# Chemical pollutants Assessment and control

Prof David Vernez | Chef de département

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Centre universitaire de médecine générale et santé publique • Lausanne

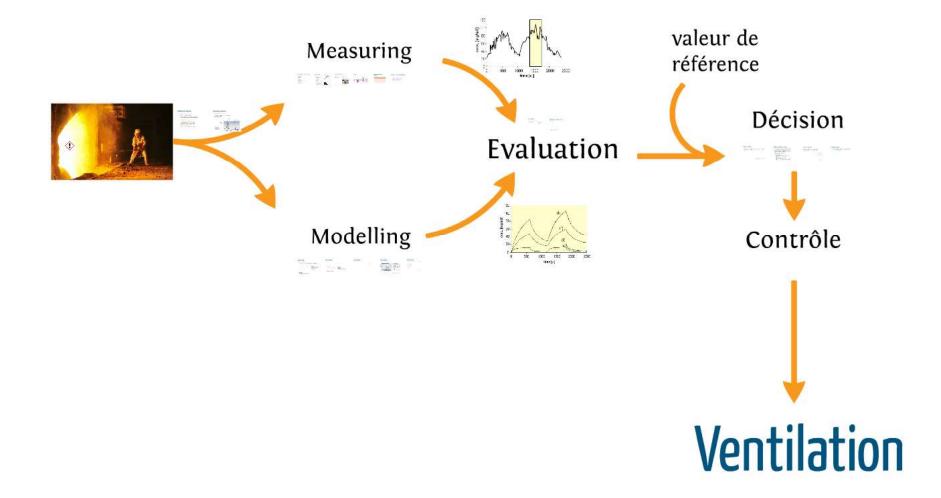
Département Santé Travail - Environnement

Rte de la Corniche 2 CH-1066 Epalinges-Lausanne Tél. +41 21 314 74 51 www.unisante.ch



# Which exposure?

# Is it acceptable?



# Variability of exposure

#### Due to the emission source

- process used, rate, quantities
- · physical properties of the material, energy used
- emissions linked to other processes, partitioning

#### Due to the work environment

- general ventilation (weather conditions)
- air currents, local mixing, thermal effects
- distance from the source (displacement)

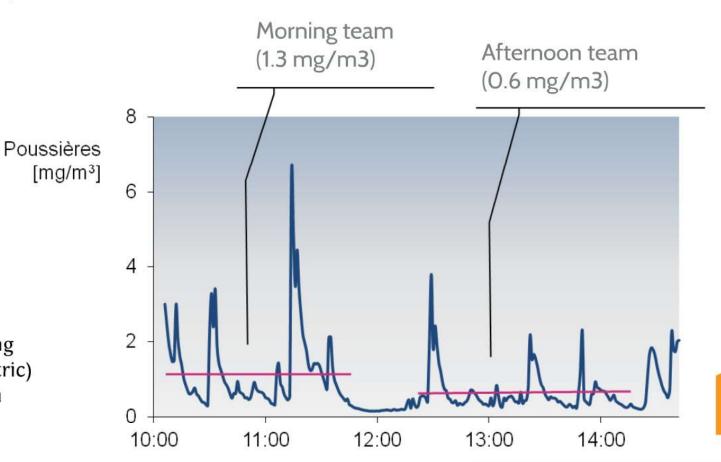
#### Due to measurement

inaccuracy of the equipment or sampling

# Variability of exposure

#### Due to human factors

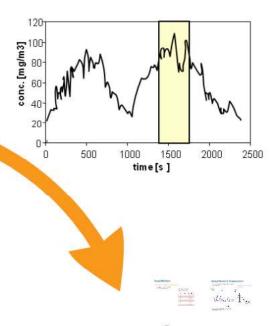
- specific tasks (postures, movements, movements...)
- · work habits, training
- measurement, control...



