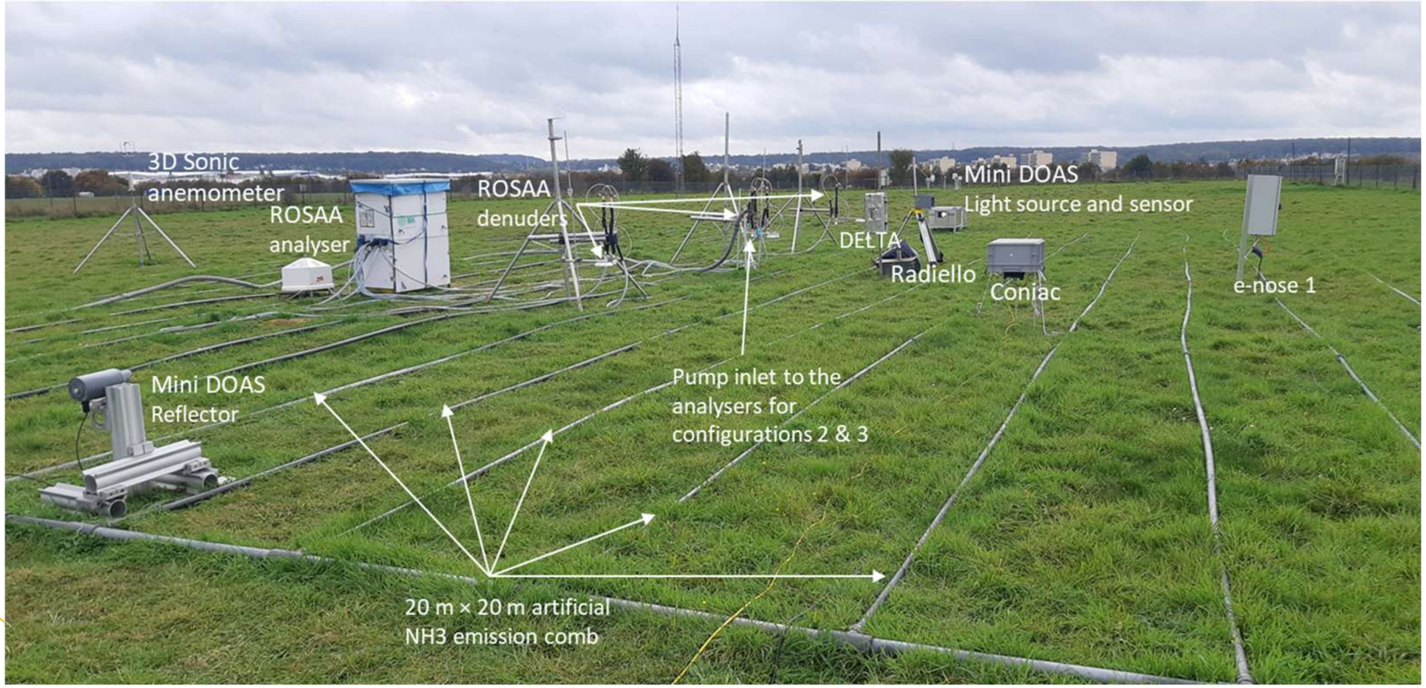




7. Calibration of IOMS for field application

B. In the field

Interlaboratory tests in the field



AMICA project, INRAE, France

Multi-Instrumental Analysis of Ammonia Concentrations 2021 on the INRAE site in Thiverval-Grignon.

https://www.inrae.fr/actualites/amica-analyser-lammoniac-latmosphere-mieux-gerer-qualite-lair

6. Take home messages

Sampling and Measurement go hand in hand:
A sensor array system will only give reliable results if the sampling is representative and “error-free”

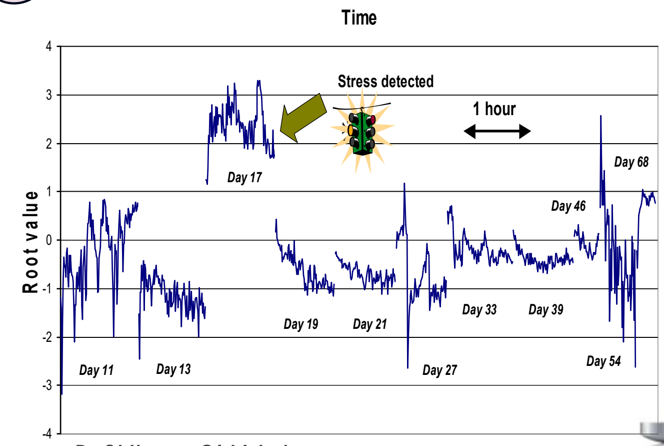
- Fundamentals of sampling (sampling plan) are important to know even if rarely applicable for environmental applications in the atmosphere
- Maintain good laboratory practices at every step to reduce sampling errors
- While tests with synthetic samples can be useful (e.g., to assess the performance of a new sensor), they are not sufficient to validate field applicability.
- At a minimum, complementary laboratory tests should be conducted under conditions that closely mimic those in the field.
- Whenever possible, prioritize real samples over synthetic ones: Given their heterogeneity, real samples ensure that all relevant conditions are properly represented.
- For source sampling and measurement, flow rate is a critical parameter that must be carefully considered.
  - Sampling procedures should always be adapted to the geometry of the source.
- The calibration of gas sensor array system for field applications should ideally be performed directly in the field, through comparison with reference methods, rather than relying solely on standard laboratory mixtures.
- In general, the simpler the technique, the lower the measurement uncertainty and associated costs, especially due to reduced maintenance requirements.

