Chemical pollutants - properties and exposure

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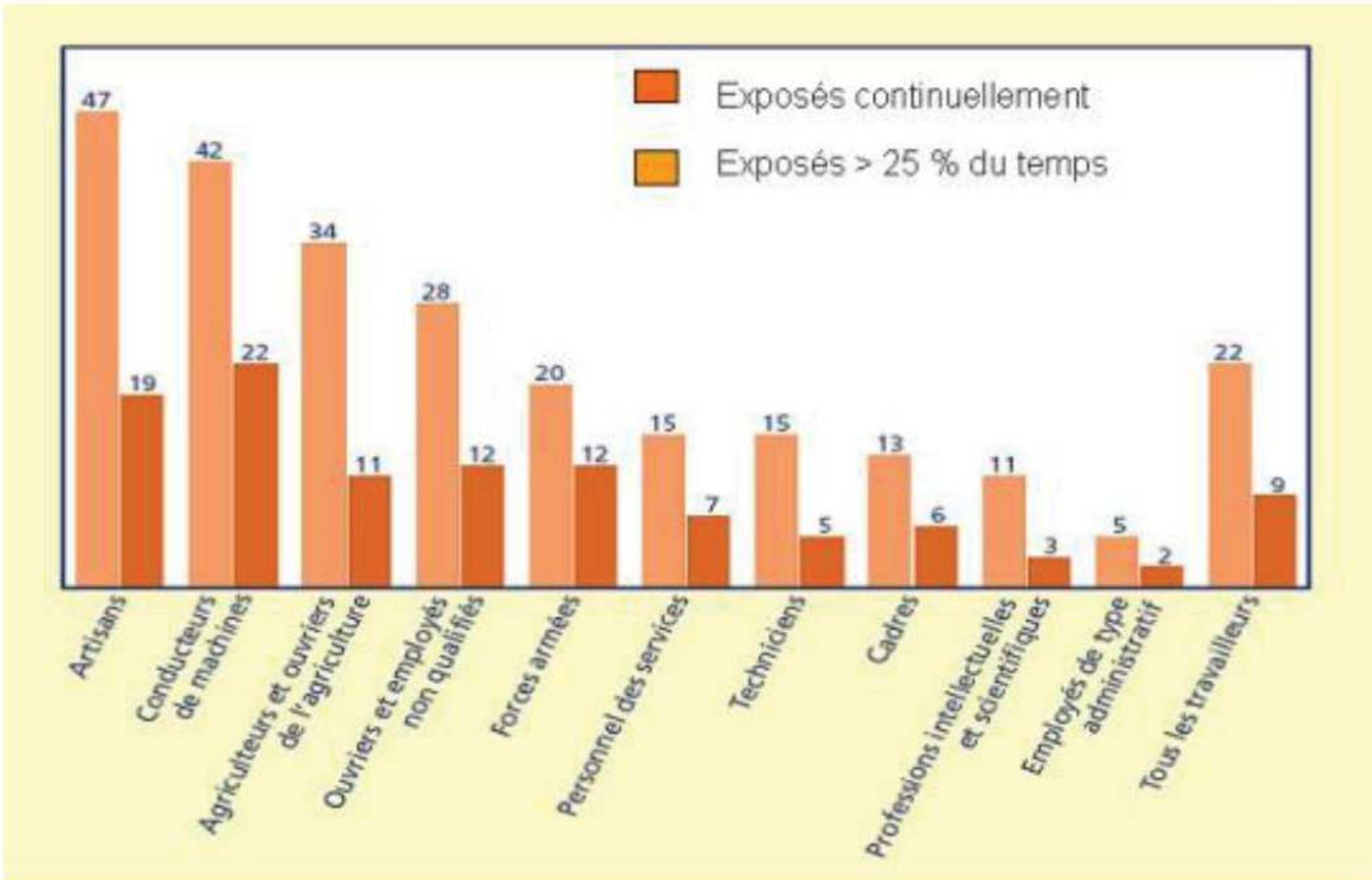
Workers exposed to chemical risks

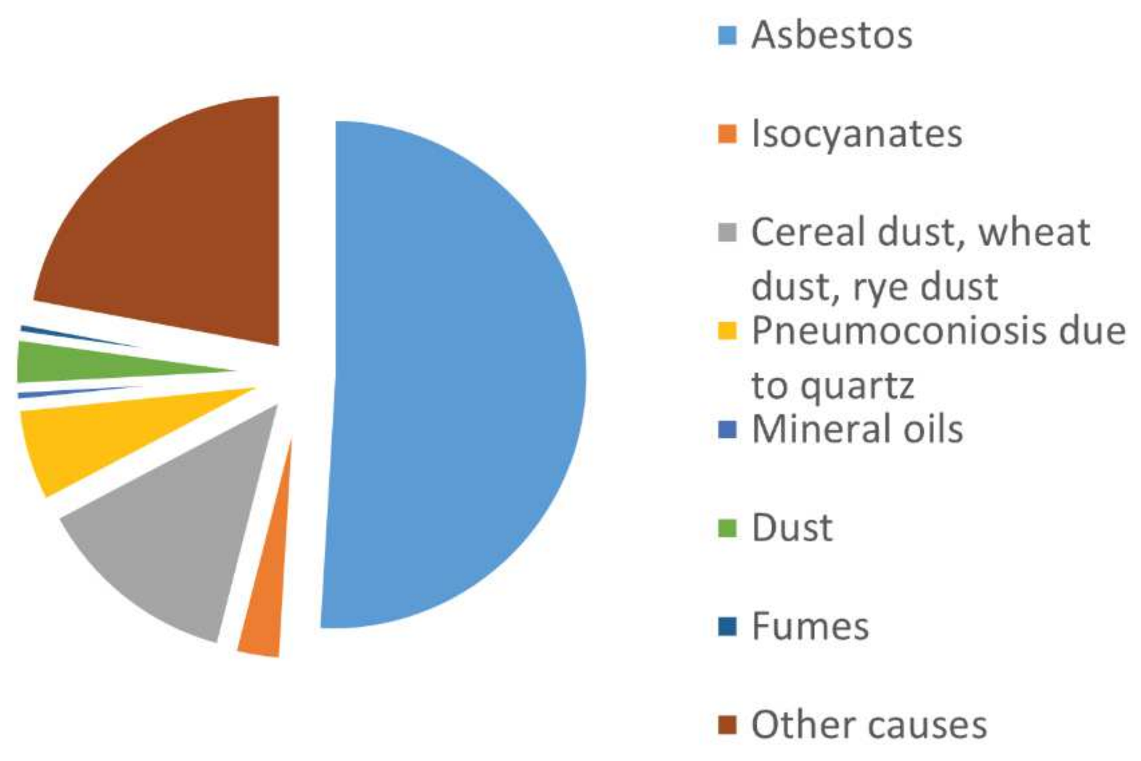
% of workers inhaling vapors, fumes and dusts in Europe, by occupational category.

