

unisanté

# Chemicals Assessment

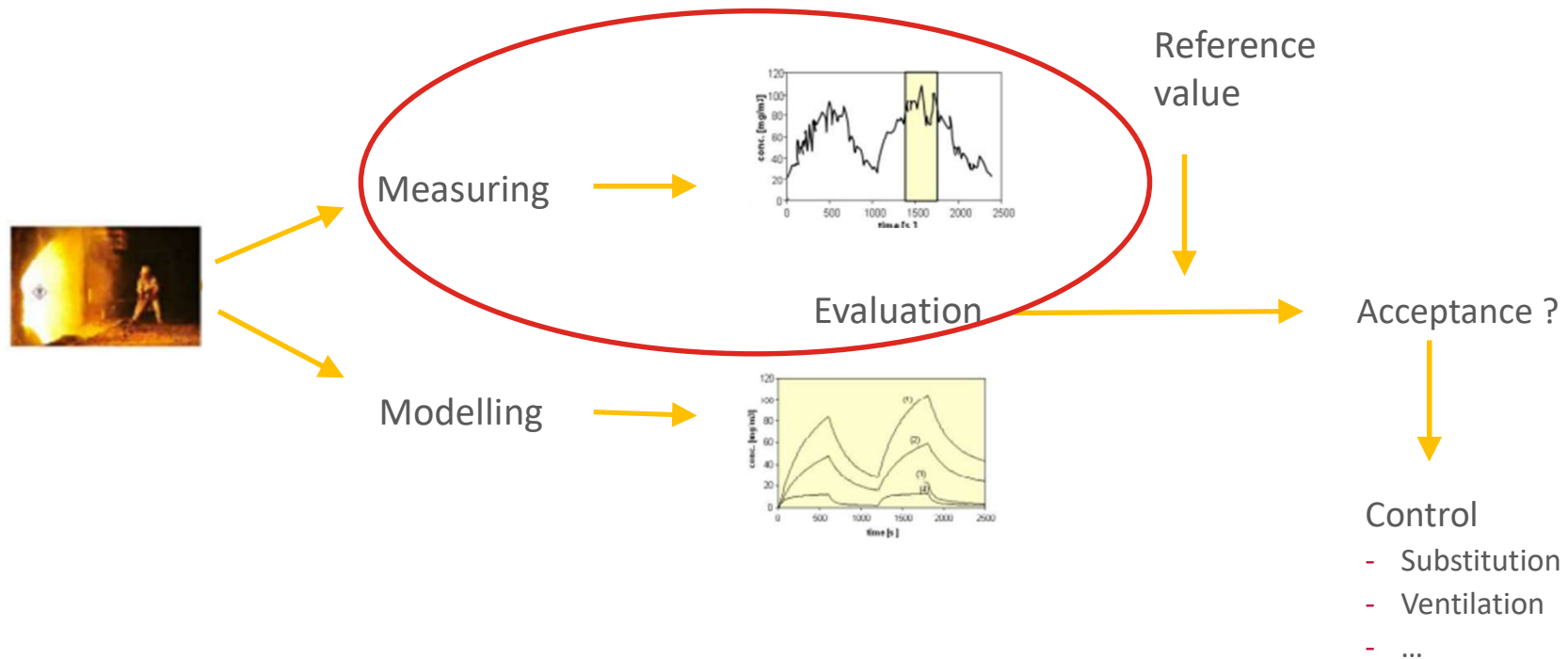
*David Vernez*





# Exposure assessment & control

## Strategy



# Exposure variability

## Due to the emission source

- Process used, rate, quantities
- Physical properties of the material, energy used
- Emissions linked to other processes

## Due to the work environment

- General ventilation (weather conditions)
- Air currents, local mixing, thermal effects
- Distance from the source (displacement)

## Due to the measurement

- Inaccuracy of the equipment or sampling

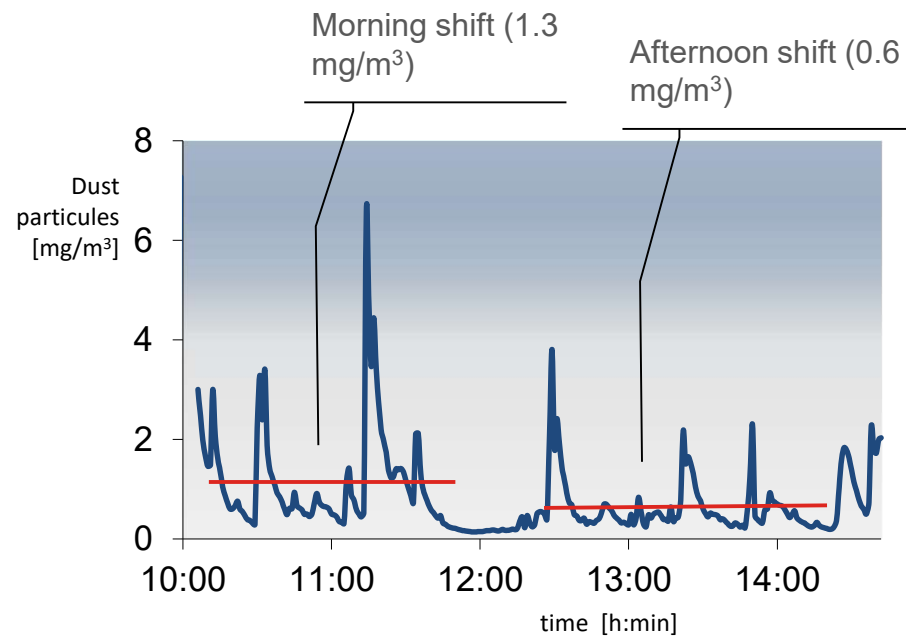
# Exposure variability

## Individual related

- Specific tasks (posture, body movements, moving around...)
- Work habits, training
- Measurement, control

## Metal industry

- Direct reading (*nephelometry*)
- Stationary position



# Airborne measurements

## Integrative measurements (dose)

### Mechanical

- Syringes
- Vacuum containers
- Plastic bags
- Cryogenic methods

### Chemisorption

- Solubilization
- Activated charcoal Chemical transformation (e.g. impregnated filters)
- Porous polymers

### Physisorption

- Various solid supports
- SPME (microextraction)

