Sediment quality assessment criteria: new approaches and views

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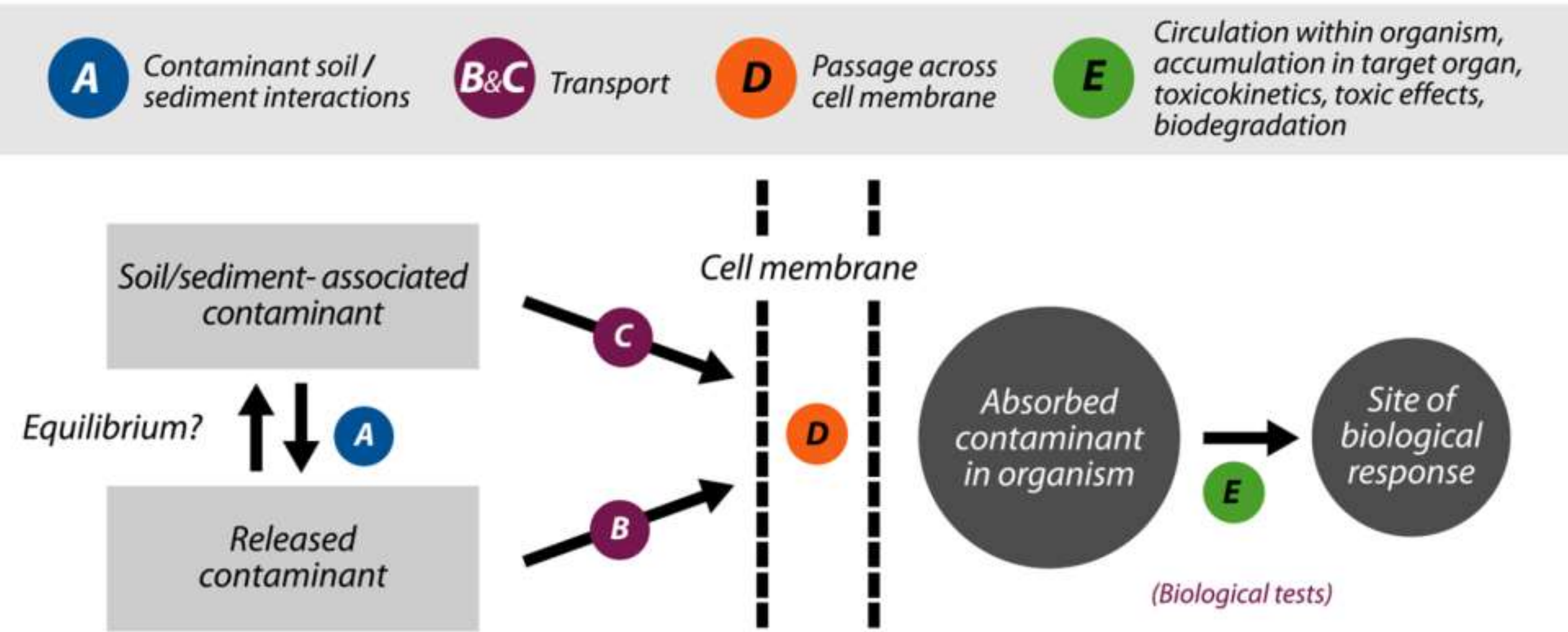
ENVIRONMENTAL RISK ASSESSMENT

Environmental Risk Assessment (ERA), including sediment assessment, is a **COMPREHENSIVE** approach to **support decision making** in the regulatory context, and covers a wide spatial set of situations under very different regulatory contexts