Trends

- Little evolution in time
- Multiplicity of sources
- point exposures



Occupational diseases in Switzerland (2016-2020)

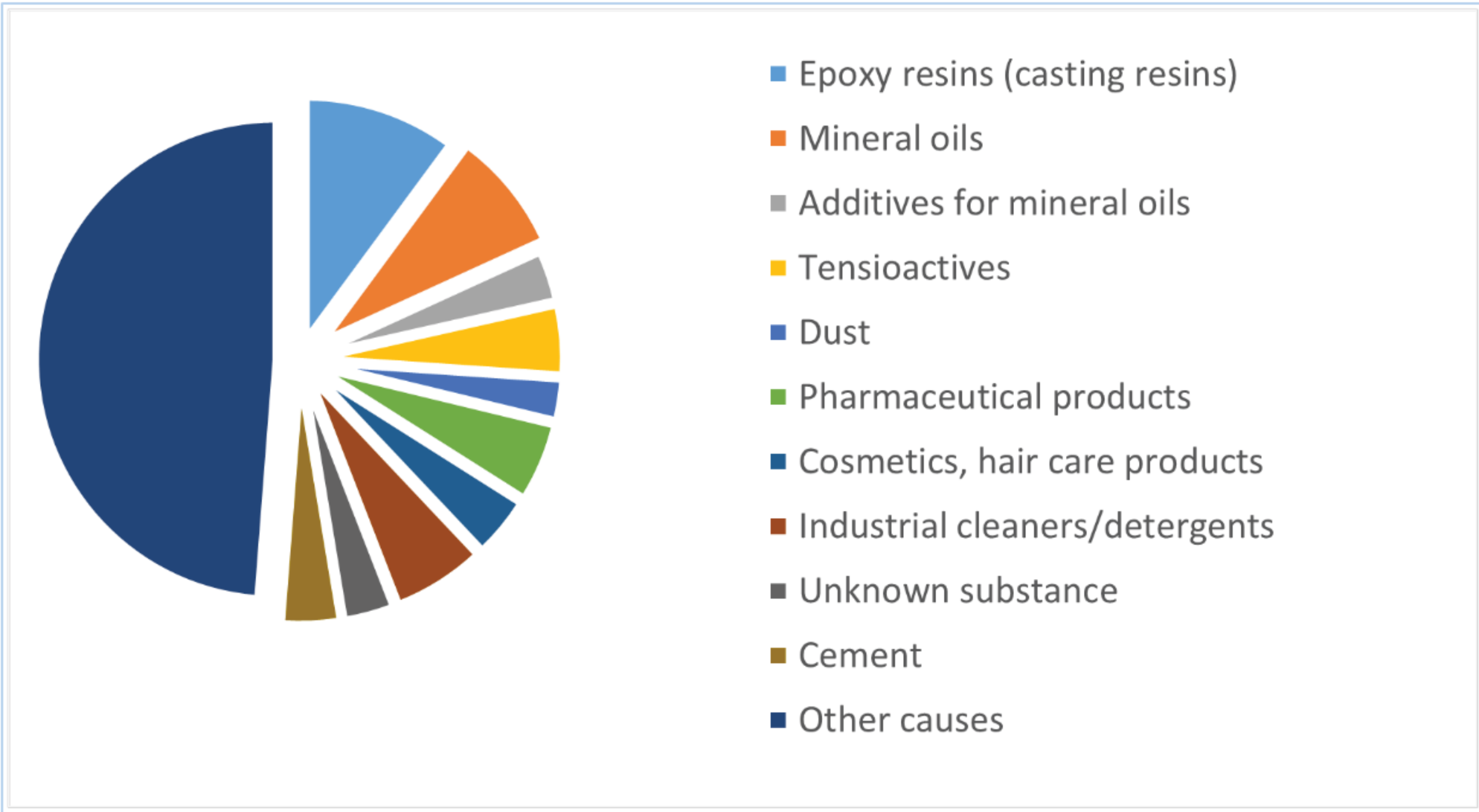


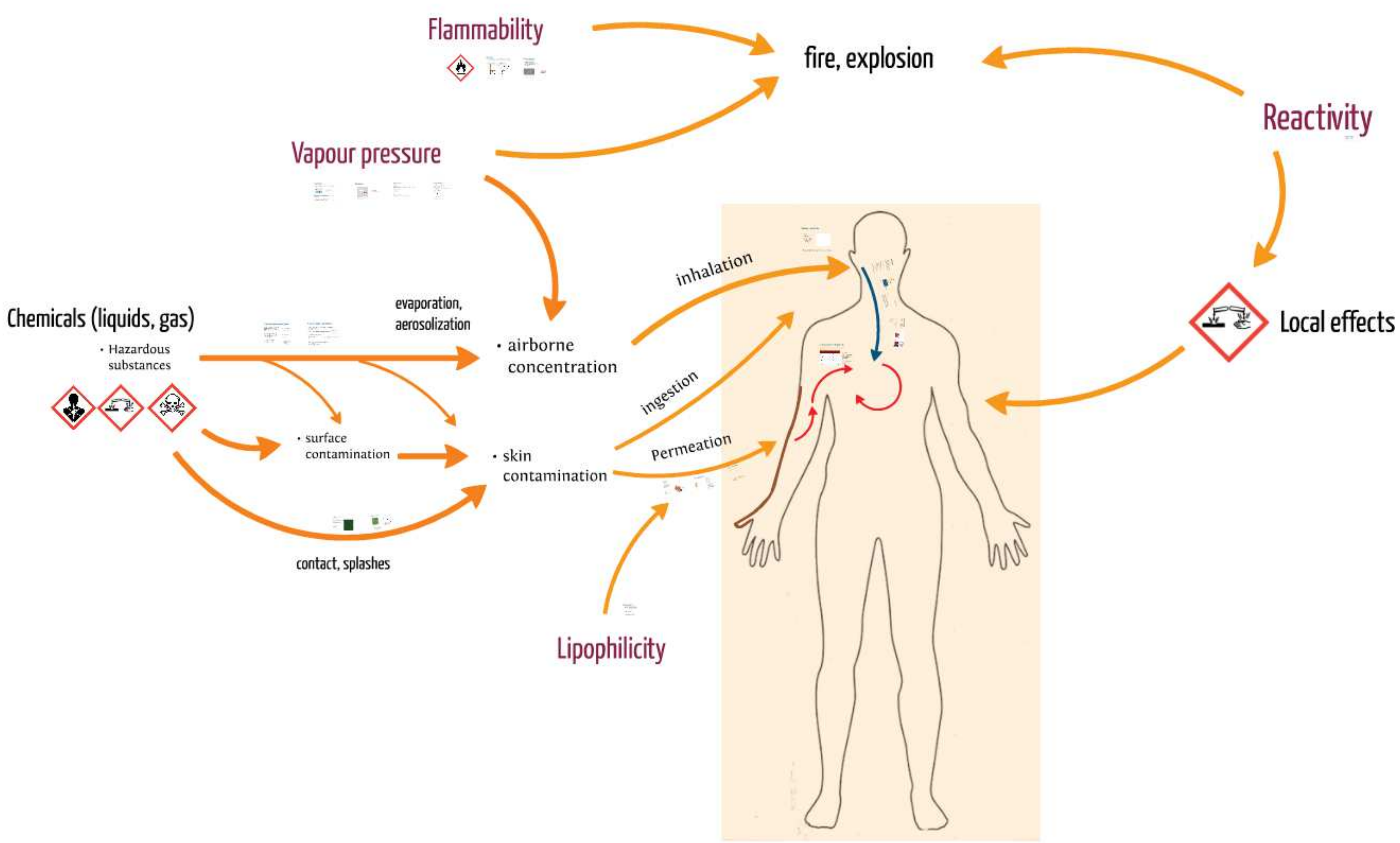
Respiratory system (n=314/year)