# Airborne measurements

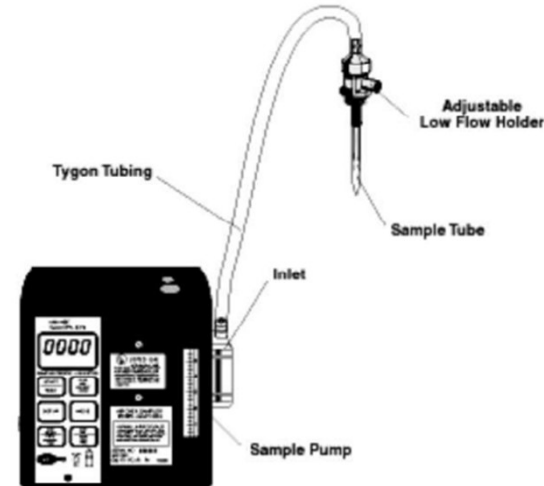
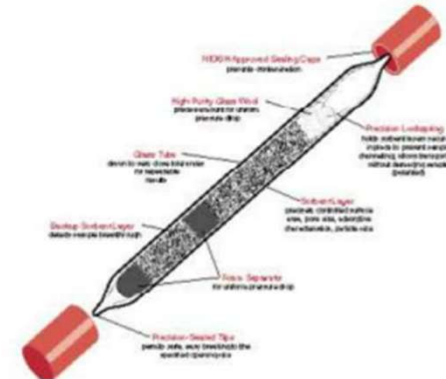
## Integrative measurements – chemisorption

### Activated charcoal tube

- Limited capacity
  - Different sizes
  - Typically 100- 1000 mg
- Control area
- Desorption
  - Solvent (often CS<sub>2</sub>)
  - Efficiency to be determined

### Various other sampling tubes

Requires laboratory analysis after desorption



# Airborne measurements

## Continuous measurements (concentration )

### Photoionization detector

- Versatile, most organics
- Direct reading
- Non-specific



ToxiRAE photo-ionization Monitor

### Electrochemical detector

- Direct reading
- Specific
- Only common gases (CO, H<sub>2</sub>S, O<sub>2</sub>, SO<sub>2</sub>...)

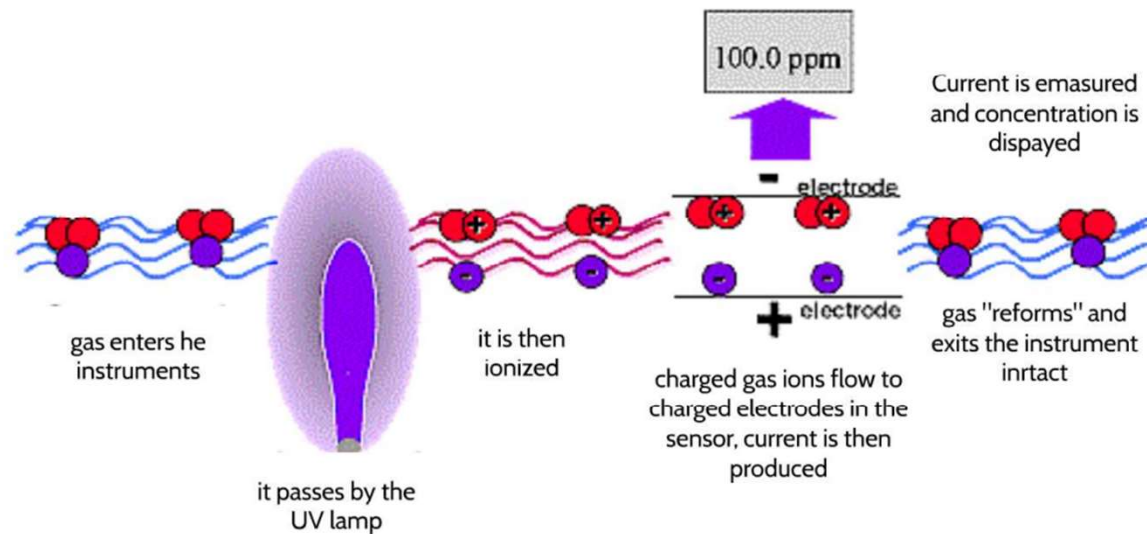


Dreager electrochemical detector

# Airborne measurements

## Photoionization detector

UV light (typically 10.6 eV)



# Airborne measurements

## Continuous measurements

Some examples

Principle	Measured substances
Electrochemical	CO, NO <sub>x</sub> , Phosgen, Cl <sub>2</sub>
Photoionisation	Most organic substances
Spectrophotometry IR	Organic and inorganic substances
Non dispersive IR	CO <sub>2</sub>
Chemiluminescence	Ozone
Combustion	Flammable substances
Spectrophotometry UV	Ozone

# Case study

## The printing industry

An industrial hygienist was tasked with assessing the inhalation exposure of press operators in a printing facility. The worker handles inks containing Toluene ( $C_7H_8$ ). OEL (TWA) : 50 ppm 8-h

Monitoring was conducted over 8-hour for 1 worker, with the following results:

Measurement	Duration (hour)	Concentration (ppm)
1	100	15
2	50 min	75
3	60	No measurement
4	150 min	120
5	40	No measurement



### Question (2.3a)

Do you think these data could be representative of the exposure?

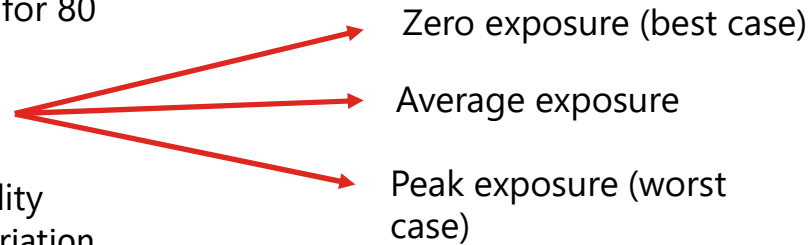
# Case-study solution

## Question 2.3a

- OEL (TWA) : 50 ppm 8-h
- Work duration : 8-hour shift
- Number of workers **1 worker**
- Insufficient sampling duration, the OEL is for an 8-hour period (8 x 60 = 480 minutes)
- Gap : no measurements for 80 minutes  
Assumptions for the unmeasured
- Lack of exposure variability data : between-worker variation

Measurement	Duration (min)	Concentration (ppm)
1	100	15
2	50 min	75
3	60	No measurement
4	150 min	120
5	40	No measurement
<b>Total : 400min</b>		

} Gaps

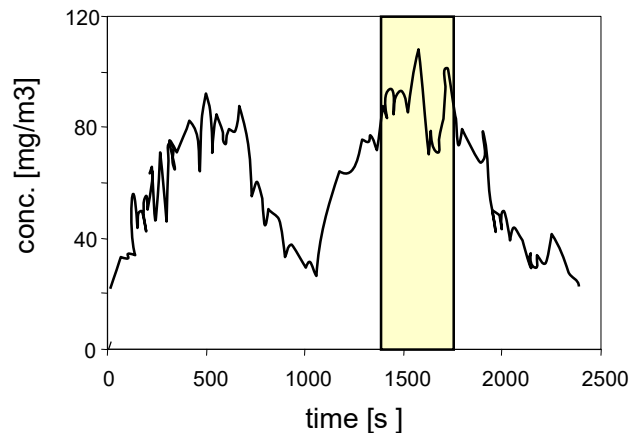


Representativeness issues become worse with less time sampled

# Representativeness of the measurements

Are the realized exposure measurements **representative** of the real exposure situation?