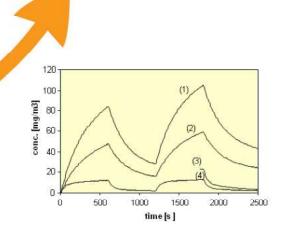
- Metallurgy
- direct reading (nephelometric)
- Fixed station

# Measuring





# Evaluation



# Modelling











# Integrated measurements, gas and vapor sampling

#### Mechanical

Syringes
Vacuum containers
Plastic bags
Measuring cells
Cryogenic method

#### Chemisorption

Solubilization
Activated carbon
Chemical transformation: impinger, impregnated
paper, porous polymers

#### Physisorption

Various solid supports, SPME (microextraction)

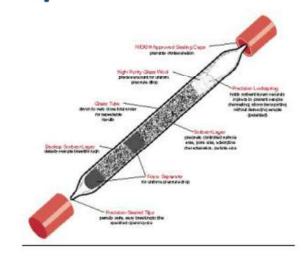
# Integrated measurements, chemisorption

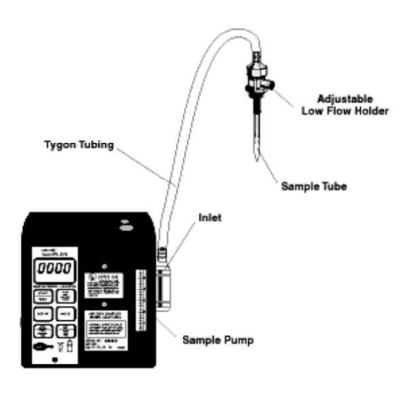
## Sampling on activated carbon

- limited capacity
  generally 10% w/w
  different sizes
  100/50, 1000/500 mg
- · control area
- desorption
   solvent (often CS2)
   efficiency to be determined

#### Various other sampling tubes

Requires laboratory analysis after desorption





# Continuous measurements

#### Photoionization detector

Most of the organics Direct reading, recording Non-specific



ToxiRAE photo-ionization Monitor

#### Electrochemical detector

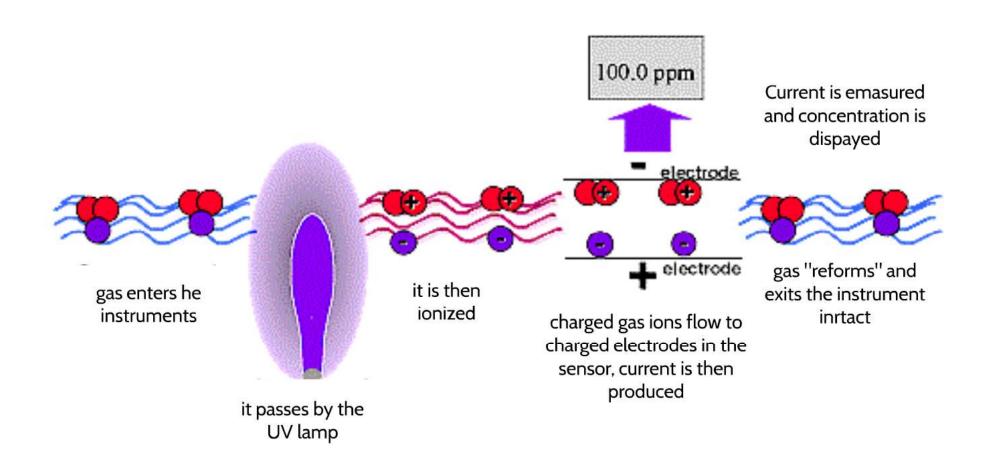
Electrochemical detector Direct reading Specific

Common gases: CO, H2S, O2, SO2,...



Dreager electrochemical detector

## **Photoionisation**



# Continuous measurements

Some examples
Typical pollutants

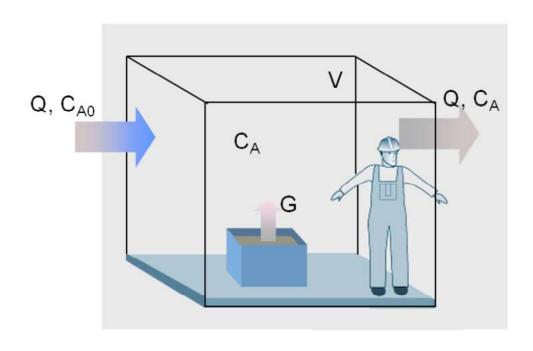
Principle	Measured substances		
Electrochemical	CO, NO <sub>X</sub> , Phosgen, Cl <sub>2</sub>		
Photoionisation	Most organic substances		
Spectrophotometry IR	Organic and inorganic substances		
Non dispersive IR	CO <sub>2</sub>		
Chemiluminescence	Ozone		
Combustion	Flammable substances		
Spectrophotometry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

# Integrated or continuous measurements?

What are the advantages and drawbacks of continuous vs. Integrated measurements?