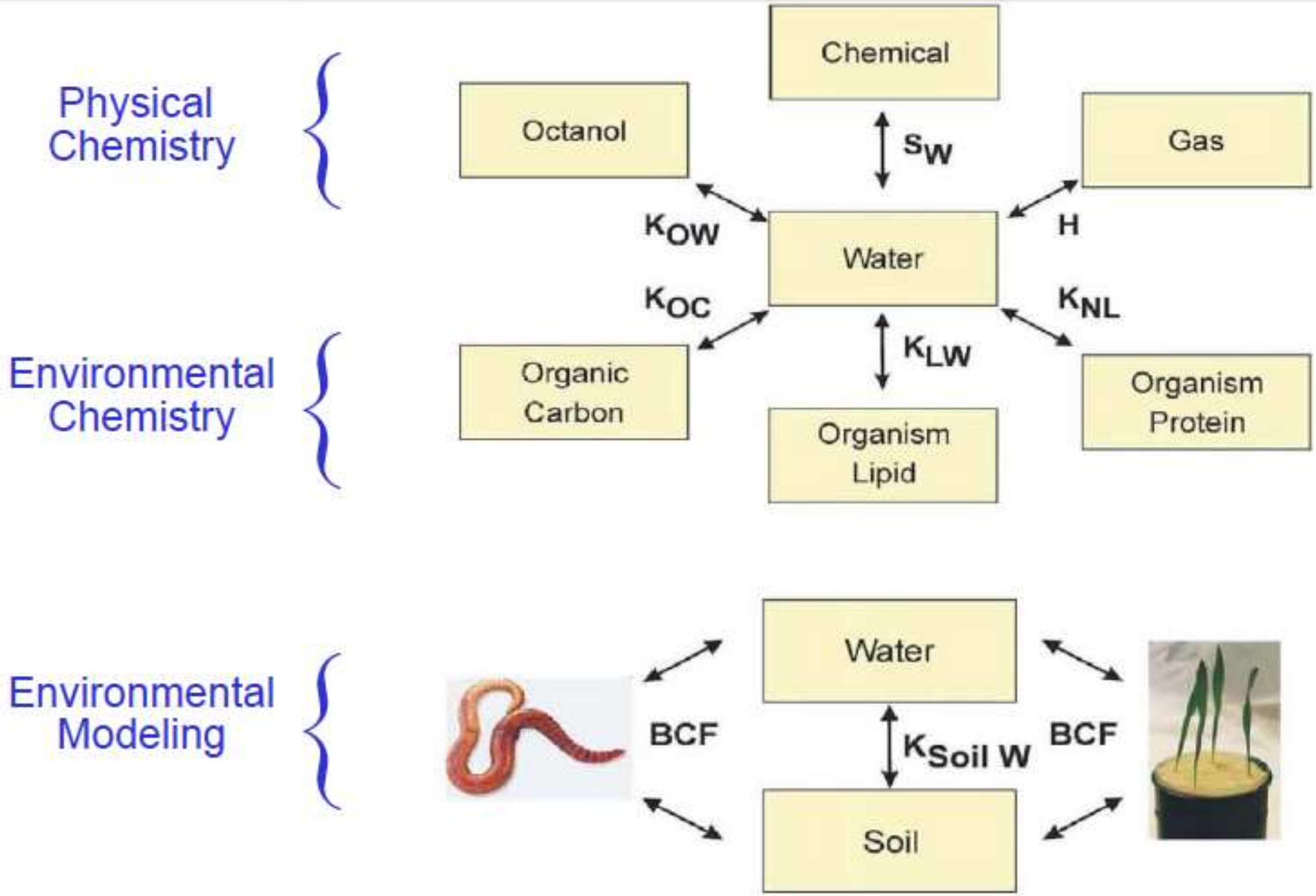
MY TODAY'S JOB…

- It is a question of interfaces
- Where the EqP model coupled to BLM, WHAM and speciation models fail
- A quick glance on the complexity of the environment
- Ecotoxicology under pressure
- Dynamics vs thermodynamics vs kinetics
- **Proposal of a systemic approach: toxicity as an emergent property**