- Exposure variability
  - intra-individual, inter-individual
- Measurement error
  - Analytical sampling

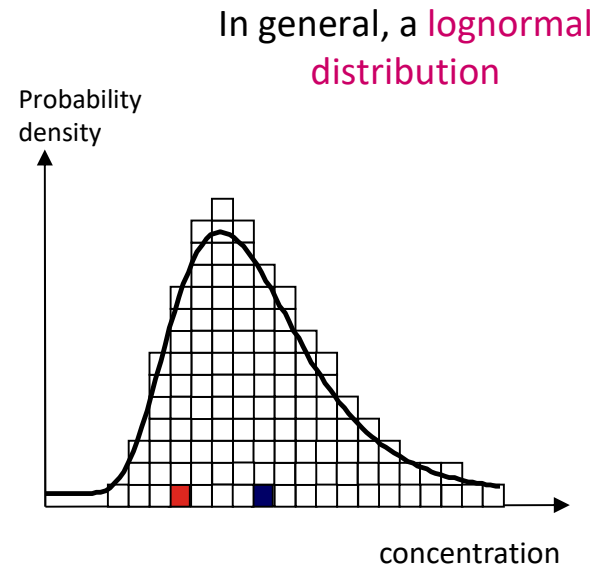
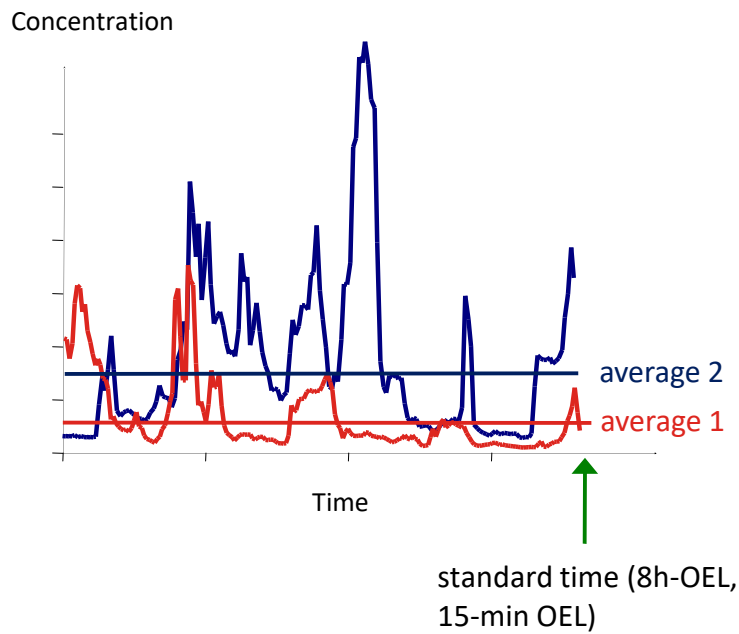


*Never measure twice on the same spot, the result will always be different*

*Tinnenberg 2001*

# Exposure distribution

To take the variability into account, we characterize the exposure distribution

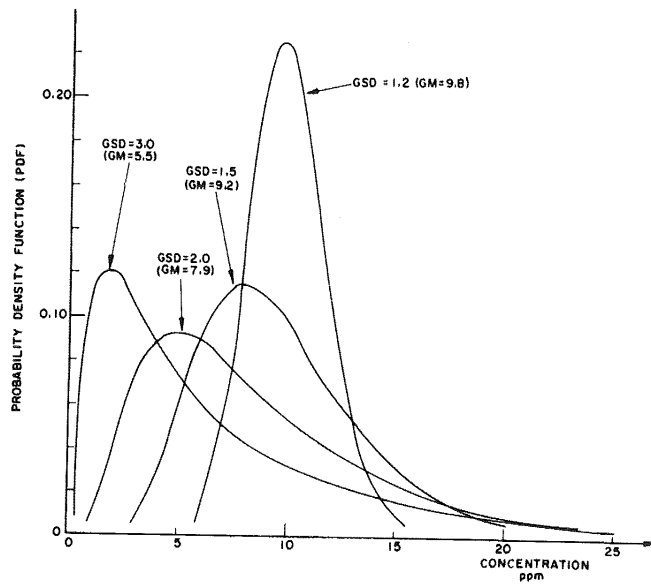


# Measurements distribution

## Observed distribution

- Widely spread GSD 1.5-3.0
- Typically GSD 2.0-2.5

For a geometric mean of 10



$\mu$	GSD	Percentile 2.5% - 97.5%
11	1.5	4-23
13	2.0	3-40
15	2.5	2-63
18	3.0	1-90
22	3.5	0.8-123

# Statistical approach (simplified)

- sampling
  - Number of samples required to ensure that at least one sample will belong to the most exposed (percentile 10%)  
confidence indice of 95% (short-term measurement)

Taille de la population	12	13-14	15-16	17-18	19-21	22-24
Nb échant.	11	12	13	14	15	16

25-27	28-31	32-35	36-41	42-50	∞
17	18	19	20	21	29

# Practical approach: “action level”

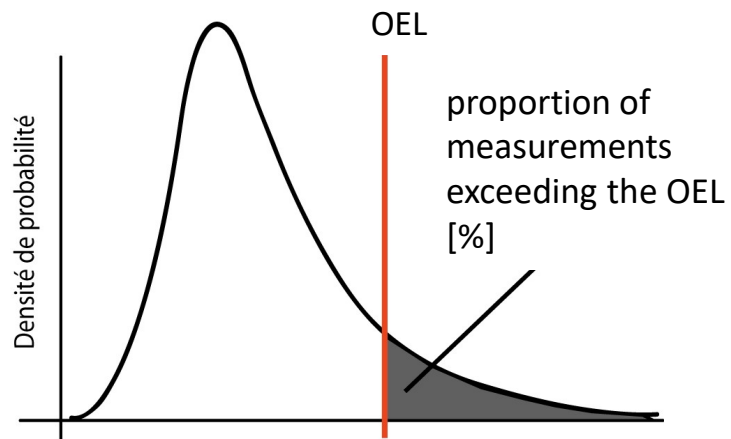
An « action level » is a level at which preventive actions have to be taken. This level is usually equivalent to the half or the third, sometimes the quarter of the OEL.

For what reason?

- taking into account exposures variability (day, week, month, year)
- taking into account the limited knowledge about OEL
- the company corporate image
- quality procedures (ISO and OSHAS standards)

# Statistical approach

Probabilistic approach: Assuming a given distribution of  $(\mu, \sigma)$ , what are the chances to exceed the reference value?