Total (diseases) in 2019: 2490

Occupational diseases in Switzerland (2016-2020)

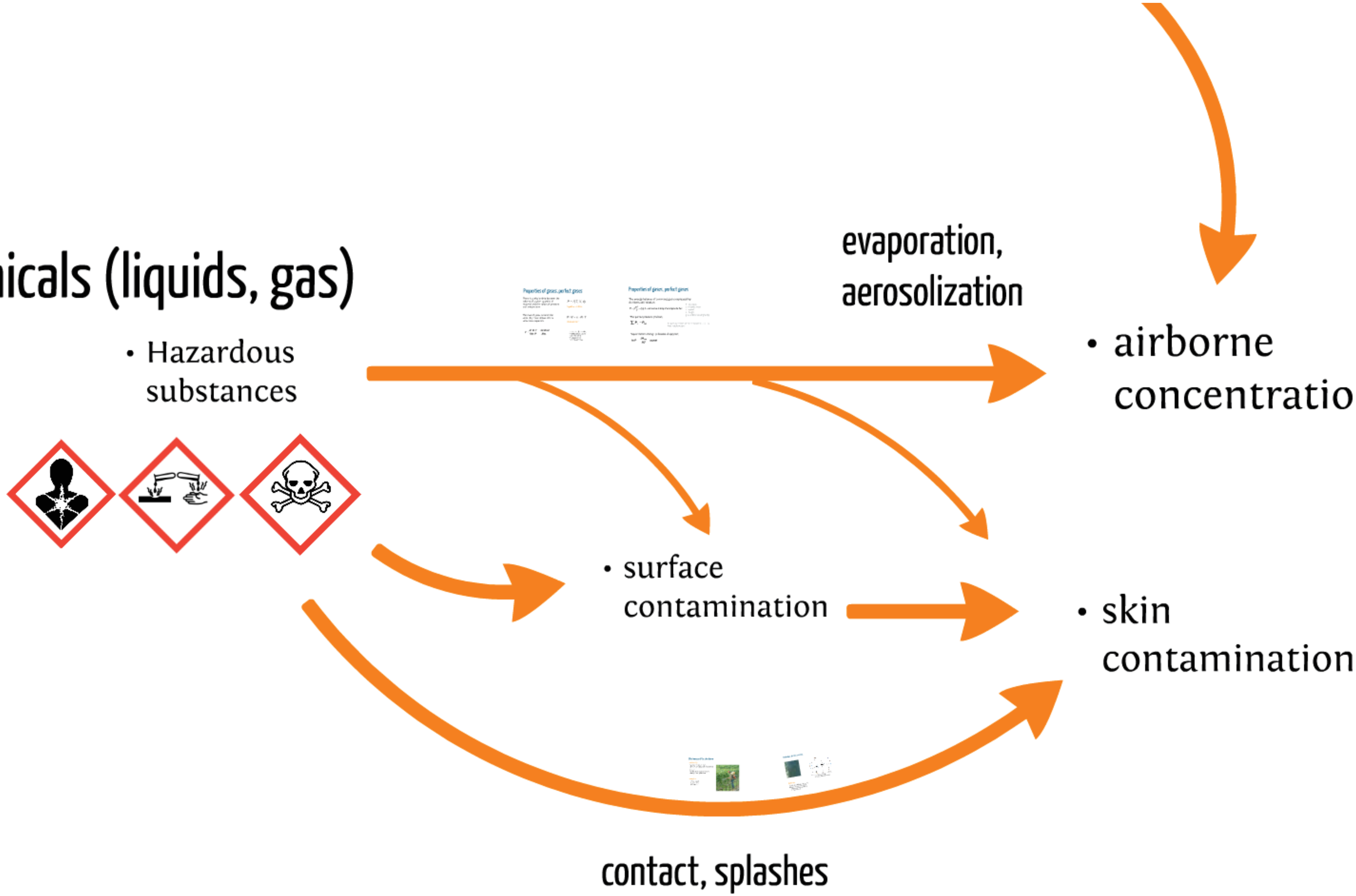
Skin (n=393/year)





The safety data sheet (SDS or MSDS)

Chemicals (liquids, gas)



Properties of gases, perfect gases

There is a relationship between the volume of a given quantity of material and the values of pressure and temperature

$$P = f(T, V, n)$$

Equation of state

The case of gases is particular since they have almost all the same state equation:

$$P \cdot V = n \cdot R \cdot T$$

Ideal gas law

$$V = \frac{M\ R\ T}{Mw\ P} = \frac{24.45\ M}{Mw}$$

R constant [J mol-1 K-1]
T temperature abs. [K]
P pressure [Pa]
V volume [m3]
n numb. of moles

Properties of gases, perfect gases

The energy balance of a moving gas is expressed by the Bernoulli relation

$$P + \varphi \frac{v^2}{2} + \varphi g z = \text{constante le long d'une ligne de flux}$$