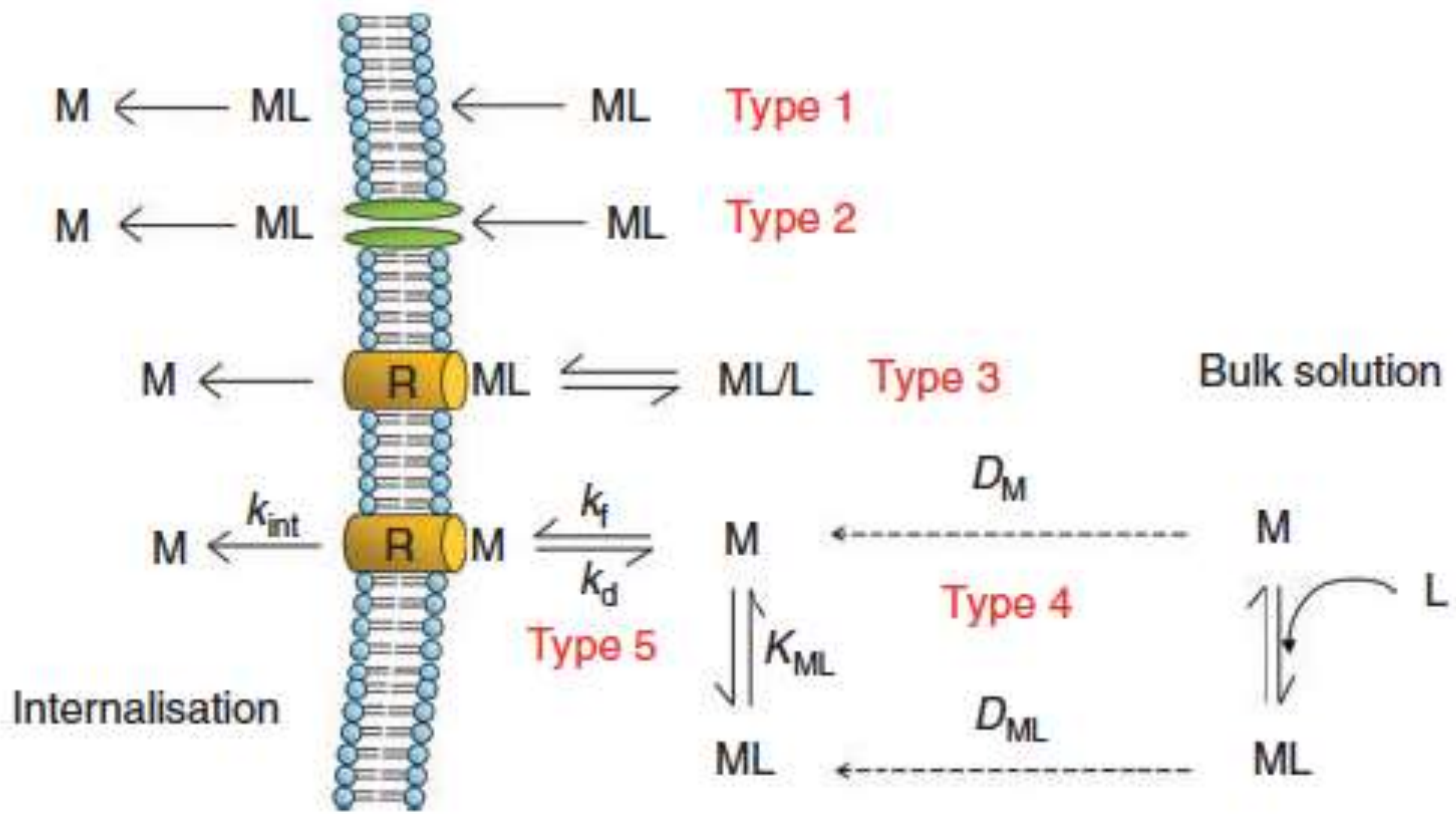
PROCESSES AT THE INTERFACE



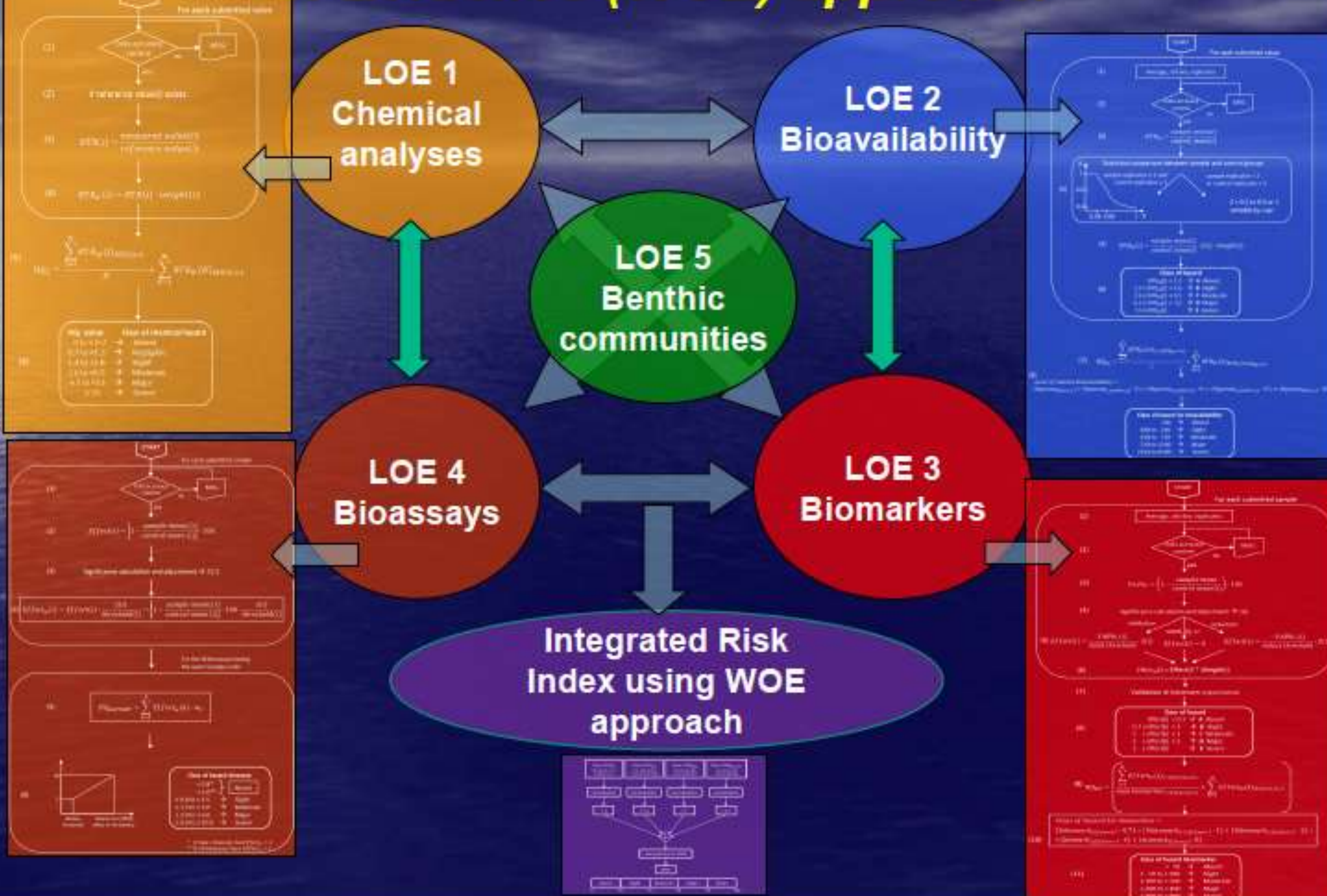
A GIANT PROBLEM OF CHEMISTRY AT THE INTERFACES