#### One compartment (1-box model)

Gases ideally mixed in a single compartment (general ventilation)



#### **Parameters:**

initial conc. CAi [mg/m3] incoming conc. CA0 [mg/m3] ventilation Q [m3 /s] volume V [m3] emission G [g/s]

#### characteristics:

- very simple
- Underestimation of exposures close to the source

#### Mass balance

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

#### Analytical solution

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

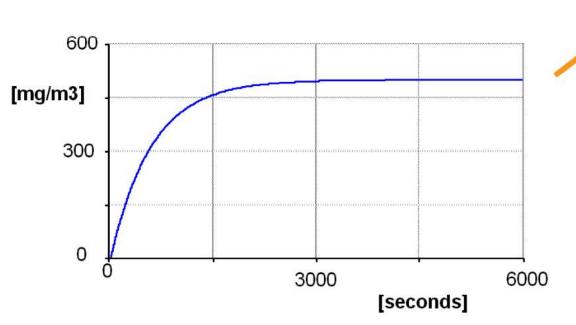
#### without contamination

$$C_A = \frac{G}{Q} \cdot \left[ 1 - e^{-\frac{Q \cdot (t - t_0)}{V}} \right]$$

#### **Assumptions:**

no sink, (Ksink= 0)
constant emission
small volume of gas generated
external concentrations are constant

## Example



#### × Parameters

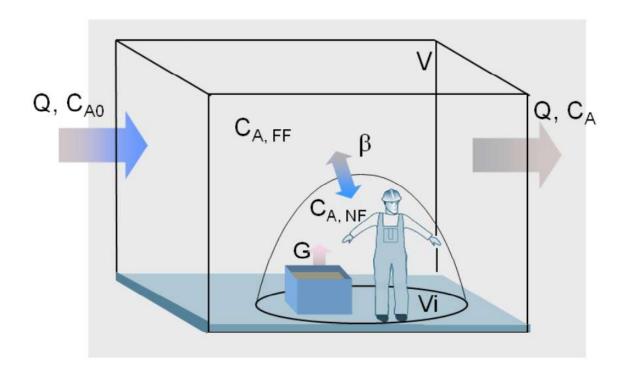
$$Arr$$
 Q = 0.1 m<sup>3</sup>/s

$$\rightarrow$$
 G = 50 mg/s

$$Arr C_{A0} = 0 \text{ mg /m}^3$$

$$ightharpoonup C_{Ai} = 0 \text{ mg/m}^3$$

## Two-compartments model



# Initial conditions initial conc. CAi [mg/m3] Incoming conc. CAO [mg/m3] Air change ventilation Q [m3 /s] compartment volume V [m3] volume (NF) Vi [m3] Inter-compartment exchange: B [m3 /s] Emission emission coefficient G [g/s]

Two compartments ideally mixed: the near field (NF) and the far field (FF)

#### Two-compartments 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

$$V_{FF} \cdot dC_{A,FF} = \beta \cdot C_{NF} \cdot dt - (\beta + Q) \cdot C_{FF} \cdot dt$$

