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Appunti universitari

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Course of RECLAMATION OF POLLUTED SITES

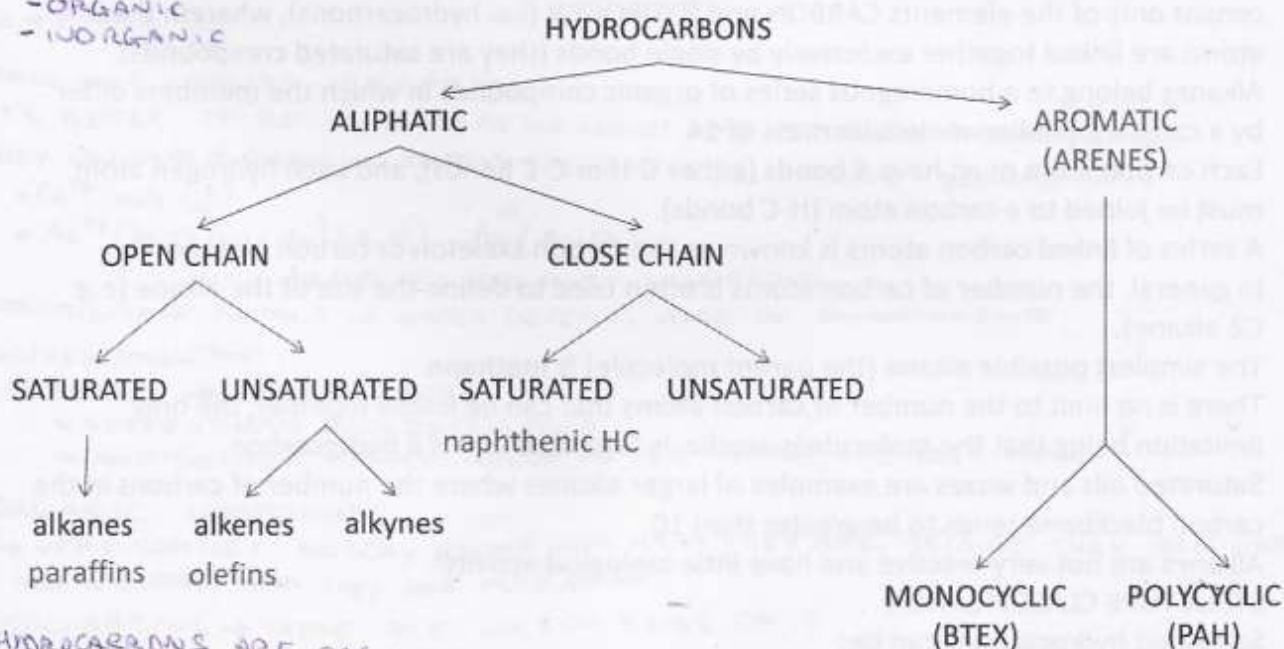
Contaminants

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October 18, 2011

IF THERE IS AN ACCIDENT, IT'S IMPORTANT TO KNOW WHICH POLLUTANT THERE IS.
THEY CAN BE (2 BIG FAMILIES):

- ORGANIC
- INORGANIC



HYDROCARBONS ARE ORGANIC.

⊗ VAI A 2B

INTRODUCTION

DIFFERENT APPROACH FROM PETROLEUM ENGINEERING: HERE, WE THINK ABOUT SURFACE, BECAUSE GENERALLY ACCIDENTS HAPPENS ON THE SURFACE

SURFACE = SOIL, AND THEN AQUIFER.

↳ WE ARE INTERESTED IN VADOSE ZONE (NOT SATURATED) AND AT THE 1° AQUIFER.

VADOSE ZONE: PORES ARE PLAW OF AIR AND WATER, NOT ONLY OF WATER.



• V_{SOIL} = VOLUME OF SOIL

• V_V = VOLUME OF VOIDS

• $V_T = V_V + V_S$

• $V_V = V_W + V_{AIR}$

POROSITY: $n = \frac{V_V}{V_T}$

SATURATION: $S = \frac{V_W}{V_V} \rightarrow \text{MAX: } S=1, \text{ IF } \theta=n$

WATER CONTENT: $\theta = \frac{V_W}{V_T} \rightarrow \text{MAX: } \theta=n$

WITHOUT POLLUTION, I HAVE 3 PHASES: WATER, AIR, SOIL.

DURING RAIN, IT COMES WATER FROM THE SURFACE.

⇒ WHAT HAPPENS TO THE VADOSE ZONE?

DARCY LAW: $q = K \cdot i \rightarrow$ IT'S THE RAW FLOW, THAT GOES TO THE AQUIFER

↳ $K = \left[\frac{m}{s} \right]$

POLLUTANTS

2 BIG FAMILIES OF POLLUTANTS = PROBLEMATIC FOR PEOPLE OR ENVIRONMENT:

• INORGANIC COMPOUNDS.

↳ HCL, SULFUR ACID (H_2SO_4), PH, NITRATES (NO_3^-), METALS (HEAVY, COPPER, COBALTIM, TITANIUM, URANIUM, CHROMIUM, ...), ARSENIC

Hg → $\rho = 15 \frac{TON}{m^3}$

Fe → $\rho = 5,5 \frac{TON}{m^3}$

METALS ARE SOLIDS, EXCEPT Hg.

IT'S BETTER TO BE SOLID, SO AS WE CANNOT HAVE A PASSAGE TO GAS PHASE.

THEY CAN HAVE ≠ OXIDATION STATE ⇒ PHENOMENA CAN CHANGE BECAUSE OF IT.

• Co^{+6} AND Co^{+3}

• $As^{+3} (As_2O_3)$, $As^{+3} (AsH_3)$, $As^{+5} (As_2O_5)$

↳ GAS, IT'S THE MOST DANGEROUS

SOLUBILITY OF METALS IN WATER DEPENDS ALSO ON OXIDATION STATE.

ANOTHER POLLUTANT:

ASBESTOS → IT COMES FROM:

↳ SERPENTINOUS ROCK ⇒ CHRISOILO

↳ ANFIBOLOUS ⇒ CROCIDOLITE → THE WORST, THE MOST TOXIC.

• ORGANIC COMPOUNDS

↳ VERY COMPLEX, NOBODY KNOWS HOW MANY THEY ARE, BECAUSE THEY ARE NATURAL AND NON-NATURAL, AND THEY ARE INCREASING.

HYDROCARBONS → THERE ARE LOTS OF KWDS OF IT.

MAIN FAMILY → THE ONE IN WHICH IN THE MOLECULA THERE ARE:

• C, H = MAIN COMPOUNDS

• O, N, P, ... = OTHER ATOMS

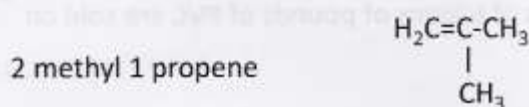
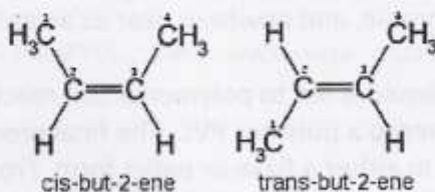
ALKENES ARE USED TO PRODUCE POLYMERS.
 IF ↑ n ⇒ ↑ MOLECULAR WEIGHT ⇒ LIQUID

An ALKENE (olefin or olefine) is an unsaturated chemical compound containing at least one carbon-to-carbon double bond. The simplest acyclic alkenes, with only one double bond and no other functional groups, form an homologous series of hydrocarbons with the general formula C_nH_{2n} . → C_nH_{2n}

The simplest alkene is ETHYLENE or ETHENE (C_2H_4). → $H-C=C-H$



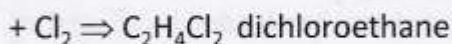
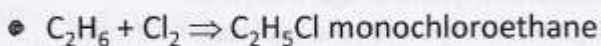
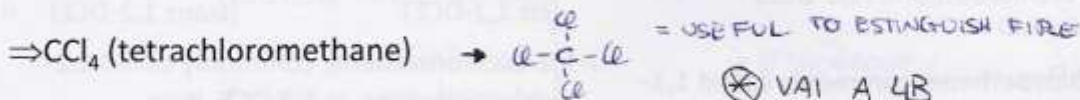
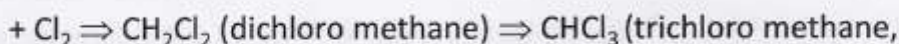
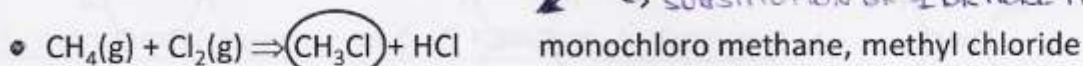
1n-butene $H_2C=CH-CH_2-CH_3$
 2n-butene $H_3C-HC=CH-CH_3$ (cis or trans)



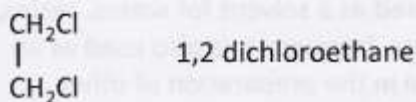
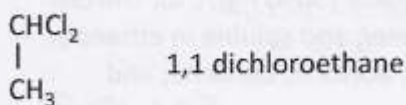
⊗ VAI A 2C

HALOGENATION REACTIONS

PROBLEM OF CH_4 = A CERTAIN [] COULD EXPLODE
 ⇒ IT IS POSSIBLE TO MAKE AN ARTIFICIAL REACTION
 (IT DOESN'T HAPPEN IN NATURE):
 REACTION WITH Cl_2
 ⇒ SUBSTITUTION OF 1 OR MORE H WITH Cl



2 isomers



The chemical compound **1,2-dichloroethane** is a chlorinated hydrocarbon, mainly used to produce vinyl chloride monomer (VCM, chloroethene), the major precursor for PVC production. 1,2 DCA is also used generally as an intermediate for other chemical compounds and as a solvent.

→ HALOGENATION REACTIONS: METHANE

PROPERTIES DUE TO Cl:

IT CAN CLEAN METAL SURFACES ⇒ VERY USED IN PAST.
 ↳ NOW NOT, THERE ARE PROBLEMS WITH IT.

• CHLOROMETHANE:

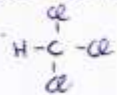
NEW CHARACTERISTICS:

- C IS +4 (Cl=-1)
- VERY DIFFICULT TO BURN IT
- MOLECULAR WEIGHT: MW=152 → VERY HIGH ⇒ IT'S A LIQUID
- Cl IS NOT BIODEGRADABLE BY MICROORGANISM (CH₄=BIODEG)
 ⇒ IT'S VERY DIFFICULT, IN THE ENVIRONMENT.
- Cl IS VERY ELECTRONEGATIVE ⇒ HIGH SOLUBILITY IN WATER ⇒ HIGH MOBILITY IN WATER
 (CH₄ IS NOT POLAR ⇒ NOT SOLUBLE IN WATER)

⇒ BAD CHARACTERISTICS FOR POLLUTION, WE CANNOT HAVE A NATURAL DECREASE OF THE POLLUTANT CONCENTRATION

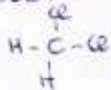
⇒ IT'S A PROBLEM IN WATER TO HAVE CHLORINATE SOLVENTS

• CHLOROFORM:



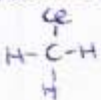
→ USED AS ANESTHETIC, DRY WASHING CLOTHES, ...

• DICHLOROMETHANE



→ USED FOR FOOD, FOR INSTANCE TO EXTRACT COFFEE FROM PLANTS

• MONOCHLOROMETHANE

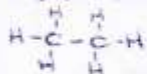


THESE SUBSTITUTIONS ARE ALSO POSSIBLE FOR ETHANE, PROPANE, ... WITH THE SAME CONSIDERATIONS:

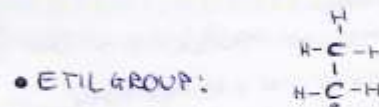
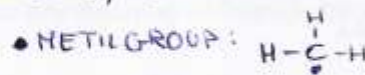
HIGH SOLUBILITY, LOW DEGRADABILITY, NOT COMBUSTIBLE, ...

→ SUBSTITUTION REACTIONS: ETHANE & PROPANE

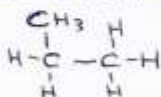
• CONSIDER ETHANE:



⇒ IT IS POSSIBLE TO SUBSTITUTE 1 OR MORE H WITH OTHER HYDROCARBURE RADICAL, FOR INSTANCE:

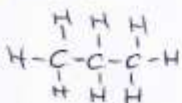


⇒ METHYLETHANE:

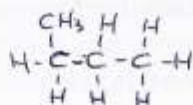


→ THE NAME WILL DEPEND ON THE POSITION IN WHICH THERE IS CH₃

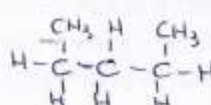
• PROPANE:



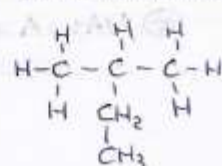
→ 1-METHYLPROPANE



→ 1,2-DIMETHYLPROPANE

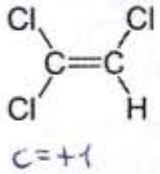


→ ETHYLPROPANE



⊗ VAI A 53

CHLORINATED ETHENES (3/4)



→ TRIELINE

Trichloroethylene (TCE) is an effective solvent for a variety of organic materials.

When it was first widely produced in the 1920s, trichloroethylene's major use was to extract vegetable oils from plant materials such as soy, coconut, and palm. Other uses in the food industry included coffee decaffeination and the preparation of flavoring extracts from hops and spices.

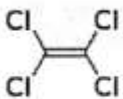
From the 1930s through the 1970s, both in Europe and North America, trichloroethylene was used as a volatile gas anesthetic. TCE was used in place of the earlier anesthetics chloroform and ether in the 1940s, but was itself replaced in the 1950s by the newer halothane, which allowed much faster induction and recovery times. Marketed in the UK by ICI under the trade name Trilene it was coloured blue (with a dye called waxolene blue) to avoid confusion with the similar smelling chloroform.

It has also been used as a dry cleaning solvent, although replaced in the 1950s by tetrachloroethylene (also known as perchloroethylene, PCE).

Perhaps the greatest use of TCE has been as a degreaser for metal parts. The demand for TCE as a degreaser began to decline in the 1950s in favor of the less toxic 1,1,1-trichloroethane. However, 1,1,1-trichloroethane production has been phased out in most of the world under the terms of the Montreal Protocol, and as a result trichloroethylene has experienced some resurgence in use as a degreaser.



CHLORINATED ETHENES (4/4)



→ PERCLORO ETILENE

Tetrachloroethylene (PCE) or tetrachloroethene is a colourless liquid widely used for dry cleaning of fabrics, hence it is sometimes called "dry-cleaning fluid".

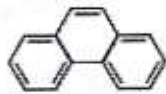
It is an excellent solvent for organic materials. Otherwise it is volatile, highly stable and nonflammable. Usually as a mixture with other chlorocarbons, it is also used to degrease metal parts in the automotive and other metal working industries.

The International Agency for Research on Cancer has classified PCE as a group 2A carcinogen, which means that is probably carcinogenic to humans.

Like many chlorinated hydrocarbons, PCE is a central nervous system depressant and can enter the body through respiratory or dermal exposure. PCE dissolves fat from the skin, potentially resulting in skin irritation.

⊗ VAI A 4C

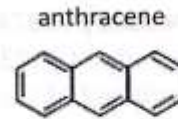
The simplest PAHs, as defined by IUPAC are **phenantrene** and **anthracene** ($C_{14}H_{10}$), which both contain three fused aromatic rings.



phenantrene

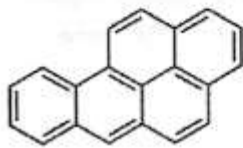


NAFTALENE

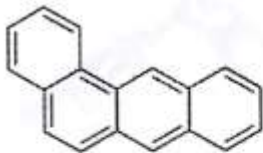


anthracene

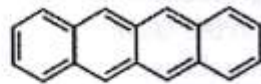
Naphthalene ($C_{10}H_8$ constituent of mothballs), consisting of two coplanar six-membered rings sharing an edge, is another aromatic hydrocarbon. By formal convention, it is not a true PAH, though is referred to as bicyclic aromatic hydrocarbon.



Benzo[a]pyrene, $C_{20}H_{12}$, is a five-ring PAH whose metabolites are mutagenic and highly carcinogenic. It belongs to a class of PA compounds known as benzopyrenes, which consist of a benzene ring fused to a pyrene molecule. B(a)P is a product of incomplete combustion at temperatures between 300 and 600°C.



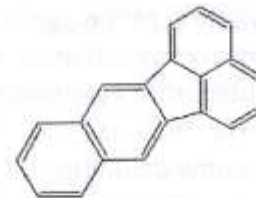
Benzo[a]anthracene



Benzo[b]anthracene
Tetracene



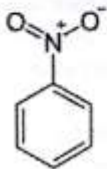
Benzo[b]fluorantene



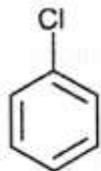
Benzo[k]fluorantene

ALL ARE VERY TOXIC, ALSO FOR VERY SMALL [·]

AROMATIC COMPOUNDS



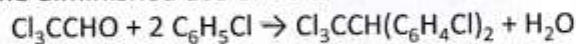
Nitrobenzene is an organic compound with the chemical formula $C_6H_5NO_2$. Nitrobenzene is a water-insoluble pale yellow oil with an almond-like odor. Although occasionally used as a flavoring or perfume additive, nitrobenzene is highly toxic in large quantities and is mainly produced as a precursor to aniline. In the laboratory, it is occasionally used as a solvent, especially for electrophilic reagents.



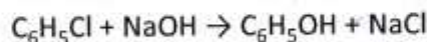
→ BENZENE = H CAN BE SUBSTITUTED

Chlorobenzene is an aromatic organic compound with the chemical formula C_6H_5Cl .