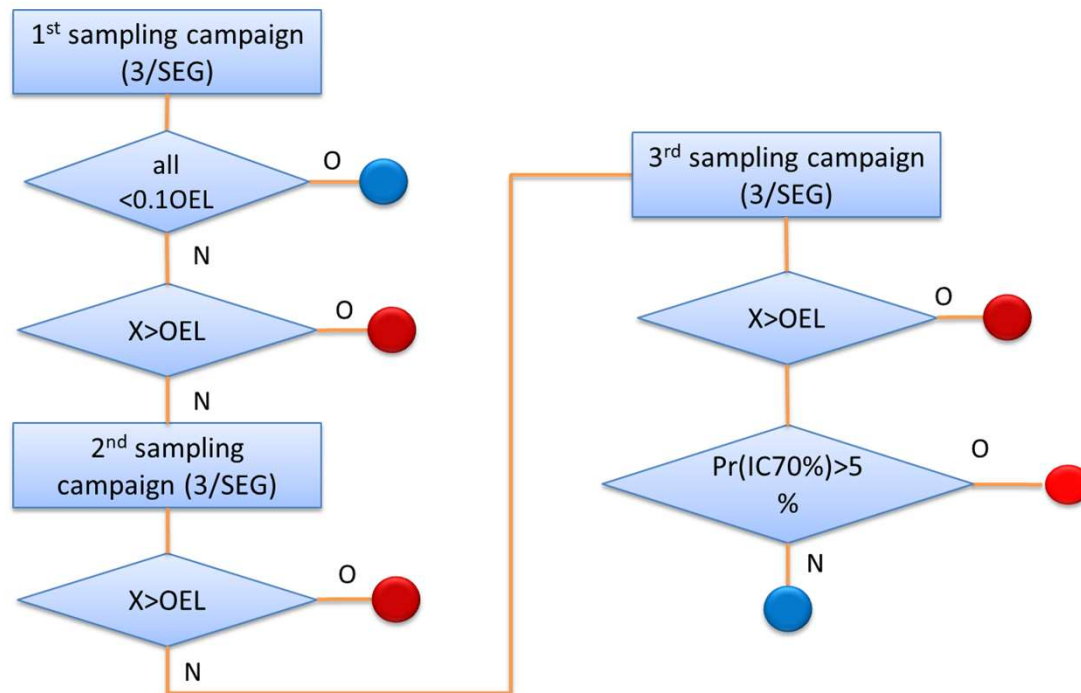


to keep in mind:

$$\mu \cong \bar{x} = \sum \frac{x_i}{n}$$

$$\sigma \cong s = \sqrt{\frac{\sum (\bar{x} - x_i)^2}{n - 1}}$$

# Statistical approach



- Iterative strategy to reduce the number of samples
- Based on the notion of SEG (Similar Exposure Groups)

HCO

## Case study

The industrial hygienist continued the assessment and conducted continuous personal exposure measurements during 8 hours in a group of operators performing the same tasks under comparable conditions.

- OEL (TWA) : 50 ppm 8-h

Measure 1: 25 ppm

Measure 2: 2 ppm

Measure 3: 3 ppm

Measure 4: 35 ppm

Measure 5: 45 ppm

Measure 6: 12 ppm

- Z-score for the 95<sup>th</sup> percentile : 1.645



### Question (2.3b)

Compare the exposure (95<sup>th</sup> percentile) with the OEL (assuming the group is homogeneous) and comment the results

### Question (2.3c)

Is the exposure group homogeneous ?

$$GM = \left( \prod_{i=1}^n x_i \right)^{\frac{1}{n}} \quad GSD = \exp \left( \sqrt{\frac{\sum_{i=1}^n (\ln x_i - \ln GM)^2}{n}} \right)$$

## Diapositive 20

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**HCO**

After slide 23

Chettou Hasnaa; 2025-10-01T12:15:54.612

# Case-study solution

## Question 2.3b

Reminder : The test shall measure, with at least 70% confidence, whether less than 5% of exposures in the HEG exceed the OEL

$$GM = \left( \prod_{i=1}^n x_i \right)^{\frac{1}{n}} \quad GSD = \exp \left( \sqrt{\frac{\sum_{i=1}^n (\ln x_i - \ln GM)^2}{n}} \right)$$



Geometric mean = 11.9  
Geometric standard deviation = 3.70

- $Z_{0.95}$  (for 95<sup>th</sup> percentile): 1.645

Using GM and GSD

$$p95 = GM * GSD^{1.65}$$

$$p95 = 11,9 * 3,7^{1.65}$$

$$p95 = 103 \text{ ppm}$$

OR

Using mean and standard deviation

$$\Rightarrow \text{Percentile Value} = \mu + z\sigma$$

$$\bar{x} = \frac{\sum \ln(x_i)}{n} \quad s = \sqrt{\frac{\sum (\ln(x_i) - \bar{x})^2}{n-1}}$$

$$\mu = 2,48$$

$$\sigma = 1,31$$

$$\text{On the log scale } p95 = 4,63 \rightarrow p95 = \exp(4,63) = 103 \text{ ppm}$$

# Case-study solution

## Question 2.3b

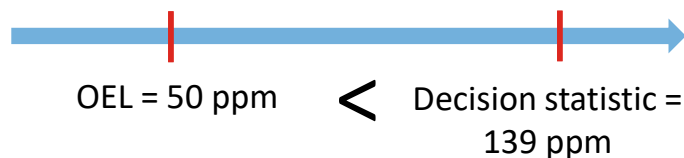
Calculate UCL of 95th percentile at 70% confidence

$$UCL_{95,0.70} = \exp(\bar{X} + t_{\alpha,df} \cdot SE_{\bar{X}} + z_{0.95} \cdot s)$$

where:

- $\bar{X}$  = mean of  $\ln(x)$
- $SE_{\bar{X}} = \frac{s}{\sqrt{n}}$  is the standard error of the mean log
- $s$  = standard deviation of  $\ln(x)$
- $t_{\alpha,df}$  = t-value from Student's t-distribution at one-tailed confidence level  $1 - \alpha$
- $z_{0.95}$  = z-value from the standard normal distribution for the 95th percentile

UCL 70% of p95 = 139 ppm



**UCL > OEL => Non-compliance**

# Case-study solution

## Question 2.3c

The dispersion of the measured values is such that the assumption of a homogeneous group is not valid

Note that before testing compliance with the OEL it is necessary to consider the validity of each measurement and to use the measurements to evaluate the constitution of the SEG... **EN 689:2018+AC:2019**