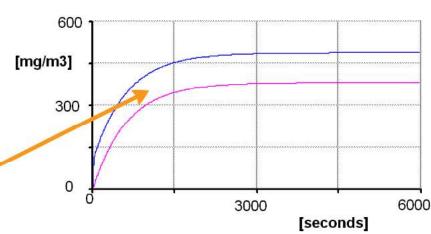
#### Example

État stationnaire

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

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

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



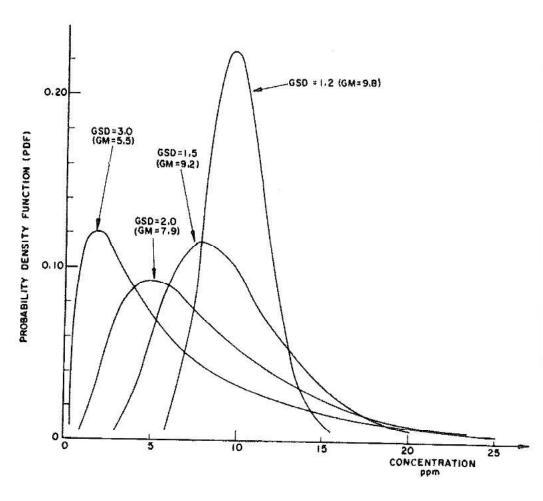
#### × Paramètres

- ▶ Q, G, V
- ▶  $V_{NF} = 2 \text{ m}^3$
- ▶  $\beta = 0.35 \text{ m}^3/\text{s}$

# Sample distribution

#### Wide range of observed distributions

extended range GSD 1.5-3.0 frequently GSD 2.0-2.5



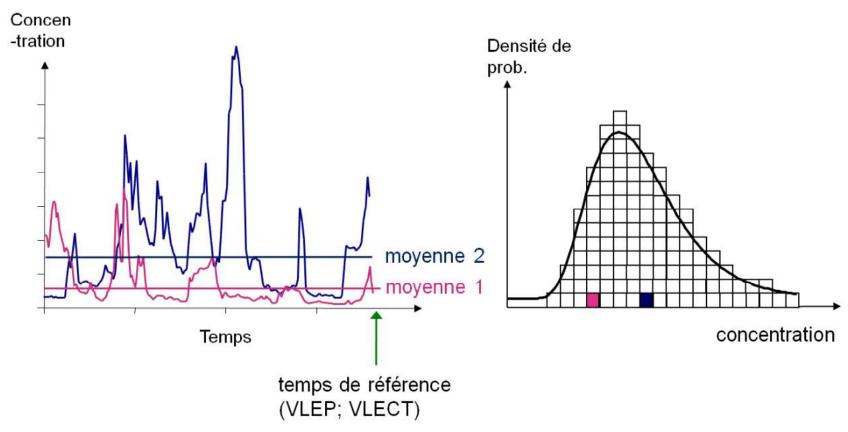
For a geometrical mean (GM) of 10

μ	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

# Representativeness of the measurements

Are the measurements performed representative of actual exposure?

"Never measure in the same place twice, you will always get different results" Tinnenberg 2001



To account for variability, we qualify the **distribution** of exposures

# How many samples?

Number of samples required to ensure that at least 1 sample is in the top 10% (95% confidence level)

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	<b>∞</b>	
	17	18	19	20	21	29	

"The more we measure, the more likely we are to exceed the norm." Tinnenberg 2001

# Pragmatic "action level" approach

An "action level" is defined as the level above which preventive measures must be taken. This level is usually set at one-half to one-third, and sometimes even one-quarter, of the official limit.

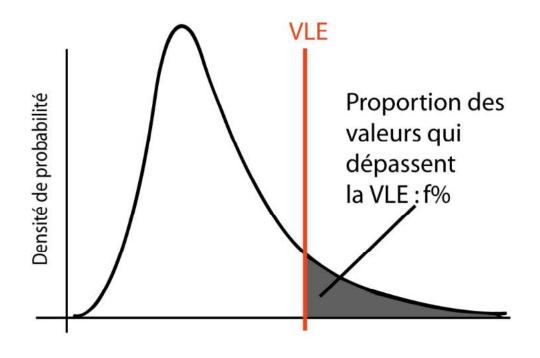
#### What are the reasons for this?