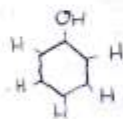
This colorless, flammable liquid is a common solvent and a widely used intermediate in the manufacture of other chemicals. Chlorobenzene once was used in the manufacture of certain pesticides, most notably DDT by reaction with chloral (trichloroacetaldehyde), but this application has declined with the diminished use of DDT.



At one time, chlorobenzene was the main precursor for the manufacture of phenol:



The major use of chlorobenzene is as an intermediate in the production of products such as herbicides, dyestuffs, and rubber. Chlorobenzene is also used as a high-boiling solvent in many industrial applications as well as in the laboratory



ESACLOROBENZENE



BENZENE ≠ PHENOL
PARTICULARLY
BECAUSE OF
SOLUBILITY IN
WATER

AVERY PROBLEMATIC FAMILY.
 DIOXINE IS NOT PRODUCED BY MAN. IT IS PRODUCED WHEN YOU BURN SOME ORGANIC
 ↓ SUBSTANCES THAT CONTAIN CL, AT HIGH T. → NOBODY WANTS TO PRODUCE IT = IT'S UNDESIRABLE.
 IT IS TOXIC WITH [] > 0g IN THE AIR.
 ⇒ ANALYSIS ARE REALLY DIFFICULT AND COSTLY TO DO.

Polychlorinated dibenzodioxins (PCDDs), or simply **dioxins**, are a group of organic polyhalogenated compounds that are significant because they act as environmental pollutants. They are commonly referred to as dioxins for simplicity in scientific publications because every PCDD molecule contains a dioxin skeletal structure. Typically, the *p*-dioxin skeleton is at the core of a PCDD molecule, giving the molecule a dibenzo-*p*-dioxin ring system. Members of the PCDD family have been shown to bioaccumulate in humans and wildlife due to their lipophilic properties, and are teratogens, mutagens, and human carcinogens.

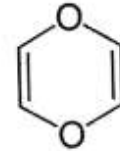
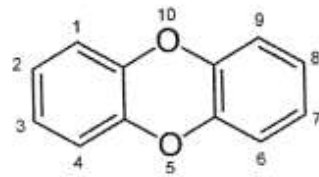
Dioxins occur as by-products in the manufacture of organochlorides, in the incineration of chlorine-containing substances such as PVC (polyvinyl chloride), in the bleaching of paper, and from natural sources such as volcanoes and forest fires.

The structure of dibenzo-*p*-dioxin comprises two benzene rings joined by two oxygen bridges. This makes the compound an aromatic diether. The name dioxin formally refers to the central dioxygenated ring, which is stabilized by the two flanking benzene rings.

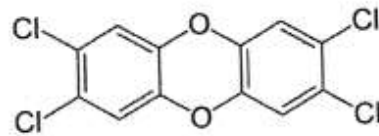
In PCDDs, chlorine atoms are attached to this structure at any of 8 different places on the molecule, at positions 1-4 and 6-9. There are 75 different PCDD congeners (that is: related dioxin compounds).

The toxicity of PCDDs depends on the number and positions of the chlorine atoms. Congeners that have chlorines in the 2, 3, 7, and 8 positions have been found to be significantly toxic.

PCDDs

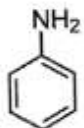


1,4-Dioxin

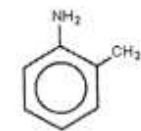


2,3,7,8-Tetrachlorodibenzodioxin

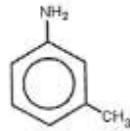
AROMATIC AMINES



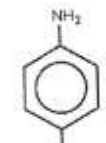
Aniline, phenylamine or aminobenzene is an organic compound with the formula $C_6H_5NH_2$. Consisting of a phenyl group attached to an amino group, aniline is the prototypical aromatic amine.



o-toluidine (o-methylaniline)

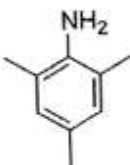


m-toluidine (m-methylaniline)

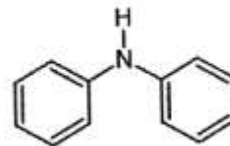


p-toluidine (p-methylaniline)

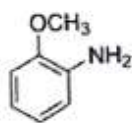
Toluidines are used in the production of dyes. They are a component of accelerators for cyanoacrylate glues. They are toxic and are suspected human carcinogens.



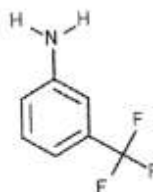
2,4,6-Trimethylaniline



Diphenylamine, $(C_6H_5)_2NH$

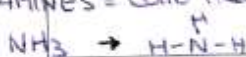


Anisidine (three possible isomers)



3-(Trifluoromethyl)aniline $CF_3C_6H_4NH_2$ is an intermediate in the production of the herbicide fluometuron

AMINES = COME FROM AMMONIA



↓ SUBSTITUTIONS →

- METHYLAMINE $\rightarrow H-N(H)-CH_3 \rightarrow$ IT'S A PRIMARY AMINE, ONLY 1 SUBSTITUTION
- DIMETHYLAMINE $\rightarrow H-N(CH_3)-CH_3 \rightarrow$ IT'S A SECONDARY AMINE
- TERTIARYAMINE $\rightarrow CH_3-N(CH_3)-CH_3$

OIL = DEPENDING ON THE PLACE WHERE YOU CULTIVATE IT,
IT WOULD HAVE ≠ COMPOSITIONS.
THESE ARE MEDIUM COMPONENTS,
THE FAMILIES PRESENT.



Raw oil characteristics.

Density [g/cm ³]	0.89
Sulphur [%]	1
Volatiles organic compounds (VOC):	
C1-C8 [%]	8
C9-C15 [%]	15
Main components:	
Alkanes [%]	33
Alkenes [%]	22
Aromatics [%]	30
Residues [%]	15
Ratio alkanes/aromatics []	1.12

TO OBTAIN A PRODUCT FROM OIL, THERE ARE ≠ PROCESSES (IN RAFFINERIES):

- DISTILLATION = PHYSICAL PROCESS.
DEPENDING ON THE T, YOU OBTAIN ≠ PRODUCTS.
- OTHER STRONGER PROCESSES.



Characteristics of common oil products.

Oil product	Distillation range	Hydrocarbon chain	General composition
Gasoline	40 ÷ 205 °C	C5 ÷ C10	alkanes - cicloalkenes - aromatics
Cherosene	175 ÷ 325 °C	C12 ÷ C16	alkanes - alkenes - cicloalkenes - PAH
Diesel	200 ÷ 400 °C	C15 ÷ C25	alkanes - cicloalkenes - PAH
Fuel oil	140 ÷ 400 °C	C10 ÷ C25	alkanes - cicloalkenes - BTEX - PAH
Oil	Residues	C20 ÷ C70	alkanes - PAH

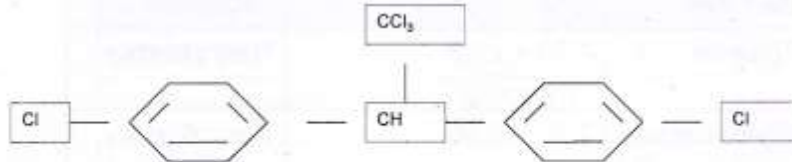
ALL THESE COMPOUNDS ARE NOT CHLORINATE, BECAUSE CL ARRIVES FROM OTHER ACTIVITIES LATER

HIGH SOLUBILITY, VOLATILITY, TOXICITY, STABILITY IN THE ENV.

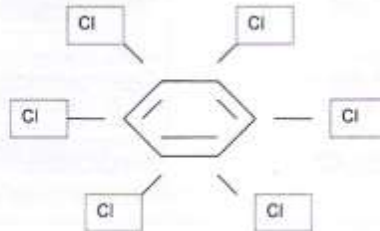


Pesticides (insetticides, erbicides, fungicides)

DDT (insetticide)



Lindane (insetticide)

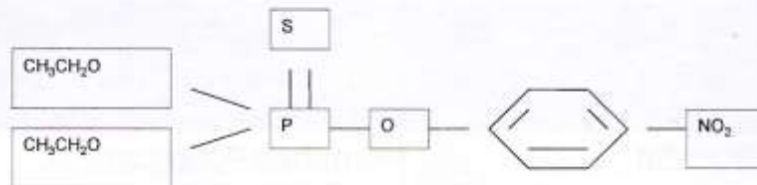


PARATHION = VERY HIGH BIODEG → NO Cl, THERE IS P
 ⇒ IN TIME, THEY WILL DISAPPEAR
 ⇒ THEY HAVE SUBSTITUTED DDT

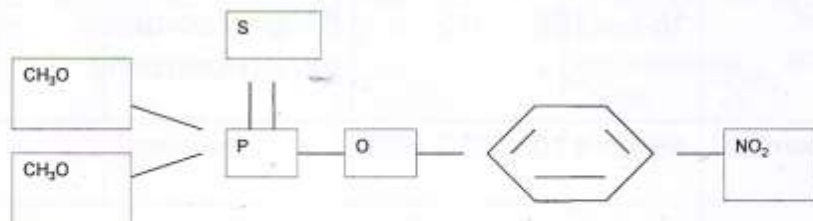


Pesticides (insetticides, erbicides, fungicides)

Etil Parathion (insetticide)



Metil Parathion (insetticide)

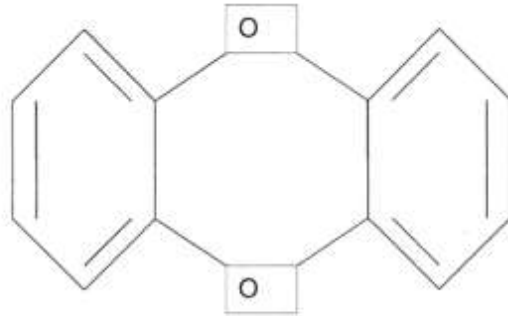


Polychlorinated byphenyls



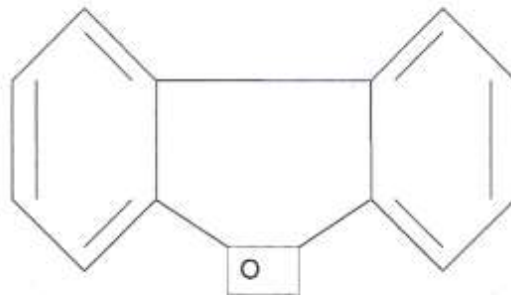
dibenzodioxines and dibenzofuranes

dibenzodioxines



VERY IMPORTANT, THEY WERE USED IN THE PAST FOR ELECTRICITY

dibenzofuranes



03/10/2013

CHEMICAL PARAMETERS TO MEASURE IN ORDER TO HAVE AN IDEA OF THE POLLUTION.

IN A SITE → 2 DIFFERENT KIND OF POLLUTION:

- OF THE SOIL
 - OF THE AIR
- } ⇒ 2 DIFFERENT SAMPLES TO TAKE

IF I TAKE A SOIL SAMPLE, WHICH POLLUTANT I SEARCH FOR?
I NEED TO KNOW WHAT KIND OF ACCIDENT.

LET ME THINK ABOUT INORGANIC.

⇒ I SEARCH FOR HEAVY METALS

UNIT MEASURE:

- ppm
- $\frac{mg}{kg}$
- %

RELATIONSHIP BETWEEN THEM?
↳ 10'000 TIMES

IF THE ACCIDENT WAS ORGANIC
⇒ DEPENDING ON THE ACCIDENT, I DECIDE WHICH SUBSTANCES TO LOOK FOR IN LAB.

⇒ THE PARAMETERS DEPENDS ON IT.

2 PARAMETERS ARE VERY INTERESTING TO UNDERSTAND IF THERE IS A BIG POLLUTION:

- COD = IDEA OF ORG. SUBSTANCES THAT ARE CHEMICAL OXIDABLE IN THE SAMPLE
- BOD = " BIOLOGICAL OXIDABLE "

BOD < COD

COD = AMOUNT OF O₂ NECESSARY IF I WANT TO OXIDATE THE C PRESENT.

BOD = DEALS WITH ONLY BIODEGR. SUBSTANCES

IF COD > 0

⇒ I CAN AVOID OTHER ANALYSIS FOR ORGANIC SUBSTANCES.

WATER SAMPLE

↳ INORGANIC
⇒ THERE IS OTHER THAN METALS:

- pH
- CONDUCTIVITY
- TEMPERATURE
- REDOX POTENTIAL VALUE

↳ TO UNDERSTAND AERO/AANAERO CONDITIONS.

WE'LL SEE THE CHARACTERISTICS THAT ARE IMPORTANT FOR ENVIRONMENT

PROPERTIES OF ORGANIC AN INORGANIC SUBSTANCES THAT INFLUENCE THE ENVIRONMENTAL DIFFUSION

- Solubility
- Density
- Chemical incompatibility
- volatility
- hydrofobicity
- biodegradability
- Chemical degradability (abiotic processes p.es. hydrolysis)

DENSITY

- Density: mass/ volume
- Specific weight = mass of 1 volume of a compound/mass of the same volume of water → UNITLESS, IT'S A NUMBER

$$d = \rho_s * \rho_{water} (4^\circ C)$$

DENSITY AND SPECIFIC WEIGHT ARE RELATED BY THIS RELATION

WATER DENSITY = VARIES WITH T (SMALL VARIATIONS)

↳ ↑ T ⇒ ↓ S_w

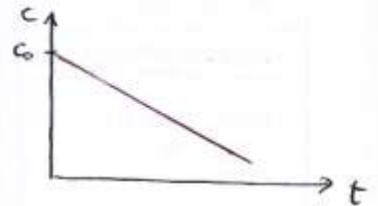
FLOW IN THE SATURATED ZONE

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} - v_e \frac{\partial C}{\partial x} - kC$$

$$v_e = q / \theta$$

$$q = Ki$$

GRAPHICALLY, TREND VELOCITY IS CONSTANT IN TIME



FOR ZERO ORDER KINETICS:

$$R = \frac{dc}{dt} = -k \Rightarrow \int_{C_0}^{C_f} dc = -k \int_0^{t_f} dt \Rightarrow C_f = C_0 - k \cdot t_f$$

IN MANY CASES, 1ST ORDER KW. IS GOOD TO DESCRIBE REAL PHENOMENA.

THESE 2 KINETICS ARE GOOD FOR BIO REACTIONS.

THERE ARE MORE DIFFICULT MODELS, BUT WE WOULD NEED MORE PARAMETERS.

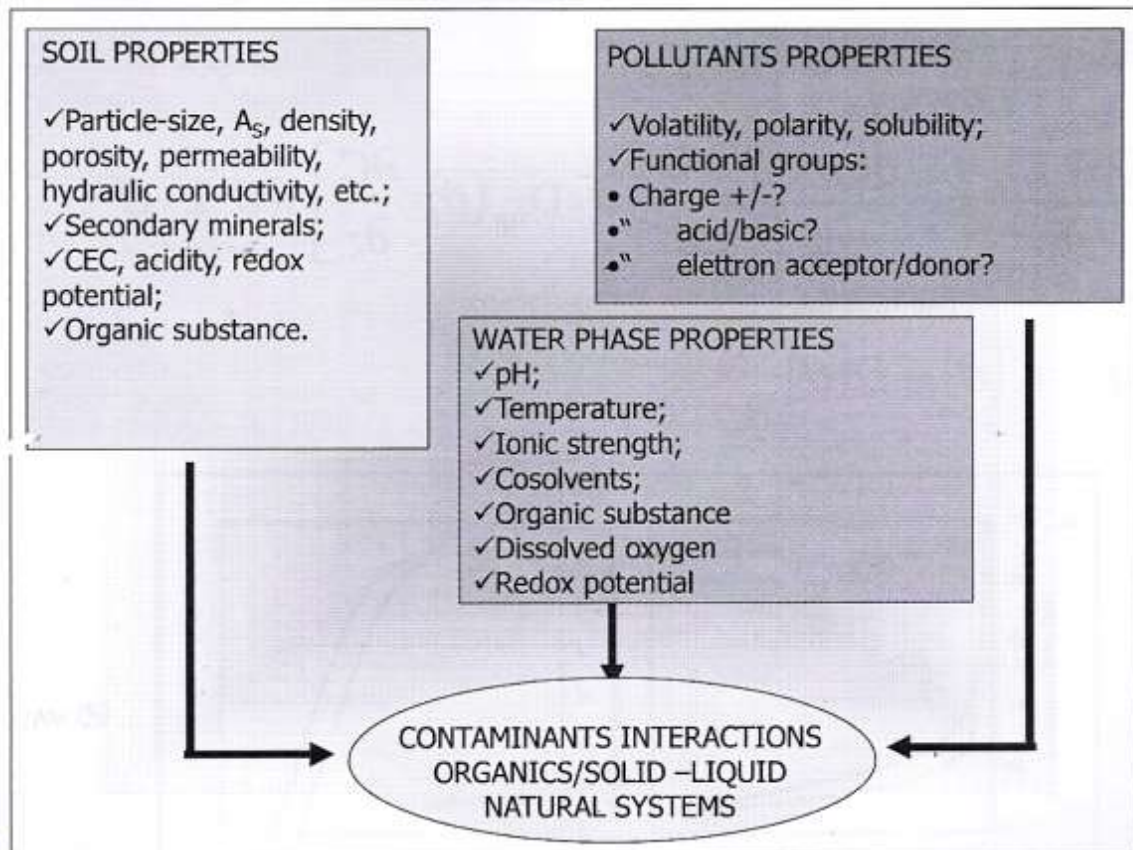
IF I HAVE A REACTION AND I WANT TO DESCRIBE IT AS A ZERO ORDER KINETICS:

I MEASURE C ON TIME → EXPERIMENTAL POINTS

⇒ I CAN HAVE THE K PARAMETER

SO, FOR 1ST ORDER, I NEED TO HAVE ONLY 1 PARAMETER.