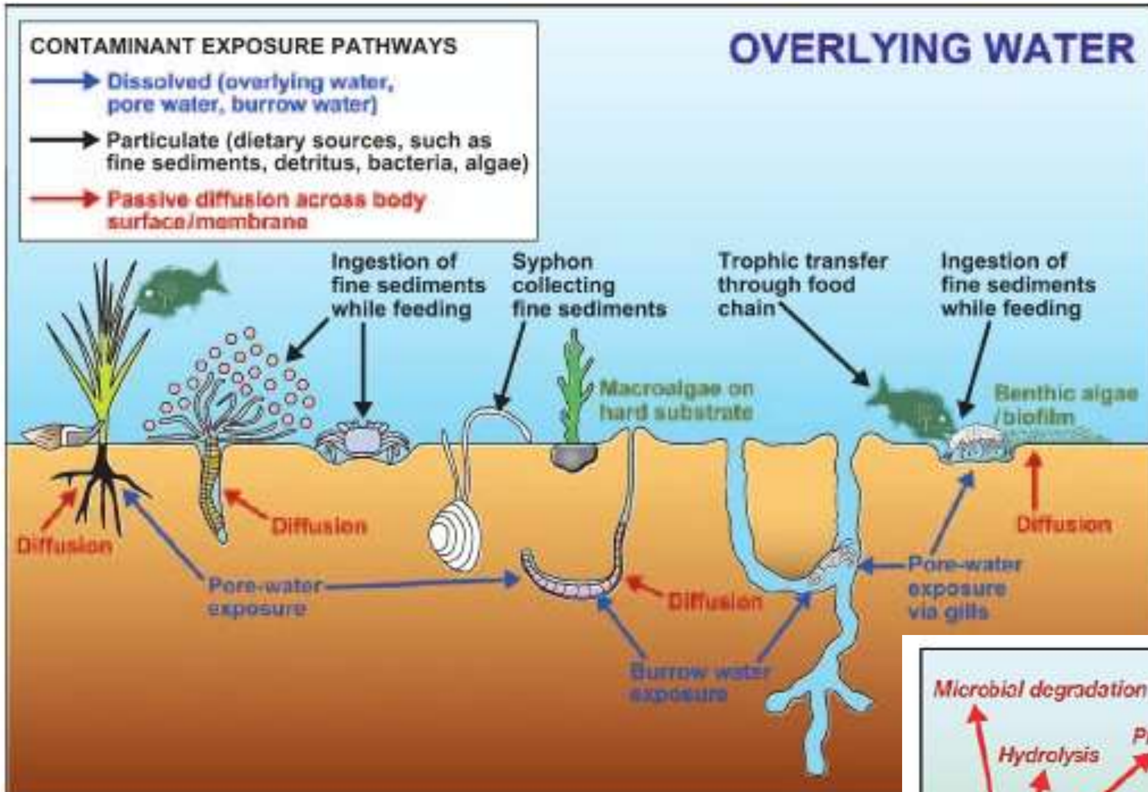
ECOTOXICOLOGY AND CHEMICAL SPECIATION: A GLANCE AT THE BOUNDARY

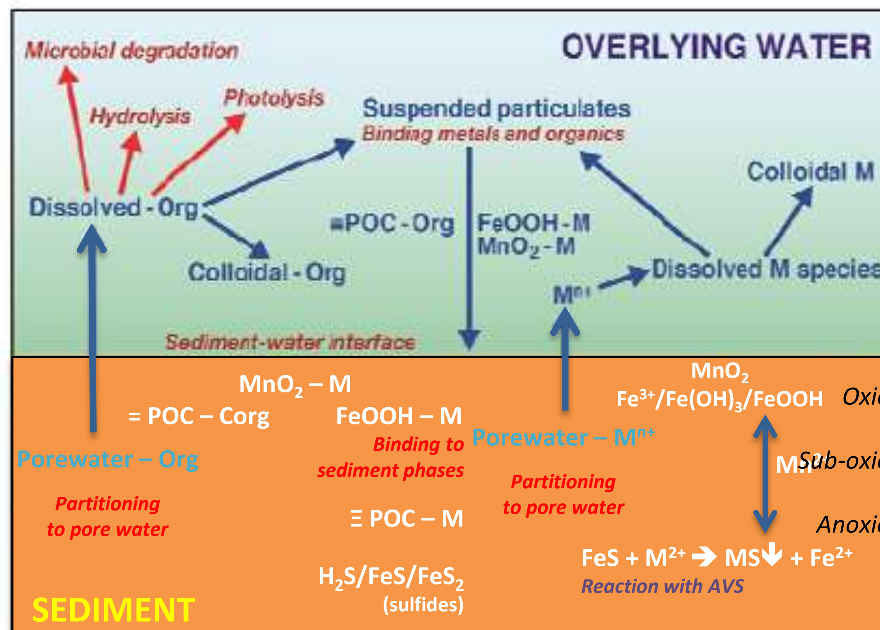


Quantitative risk assessment model on Weight of Evidence (WOE) approach



THE SEDIMENT PUZZLE