P : pressure
j :volumic mass
v : speed
z : height
g :acceleration of gravity

The partial pressure (Dalton)

$$\sum P_i = P_{tot}$$

Pi :partial pressure of the components (1,2,......i)
Ptot : total pressure

Vaporization energy (Clausius Clapeyron)

$$\ln P = \frac{\Delta H_{vap}}{RT} + const$$

Effectiveness of the skin barrier

Historically

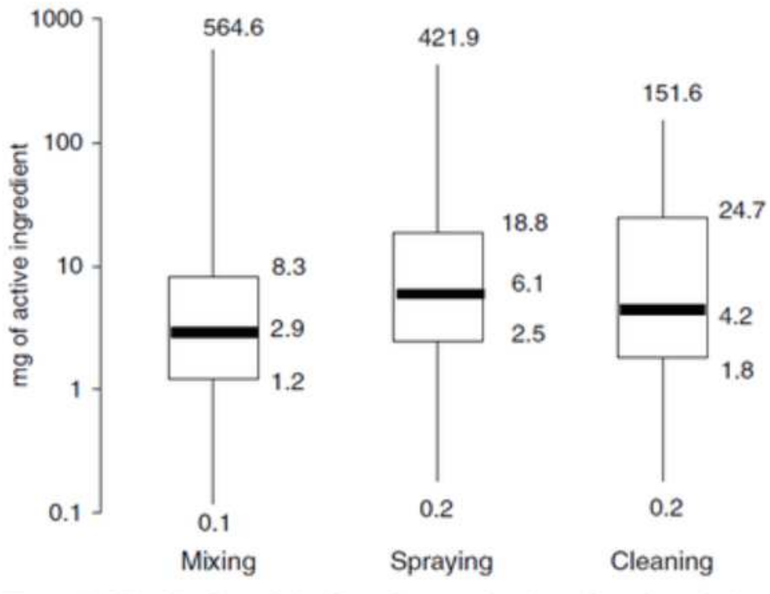
focus on the inhaled route
which is considered to be predominant

And yet...
possible transcutaneous passage
damaged skin, permeation

Examples

scrotal cancer
glycol ethers
pesticides...

Pesticides, dermal exposure



Contamination of the winegrowers' skin (Baldi 2006)

Pestexpo

dermal and inhalation exposure to dithiocarbamates in viticulture

- 40-50% by hands permeation
- 1% by inhalation

Partition coefficient

- Octanol-water partition coefficient. Differential solubility in two solvents (hydrophilic or lipophilic character)

$$\mathrm{Log}K_{OW} = \mathrm{Log}\left(\frac{C_{oct}}{C_{water}}\right)$$

- Typical partition coefficients

Ethanol	-0.28
Ethyl acetate	0.69
Benzène	2.14
Biphenyl	3.96

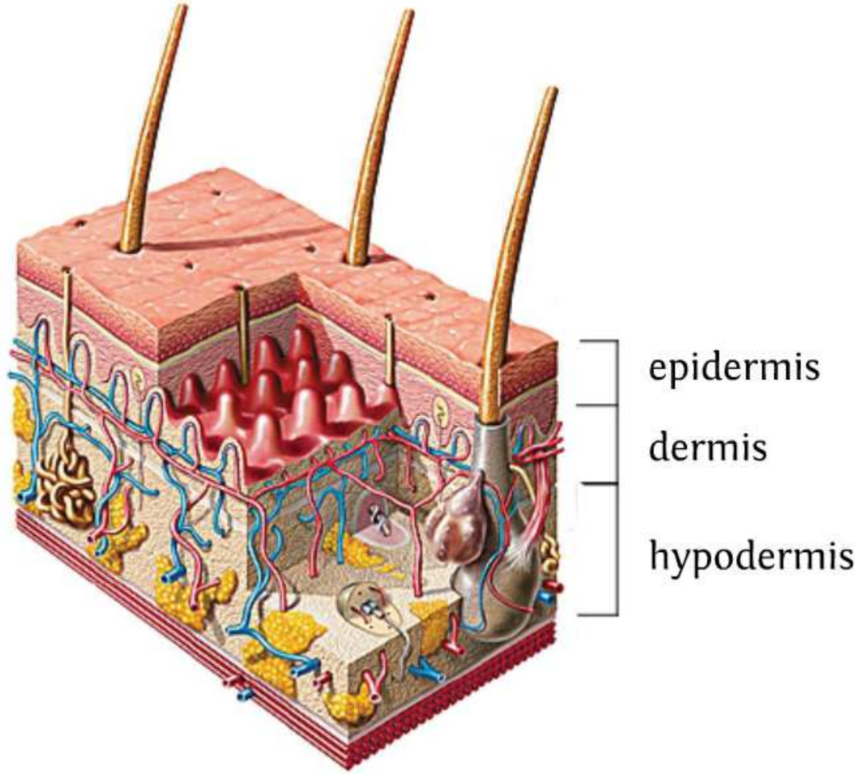
The skin

Functions

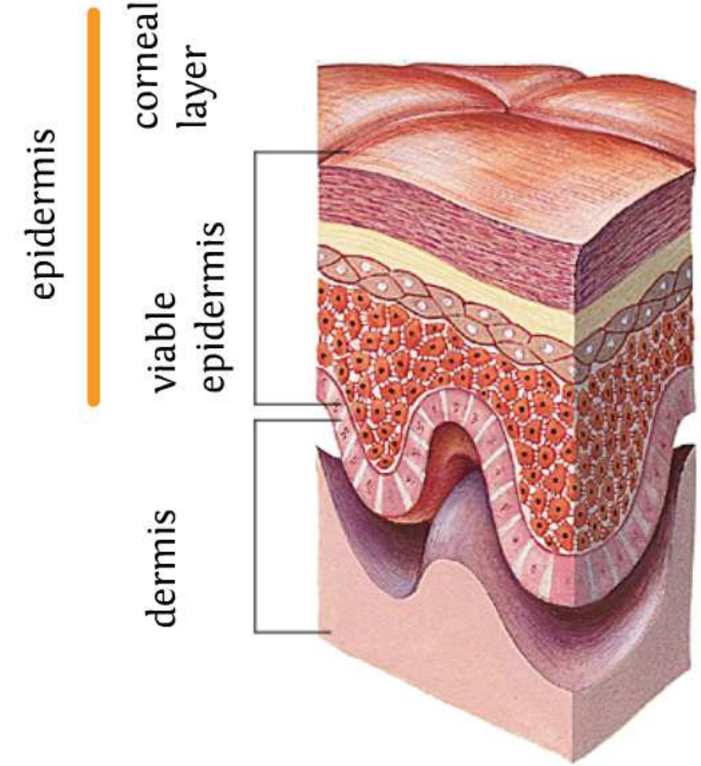
- aesthetic, social,
- tactile, thermoregulation,
- barrier against physical, biological, chemical aggressions