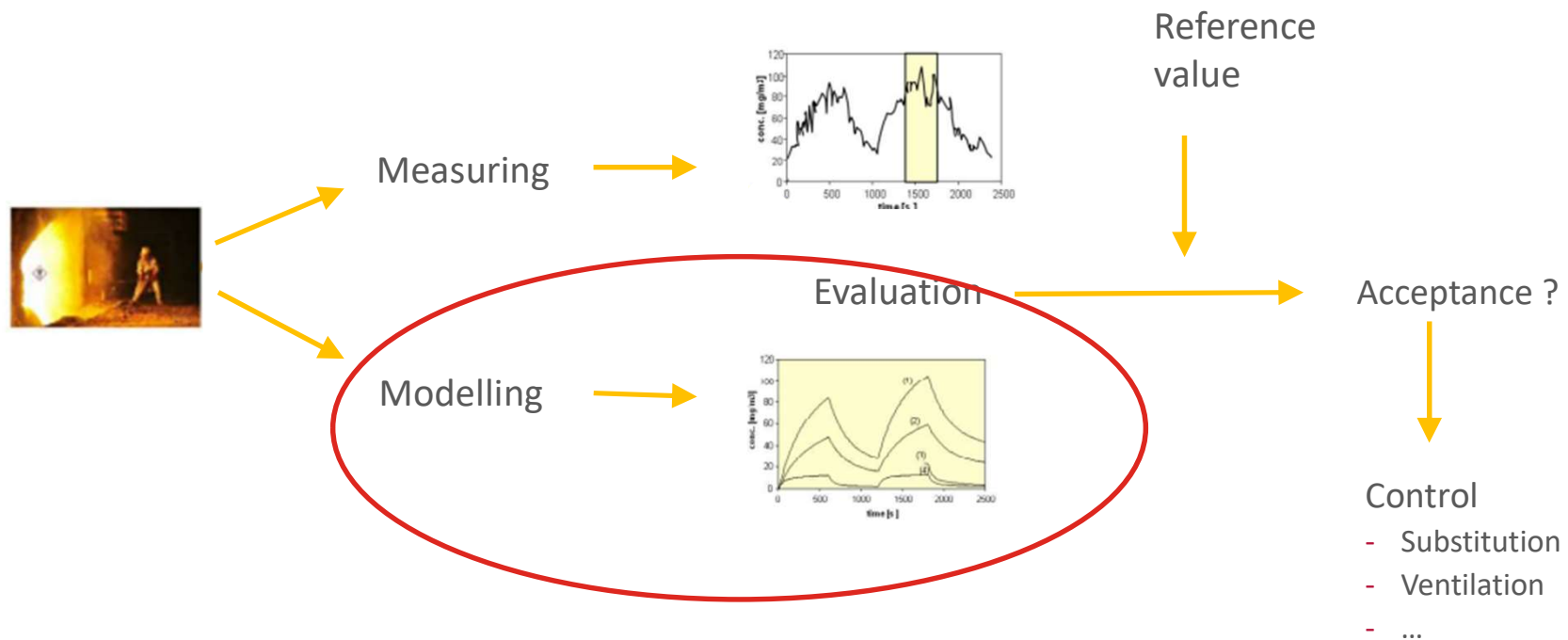
### 5.4.2 Validation of measurement results

When the measurement results are available, each measurement shall be evaluated using the information collected during measurement, and by comparison with the other measurements of the SEG.

If the result is unusually high or low, the possibility that this is because of errors of sampling or analysis shall be considered, and if this is the case then the result shall be excluded.... **EN 689:2018+AC:2019**

# Exposure assessment & control

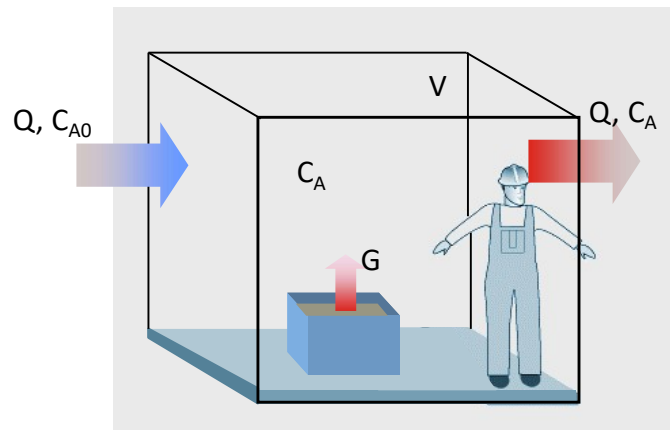
## Strategy



# Exposure modelling

## 1 - box model

- the gas/vapour is homogeneously diluted in a single compartment (with a general ventilation)



- Parameters:
  - Volume  $V$  [ $m^3$ ]
  - initial conc.  $C_{Ai}$  [ $mg/m^3$ ]
  - incoming air conc.  $C_{A0}$  [ $mg/m^3$ ]
  - ventilation  $Q$  [ $m^3/s$ ]
  - emission rate  $G$  [ $g/s$ ]
- Characteristics :
  - easy to use
  - underestimates exposures close to the source

# Exposure modelling

## 1 - box model

### MASS BALANCE

$$V \cdot \frac{dC_A}{dt} = Q \cdot C_{A0} + G - Q \cdot C_A - \underbrace{K_{\text{sink}} \cdot C_A}_{\text{Sinking}}$$

### ALGEBRAIC SOLUTION

- integrative solution

$$C_A = \left( C_{Ai} - C_{A0} - \frac{G}{Q} \right) \cdot e^{-\frac{Q(t-t_0)}{V}} + C_{A0} + \frac{G}{Q}$$

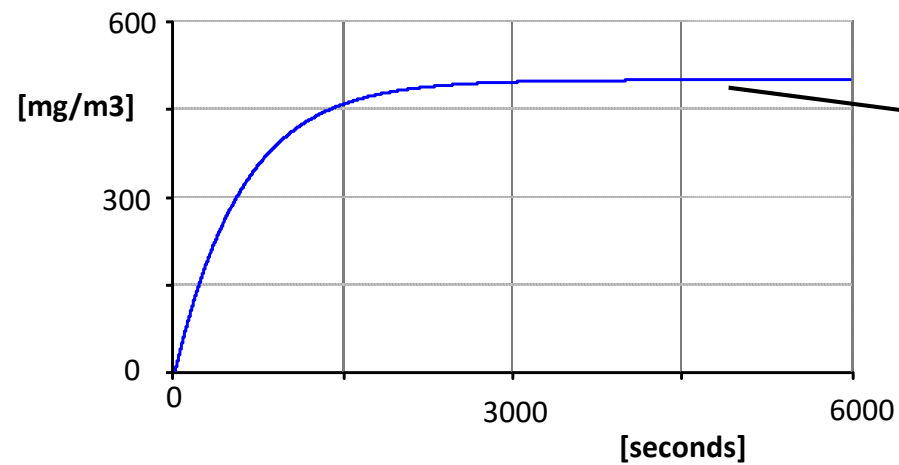
Hypothesis:

- no sinking, ( $K_{\text{sink}} = 0$ )
- constant emission rate
- small emission volume
- constant conc. in the incoming air

# Exposure modelling

## 1 - box model

EXAMPLE



- Stationary state

$$\frac{dC_A}{dt} = 0$$

$$C_A = \frac{G}{Q}$$

× Parameters

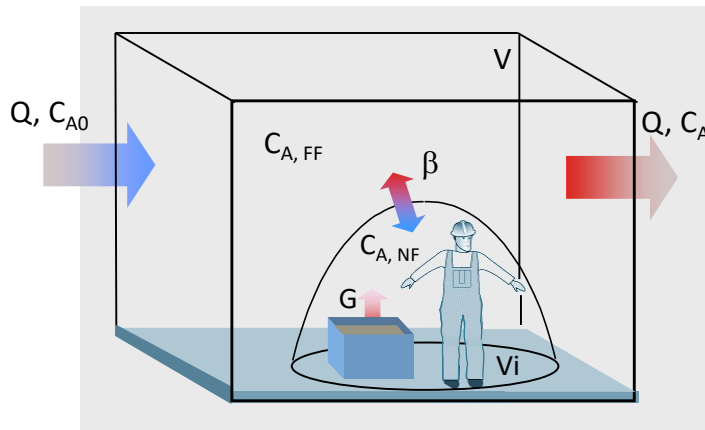
- $Q = 0.1 \text{ m}^3/\text{s}$
- $G = 50 \text{ mg/s}$
- $V = 60 \text{ m}^3$
- $C_{A0} = 0 \text{ mg/m}^3$
- $C_{Ai} = 0 \text{ mg/m}^3$

# Exposure modelling

## 2 - boxes model

### TWO HOMOGENOUS VOLUMES:

- the Near-Field compartment (NF)
- the Far-Field compartment (FF)



- Initial conditions
  - ▶ initial conc.  $CA_i$  [ $\text{mg}/\text{m}^3$ ]
  - ▶ incoming air conc.  $CA_0$  [ $\text{mg}/\text{m}^3$ ]
- Air exchanges
  - ▶ ventilation  $Q$  [ $\text{m}^3/\text{s}$ ]
  - ▶ room volume  $V$  [ $\text{m}^3$ ]
  - ▶ near-field volume  $V_i$  [ $\text{m}^3$ ]
  - ▶ inter-compartment exchange rate :  $\beta$  [ $\text{m}^3/\text{s}$ ]
- Emission
  - ▶ emission coefficient  $G$  [ $\text{g}/\text{s}$ ]

# Exposure modelling

## 2 - boxes model

### MASS BALANCE

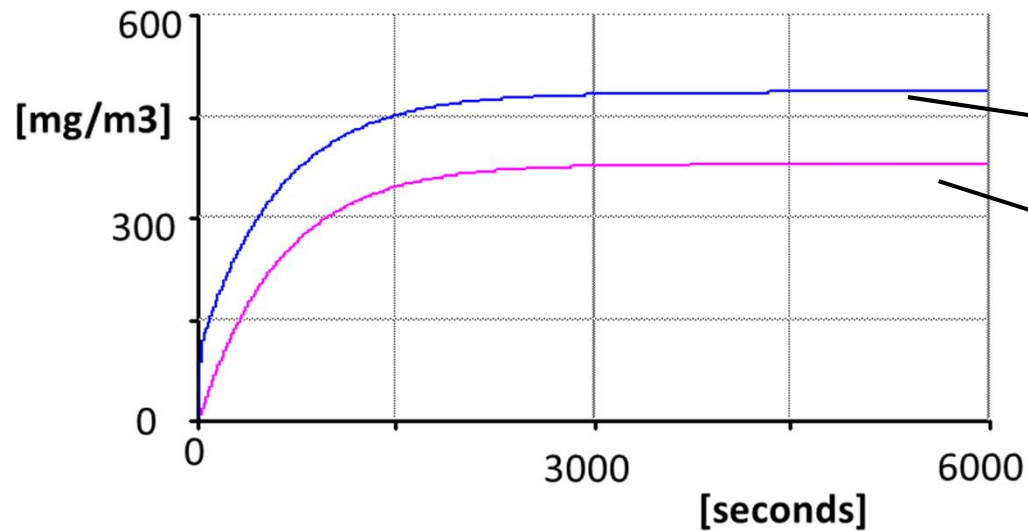
- near field.  $V_{NF} \cdot dC_{A,NF} = G \cdot dt + \beta \cdot C_{FF} \cdot dt - \beta \cdot C_{NF} \cdot dt$
  - far field  $V_{FF} \cdot dC_{A,FF} = \beta \cdot C_{NF} \cdot dt - (\beta + Q) \cdot C_{FF} \cdot dt$
- } With
- $C_{A0} = 0$
  - $C_{Ai} = 0$

- an analytical solution exists

# Exposure modelling

## 2 - boxes model

EXAMPLE



- Parameters
  - ▶ Q, G, V
  - ▶ VNF = 2 m<sup>3</sup>
  - ▶ β = 0.35 m<sup>3</sup>/s

- stationary state

$$C_{A,NF} = \frac{G}{Q} + \frac{G}{\beta}$$
$$C_{A,FF} = \frac{G}{Q}$$

HCO

## Case study

It is assumed that the printing facility is not equipped with ventilation and that:

- The air exchange rate of the room is low ( $0.5 \text{ h}^{-1}$ ).
- The emission rate  $G$  [mg/h] of the solvent can be estimated by assuming that over the 8 working hours. The operator uses a total volume of 250 ml of toluene ( $d_{\text{toluene}} = 0.8669 \text{ g/mL}$ ).
- The volume of the facility is  $50 \text{ m}^3$ .



### Question (2.3d)

From the one-compartment model, evaluate if the toluene TWA of 50 ppm ( $190 \text{ mg/m}^3$ ) is exceeded at equilibrium.