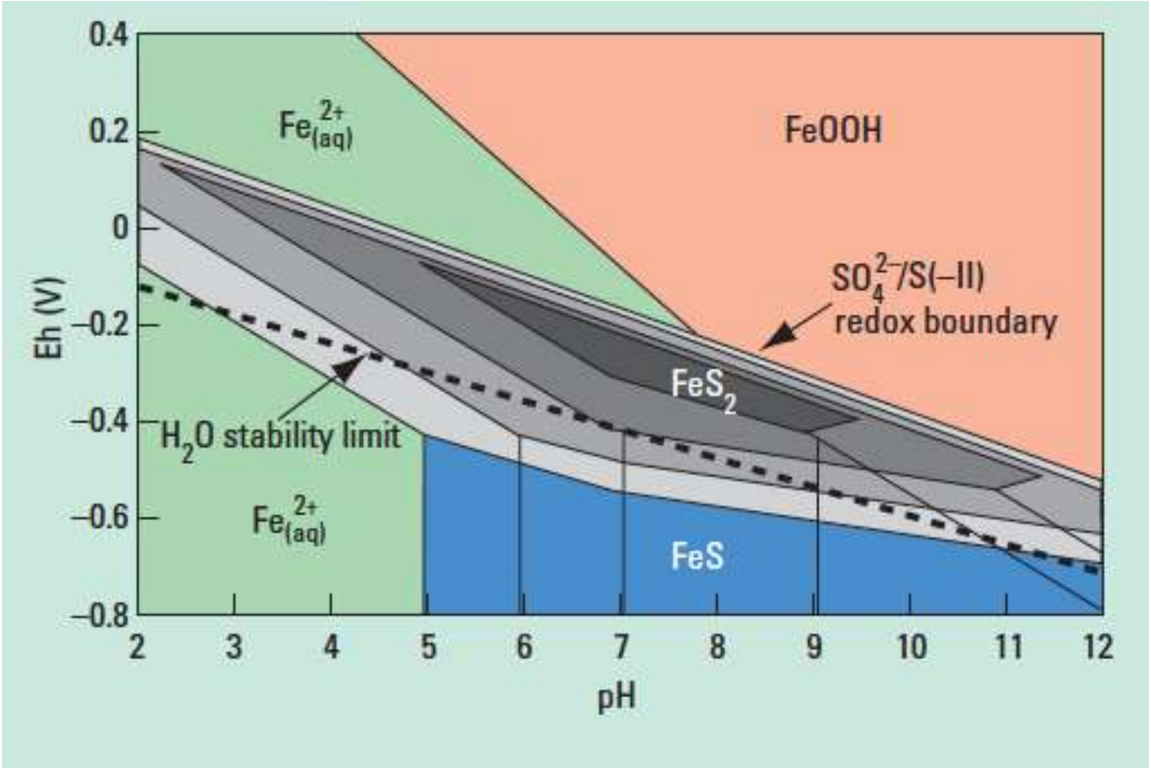
BIOAVAILABILITY…A CHALLANGE IN ITSELF

- **Equilibrium Partitioning [EqP] model (Di Toro et al., 2005) for metals**
  - ✓ Simultaneously Extracted Metals [SEM] (Di Toro et al., 2005)
  - ✓ Acid Volatile Sulphide [AVS]