IF ↑ ORDER OF KINETICS ⇒ ↑ N° OF PARAMETERS NEEDED.

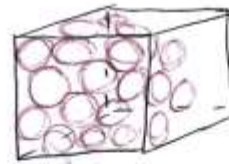


WE SEE INTERACTIONS BETWEEN ≠ PHASES IN SOIL → WATER, SOIL, POLLUTANT.

CEC = CATION EXCHANGE CAPACITY.

TO PASS FROM RIVER TO SOIL:

WE JUST ADD THE TERM: $\theta = \frac{V_w}{V_f}$
 $\Rightarrow \frac{\partial \theta C}{\partial t} \rightarrow$ BECAUSE POLLUTANT CAN BE ONLY IN THE V_w



$$\Rightarrow \frac{\partial \theta C}{\partial t} = \frac{\partial (qC)}{\partial x} + \frac{\partial}{\partial x} \left(\theta D(\theta) \frac{\partial C}{\partial z} \right) + \theta R$$

q DERIVES FROM DARCY LAW $\rightarrow q = K \cdot i$, IN THE AQUIFER
 (IN VADOSE ZONE \Rightarrow NO MORE \sim)

$$\Rightarrow q = K(\theta) \left(1 - D(\theta) \frac{\partial \theta}{\partial z} \right)$$

\downarrow NOW, K VARIES WITH θ \downarrow WATER DIFFUSION TERM

IF I PASS FROM VADOSE ZONE TO THE AQUIFER:

- θ = POROSITY = COST (TIME & SPACE)
 \Rightarrow I CAN EXTRACT IT FROM $\partial \theta / \partial z$.
- $q = K \cdot i$
- \Rightarrow THE EQUATION IS EASIER, I NEED LESS DATA.

REACTIONS KINETICS

A GENERAL REACTION BIO CAN BE:

• NON REVERSIBLE:



• REVERSIBLE:



IN ORDER TO HAVE AN IDEA OF VELOCITY OF POLLUTANT TRANSFORMATION DUE TO THE REACTION:

$$R = \frac{dc}{dt} \rightarrow C = [\text{pollutant}] = \left[\frac{kg}{m^3} \right] \left[\frac{mol}{m^3} \right]; \quad t = [s], \quad R = \left[\frac{kg}{m^3 \cdot s} \right]$$

TO EXPRESS $R \rightarrow R = -k[A]^a[B]^b$

\ominus = BECAUSE, IN GENERAL, POLLUTANT (IN SOIL, AIR, WATER, ...) WILL DECREASE.
 BUT IF I WANT TO PRODUCE A CERTAIN PRODUCT C , THE CONCENTRATION WILL $\uparrow \Rightarrow$ NO MORE \ominus

POSSIBLE SIMPLIFICATIONS:

1) FIRST ORDER KINETICS
 GENERALLY IT IS USED. IT MEANS THAT: $\begin{cases} b=0 \\ a=1 \end{cases}$
 \Rightarrow IT WILL BECOME: $R = -k[A]$

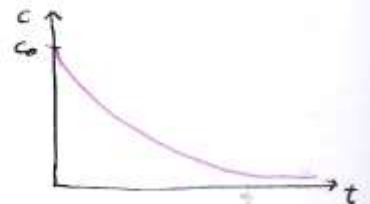
2) ZERO ORDER KINETICS.
 $\begin{cases} a=0 \\ b=0 \end{cases} \Rightarrow R = -k$

LET US UNDERSTAND WHY I SIMPLIFY:

I HAVE A POLLUTANT IN SOIL WITH AN INITIAL $[C] = C_0$. FOR 1ST ORDER KINETICS:

$$R = \frac{dc}{dt} = -kC$$

$$\Rightarrow \int_{C_0}^{C_f} \frac{dc}{C} = - \int_0^{t_f} k dt \Rightarrow R_n \frac{C_f}{C_0} = -k t_f \Rightarrow C_f = C_0 \cdot e^{-k \cdot t_f}$$



\Rightarrow THERE WILL BE AN EXPONENTIAL DECREASE:

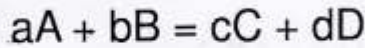
WHEN C_0 IS HIGH, AT THE BEGINNING
 \Rightarrow HIGH VELOCITY OF DECREASE
 THEN, $\downarrow C \Rightarrow \downarrow R$, THE DECREASE IS SLOWER

SO, IF I HAVE A WAY TO CLEAN IT, IN TIME EFFICIENCY WILL $\downarrow \Rightarrow \uparrow$ COSTS

⊗ VAI A 20

LIQUID PHASE REDOX POTENTIAL

The tendency of an oxidation reduction reaction is measured by means of an oxidation reduction potential $E(V)$.



$$E = E^0 - 0,059/n \log [C]^c \cdot [D]^d / [A]^a \cdot [B]^b \quad (\text{Nernst})$$

n is the number of electrons transferred by means of a redox reaction.

Redox intensity: $pE = - \log (e^-)$

$$pE = E (V) / 0,059$$

IF I READ A VALUE $\sim 0V$
 \Rightarrow I KNOW THAT I HAVE:
 $\begin{cases} Mn^{+4} \rightarrow Mn^{+3} \\ Fe^{+3} \rightarrow Fe^{+2} \end{cases}$

LIQUID PHASE REDOX POTENTIAL

REDOX POTENTIAL IS VERY IMPORTANT. ACCORDING TO ITS VALUE, I CAN UNDERSTAND WHAT IS GOING ON IN THE SOIL. IF I HAVE AN AQUIFER AT A CERTAIN T, I CAN HAVE A CERTAIN AMOUNT OF O_2 DISSOLVED IN WATER (DEPENDS ON T).

FOR EXAMPLE:
 $T=20^\circ C \Rightarrow 8 \text{ mg/l}$, IT IS THE MAX VALUE POSSIBLE.
 IF I HAVE THIS VALUE \Rightarrow IT'S A COMPLETELY AEROBIC WATER

\Rightarrow I WILL FIND $V = +0,82$.
 \Rightarrow I CAN KNOW I WILL HAVE AN AEROBIC DEGRADATION OF CELLULOSES AND SUBSTANCES.

IF, AT $20^\circ C$, I FIND 6 mg/l
 \Rightarrow IT IS NOT A COMPLETELY AERO ENV.
 \Rightarrow I NEED SOME OTHER SUBSTANCES TO OXIDATE. IN WATER, NO_3^- WILL BE USED
 \Rightarrow IT WILL BE REDUCED TO N_2 IN ORDER TO OXIDATE SUBSTANCES.

IF, AT $20^\circ C$, I FIND 4 mg/l
 \Rightarrow I COULD FIND O_2 AND ALSO NO_3^-
 \Rightarrow Mn^{+4} COULD BE USED: $Mn^{+4} \rightarrow Mn^{+2}$
 THEN, IRON: $Fe^{+3} \rightarrow Fe^{+2}$
 THEN, $SO_4^{2-} \rightarrow H_2S$

AT THIS LEVEL, THE V IS SO THAT WE ARRIVE AT A QUITE ANAERO ENVIRONMENT

⊗ AT LAST, ANAERO REACTION:
 $C_6H_{12}O_6 \rightarrow 3CO_2 + 3CH_4$

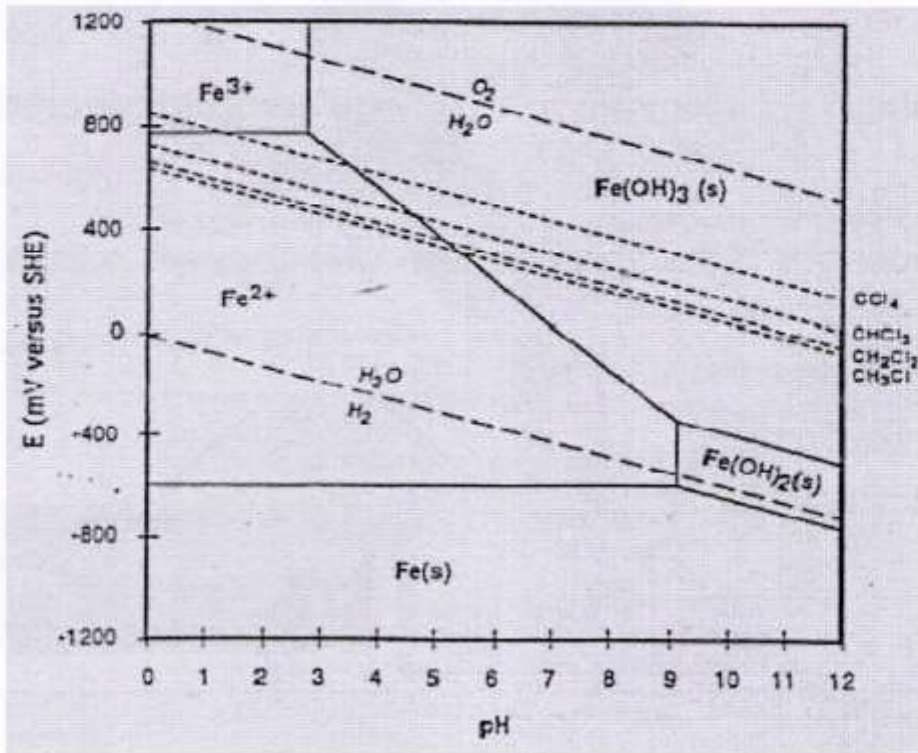
SOLUBILITY OF:
 $Fe^{+2} \gg Fe^{+3}$
 \Rightarrow UNDERSTANDING THE KIND OF ENV. (THE REDOX POTENTIAL) I CAN ALSO UNDERSTAND THESE THINGS

	Biodegradation mechanism	Redox potential (V)
Free oxygen	Aerobic environment	+0.82
Nitrate	Anaerobic environment	+0.74
Mn(IV)		+0.52
Fe(III)		-0.05
SO_4^{2-}		-0.22
CO_2		-0.24

WE CAN HAVE A DIAGRAM LIKE THAT FOR EACH METAL. HERE, WE HAVE Fe.
 PH CAN DEFINE (TOGETHER WITH E) THE KIND OF Fe COMPOUND I WILL HAVE IN THE WATER.
 ⇒ PH IS IMPORTANT FOR SOLUBILITY.
 FOR ↓ PH ⇒ ↑ SOLUBILITY OF Me. (FOR EVERY Me WE FIND THIS TREND)
 BUT THE VALUES ARE ≠ FOR EACH Me

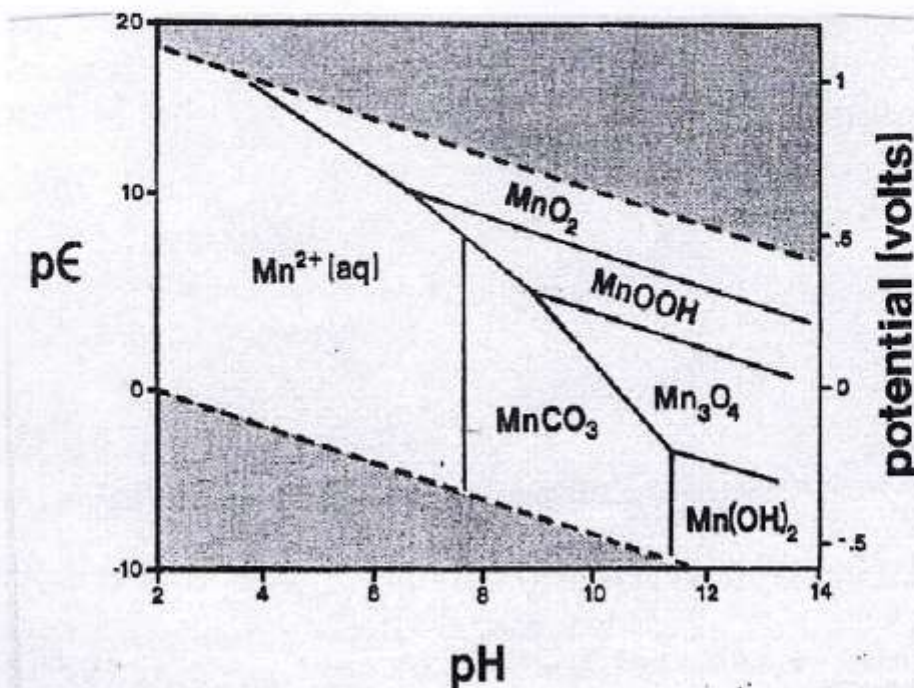
GENERALLY, FOR THE ACQUIFER pH ~ 6-7, WITHOUT POLLUTION ACQUIFER.

REDOX POTENTIAL AND LIQUID PHASE pH



I HAVE A DIFFERENT GRAPH FOR EACH Me.
 IF I ENTER WITH THE VALUE OF PH AND REDOX POTENTIAL MEASURED, I CAN KNOW WHICH FORM OF Me I'LL FIND.

REDOX POTENTIAL AND LIQUID PHASE pH



INORGANIC POLLUTANTS

It is important to keep into account the following properties:

- solubility → IN GENERAL, ↑ SOLUB IF ↓ pH
- chemical degradability (redox reactions, precipitation, complexation, etc.)

ORGANIC POLLUTANTS

It is important to keep into account the following properties:

- solubility
- density → IF > OR < WATER
- volatility → TENDENCY OF THESE SUBSTANCES TO PASS TO GAS PHASE
↳ HENRY CONSTANT
- hydrofobicity
- biodegradability → AERO IS BETTER THAN ANAERO, BECAUSE IS:
- FASTER
- EASIER TO MANAGE
BUT WE MUST CHOSE DEPENDING ON THE SUBSTANCES WE HAVE.
↳ NOT EASY DEGRADABLE SUBSTANCES, DUE TO THE PRESENCE OF HALOGENATE (Cl, I, I)
- chemical degradability (abiotic processes p.es. hydrolysis)
↳ WORST THAN BIODEG, BECAUSE YOU HAVE TO ADD COMPOUNDS
⇒ EXPENSIVE, THAT IS A BIG REAL PROBLEM, WE MUST HAVE AFFORDABLE SOLUTIONS
↳ SUSTAINABILITY OF THE REMEDIATION → ENVIRONMENTAL
↳ ECONOMIC

RAOULT LAW

Liquid-vapour equilibrium

- 1: component
- 2: component
- P: total pressure
- P1: partial pressure of component 1 in the gas phase
- P2: partial pressure of component 2 in the gas phase
- Pv1: vapour pressure of component 1 at the temperature T
- Pv2: vapour pressure of component 2 at the temperature T
- x1: molar fraction of component 1 in the liquid phase
- x2: molar fraction of component 2 in the liquid phase
- y1: molar fraction of component 1 in the gas phase
- y2: molar fraction of component 2 in the liquid phase

AS THE 2 COMPONENTS COULD BE NOT SIMILAR, GENERALLY WE APPROXIMATE RAOULT LAW WITH THE HENRY LAW.

HENRY IS VALID ONLY WHEN COMPONENT ① IS WATER AND ② IS A SMALL AMOUNT OF OTHER POLLUTANT.

IF I CONSIDER ① = POLLUTANT

⇒ c_{iL} AND c_{iG} ARE THE 2 [...] IN THE 2 PHASES.

⇒ $c_{iG} = H \cdot c_{iL}$ → HERE, IT'S DIMENSIONAL: $H = H^*$

BUT I COULD ALSO WRITE:

$$P_i = H \cdot c_{iL} \rightarrow \begin{cases} P_i = \text{PARTIAL PRESSURE} \\ H = \left[\frac{\text{atm} \cdot \text{m}^3}{\text{mol}} \right] \end{cases}$$

REAL SITUATION

Liquid-vapour equilibrium

$$x_1 + x_2 = 1$$

$$y_1 + y_2 = 1$$

$$P_1 = y_1 P = P_{v1} \cdot x_1 \cdot \gamma_1$$

γ_1 = activity coefficient, it is the deviation from the Raoult law

γ_1 is equal to 1 (Raoult law) when x_1 is equal to 1 (one component)

$$\gamma_1 = P_1 \text{ real} / P_1 \text{ Raoult}$$

γ_1 is very different from 1 when x_1 is equal to 0

$$P_2 = y_2 P = P_{v2} \cdot x_2 \cdot \gamma_2$$

$$P = P_1 + P_2 = P (\gamma_1 + \gamma_2)$$

Henry Law when x_1 is about equal to zero and the component

1 and 2 have very different physical properties ($P_1 = H^* x_1 \gamma_1$

and $H = f(T)$)

TO PASS FROM H TO H* → USE $pV = nRT$

ORGANIC POLLUTANTS: K_{OW} AND SOLUBILITY

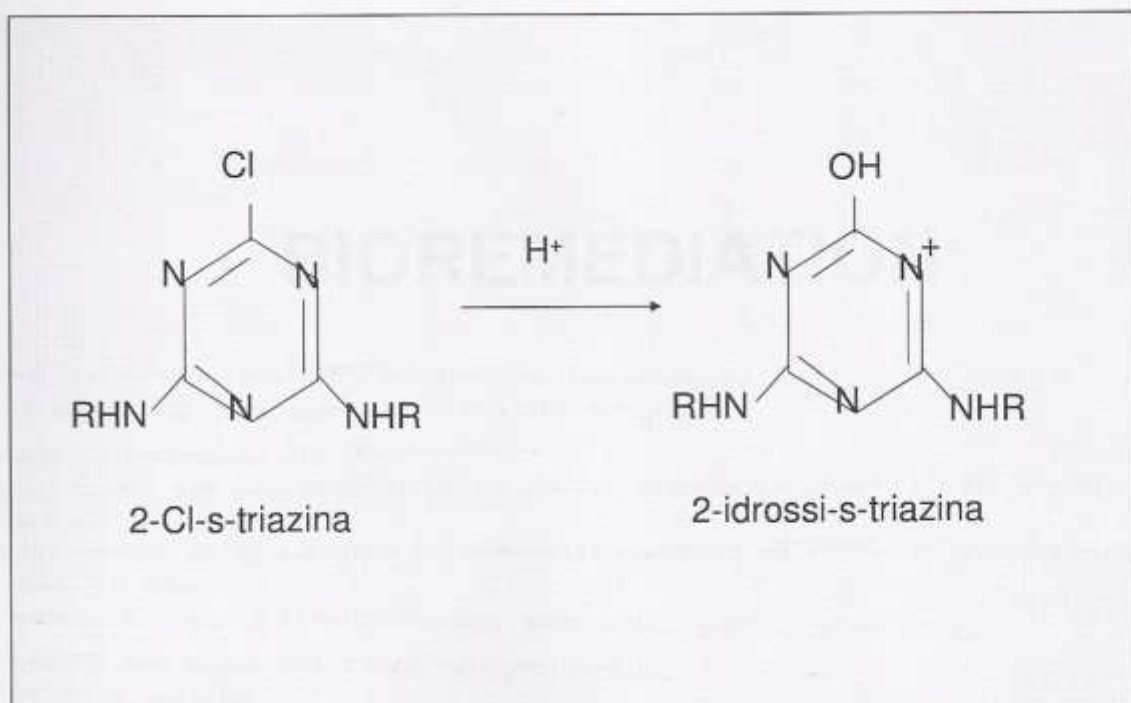
Solute	K_{OW} [(mol/l octanol)/(mol/l water)]	K_{HW} [(mol/l esane)/(mol/l water)]	C_{acq}^{sat} (mol/l water)
nitrobenzene	130	170	0.023
Phenol	28	0.1	0.89

$$\log K_{OC} = a \log K_{OW} + b$$

ORGANIC POLLUTANTS

BIODEGRADATION

The biodegradation of a chemical substance may be estimated on the basis of the chemical structure. Generally the molecules with a branched structure are more difficult to be biodegraded of those ones with a linear structure, the molecules with a short chain are more difficult to be biodegraded of those ones with a long chain and, not saturated hydrocarbons are easier to be biodegraded than saturated ones. The reductive dehalogenation is the more significant degradation mechanism for pesticides, biphenyls and polychlorinated solvents.