The first organ of the body

- weight 4-6 kg
- surface area: 1.7-2 m2 in adults



The permeation process



Corneal layer

- lipophilic
- 8 -20 um
- main barrier

Viable epidermis

- hydrophilic

Percutaneous passage

- multiple layers
- favoring moderately lipophilic molecules
  1 < Log Kow < 3
- limited size < 500 Da
- a molecular diffusion process

The permeation process

Molecular diffusion

$$F = \frac{C_{sat}}{15}(0.038 + 0.153\,\mathrm{Pow})\,e^{-0.016\mathrm{MW}}$$

F:	Flux in $mg/cm^2.h$
Csat:	Concentration of the saturated substance in water (mg/mL)
P_{OW}:	Octanol-water partition coefficient
MW:	Molecular Weight

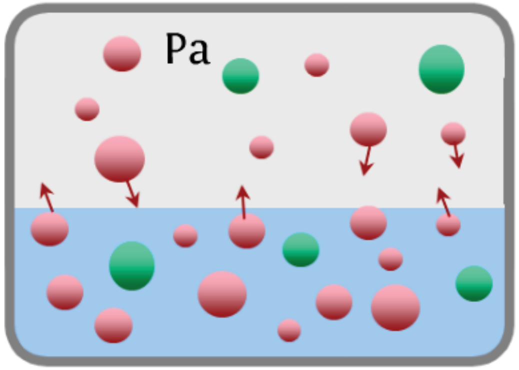
Diff coeff hydrophilic: 0.038 cm^2/h
Diff coeff lipophilic: 0.153 cm^2/h

Factors of influence

Skin condition, Temperature, Humidity, Co-formulants

Vapor pressure

The liquid-vapor equilibrium is reached when the evaporation and condensation rates are equal



Pa :partial pressure of A
Xa :molar fraction of A
P0 :saturation vapour pressure (pure substance)
Kh: Henry's ratio

Raoult's Law

The vapour pressure of an ideal solution depends on the partial pressure of each component and their respective molar fractions

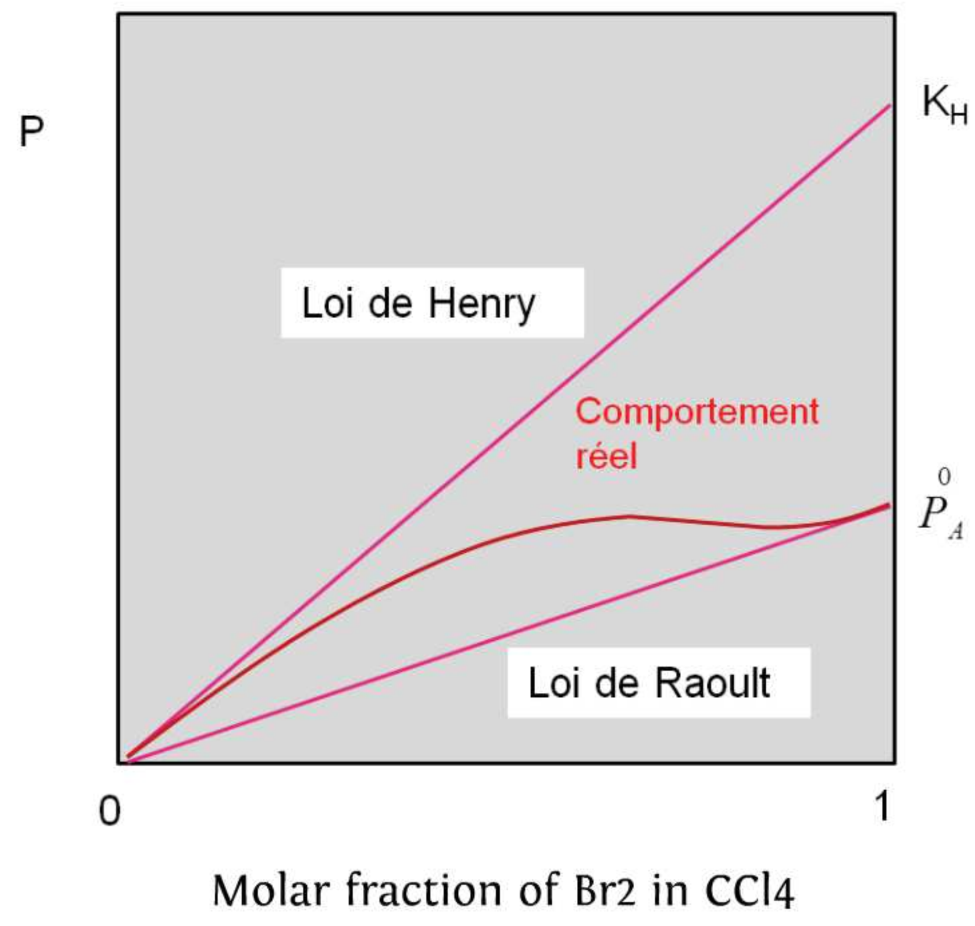
$$P_A = X_A \cdot P_A^0$$

Henry's Law

the quantity of gas dissolved in a liquid is proportional to the partial pressure that this gas exerts on the liquid.

$$P_A = X_A \cdot K_H$$

Vapor pressure



The real behavior is between the two models

Vapor pressure

Example

epichlorohydrin at 20°C
What is the concentration of this saturated vapor in mg/m3 ?