## Diapositive 31

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**HCO**

After slide 30

Chettou Hasnaa; 2025-10-01T12:16:39.932

# Case-study solution

## Question 2.3d

- Room volume:  $V = 50 \text{ m}^3$
- Air exchange rate:  $R = 0.5 \text{ h}^{-1}$
- Volume of Toluene used: 250 mL in 8 h
- $d_{\text{toluene}} = 0.8669 \text{ g/mL}$

$$R = \frac{Q}{V} \Rightarrow Q = R \cdot V = 0,5 \cdot 50 = 25 \text{ m}^3/\text{h}$$

$$\text{Mass (Toluene)} = \text{Volume} \cdot \text{Density} = 250 \cdot 0,8669 = 216,72 \text{ g in 8 h}$$

$$G = 216,72 / 8 = 27,09 \text{ g/h}$$

$$\frac{dC_A}{dt} = 0 \Rightarrow C_A = \frac{G}{Q}$$

•  $G$  (mg/h) : emission rate

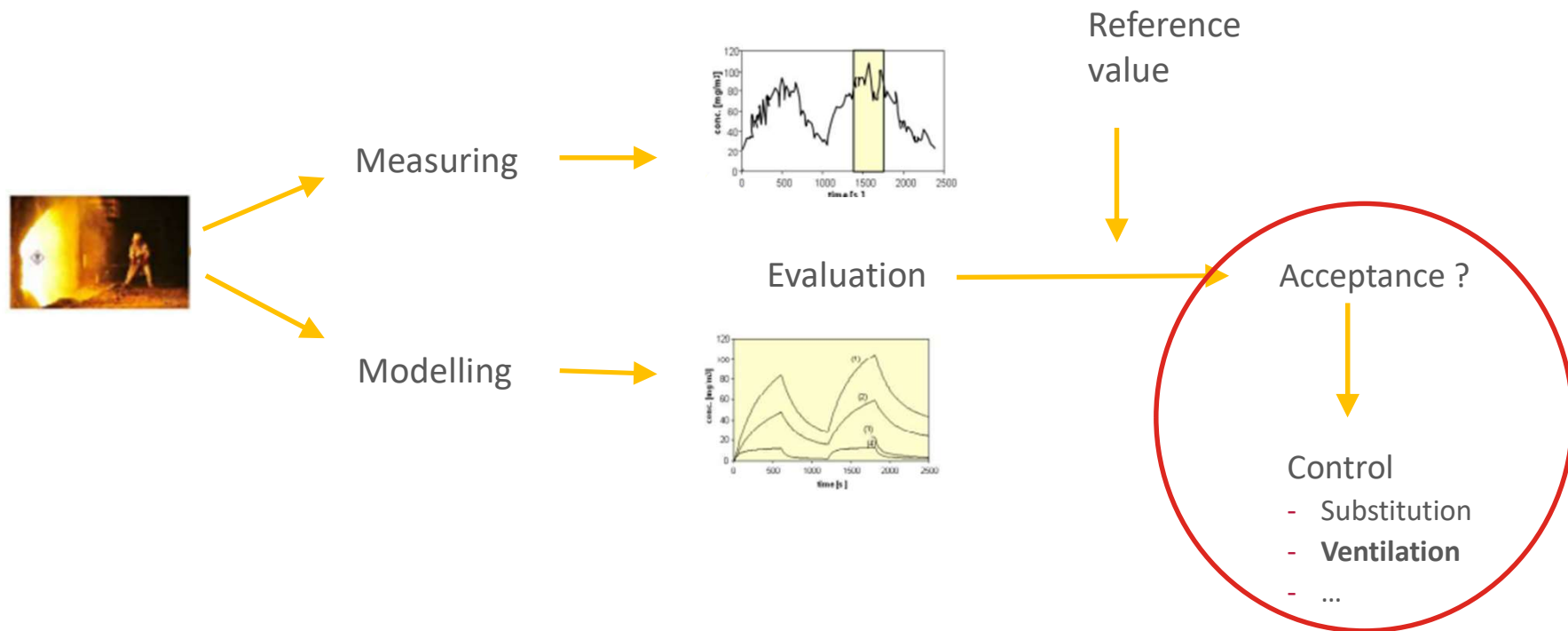
•  $Q$  ( $\text{m}^3/\text{s}$ ) : Ventilation

$$\longrightarrow C = \frac{27,09 \cdot 1000}{25} = 1083,6 \text{ mg/m}^3$$

The concentration exceed the OEL

# Exposure assessment & control

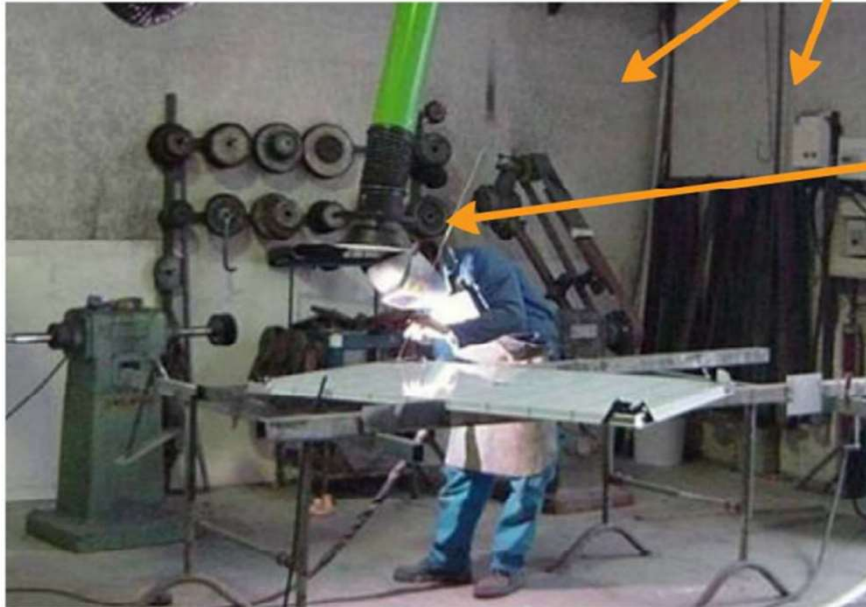
## Strategy



# Airborne measurements

## Ventilation

General ventilation



Local ventilation

# Ventilation, principles

## Allows to:

- Dilute gases, vapors and aerosols (general ventilation)
- Extracting gases, vapors and aerosols (local ventilation)
- Ensure sufficient air velocity
- Supply fresh air
- Provide air conditioning

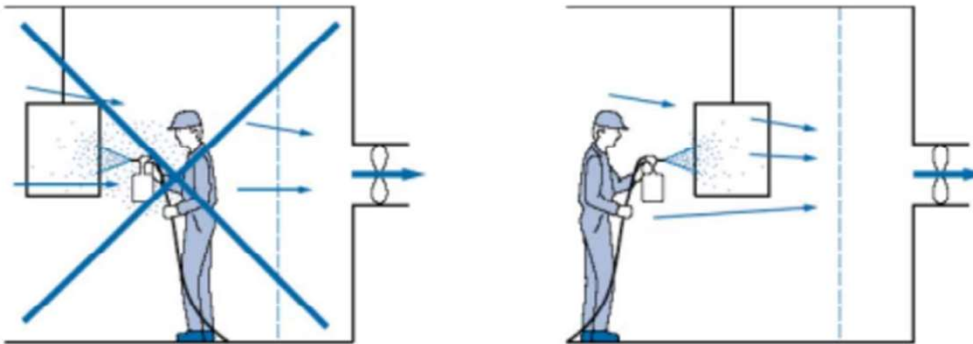
## Legal basis: OLT3, OLT4 (approval of plans)