ARTIFICIAL ORGANIC SUBSTANCES



xenobiotic substances

Xenobiotic, substances not present in natural environments.

They cumulates in the environment. They may be classified

in the following categories:

SIMILAR TO NATURAL

⇒ GOOD CONDITIONS

↳ **biodegradable**, they are similar to natural compounds, they are easily biodegradated producing compounds similar to natural compounds

i.e.:

ALCOHOLIC SUBSTANCES

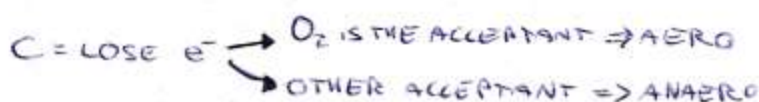
↳ **persistent**, they have a structure that is unknown to biological systems and they are degradated with difficulty. They are persistent so they may diffuse also at a great distance from the pollution point

THE WORST ONES

↳ **recalcitrant**, they resist to degradation in many environments and they may cumulate.

Cellular metabolism

The cellular metabolism involves the acceptance, from an external compound, of two electrons coming from the respiration chain. When this function is performed by free oxygen this is the aerobic metabolism; in the absence of free oxygen the anaerobic metabolism takes place.



Different kinds of metabolisms

Kind	Electrons acceptor
Aerobic respiration	Molecular O_2
Anaerobic respiration	
Denitrification	NO_3^-
Nitrates reduction	NO_3^-
Sulfates reduction	SO_4^-
Iron reduction	Fe^{3+}
Protonic reduction	H^+
Sulphur reduction	S
Organic compounds reduction	Organic compounds
Methanogenic respiration	HCO_3^-

TO HAVE AN IDEA OF HOW IT'S POSSIBLE TO DEGRADATE EVERYTHING HERE



Chlorinated hydrocarbons degradation

CAH	Aerobic oxidation		Anaerobic dechlorination	
	Direct	Cometabolic	Direct	Cometabolic
ChloroEthenes				
PCE	x	x	o	o
TCE	x	o	o	o
cis-DCE	x	o	o	o
trans-DCE	x	o	o	o
1,1-DCE	x	o	o	o
VC	o	o	o	o
CloroEthanes				
1,1,1-TCA	x	o	x	o
1,2-DCA	o	x	x	o
1,1-DCA	o	x	x	o
CA	x	x	x	x
CloroMethanes				
CT	x	x	x	o
CF	x	o	x	o
MC	o	o	o	o
CM	o	o	x	x

o = Typical x = Atypical

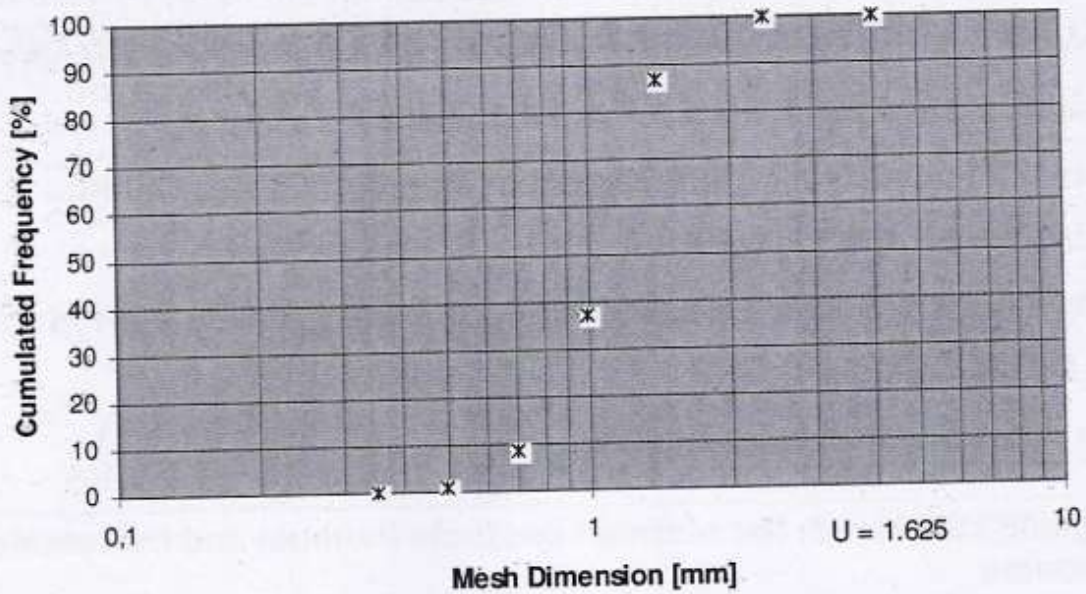
↳ POSSIBLE ↳ NON POSSIBLE OR DIFFICULT

Bioavailability

- The presence of chlorine atoms decreases the biodegradation velocity
- Organic compounds solved in water are easily biodegradated

SOLID PHASE: SOIL

PARTICLE-SIZE ANALYSIS



SOLID PHASE: SOIL

SPECIFIC SURFACE

$A_s = S/V$ $S = \text{surface [m}^2\text{]}$ e $V = \text{volume [m}^3\text{]}$
↓
 V_{TOT} OF THE SAMPLE OF SOIL

DENSITY

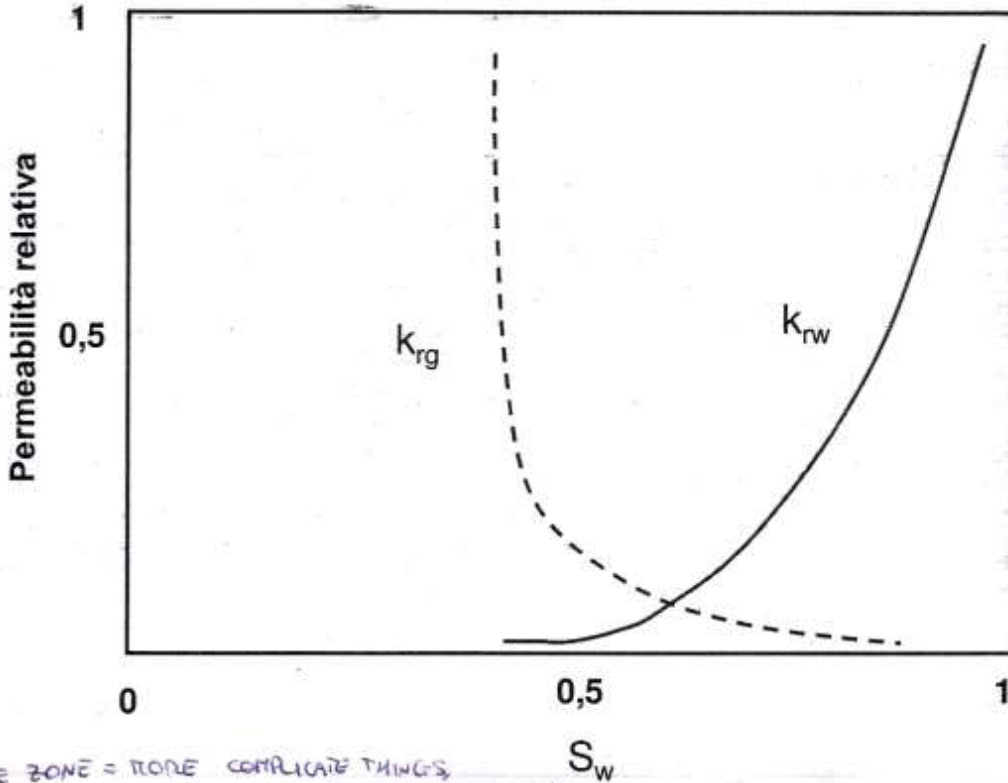
Apparent density = $\rho_b = M_{tot}/V$
 Solid phase density = $\rho_s = M_{tot}/V_s$
 $M_{tot} = \text{total mass of dry soil [kg]}$
 $V_s = \text{Volume of solid phase [m}^3\text{]}$

M_{TOT} = OF THE SAMPLE OF SOIL
 DENSITY OF SILICA PARTICLES $\rightarrow S = 2,65 \frac{kg}{dm^3}$
 \Rightarrow APPARENT DENSITY, WITH:
 $\left\{ \begin{array}{l} V_{TOT} = 1 \\ \% \text{ OF SILICA} = 70\% \end{array} \right. \Rightarrow S_{APP} = S \cdot 0,7$

DENSITY OF THE ORGANIC FRACTION
 $\hookrightarrow S \approx 1 \frac{kg}{m^3}$

INTRINSIC PERMEABILITY: IMPORTANT PARAMETER OF SOIL

FASE SOLIDA: SUOLO



IN VARIOSE ZONE = MORE COMPLICATE THINGS WE HAVE AT LEAST 3 PHASES (SOIL, AIR, FLUID).
 => WE CANNOT HAVE ONLY 1 VALUE, WE HAVE MORE VALUES, RELATED TO THE WATER CONTENT.
 IF WE ARE NOT IN SATURATED CONDITIONS, WE CAN HAVE A NEGATIVE PRESSURE HEAD.

FASE SOLIDA: SUOLO

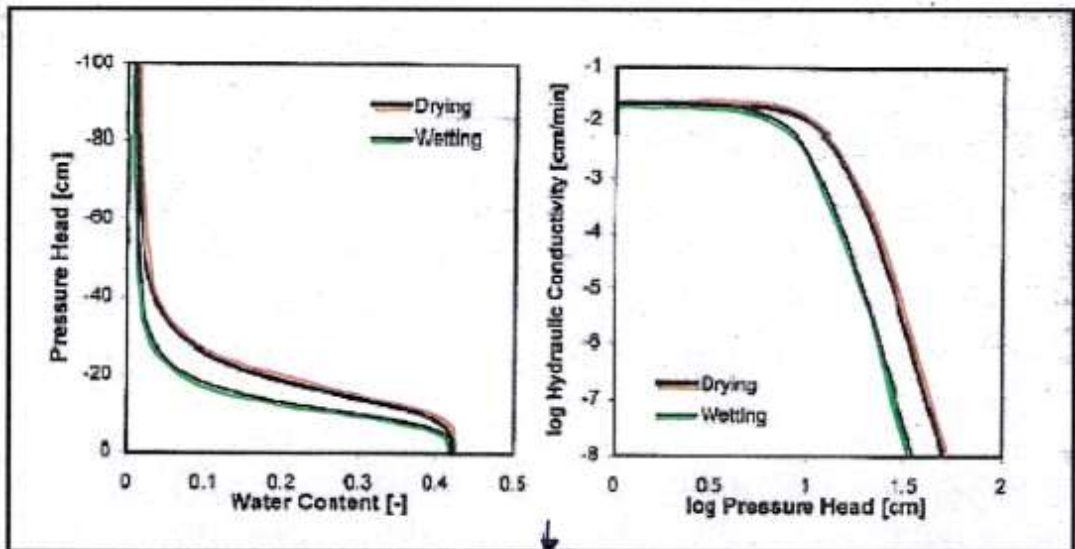
CONDUCIBILITA' IDRAULICA K

$$K = (\rho_w * g / \mu) k_i$$

In cui μ è la viscosità dinamica dell'acqua

ρ, μ ARE RELATIVE TO THE KIND OF FLUID WE HAVE

DOMANDA D'ESAME
 6. DESCRIVI QUESTI 2 GRAFICI



ENTER IN THE GRAPHIC WITH THE PRESSURE AND I DISCOVER WHICH HYDRAULIC CONDUCTIVITY I HAVE

45

MAX WATER CONTENT = POROSITY

FASE SOLIDA: SUOLO

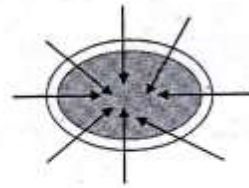
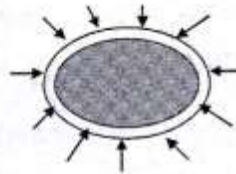
Assorbimento



Adsorbimento

+

Absorbimento



ADSORPTION = A LAYER OF POLLUTANT AROUND
↓ THE PARTICLE IS FORMED.
IT WILL BE MORE IMPORTANT IN THE HIGHEST PART OF SOIL,
AS I HAVE A GREATER AMOUNT OF ORGANIC
IF ↑ DEPTH ⇒ ↓ ADSORPTION

FASE SOLIDA: SUOLO

Adsorbimento

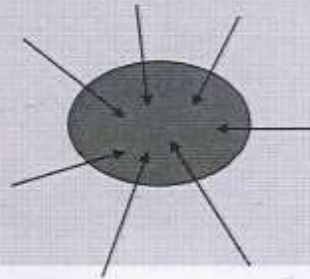
- **Forze di tipo fisico: elettrostatico.** La superficie del mezzo adsorbente può essere carica elettricamente e le particelle di inquinante di carica opposta sono trattenute mediante forze di tipo elettrostatico (adsorbimento in superficie).



FASE SOLIDA: SUOLO

Absorbimento

Le forze che entrano in gioco tra l'inquinante presente in fase liquida e il mezzo adsorbente sono di tipo fisico: di Van Der Waals (dovute alla ridistribuzione degli elettroni) e legami idrogeno. Se il tempo di contatto è sufficientemente lungo l'inquinante può diffondersi all'interno del mezzo adsorbente fino a raggiungere le condizioni di equilibrio secondo un vero e proprio fenomeno di ripartizione.



contaminante	affinità per	interazioni	isoterme
apolare e debolmente polare	fase organica idrofobica delle sostanze umiche	elettrostatiche deboli (Van der Waals) e attrazione idrofobica	tipo C o S
polare neutro	gruppi polari delle sost.umiche, gruppi polari sulla superficie minerale	elettrostatiche forti e deboli (dipolo-dipolo e ione-dipolo)	tipo L
polare cationico	gruppi COO ⁻ delle sostanze umiche, siti di scambio cationico sulla superf.minerale	elettrostatiche forti	tipo H
polare anionico	siti a carica variabile sulla superficie minerale	forte (coordinazione metallo-legante)	tipo L

CHARACTERIZATION OF POLLUTED SITES



PLUME = SOLVED COMPOUNDS → POLLUTANTS.
WE HAVE TO COLLECT SOIL SAMPLES AND WATER SAMPLES, AT DIFFERENT DEPTHS AND POSITIONS → CAUSE IT'S VERY EASY TO HAVE A STRATIFICATION OF THE POLLUTANT.
↳ MULTILEVEL WELLS

LNAPL dynamic



WE MUST REBUILD THIS SITUATION, WE HAVE TO UNDERSTAND HOW BIG IS IT. → ↑ DATA ⇒ ↑ COSTS

OF "POTENTIAL" POLLUTED SITE, WE ARE SURE ABOUT IT AFTER THE CHARACTERISATION.
⊕ UNDERSTAND THE PHYSICS OF THE PHENOMENA AND THE DYNAMIC OF THE POLLUTANT-SOURCE.
ONE POSSIBLE REMEDIATION COULD BE TO CLEAN THE SOURCE, AND THEN WE CLEAN THE GROUND WATER.
TO THE CONTRARY IS A PROBLEM, WE WILL HAVE CONTINUOUS CONTRIBUTIONS OF POLLUTANT FROM AN UNKNOWN SOURCE
⇒ WE HAVE TO WAIT FOR THE EXHAUSTION OF THE SOURCE.
↓
IF I CANNOT FIND A SOURCE, I WILL HAVE TO REMEDIATE THE SOURCE FOR A LONG TIME.