To take into account

- the variability of exposures (day, weeks, months, years)
- the limited knowledge of values
- Corporate image
- Quality procedures (ISO and OSHAS standards)

# Statistical approach

Probabilistic approach: knowing the distribution, what are the chances of exceeding the reference value?



for the record:

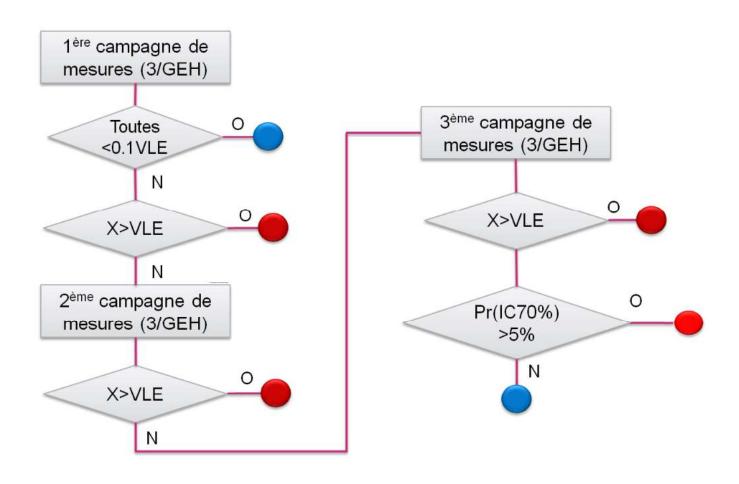
$$\mu \cong \bar{x} = \sum \frac{x_i}{n}$$

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

$$CV = \frac{s}{\bar{x}} \cdot 100\%$$

# Statistical approach

• HEG: homogeneous exposure group (workers exposed under similar conditions):



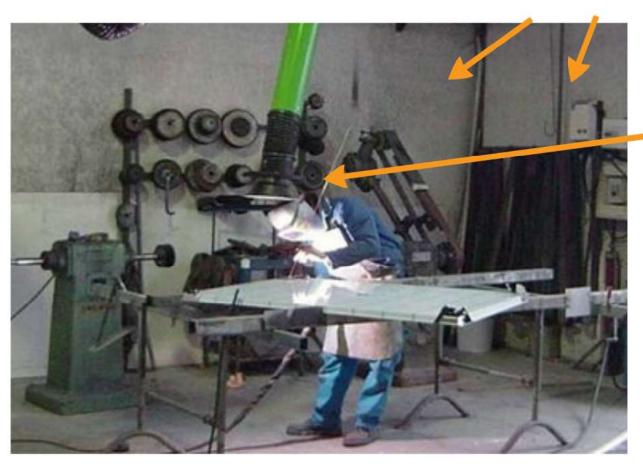
# Ventilation

## principles





## general ventilation





















#### individual protection























## Ventilation: principles

#### Objective, control:

- Risks of intoxication
- · Risk of fire or explosion
- · Climate and odor

#### 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 strategy

## Gas, vapors and aerosols

Behavior of pollutants similar to air

- Diluted gases, vapors (less than 1% by volume)
- · Same temperature
- · Aerosols less than 20 um

#### Local ventilation

- Evacuation of pollutant before its dispersion (low flow rates)
- Priority in all cases and in particular when toxic products are used

## Ventilation générale

- Dilution of pollutants with fresh air (high flow rates), possible if.....
- Controllable pollutant with reasonable air flow
- Low toxicity pollutants
- · Uniform emission