MW = 92.5 [g/mol]

$$P_A^0 = 1.73\, kPa$$

Answer

P • Mw / R T = M/V

1.73 103 • 92.5 103 / 8.314 • 293.15 = 65'700 mg/m3

Gas concentrations

Concentrations: parts per million or ppm (v/v)

- 1 ppm = 1 cm3 par m3 d'air

Example: Conversion mg/m3 to ppm

- Give the equivalent in ppm of 10 mg/m3 of Chloroform at 12°C and 96 kPa
- Chloroform (MW = 119.4)

Answer:

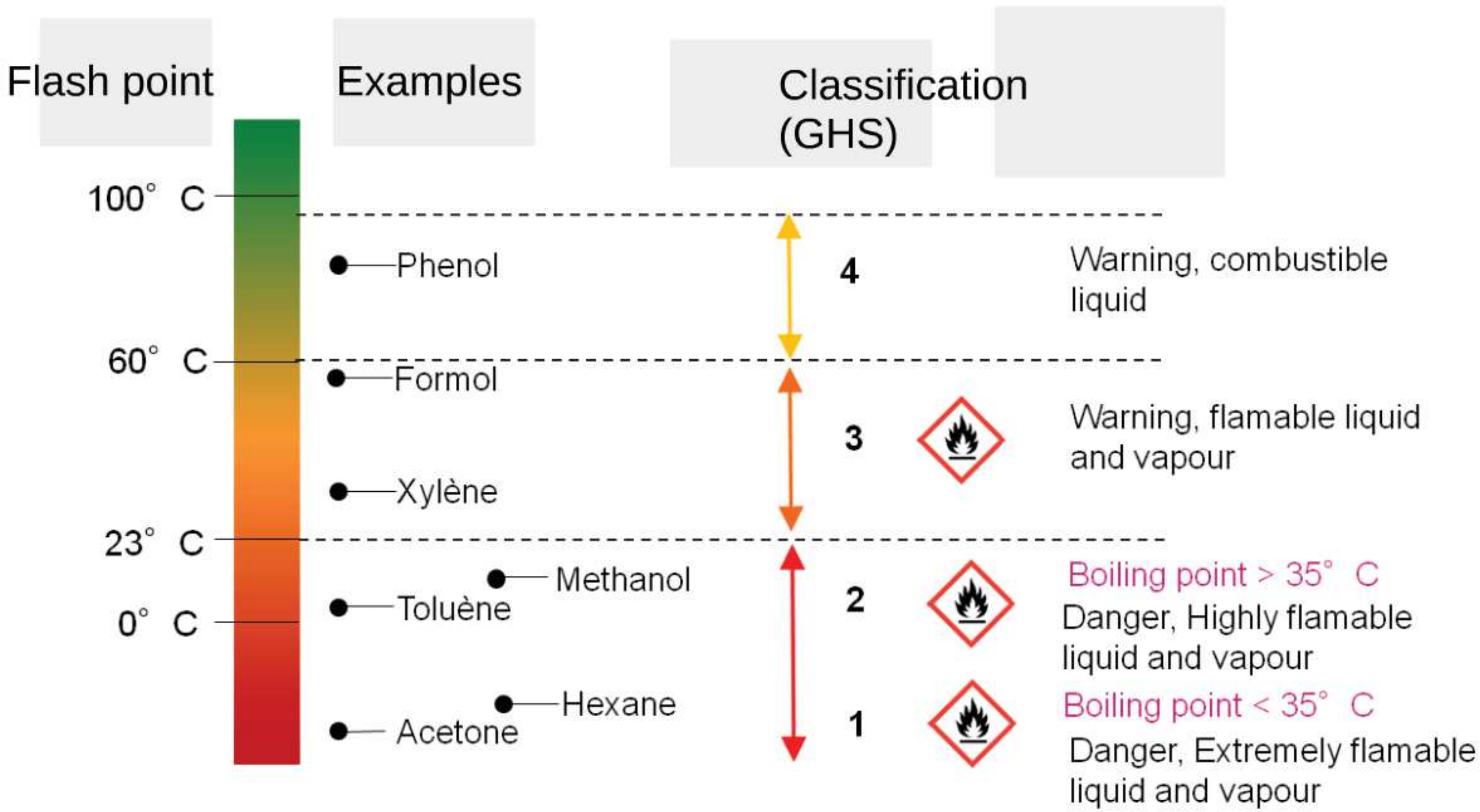
$$V = \frac{M\ R\ T}{Mw\ P} = \frac{10 \cdot 10^{-3} \cdot 8.314 \cdot 285.15}{119.4 \cdot 96 \cdot 10^{3}}$$

2.07 cm3/m3 2.1 ppm

Alternative:
Use molar volume 24.055 l/mol (20°C)

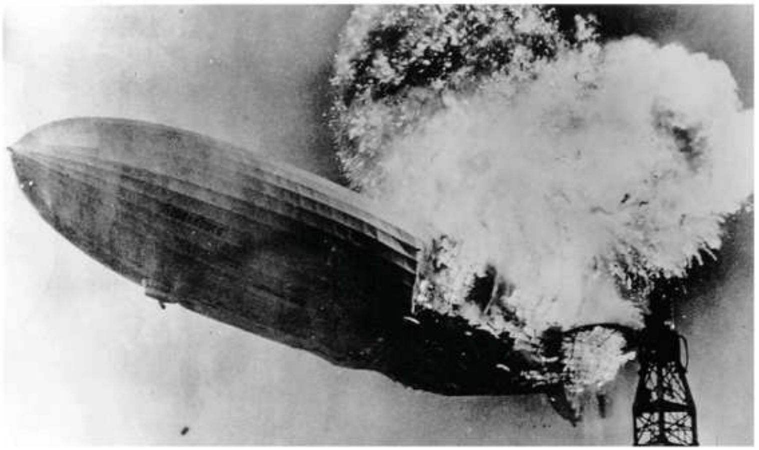
Flash point

The lowest temperature at which a sample gives off enough vapor to form a flammable mixture with the surrounding air - fire is a gaseous phenomenon!

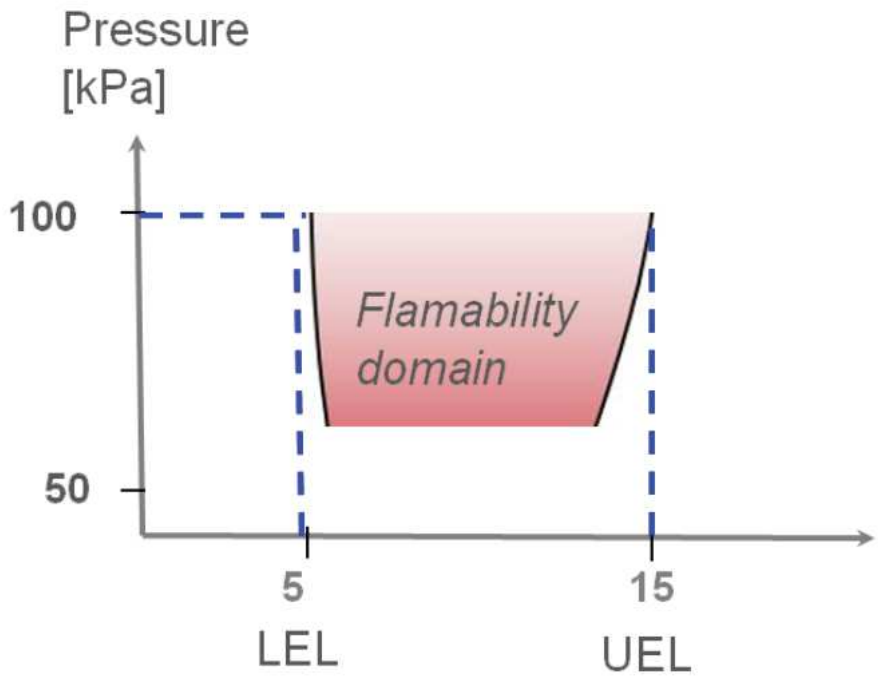


Flammability limits

- LEL Lower explosibility limit
- UEL Upper explosibility limit
- LEL and UEL are concentrations of gases, vapors or dusts in air that form a flammable mixture.