I. Characterization of polluted sites

I.1 Data collection



I.2 Site characterization and conceptual model

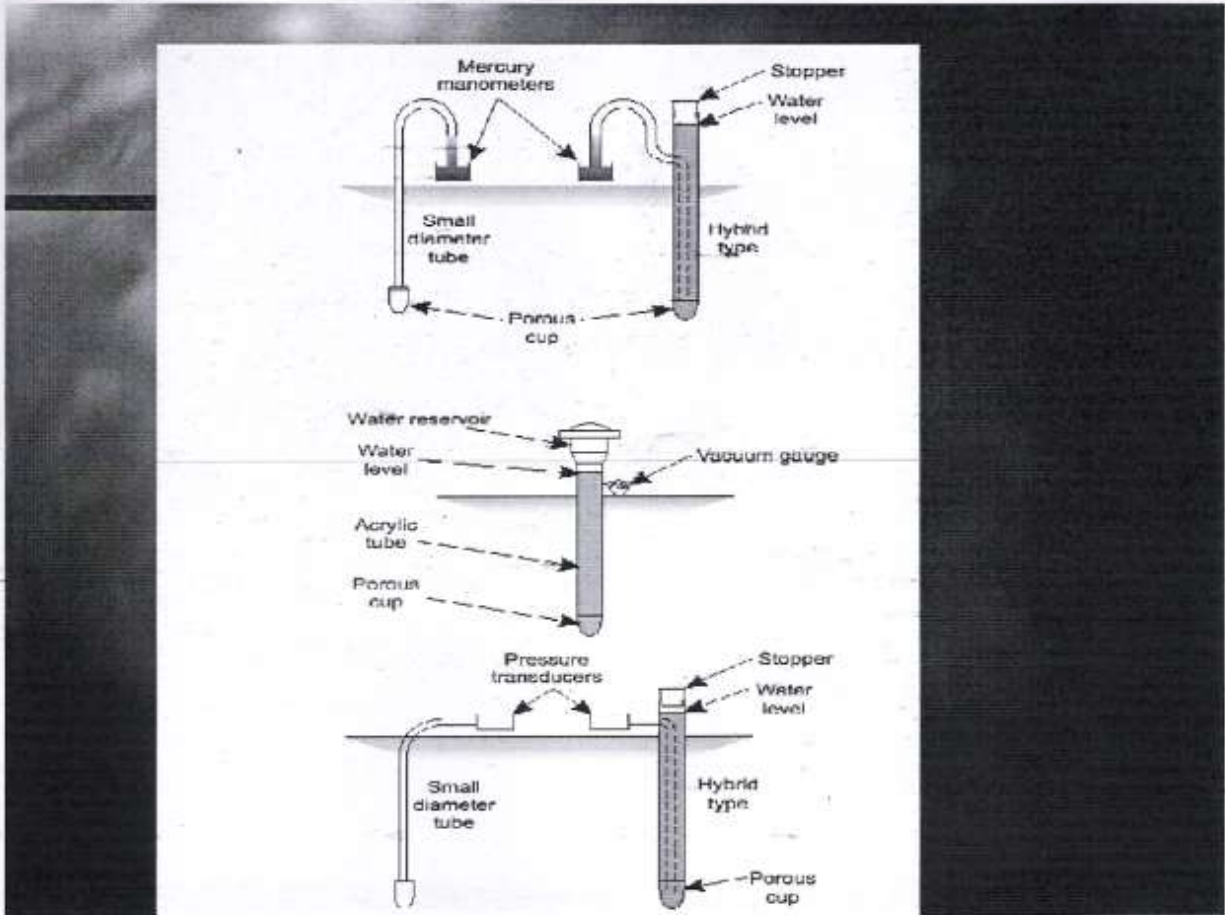
Site characterization

Aims:

- To single out pollutant sources
 - To collect and gain new data concerning geology, hydrogeology and pollution
- To define the extension and characteristics of pollution in different matrices: soil, groundwater, surfacial water

↓
WE ARE NOT ONLY INTERESTED IN POLLUTANT DATA.
GEOLOGICAL → PHYSICS OF SUBSOIL

THERE ARE 3 KINDS OF DEVICES ABLE TO MEASURE THE PRESSURE.



SOIL CHARACTER → PARTICLE SIZE IS VERY IMPORTANT.

POC = IMPORTANT FOR ADSORPTION

Vadose zone characterization

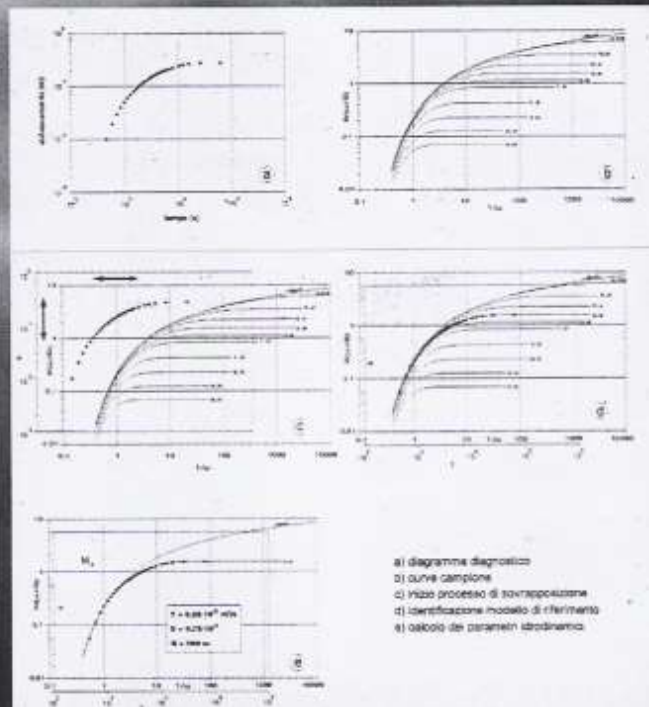
– Aim:

Soil characterization

Main instrument:

Particle-size analysis, organic carbon content, CEC, mineralogic analysis, intrinsic permeability, total porosity, field capacity

Interpretation methods



↳ I HAVE TO FIND WHICH CURVE FIT BETTER MY CURVE

Pollution characterization

- Aim:

Pollutant typology definition, pollutant extension and concentration

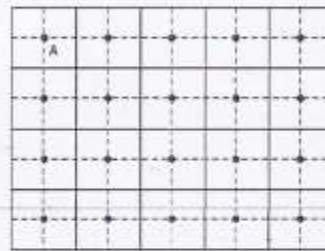
Main instrument:

Correct sampling procedure

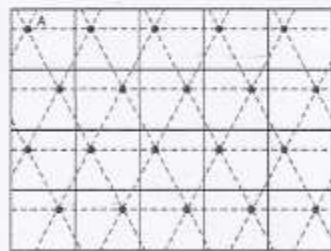
Systematic sampling



(a)



(b)



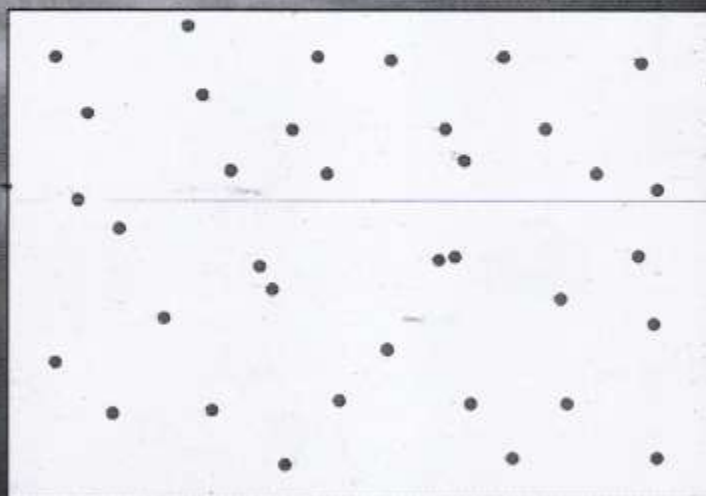
(c)



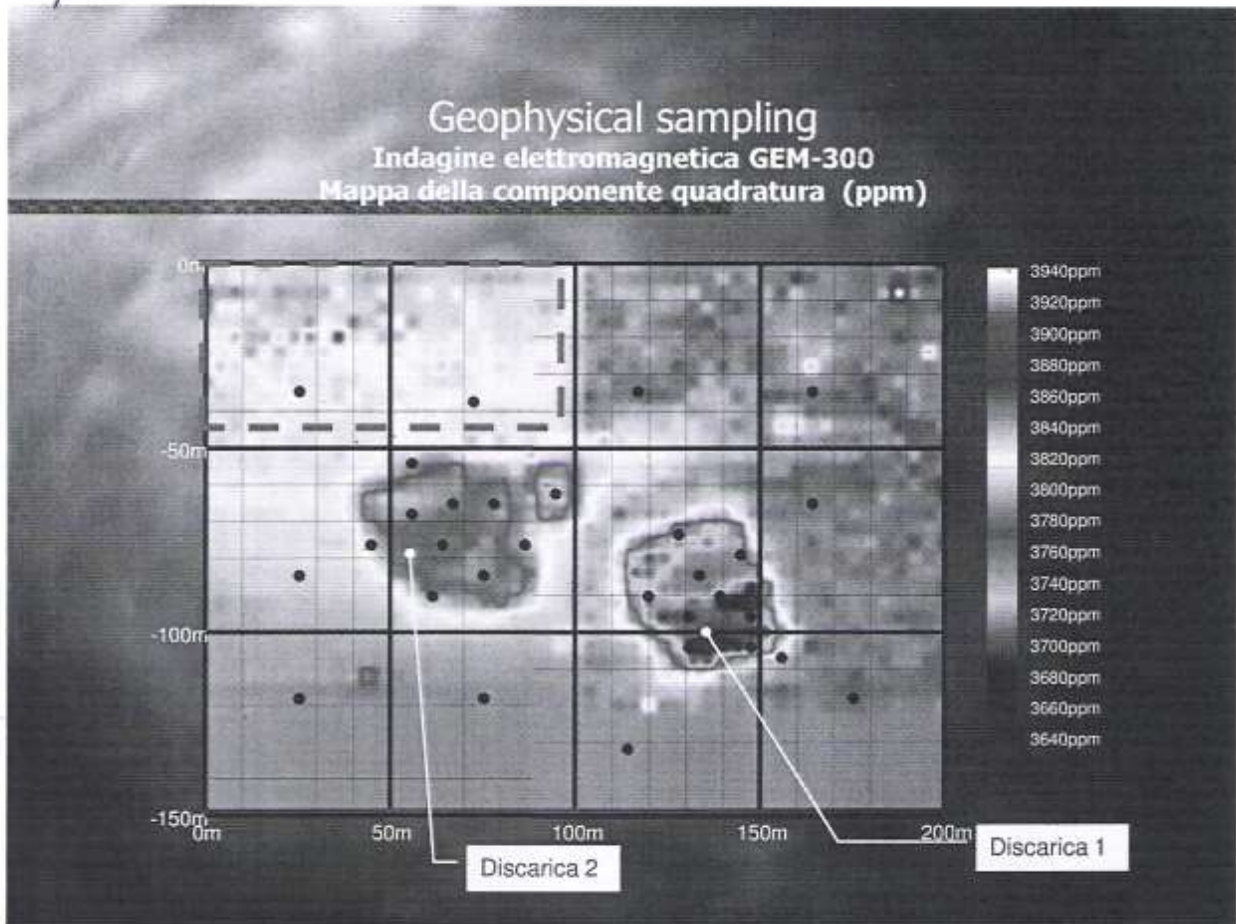
(d)

↳ THESE ARE ACCORDING TO STATISTICAL BASIS

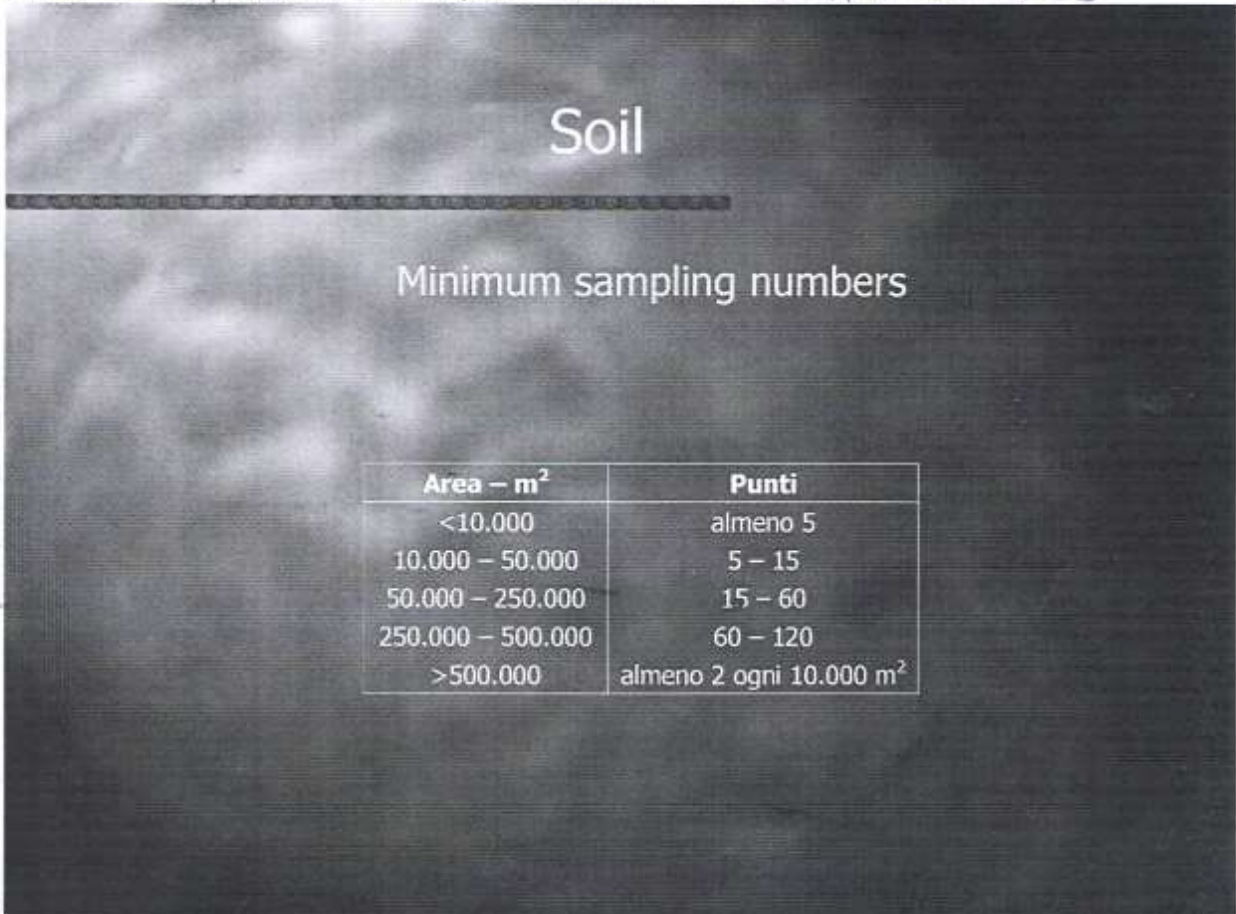
Random sampling



CI SA' SOLO INDICAZIONI DI ANOMALIE, POI SERVONO
ALTRE INDAGINI PER CAPIRE BENE



THIS IS THE MINIMUM N° OF POINTS NEEDED, FOR THE ITALIAN LAW.
IN EACH POINT, I CAN HAVE MORE SAMPLES AT \neq DEPTHS
 \Rightarrow BIG N° OF SAMPLES.
FOR EACH SAMPLE, I DO MANY ANALYSIS \Rightarrow HIGH COMPLEXITY OF PROCEDURES



SOIL SAMPLING

METHODS

- Continuous drilling
- Direct push

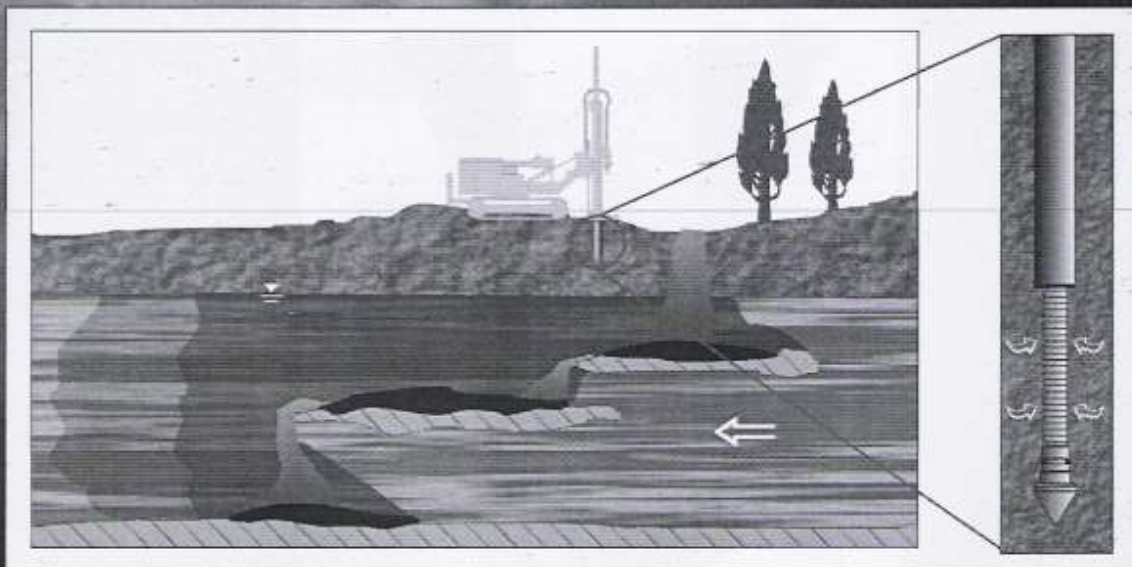
WITHOUT WATER, OR WE RISK TO CHANGE THE [POLLUTANT]!