  - ✓ Organic Carbon
  - ✓ Fe,Mn hydroxide
  - ✓ Grain Size

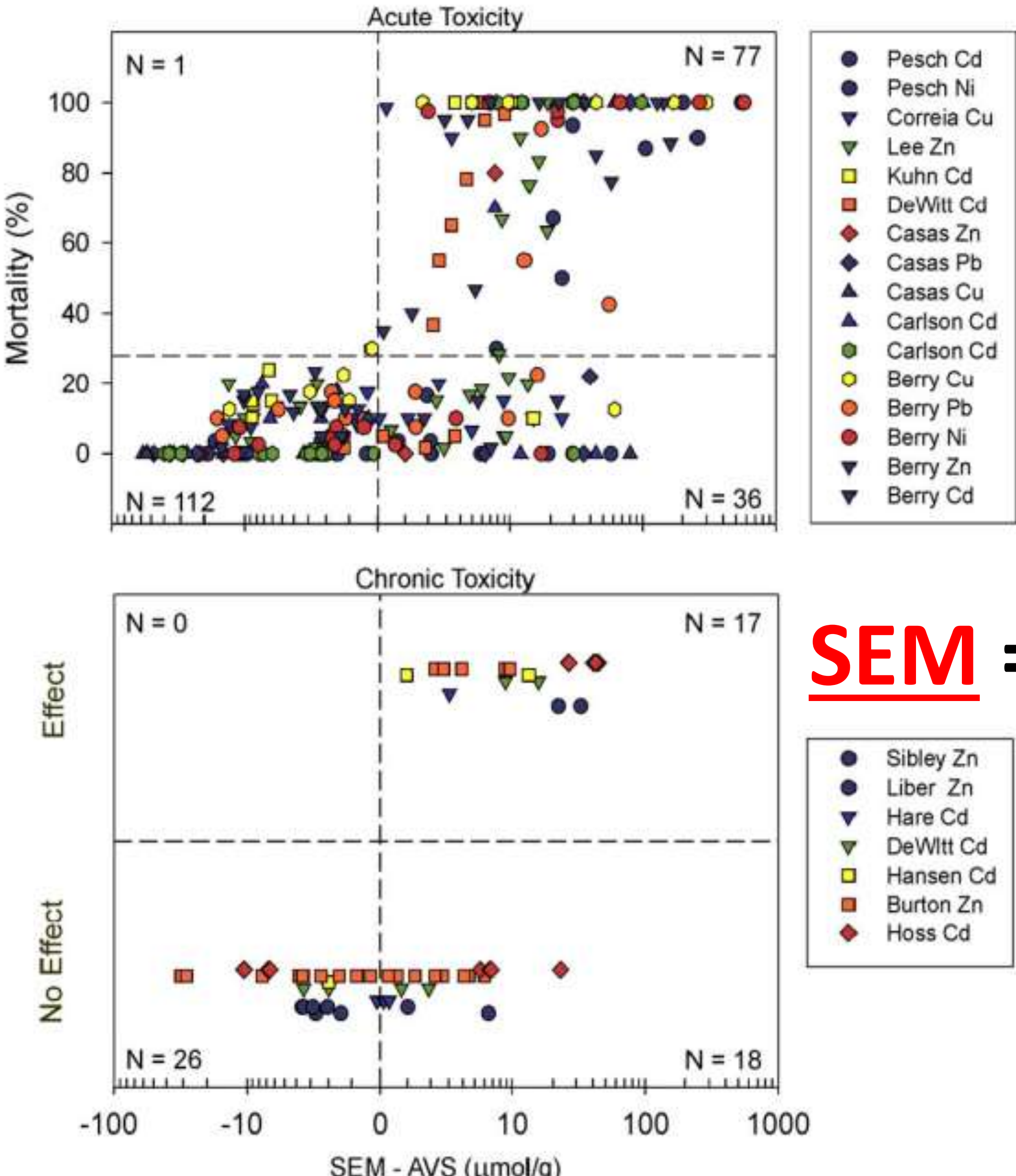
- **Equilibrium Partitioning [EqP] model (Di Toro et al., 2005) for POPs**
  - ✓ Grain size
  - ✓ Organic Carbon
  - ✓ Black carbon
  - ✓ Aging