LEL-UEL Hydrogen: 4-75% (% volumic)



Olfactory threshold, odor

The nose:

+ Selective
+/- Calibration
+/- Detection limit
- Interference
- Intoxication

Substance	Seuil olfactif	Odeur	VME
Acétaldéhyde	0.21	pomme, doux	50
Acide acétique	1.0	amère	10
Acide butyrique	0.001	amère	-
Acetone	100	doux, chimique	500
Dimethylformamide	100	poisson	5
Methanol	100	doux	200
Hydrogène sulfuré (gaz)	0.0005	oeuf pourri	5
Nitrobenzene	0.005	amande	1
Benzene	4.7	cirage	0.5
Azote	n.d		-
Hg	n.d		0.005
CO	n.d		30

Olfactory thresholds of some common organic compounds.

Inhalation

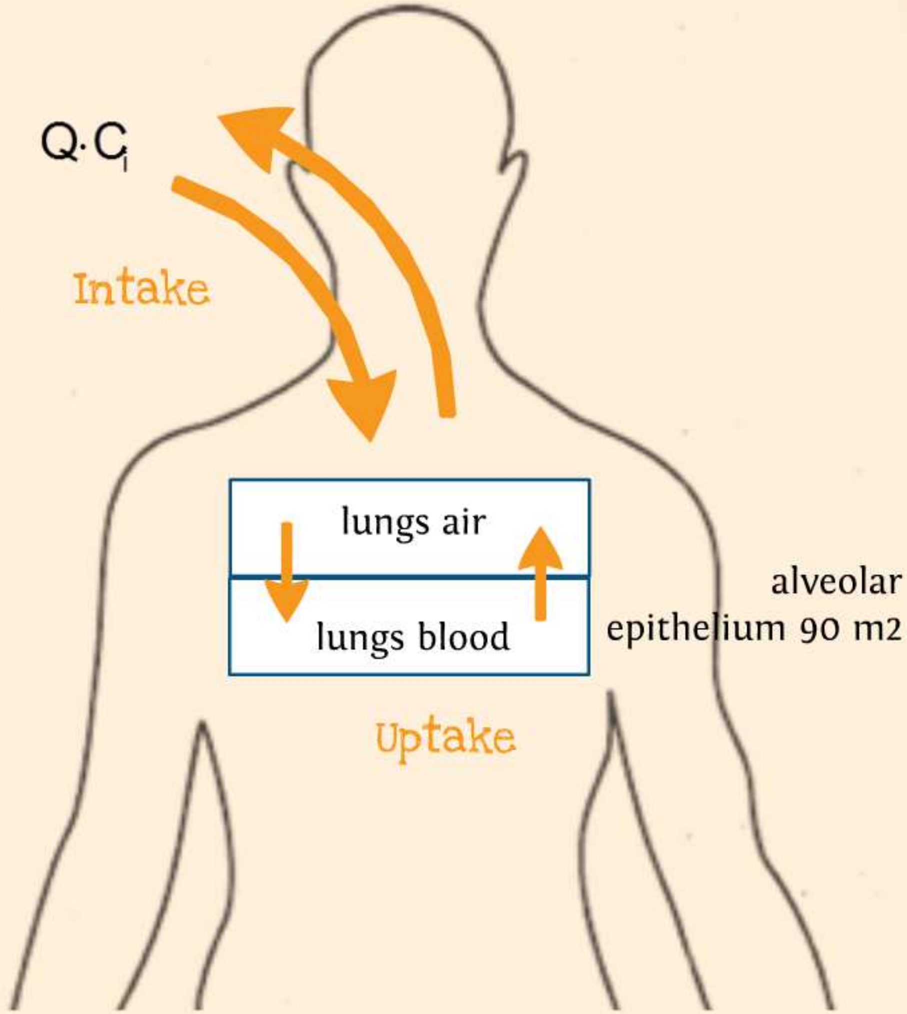
The dose received is proportional to the pulmonary ventilation, and the concentration of the pollutant