↑ => DIFFICULT

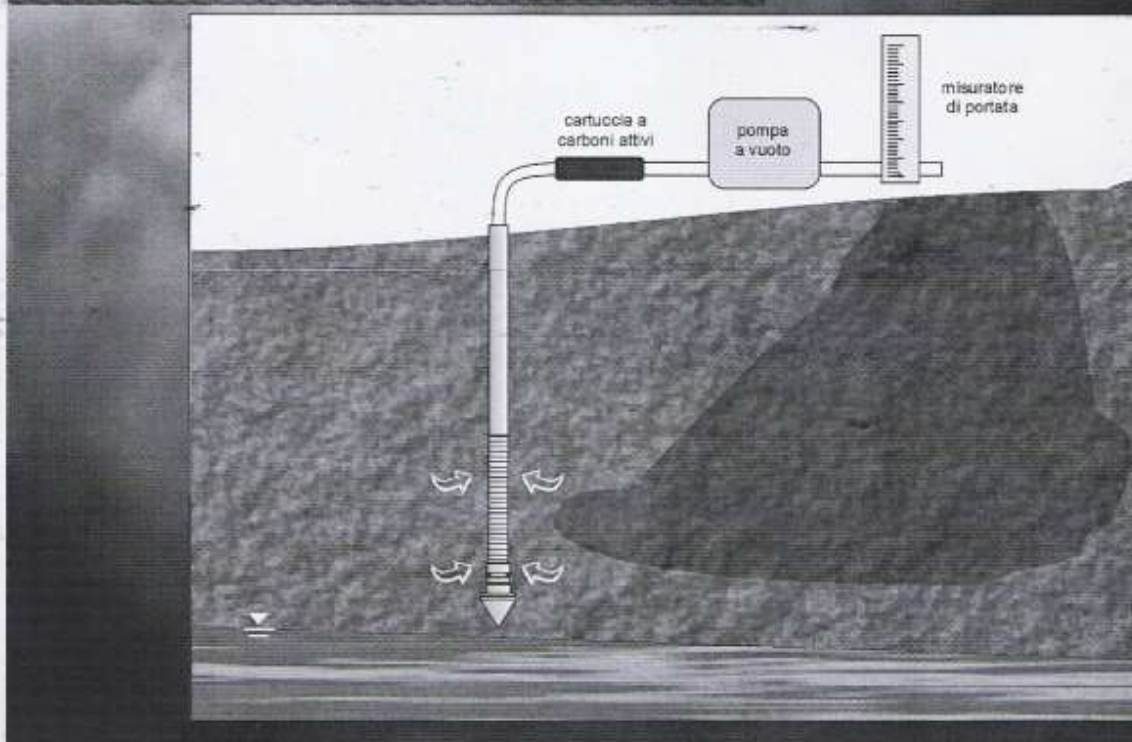
Continuous drilling



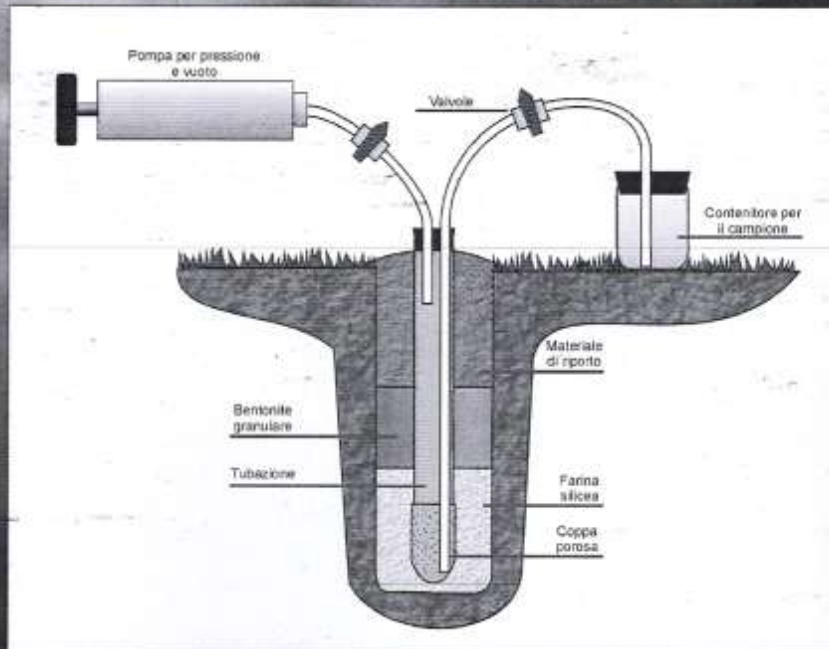
Active sampling



Active sampling

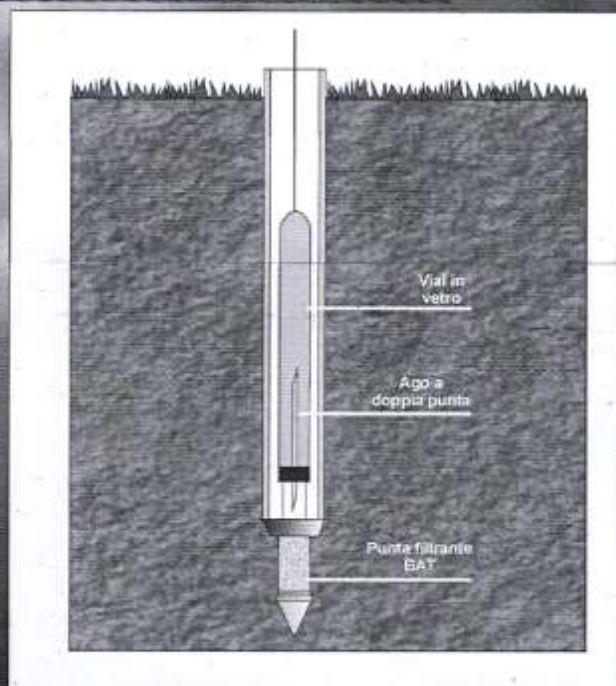


Lisimeter



↓
KIND OF DEVICES
↑

Filtering sampler (BAT)



50 POINTS ⇒ 120 SOIL SAMPLING.
 IT'S AN EXAMPLE OF A REAL CASE OF AN ALMOST SMALL AREA, BUT A HIGH N° OF SAMPLES
 ↳ IT'S NORMAL. FOR A BIGGER AREA → ↑↑↑ n°

Chlorinated solvents pollution

Area: 77.400 m²

50 GEOPROBE drillings

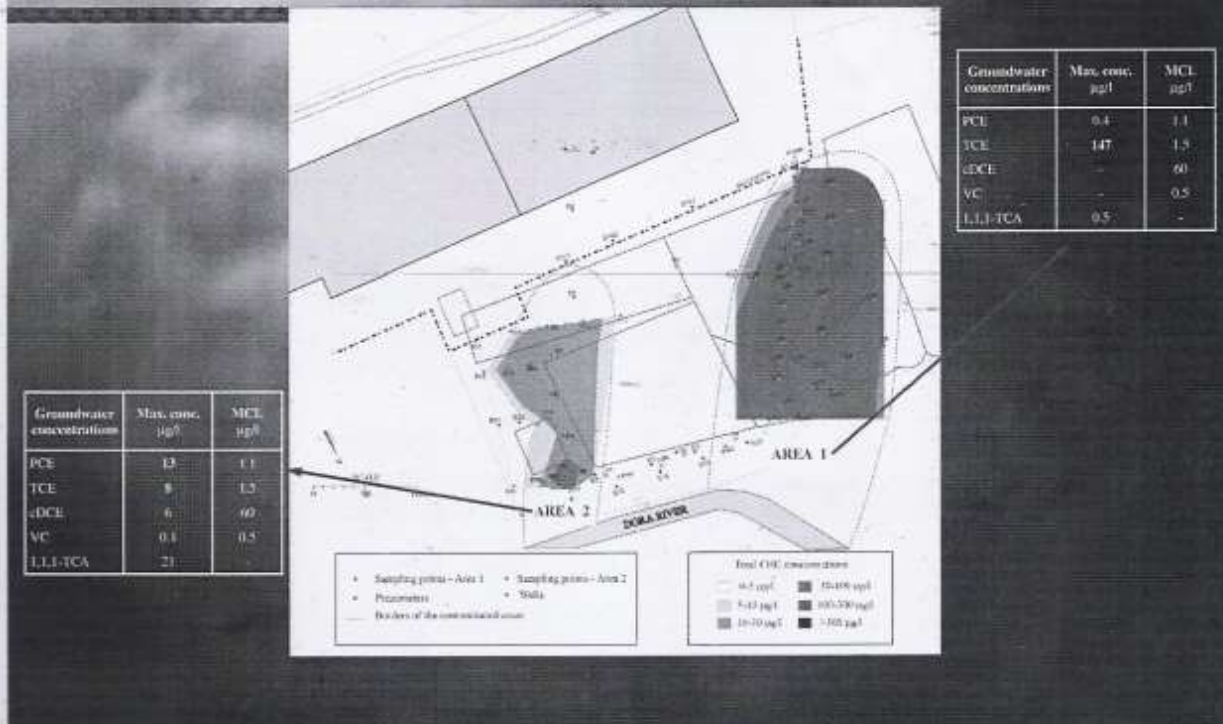
95 interstitial gas sampling

120 soil sampling

463 groundwater sampling

DATA EXTRACTED, AND WE HAVE
 TO COMPARE THEM WITH TABLE
 LIMITS, TO FIND IF THERE ARE PROBLEMS

Inquinamento da solventi clorurati



ASTM RBCA STANDARD AND ENVIRONMENTAL AND SANITARY RISK ANALYSIS

P. A. C. Marescalco, Ph.D. Eng.
7th October 2008

FOR ITALIAN LAW, THIS PROCEDURE IS IMPORTANT TO DEFINE IF A SITE IS POLLUTED.
IT'S AN INTERNATIONAL PROCEDURE, WE CAN HAVE 4 LEVELS.

ENVIRONMENTAL AND SANITARY RISK ANALYSIS

With the words **environmental and sanitary risk analysis** it is meant the **quantification of the toxicological damage to the environment or to human beings as a result of the presence of a contaminating source, whose releases can reach, following several migration paths, a potentially exposed subject (receptor).**

Background:

Introduced at the end of the '80es in the U.S.A. (1989, EPA*).

Codification:

1995, ASTM (American Society for Testing and Materials) E1739;

1998, ASTM PS104 → RBCA** procedure.

*Environmental Protection Agency

**Risk Based Corrective Action

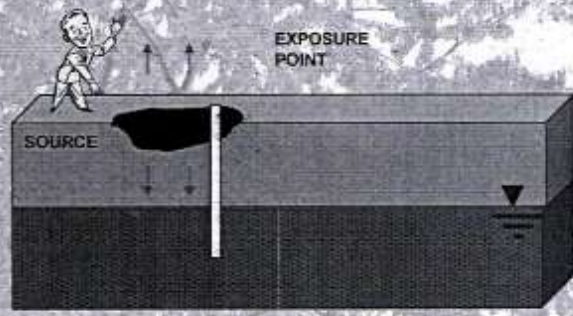
LEVEL I → WHAT DO WE NEED TO DO THE MODEL? →

- KNOW POLLUTION SOURCE
 - UNDERSTAND WHICH ARE THE SUBJECTS POTENTIALLY EXPOSED TO POLLUTION
 - THE WAY IN WHICH SUBJECTS WILL COME IN CONTACT WITH POLLUTION
- DERMAL EXPOSURE, EAT, INHALATION, DRINK POLLUTED WATER FROM GROUNDWATER, USE POLLUTED WATER TO IRRIGATE, ...

WHEN WE HAVE THEM, WE HAVE A MODEL TO START THE RISK ANALYSIS

RISK ANALYSIS: LEVEL I

- ✓ SITE-GENERIC;
- ✓ ON-SITE RECEPTORS;



PROs:

1. We only need to know the source concentration and targets position;
2. Analyses are cheap.

CONs:

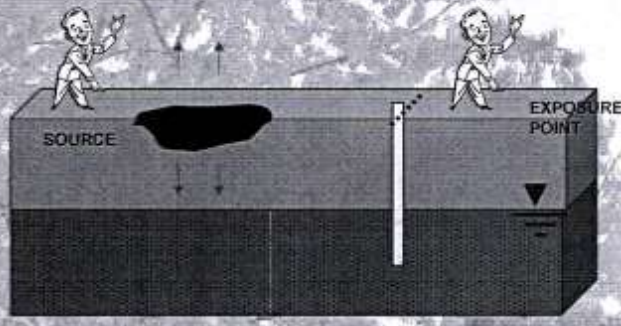
1. Extremely conservative results

LEVEL II → WE NEED SITE SPECIFIC PARAMETERS, AND ALSO THE 3 THINGS SEEN FOR LEVEL I.

→ BUT NOW, WE MUST MEASURE MORE PARAMETERS.

RISK ANALYSIS: LEVEL II

- ✓ SITE-SPECIFIC;
- ✓ ON-SITE AND OFF-SITE RECEPTORS;
- ✓ ANALYTICAL MODELS TO SIMULATE FATE AND TRANSPORT;



PROs:

1. More detailed and precise analysis

CONs:

1. Site-specific parameters are needed;
2. More expensive.

Frequent QUESTION

RISK EVALUATION

THEORETICAL DEFINITION OF RISK. THIS KIND OF DEFINITION IS VALID FOR EVERYTHING.

SAME DEFINITION AS IN INDUSTRIAL SAFETY PROCEDURES:

$$R = P \times D = P \times F_p \times F_e$$

- R: risk associated to a certain event
- P: occurring probability
- D: damage caused by the event
- F_p: danger factor (damage importance – death, injuries, poisoning)
- F_e: contact factor (is a function of exposure duration)

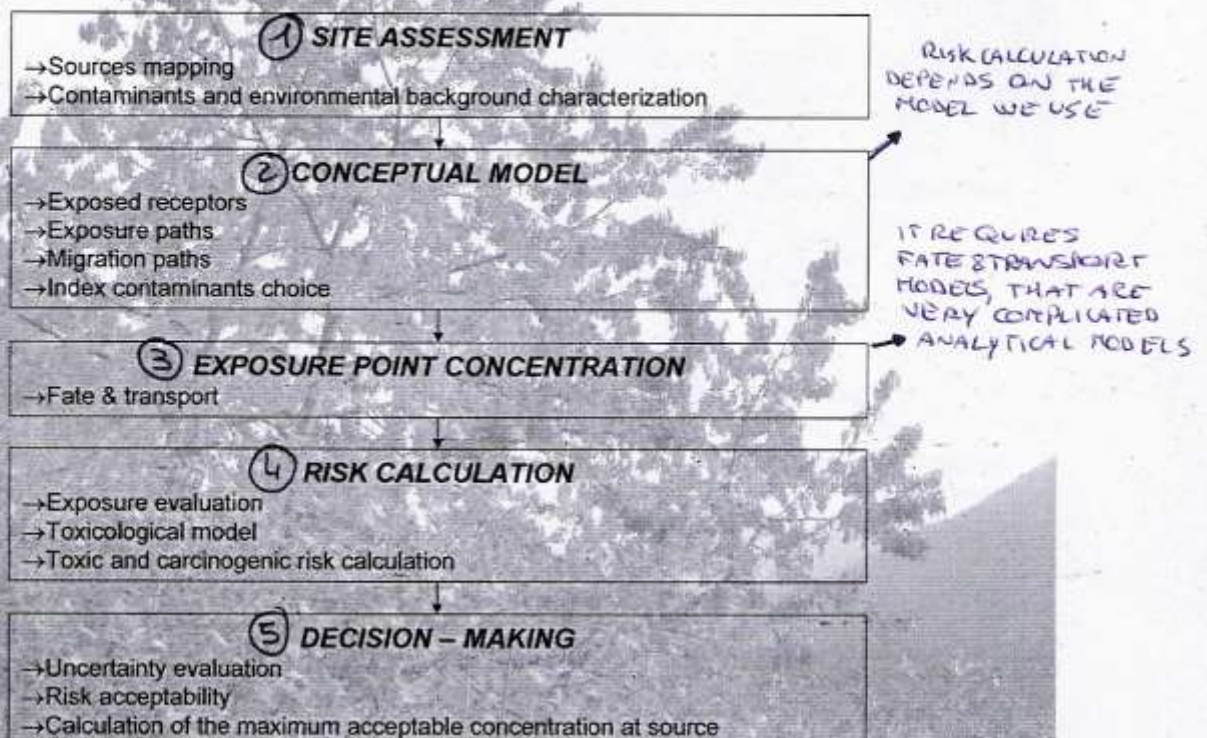
CONTAMINATED SITES:

$$R = E \times T$$

- P = damage occurring probability assessed (P = 1)
- F_p = T [mg/kg d]⁻¹ (contaminant toxicity)
- F_e = E [mg/kg d] (rate of exposure)

IN THIS PROCEDURE, THERE IS A PROBLEM → UNCERTAINTY, BECAUSE WE MUST MAKE SOME ASSUMPTION TO DO CALCULATIONS.

RBCA (ASTM PS104) – RISK ANALYSIS WORKFLOW



ORGANIC/INORGANIC CONTAMINANTS

✓ Generally inorganic contaminants behave as a liquid phase miscible with water while most of organic contaminants are a liquid phase immiscible with water. Immiscible compounds are called NAPLs (Non Aqueous Phase Liquids).

✓ NAPLs are divided in LNAPL (Light NAPLs), which float onto water table (i.e. BTEX), and DNAPL (Dense NAPLs), which tend to cross the saturated zone (i.e. pesticides).