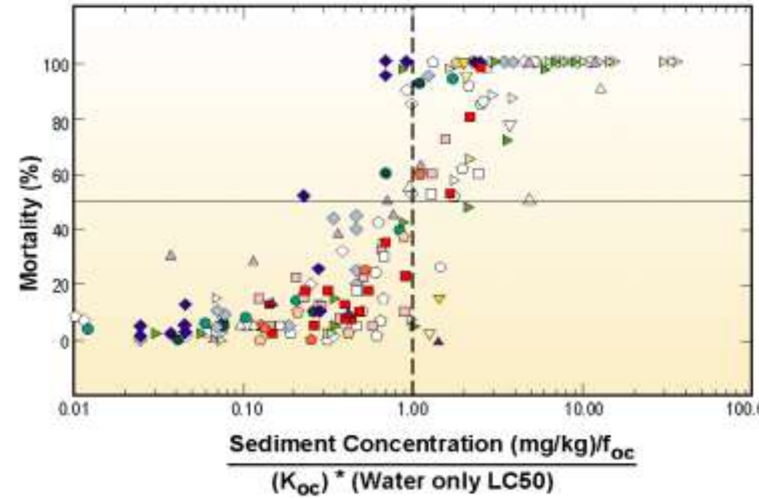
EqP-MODEL FOR METALS

$$\underline{SEM} = AVS + F_{OC}K_{OC}C_W + K_d(a+b[FeO_x+MnO_x])$$



AN OPERATIONAL APPROACH



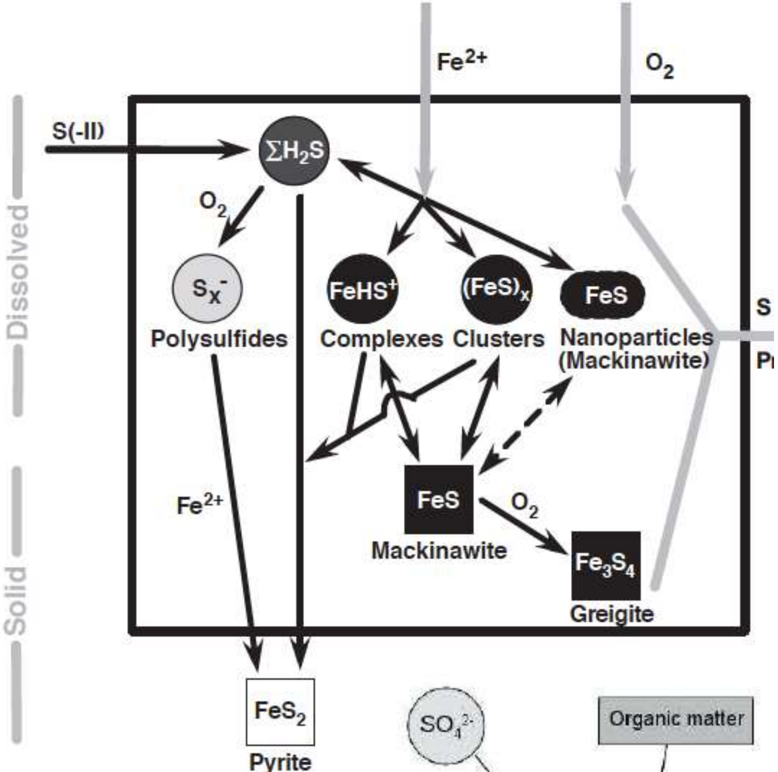


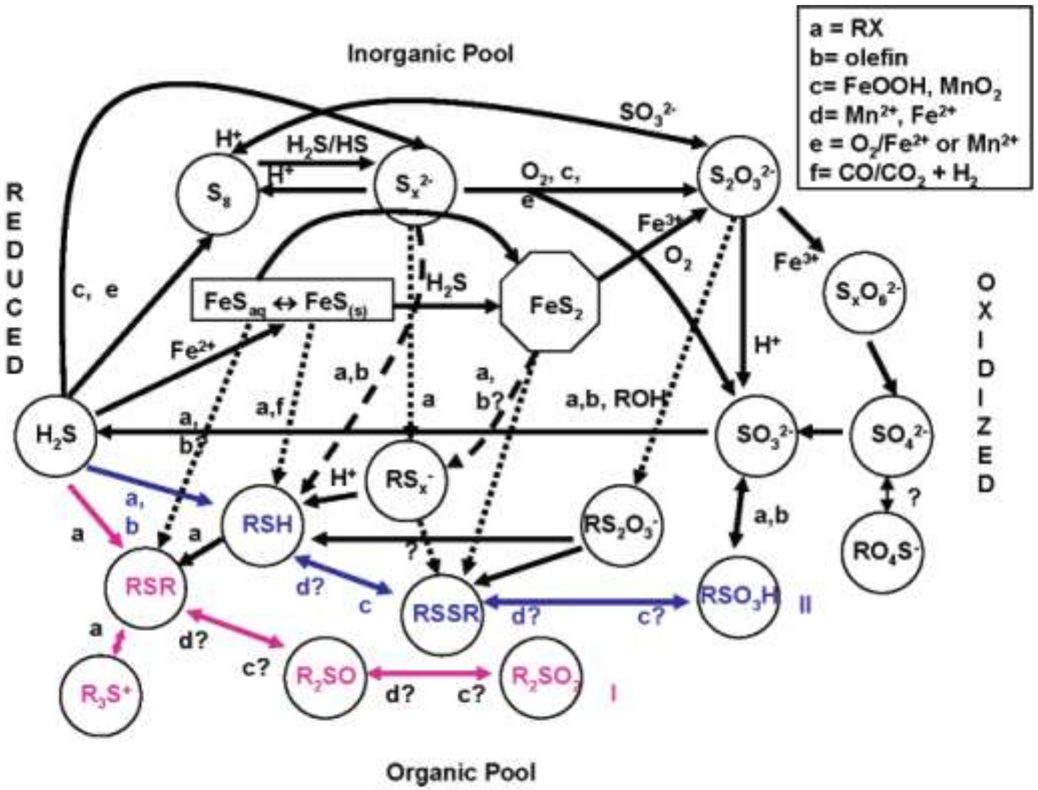
$$\underline{\textbf{SEM}} = \textbf{AVS} + F_{OC}K_{OC}C_W$$