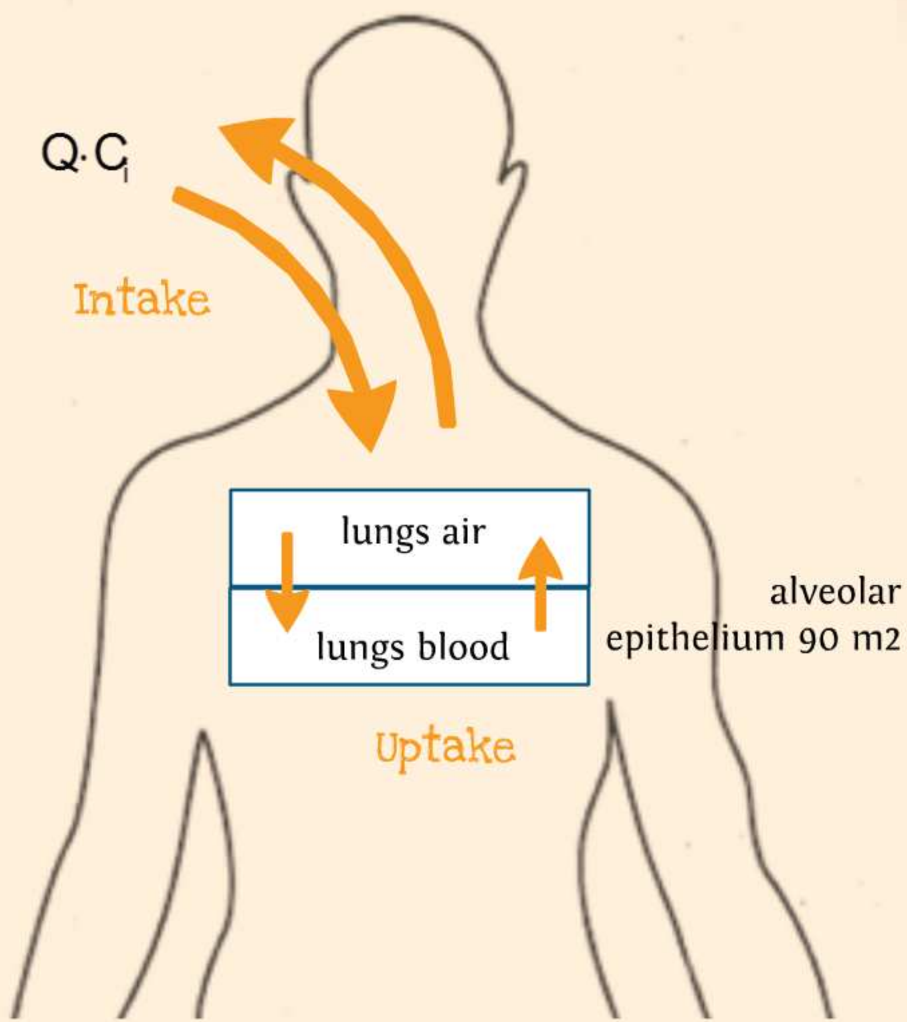
Ventilation flow, Q

adult male,
- at rest: 7.5 l/min
- light activity 20 7/min

adult female
- at rest 6.0 l/min
- light activity 19 l/min

About **10 m3** per working day





Estimate of intake (potential dose)

$$D_{pot} = \int_{t1}^{t2} C_i(t) \cdot Q \cdot dt$$

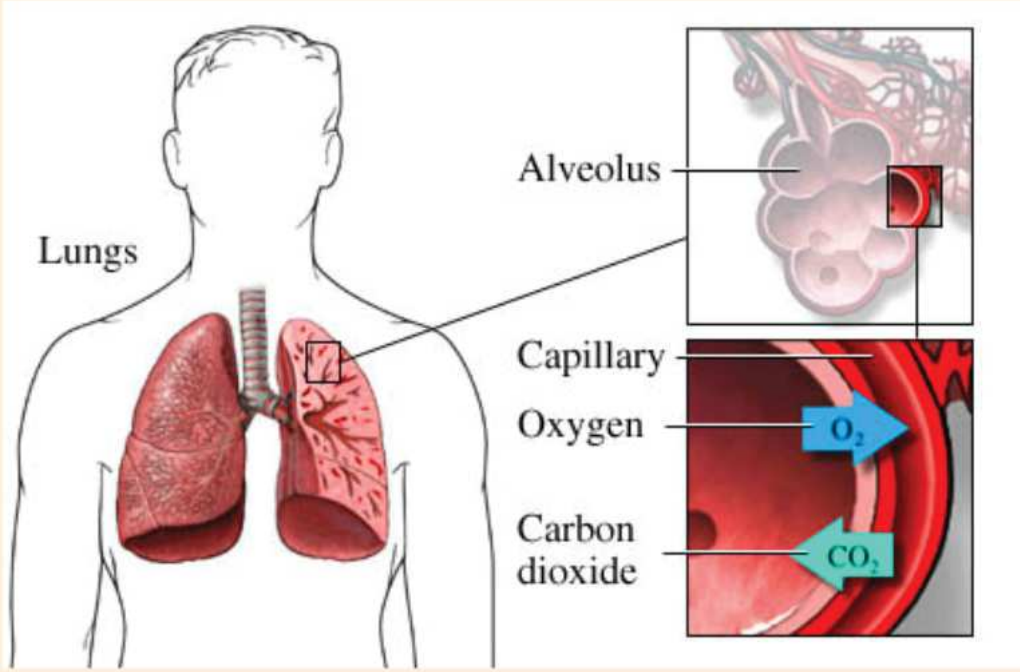
Dpot: potential dose (mg)
Ci: concentration (mg/m3)
Q pulm. ventilation (m3/min)

Uptake ?

- lipophilic gases and vapors reach the systemic circulation via the alveoli
- hydrophilic gases and vapors dissolve in the respiratory tract

Gas exchange

The blood-air balance is achieved in the alveoli



Composition of the alveolar gases (sea level)

P_O2 13.2 %
P_CO2 5.3 %
P_H2O 6.2 %

Sustance	blood/air partition coefficient
Methy alcohol	1700
Acetone	330
Diethyl Ketone	157
Ethyl ether	15
Benzene	6.6

Cutaneous route vs. pulmonary route

Comparison between inhalation and dermal route (theoretical)

Substance	Flux $mg/cm^2/h$	Poumons* mg	Peau** mg
Aniline	0.6405	58.4	72
Biphenyl	0.0759	9.98	8.5
o-Crésol	4.5338	169	510
Dieldrine	0.0013	1.92	0.15
DMF	1.0347	230	116
2-Ethoxéthanol	1.2054	138	136
Lindane	0.0087	3.84	0.98
Dichlorométhane	0.14	1337	16

Hypothesis

*alveolar ventilation of 16 l/min and alveolar absorption of 100% (over 8 hours)

**assuming hand contact (450 cm2) for 15 min

The safety data sheet (SDS or MSDS)

- Can be obtained from any product manufacturer or supplier
- Contains 16 chapters

1. Identification of the substance/product
2. Information on ingredients
3. Hazard identification
4. First aid measures
5. Fire fighting measures
6. Accidental release measures
7. Handling and storage
8. Exposure control/personal protection
9. Physical and chemical properties
10. Stability and reactivity
11. Toxicological information
12. Ecological information
13. Disposal considerations
14. Transport information
15. Regulatory information
16. Other information

Ordinance on Safety Data Sheets for Toxic and Environmentally Hazardous Substances of 9 November 1998
813.013.4

The safety data sheet (section 9)

Section 9: Physical and Chemical Properties

This section identifies physical and chemical properties associated with the substance or mixture. The minimum required information consists of:

- Appearance (physical state, color, etc.);
- Odor;
- Odor threshold;
- pH;
- Melting point/freezing point;
- Initial boiling point and boiling range;
- Flash point;
- Evaporation rate;
- Flammability (solid, gas);
- Upper/lower flammability or explosive limits;
- Vapor pressure;
- Vapor density;
- Relative density;
- Solubility(ies);
- Partition coefficient: n-octanol/water;
- Auto-ignition temperature;
- Decomposition temperature; and
- Viscosity.

The SDS may not contain every item on the above list because information may not be relevant or is not available. When this occurs, a notation to that effect must be made for that chemical property. Manufacturers may also add other relevant properties, such as the dust deflagration index (Kst) for combustible dust, used to evaluate a dust's explosive potential.

according to standardized test results