✓ Two different approaches: MADEP (distinction between light and heavy TPH is a function of the number of C atoms) o TPHCWG (TPHs are divided into groups with similar soil mobility – based on “fate & transport” models).

⊕ SUBJECTS:

- ONSITE → PHYSICALLY PEOPLE TOUCHING, EATING, ...
- OFFSITE → AT A CERTAIN DISTANCE FROM THE POLLUTED SITE
↳ I.E.: NEAR TO IT THERE IS A WELL, THAT BRINGS WATER TO HOUSES THAT ARE FAR.

② RBCA (ASTM PS104) – CONCEPTUAL MODEL

Exposed subjects (receptors):

- On site, off site; ⊕
- Residents – adults and kids;
- Workers – remediation operators, other workers.

Use of the site:

- Residential;
- Recreational;
- Industrial and commercial.

Migration paths:

- Unsaturated soil;
- Saturated soil;
- Groundwater;
- Surface water;
- Indoor air;
- Outdoor air.

FIRST HYPOTHESES

For the level II analysis, we assume that:

- ✓ Contaminants soil concentration is homogeneously distributed and is constant for the entire exposure duration;
- ✓ Soil is assumed homogeneous, isotrope, incoherent;
- ✓ No biodegradation mechanisms (except for DAF) and neither decay nor transformation of substances in soil or in water or vapor solutions are considered.

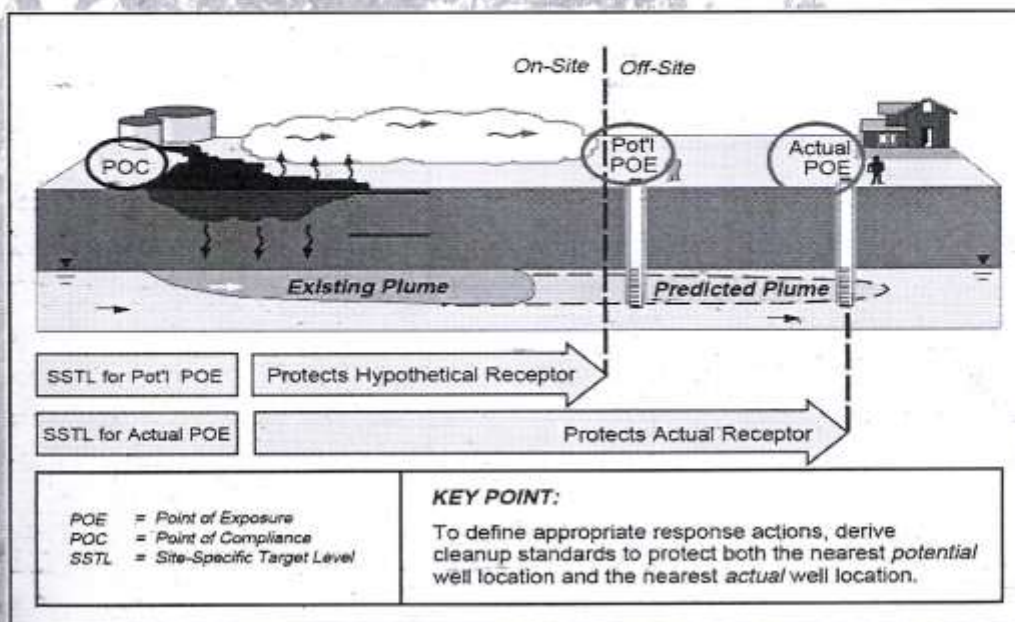
I CAN HAVE A LOT OF DATA BY SAMPLING, BUT IN THE MODEL I HAVE TO PUT ONLY 1 PARAMETER
 => WE HAVE TO CHOOSE THE BEST REPRESENTATIVE DATA

NO BIODEG, BECAUSE THE ANALYSIS MUST BE CONDUCTED IN ABSOLUTELY CONSERVATIVE CONDITION

③ RBCA – FROM POC (SOURCE) TO POE (EXPOSURE POINT)

$$C_{POC} \text{ (mg/l)} = C_{\text{source}} \text{ (mg/kg o mg/l)} / NAF$$

$$C_{POE} \text{ (mg/kg o mg/m}^3 \text{ o mg/l)} = C_{\text{source}} \text{ (mg/kg o mg/l)} / NAF$$



POLLUTION IN SOIL, RAW → TRANSPORT TO GROUNDWATER → PLUME
 ↳ WE HAVE THIS EQUATION TO DESCRIBE IT.
 WE NEED 4 KINDS OF PARAMETERS, DEPENDING ON WHICH EQUATION WE USE

RBCA (ASTM PS104) – TRANSPORT AND TRANSFER MODELS

Soil to leachate partition coefficient:

$$K_{sw} \left[\frac{(mg/L - H_2O)}{(mg/kg - soil)} \right] = \frac{\rho_s}{\theta_{ws} + k_d \rho_s + H \theta_{as}}$$

$$NAF = \frac{C_{source}}{C_{leachate}}$$

Hypotheses for soil-leachate partition calculation:

- Immediate balance between leachate and soil source concentration
- Soil or leachate decay negligible
- Mass in source infinitely bigger than possible leachate release

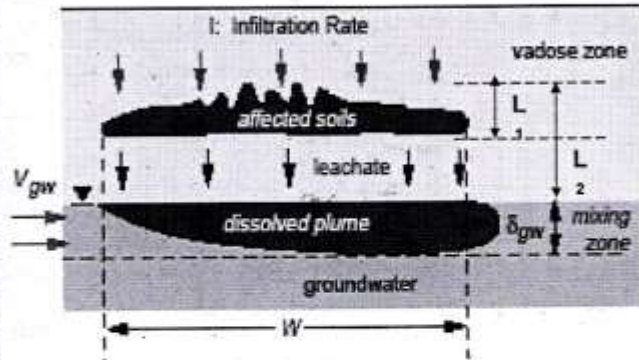
- Source and site geometry parameters
- Soil or groundwater specific parameters
- Substance specific parameters

Soil attenuation model:

$$SAM[-] = \frac{L_1}{L_2}$$

Hypotheses for SAM:

- Volatilization and biodegradation are negligible
- Mass conservation per each contaminant



Leachate dilution factor:

$$LDF [dimensionless] = 1 + \frac{V_{gw} \delta_{gw}}{W}$$

$$\delta_{gw} = \sqrt{2 \cdot \alpha_t \cdot W + d_s} \cdot \left[1 - e^{-\frac{W}{d_s}} \right]$$

RBCA INPUT PARAMETERS

WE NEED A LOT OF PARAMETERS

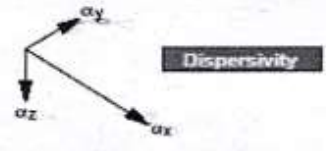
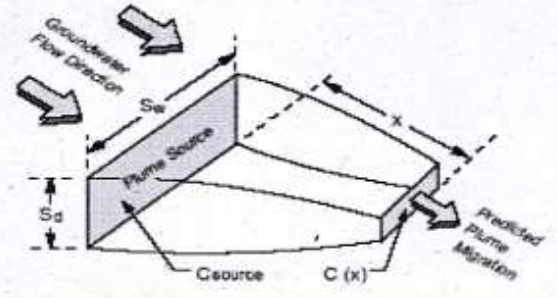
TABLE 2. PARAMETER SELECTION GUIDELINES: SOIL-TO-GROUNDWATER LEACHATE MODELS (EQUATIONS CM-7 AND CM-8)

Symbol ⁽¹⁾	Description	Typical Range	Parameter Measurement or Estimation Guidelines	Reference
SITE-SPECIFIC PARAMETER MEASUREMENTS				
W	Soil source zone dimension parallel to groundwater flow direction (cm)	Site-specific	Measure lateral extent of soil zone serving as source of leachate release to underlying groundwater (e.g., exceeding Tier 1 limits) along line parallel to natural groundwater flow.	Conner et al., 1995
f _{oc}	Fraction of organic carbon in soil (g-C/g-soil)	0.001 - 0.03	Measure on representative unaffected soil samples over vertical depth interval of vapor migration or use generic lowerbound value of 0.01 for vadose zone.	La Grega, 1994
V _{gw}	Groundwater Darcy velocity (cm-w)	Site-specific	Estimate as follows: V _{gw} = K * i where K and i are defined as noted below.	Bedient et al., 1994
K	Hydraulic conductivity of water-bearing unit (cm-sec)	Site-specific	Measure K values varied upon either i) ring-based slug tests or ii) constant-rate aquifer pumping tests conducted on wells properly installed and developed in water-bearing unit. Re-evaluate test results if measured values fall outside typical range for predominant soil type, as follows: Clays: 1×10^{-6} cm/s Silts: 1×10^{-6} - 1×10^{-3} cm/s Silty Sands: 1×10^{-4} - 1×10^{-2} cm/s Clean Sands: 1×10^{-2} - 1 cm/s Gravels: > 1 cm/s	Bedient et al., 1994
i	Lateral hydraulic flow gradient of water-bearing unit (cm/cm)	0.001 - 0.1	Measure lateral flow gradient in area beneath soil source zone based on triangulation among 3 or more monitoring wells or piezometers screened within water-bearing unit.	Newell et al., 1992
delta _{gw}	Groundwater mixing zone thickness (cm)	Site-specific	Measure vertical extent of affected groundwater zone within water-bearing unit in area underlying soil source zone. If vertical plume extent undetermined at this location, use lowerbound estimate (e.g., 200 cm).	ASTM, 1995
REASONABLE PARAMETER ESTIMATES				
i	Infiltration rate of water through soil (cm-year)	-----	Estimate i as fraction of annual rainfall (P) in site area, depending on predominant surface soil type, as follows: Clayey Soils: $i = (1 - 2\%) \times P$ Sandy Soils: $i = (3 - 10\%) \times P$ Paved Slur: $i = (0.1 - 1\%) \times P$	(NOTE: Values are preliminary. Supporting guidelines under development.)
rho _s	Soil bulk density (g-soil/cm ³ -soil)	-----	Use median soil value of 1.7 g/cm ³	ASTM, 1995
theta _{ws}	Volumetric water content in vadose zone soils (cm ³ -H ₂ O/cm ³ -soil)	-----	Estimate based on predominant soil type as follows: Uniform Sand: 13% Soft Clay: 5% Mixed-Grain-Sand: 16% Stiff Clay: 34% Silt: 4% NOTE: Typical theta _{ws} values approximated as saturated water content minus specific yield of soil.	Beck et al. 1974 Todd, 1980
theta _{as}	Volumetric air content in vadose zone soils (cm ³ -air/cm ³ -soil)	-----	Calculate as theta _{as} = theta _v - theta _{ws} , where theta _{ws} and theta _v estimated per predominant soil type as above. NOTE: Values correspond to drained conditions. Dry weather may increase theta _{as} in near-surface silts and clays (< 6 ft depth).	Beck et al. 1974 Todd, 1980
NOTE: See Equations CM-7 and CM-8 on Figure 2 regarding use of the above parameters for estimation of soil-to-groundwater leaching factor for affected soils. Detailed discussion of this soil leachate model is provided in the Tier 2 RBCA Guidance Manual (Conner et al., 1995).				

RBCA (ASTM PS104) – TRANSPORT AND TRANSFER MODELS

Lateral groundwater dilution-attenuation:

- DOMENICO SOLUTION**
- Spatial 3D domain
 - Natural decay (first order kinetics)
 - Areal source with continuous release
 - Advection, hydrodynamic dispersion, adsorbing
 - Vertical and transversal dispersion in two directions



$$\frac{C(x)_i}{C_{si}} = \exp\left(\frac{x}{2\alpha_x} \left[1 - \sqrt{1 + \frac{4\lambda_i \alpha_x R_i}{v}}\right]\right) \operatorname{erf}\left(\frac{S_w}{4\sqrt{\alpha_x x}}\right) \operatorname{erf}\left(\frac{S_d}{4\sqrt{\alpha_z x}}\right)$$

Solution on the plume centerline at steady state condition

$$v = \frac{K \cdot i}{\theta_e}$$

THERE ARE 7 EQUATIONS FOR 7 TRANSPORT MODELS

RBCA INPUT PARAMETERS

TABLE 3. PARAMETER SELECTION GUIDELINES: LATERAL GROUNDWATER TRANSPORT MODEL (EQUATION LT-1) continued

Input Parameter		Typical Range	Parameter Measurement or Estimation Guidelines	Reference
Symbol	Description			
SITE-SPECIFIC PARAMETER MEASUREMENTS (CONT'D)				
k_d	Soil-water sorption coefficient (g-H ₂ O/g-soil)		For organics, estimate as $k_d = K_{oc} \times f_{oc}$. For ionizing organics (e.g., chlorophenols), estimate k_d based on published pH dependent partitioning coefficients for ionized and neutral forms. For inorganics, estimate k_d as published pH-dependent isotherms, based on measured groundwater pH. See EPA SSL Guidance for detailed information.	U.S. EPA, 1996
f_{oc}	Fraction of organic carbon in soil (g-C/g-soil)	0.001 - 0.03	Measure depth from ground surface to top of affected source zone. Measure average vertical dimension from top to base of affected soil zone over area corresponding to W. Generic lowerbound value of 0.001.	Larega, 1994
BC_i	Biodegradation capacity for constituent i	Site-specific	If using electron-acceptor superposition form of Domenico model (Equation LT-1b), calculate BC_i value as indicated on Figure 3. Detailed instructions for BC_i and BC_j estimation are provided in BIOSCREEN user's manual (Newell et al., 1996). Calculation must be based on site-specific measurement of principal electron acceptor concentrations in site groundwater.	Newell et al., 1996 Connor et al., 1995
X	Distance from source to downgradient POE (cm)	Site-specific	Measure from source term location to downgradient POE location along line of groundwater flow.	Connor et al., 1995
S_w	Groundwater source term width (cm)	Site-specific	See Figure 4 for guidelines regarding site-specific determination of source width of water-bearing unit.	Connor et al., 1995
S_d	Groundwater source term thickness (cm)	Site-specific	See Figure 4 for guidelines regarding site-specific determination of source thickness in water-bearing unit.	Connor et al., 1995
REASONABLE PARAMETER ESTIMATES				
n_e	Effective porosity of water-bearing unit (cm ³ -pore/cm ³ -soil)	0.001 - 0.1	Match to representative value for predominant soil type in water-bearing unit as follows: Clay = 0.01 - 0.20 Silt = 0.01 - 0.30 Fine Sand = 0.10 - 0.30 Med. Sand = 0.15 - 0.30 Coarse Sand = 0.20 - 0.33 Gravel = 0.10 - 0.35	Domenico et al., 1990 Walton, 1983

RBCA INPUT PARAMETERS

TABLE 1. PARAMETER SELECTION GUIDELINES: VOLATILIZATION MODELS

Input Parameter		Typical Range	Parameter Measurement or Estimation Guidelines	Reference
Symbol	Description			
SITE-SPECIFIC PARAMETER MEASUREMENTS				
W	Soil source zone dimension parallel to wind direction (cm)	Site-specific	Measure lateral extent of soil zone serving as source of vapor release (e.g., zone exceeding Tier 1 limits). For on-site POE, use maximum lateral source dimension. For off-site POE, use dimension measured along line passing from source zone to nearest downwind off-site POE location.	Connor et al, 1995
L _{GW}	Depth to groundwater	Site-specific	For unconfined unit, measure depth to static water level. For confined unit, measure depth to top of water-bearing stratum.	Connor et al, 1995
L _s	Depth to subsurface soil source (cm)	Site-specific	Measure depth from ground surface to top of affected source zone.	Connor et al, 1995
d or d _s	Thickness of affected soil zone	Site-specific	Measure average vertical dimension from top to base of affected soil zone over lateral area corresponding to W.	Connor et al, 1995
h _v	Thickness of vadose zone (cm)	Site-specific	Measure from ground surface to depth of static water level in unconfined unit. In confined unit, measure from ground surface to depth of soil saturation (often corresponding to potentiometric surface elevation).	Connor et al, 1995
f _{oc}	Fraction of organic carbon in soil (g-C/g-soil)	0.001 - 0.03	Conduct lab analyses on representative unaffected soil samples over depth interval of vertical vapor migration or use generic value of 0.01 for vadose zone.	LaGrega, 1994
REASONABLE PARAMETER ESTIMATES				
U _{air}	Wind speed above ground surface in ambient mixing zone (cm/s)	45 - 450 cm/sec	Match to average annual windspeed for site area, based on published climatic data.	Connor et al, 1995
O _{air}	Ambient air mixing zone height (cm)	200 cm	Match to typical height of human breathing zone (6 ft or 2m).	Connor et al, 1995
k _s	Soil-water sorption coefficient (g-H ₂ O/g-soil)	---	For organics, estimate as: k _s = k _{oc} × f _{oc} . For ionizing organics (e.g., chlorophenols), estimate k _s based on published pH-dependent partitioning coefficients for ionized and neutral forms. For inorganics, estimate k _s per published pH-dependent isotherms, based on measured groundwater pH. Detailed guidelines provided in U.S. EPA SSL Background Document (1996).	U.S. EPA, 1996
ρ _s	Soil bulk density (g-soil/cm ³ -soil)	1.6 - 1.75	Use median soil value of 1.7 g/cm ³ .	ASTM, 1995
θ _T	Total soil porosity (cm ³ -pore space/cm ³ -soil)	35 - 55%	Estimate based on predominant soil type as follows: Uniform Sand: 40% Soft Clay: 55% Mixed-Grain-Sand: 35% Silt Clay: 37% Silt: 50%	Peck et al, 1974
θ _{wt}	Volumetric water content in vadose zone soils (cm ³ -H ₂ O/cm ³ -soil)	13 - 52%	Estimate based on predominant soil type as follows: Uniform Sand: 13% Soft Clay: 52% Mixed-Grain-Sand: 18% Silt Clay: 34% Silt: 42% NOTE: Typical θ _{wt} values approximated as saturated water content initial specific yield of soil.	Peck et al, 1974 Todd, 1980
θ _{at}	Volumetric air content in vadose zone soils (cm ³ -air/cm ³ -soil)	3-27%	Calculate as θ _{at} = θ _T - θ _{wt} , where θ _{wt} and θ _T estimated per predominant soil type as above.	Peck et al, 1974 Todd, 1980
NOTE: See Equation CM 1 through CM 6 on Figure 2 regarding use of the above parameters for estimation of steady-state volatilization factors for affected soils. Detailed discussion of these volatilization models is provided in the Tier 2 RBCA Guidance Manual (see Connor et al, 1995).				