This is not yet the end

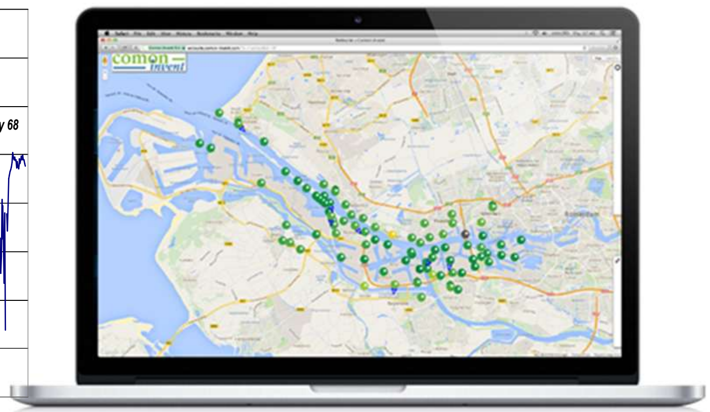
"My favourite approach for successful application of IOMS in real life,
for environmental monitoring in the ambient air (fenceline or close to the neighborough)

(Extreme) event detection
Combine sensors measurements with wind direction (knowledge of dispersion)
Simple and cheap gas sensors system chamber
- *Without pump*
- *if filters: check if the filters are not clogged*
- *Without complex sampling line (passive)*

and numerous sampling sites". AC Romain



Ref ULiege, SAM Lab



https://www.comon-invent.com/real-time-monitoring/

Personal reflection

Our community is multidisciplinary.
We need stronger collaborate between disciplines,
statisticians with chemist, material sciences with end-users etc…

E-Noses in the real world and for some scientists NO LONGER HAVE A VERY GOOD PRESS.

Let's be rigorous in our work and honest about the true current possibilities of our instruments!

Even the best "lab" sensor is useless in the field without real-world testing ultimately, sample/sampling quality is as important as sensor quality.

If you can, b … ***g and rough…***

Imitate the sense of smell?

"machines to perform tasks that previously only humans can do"

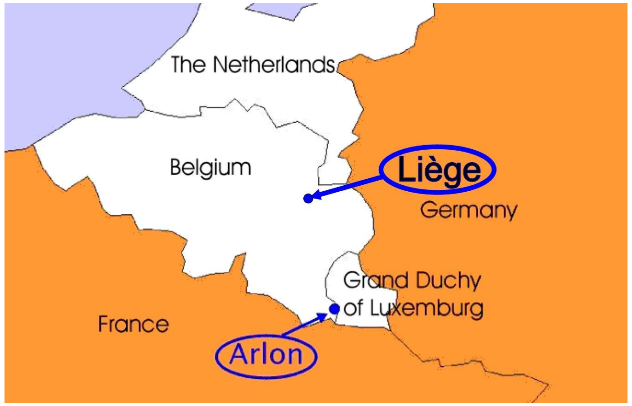
« In 1982, Persaud and Dodd, from the University of Warwick, introduced the concept of artificial olfaction. They present this new technology as an intelligent system based on a network of chemical sensors for odor classification.
But the pioneer was undoubtedly Moncrieff, who in 1961 proposed an instrument for detecting odours, based on a thermistor, covered with an adsorbent film, integrated into a Wheatstone bridge.

It was only in 1991 that the term "electronic nose" was accepted and that a first conference was dedicated to it [NATO Advanced research workshop on sensors and sensory systems].
J. Gardner in 1994 offers a definition of this nose:

an instrument comprising a network of partially specificity chemical sensors and
a pattern recognition system,
able to recognize simple or complex odors….

Plagiarism of my Thesis, 2006

Thank you for your attention



The best representative sample of my lab

5. Odor sampling: Technical considerations (how)

Source geometry

- « Fugitive » source and for unsampled source

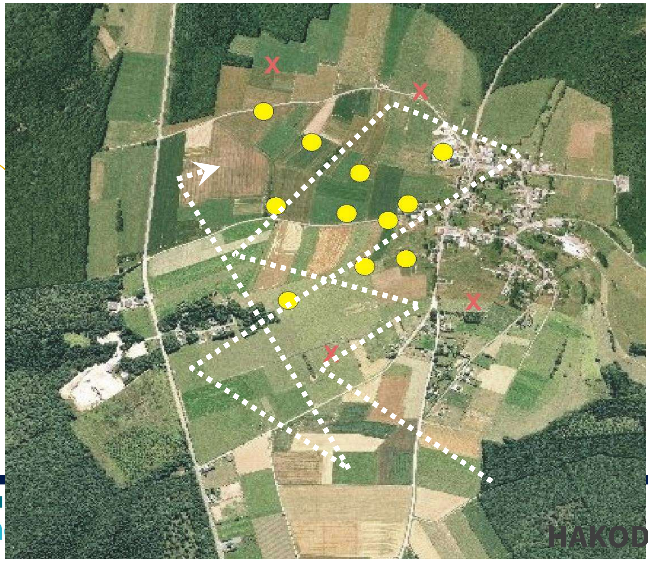
The field inspection method (EN 16841-2 –plum- or 1 –grid-)

Concise explanation

- introduce in the model a odour flowrate that generates an odour iso-curve 1su / m³, and the curve has to include all the point

- deduce the flow of the odour source that led to the perception limit curve measured on the site

Walk and smell in the receptor field
Determine the limit « odour-no odouir »
This limit is evalaute to 1 su/m³



Big uncertainty of the uncertainty estimation

reverse modelling to find the odour flow rate that generate 1 su/m³ (lagrangian model)