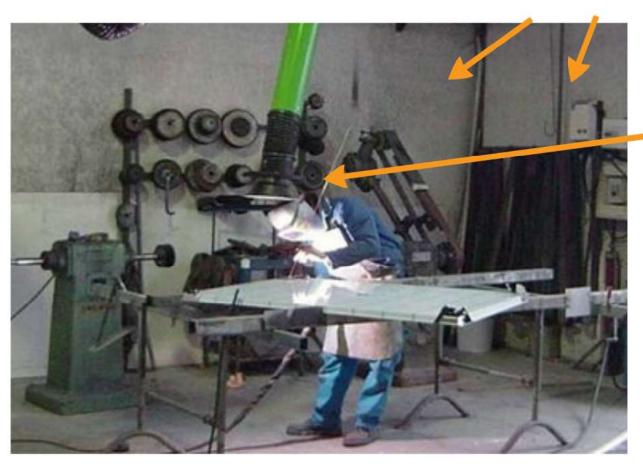
# Ventilation

## principles





## general ventilation





















#### individual protection



















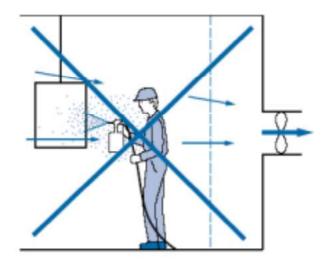


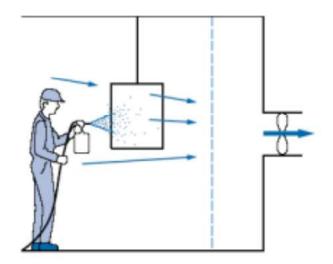


## General ventilation

## 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





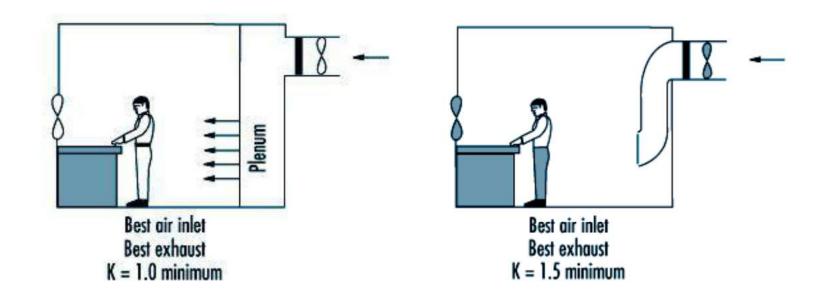
## General ventilation

### 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



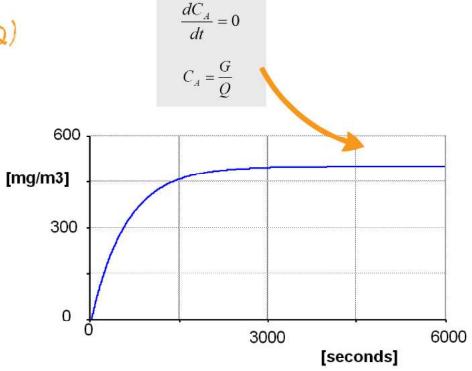
# General ventilation

#### 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



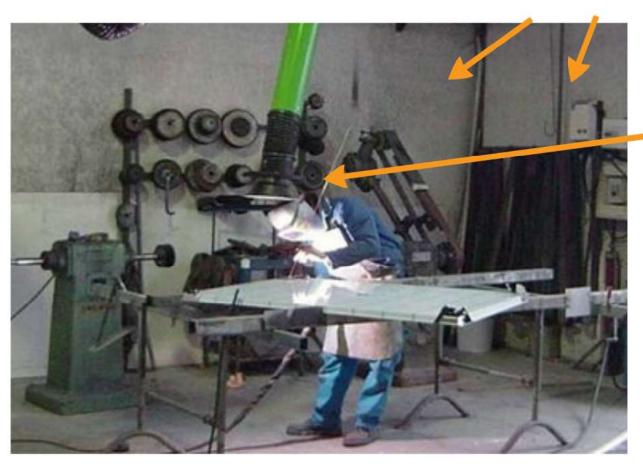
# Ventilation

## principles





## general ventilation





















#### individual protection























# 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



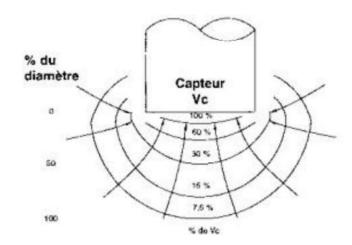
# Local ventilation

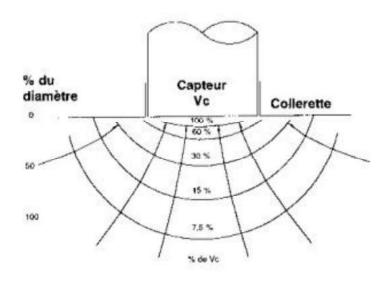
## Aspiration

- 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)

# 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

# Example

What are the advantages and disadvantages of each ventilation situation?

It is assumed that the source of the pollutant is located on the work surface (e.g. solvent handling)..