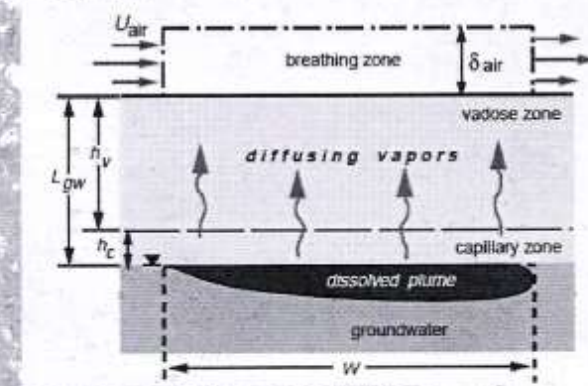
RBCA INPUT PARAMETERS

TABLE 1. PARAMETER SELECTION GUIDELINES: VOLATILIZATION MODELS

continued

Input Parameter		Typical Range	Parameter Measurement or Estimation Guidelines	Reference
Symbol	Description			
REASONABLE PARAMETER ESTIMATES (CONT'D)				
k _{cap}	Thickness of capillary fringe (cm)	2 - 300 cm	Estimate based on predominant soil type, as follows: Medium Sand: 25 cm Clayey Silt: 200 cm Fine Silt: 43 cm Silt: 105 cm	Todd, 1980
P _e	Particulate emission rate (g/cm ² -s)	---	Use generic upperbound value (e.g., 6.9 × 10 ⁻¹⁴ g/cm ² -sec) or estimate reasonable site-specific value using method outlined in U.S. EPA SSL guide.	ASTM, 1995 EPA, 1996
τ	Averaging time for vapor flux (s)	---	Match to assumed exposure duration (in seconds).	ASTM, 1995
ER	Enclosed space air-exchange rate (L/s)	---	Use generic lowerbound value (e.g., 0.00014 L/s for residential, 0.00023 L/s commercial) or match to minimum allowable indoor air ventilation rate per local building code.	ASTM, 1995
L _B	Ratio of enclosed space volume to infiltration area (cm)	---	Use generic lowerbound value (e.g., 200 cm) or develop reasonable estimates based on size (no. of floors) and area (foundation outline) of typical residential or commercial structures in site area.	ASTM, 1995
L _{crack}	Enclosed space foundation or wall thickness (cm)	---	Use generic upperbound value (e.g., 15 cm) or match to local building code specifications for residential or commercial structures.	ASTM, 1995
Z	Areal fraction of cracks in foundations/walls (cm ² -cracks/cm ² -total area)	---	Use generic upperbound value (e.g., 1%) or estimate based on observed site conditions.	ASTM, 1995
CHEMICAL-SPECIFIC PARAMETER VALUES				
H	Henry's Law Constant (cm ³ -H ₂ O/cm ³ -air)	---	Use median value reported for each constituent of concern in published chemical reference.	Connor et al, 1995 a
k _{oc}	Carbon-water sorption coefficient (g-H ₂ O/g-C)	---	Use median value reported for each constituent of concern in published chemical reference.	Connor et al, 1995 a
D ^{air}	Diffusion coefficient in air (cm ² -s)	---	Use median value reported for each constituent of concern in published chemical reference.	Connor et al, 1995 a
D ^{wat}	Diffusion coefficient in water (cm ² -s)	---	Use median value reported for each constituent of concern in published chemical reference.	Connor et al, 1995 a
D ^{soil}	Effective diffusivity in vadose zone soils (cm ² -s)	---	Estimate as shown on Figure 2.	---
D ^{at}	Effective diffusivity above the water table (cm ² -s)	---	Estimate as shown on Figure 2.	---
NOTE: See Equation CM 1 through CM 6 on Figure 2 regarding use of the above parameters for estimation of steady-state volatilization factors for affected soils. Detailed discussion of these volatilization models is provided in the Tier 2 RBCA Guidance Manual (see Connor et al, 1995).				

RBCA (ASTM PS104) – TRANSPORT AND TRANSFER MODELS



Groundwater volatilization factor:

$$VF_{wamb} \left[\frac{(mg/m^3 - air)}{(mg/L - H_2O)} \right] = \frac{H}{1 + \left[\frac{U_{air} \delta_{air} L_{GW}}{WD_{ws}^{eff}} \right]} \times 10^3$$

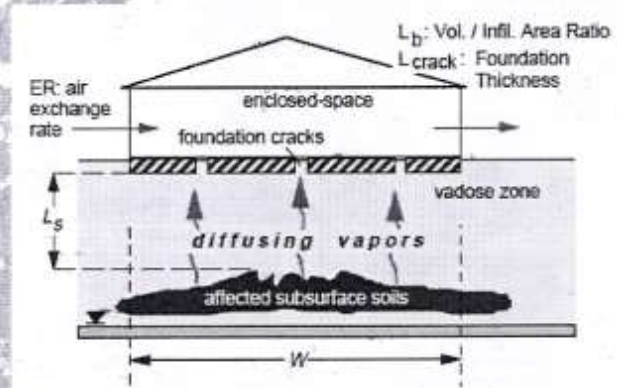
D_{vs}^{eff} Effective diffusivity above the water table:

$$D_{vs}^{eff} \left[\frac{cm^2}{s} \right] = (h_{cap} + h_v) \left[\frac{h_{cap}}{D_{cap}^{eff}} + \frac{h_v}{D_s^{eff}} \right]^{-1}$$

D_{cap}^{eff} Effective diffusivity in the capillary zone:

$$D_{cap}^{eff} \left[\frac{cm^2}{s} \right] = D_{air}^{eff} \frac{\theta_{acap}^{3.33}}{\theta_1^2} + \left[\frac{D^{wat}}{H} \right] \left[\frac{\theta_{wcap}^{3.33}}{\theta_1^2} \right]$$

RBCA (ASTM PS104) – TRANSPORT AND TRANSFER MODELS



Soil to enclosed space volatilization factor:

$$VF_{seep} \left[\frac{(mg/m^3 - air)}{(mg/kg - soil)} \right] = \frac{H \rho_s}{\left[\theta_{ws} + k_s \rho_s + H \theta_{as} \right]} \left[\frac{D_s^{eff} / L_s}{ER L_b} \right] \times 10^3$$

$$1 + \left[\frac{D_s^{eff} / L_s}{ER L_b} \right] + \left[\frac{D_s^{eff} / L_s}{(D_{crack}^{eff} / L_{crack}) \eta} \right]$$

D_{crack}^{eff} Effective diffusivity through foundation cracks:

$$D_{crack}^{eff} \left[\frac{cm^2}{s} \right] = D_{air}^{eff} \frac{\theta_{acrack}^{3.33}}{\theta_1^2} + \left[\frac{D^{wat}}{H} \right] \left[\frac{\theta_{wcrack}^{3.33}}{\theta_1^2} \right]$$

RBCA INPUT PARAMETERS

TABLE 4. PARAMETER SELECTION GUIDELINES: LATERAL AIR TRANSPORT MODEL (EQUATION LT-2)

Input Parameter		Typical Range	Parameter Measurement or Estimation Guidelines	Reference
Symbol	Description			
SITE-SPECIFIC PARAMETER MEASUREMENTS				
L	Length of affected soil zone parallel to wind direction (cm)	Site-specific	Determine lateral extent of affected soil zone serving as source of vapor release (e.g., zone exceeding Tier 1 limits) measured along line passing from source zone to downwind off-site POE	Connor et al, 1995
A	Lateral area of affected soil zone (cm ²)	Site-specific	Measure areal extent of affected soils serving as source of vapor release (e.g., zone exceeding Tier 1 limits)	Connor et al, 1995
X	Lateral distance downwind of source zone (cm)	Site-specific	For most conservative evaluation, measure as distance from edge of affected soil zone to nearest off-site POE location (in same direction as L above). For typical case, measure this distance along line of predominant annual wind direction.	Connor et al, 1995
REASONABLE PARAMETER ESTIMATES				
U _{air}	Windspeed above ground surface in ambient mixing zone (cm/s)	45 - 450 cm/sec	Match to average annual windspeed for site area, based on published climatic data	Connor et al, 1995
δ _{air}	Ambient air mixing zone height (cm/s)	200 cm	Match to typical height of human breathing zone (6 ft or 2m)	ASTM, 1995
γ	Transverse distance off air plume centerline (cm)	----	To evaluate exposure concentrations along plume centerline, γ is set equal to zero	Connor et al, 1995
z	Height of breathing zone (cm)	----	Assume equal to δ _{air} above.	Connor et al, 1995
σ _y , σ _z	Air dispersion coefficients (cm) in the transverse (y) and vertical (z) directions	----	For average annual climatic conditions, characterize σ _y , σ _z based on Stability Class C (slightly unstable) using the following relationships: $\sigma_y = 10(\text{Log}(x) + 0.941 - 0.041)$ $\sigma_z = 10(\text{Log}(x) + 0.827 - 1.01)$ If Stability Class C determined to be inapplicable, estimate air dispersion coefficient values using Pasquill-Gifford system as discussed in DeVull et al. 1994.	Connor et al, 1995 DeVull et al, 1994 U.S. EPA, 1988
C _g	Concentration of constituent i in ambient air at point source	----	Estimate based on appropriate soil-to-air volatilization model (see Equations CM-1 through CM-3 on Figure 2) or conduct site-specific measurements in breathing zone air overlying affected soil source area.	Connor et al, 1995

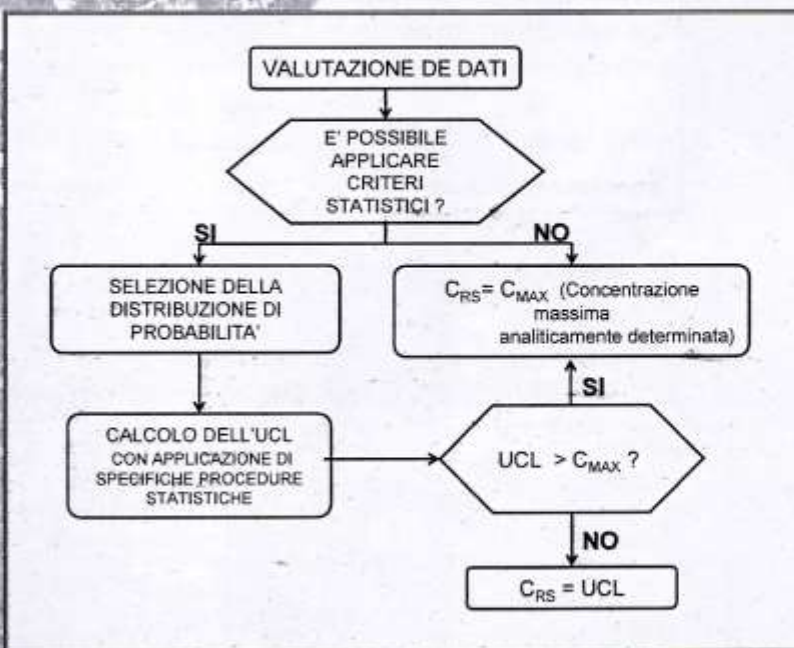
NOTE: See Equation LT-2 on Figure 3 regarding use of the above parameters for estimation of lateral air dispersion factor for wind-borne contaminant transport to downwind receptor. Detailed discussion of this air dispersion model is provided in the Tier 2 RBCA Guidance Manual (see Connor et al. 1995).

IN GENERAL, WE HAVE SEVERAL VALUES FOR EACH PARAMETER. ⇒ THE MORE CONSERVATIVE VALUE IS NOT ALWAYS THE MAXIMUM VALUE (BUT IT IS VERY OFTEN SO).
 ⇒ WE NEED TO CHOOSE WHICH ONE TO USE.
 IF WE HAVE N/A VALUES FOR A PARAMETER, WE CHOSE THE MORE CONSERVATIVE ONE → THE MAXIMUM VALUE.
 BECAUSE IT'S NOT POSSIBLE TO DO A STATISTICAL ANALYSIS
 SPECIFIC ANALYSIS → IT'S POSSIBLE TO DO IT
 ⇒ I.E. IF I HAVE A GAUSSIAN DISTRIBUTION THE MORE CONSERVATIVE VALUE IS THE ONE FOR WHICH I HAVE THE 95% OF DATA

DATASET EVALUATION



- ✓ Number of data available (surveys within the investigated area): $N \geq 10$
- ✓ Sampling of the source homogeneously distributed
- ✓ Outlier/Non detected
↓
ERRORS



DATA DISTRIBUTION

Gaussian or normal distribution: symmetrical distribution whose central value is given by the arithmetic mean of the parameter values. $x_1, x_2, x_3, \dots, x_n$

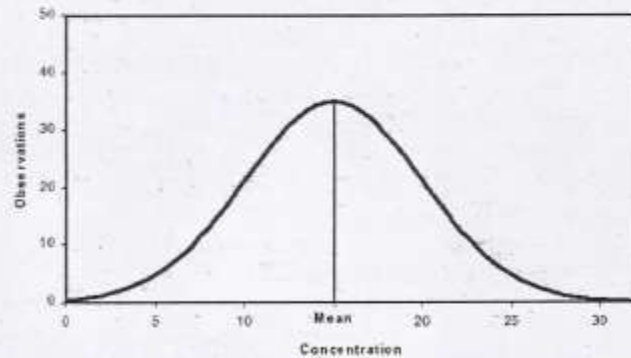
The normal distribution shape is given by the probability density function, determined by two parameters: the arithmetic mean and the sample variance, which represents the data dispersion from the mean value.

Function $f(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{1}{2\sigma^2}(x-\bar{x})^2\right]$

Mean $\bar{x} = \frac{1}{n} \sum_{i=1}^n x_i$

Variance $\sigma^2 = \frac{1}{n-1} \sum_{i=1}^n (x_i - \bar{x})^2$

EXAMPLE OF A NORMAL DISTRIBUTION



DATA DISTRIBUTION

Lognormal distribution: the lognormal distribution is an asymmetric distribution, which follows from the geometric mean calculation. Its shape is delimited on the left by the zero value, while on the right is kind of leaning.

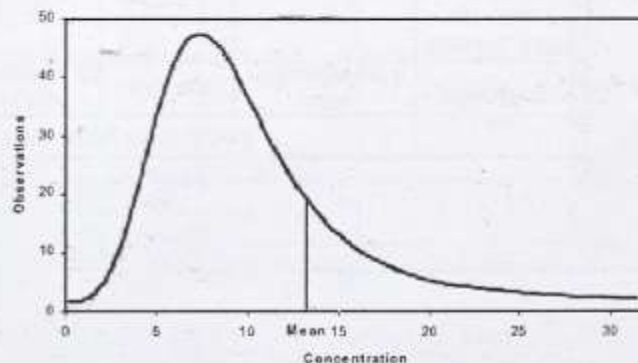
Lognormal distribution is defined by two parameters \bar{y} and σ_y^2 (where $y = \ln x$).

Function $f(x) = \frac{1}{x\sigma_y\sqrt{2\pi}} \exp\left[-\frac{1}{2\sigma_y^2}(\ln x - \bar{y})^2\right]$ $x > 0$ $-\infty < \bar{y} < \infty$ $\sigma_y > 0$

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

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

EXAMPLE OF A LOGNORMAL DISTRIBUTION



METHODS TO ESTIMATE THE REPRESENTATIVE CONCENTRATION

UCL

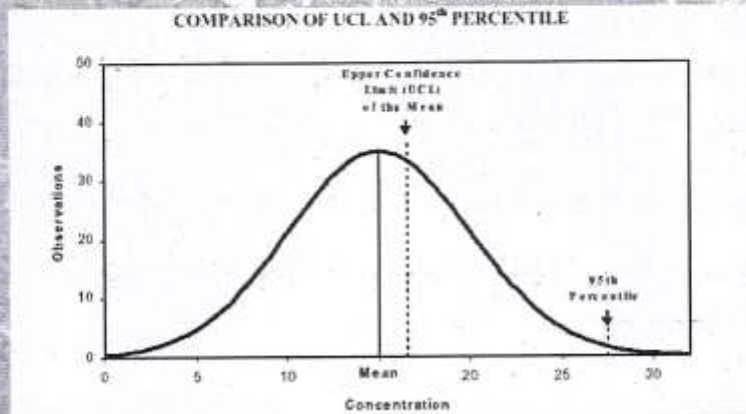
Normal distribution

1. Student "t" method

Log normal distribution

1. Land method
2. Chebyshev method

Percentile



METHODS TO ESTIMATE THE REPRESENTATIVE CONCENTRATION

Pro-UCL Software

Statistical tests

TIPO DI TEST [software ProUCL ver. 3.0]	TIPO DI DISTRIBUZIONE			
	NORMALE	LOG NORMALE	GAMMA	NON PARAMETRICA
"Normal Quantile-Quantile (Q-Q) Plot"	X	X	—	—
"Shapiro e Wilk test" (n < 50)	X	X	—	—
"Lilliefors Test"	X	X	—	—
"Gamma Quantile-Quantile (Q-Q) Plot"	—	—	X	—
"Kolmogorov-Smirnov test"	—	—	X	—
"Anderson Darling test"	—	—	X	—