- Atmosphere of the premises: ventilation and air pollution (art 17 and 18)
- Minimum air volume (art 12)
- Climate of the building (art 16)
- Sunlight and heat radiation (art 20)
- Windows and natural ventilation (art 17)
- Construction materials for ventilation systems, control openings ... (art 18)

# Ventilation, general ventilation

## The basic principles...

- Correct positioning of the inlet and outlet
- Flow from "clean" to "dirty" areas
- Induce the maximum flow in the polluted areas
- Make sure there are no dead zones
- Do not position individuals between sources and extraction



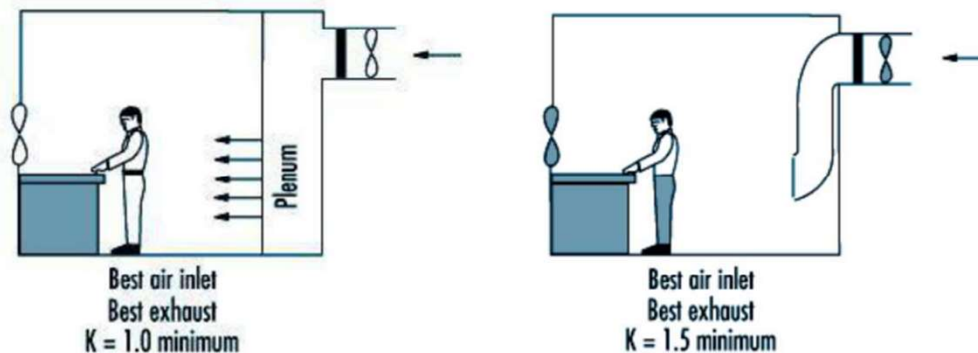
# Ventilation, general ventilation

## The basic principles..... (continued)

- Use the natural movement of the air
- Remember that the pulse is more directional than the suction
- be careful of air movements

## Efficiency

Increase in ventilation rate by the safety factor K, to take into account non-ideal behaviour



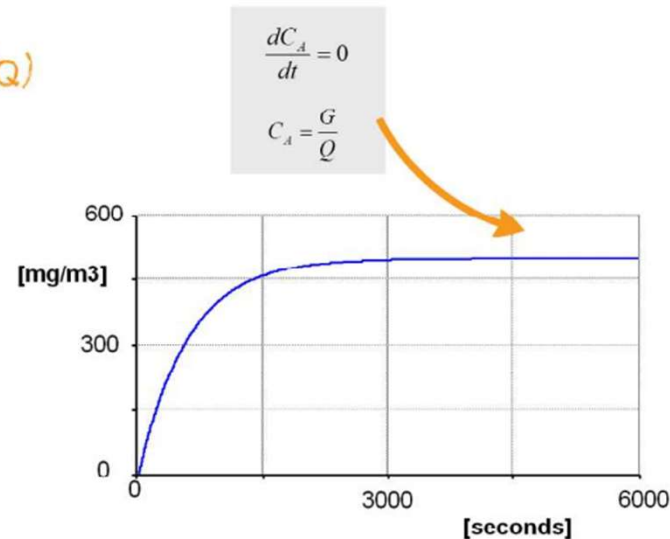
# Ventilation, general ventilation

## Drawbacks

- Residual pollution
- Poor protection of individuals close to the pollution source
- Requires large flows
- Difficulties to absorb concentration peaks
- Air treatment

For a given émission (G) and flow (Q)

- The final (stationary) concentration does not depend on the room volume



# Ventilation, local ventilation

## Benefits

- Reduction of local exposure
- Limitation of the number of exposed individuals
- Reduction of the required flow rates
- Reduction in heating costs
- Improved purification efficiency



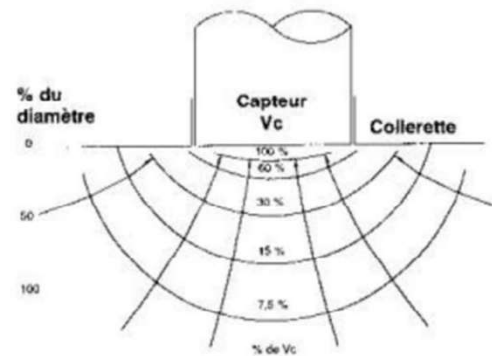
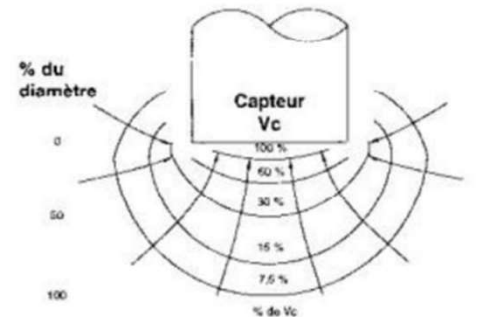
# Ventilation, local ventilation

## ASpiration

- Flow decrease propotionaly to the square of the distance
- The shape of the aspiration mouth must be taken into account
- 10% of the flow at only 1 diameter of distance

## Pulsion

- 10% of the flow at another 60 diameters



(Beaudet et coll., 1998)

# Ventilation, local ventilation

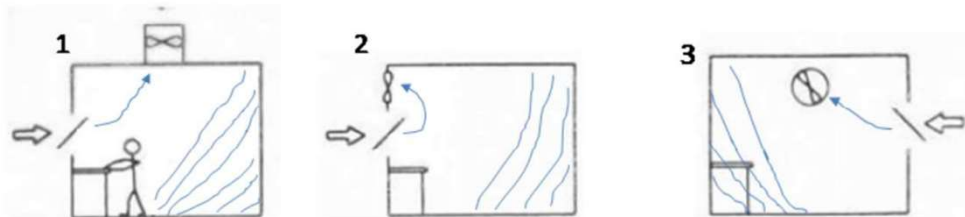
## The basic principles

- Enclose the pollutant production area as much as possible
- Capture as close as possible to the emission zone
- Place the aspiration device so that the operator is not between it and the source of pollution
- Use the natural movements of the pollutants
- Induce a sufficient air speed (capture speed 0.5-1 m/s)
- Distribute the air velocities evenly over the collection area
- Compensate each air outflows with corresponding air inlets
- Avoid air movements and thermal discomfort
- Discharge polluted air away from the fresh air intake zones

HCO

## Case study

Three ventilation designs are considered to reduce the exposure close to the printing machine.



Question (2.3e)

What are the pros and cons of these 3 options ?

## Diapositive 42

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**HCO**

After slide 30

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