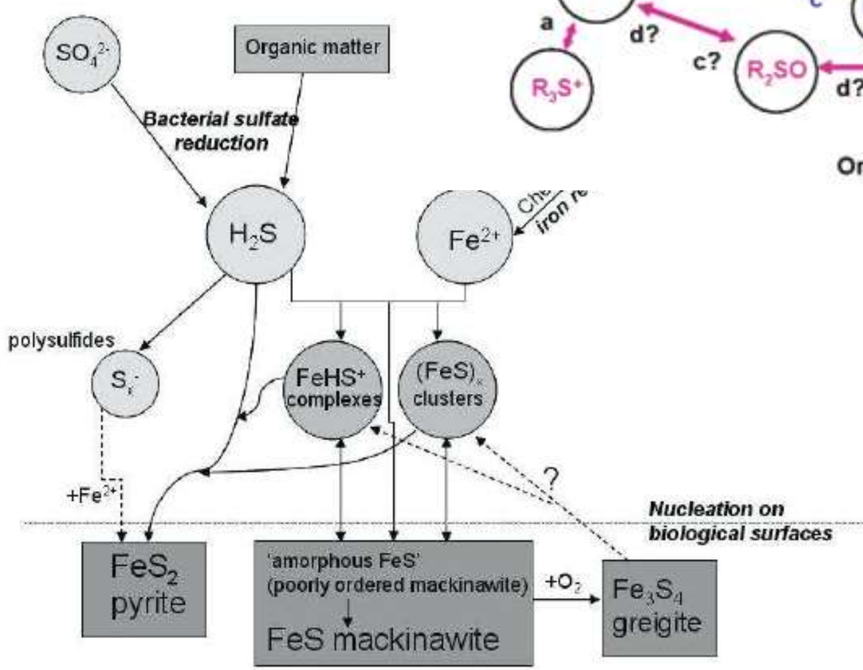
AVS, SEM…
DEFINITIONS AT WORK

$$\text{AVS} = \text{FeS}_{mackinawite} + \text{FeS}_{greigite} + \text{FeS}_{aquo} + \text{FeS}_{clusters} + \ldots$$

- SEM= [Ni]+[Cd]+[Zn]+[Sn]+[Ag]+[Hg]; $K_{sp} > K_{sp,\ Pyrite}$
- $F_{OC}K_{OC}C_W$
- $K_d(a+b[FeO_x+MnO_x])$

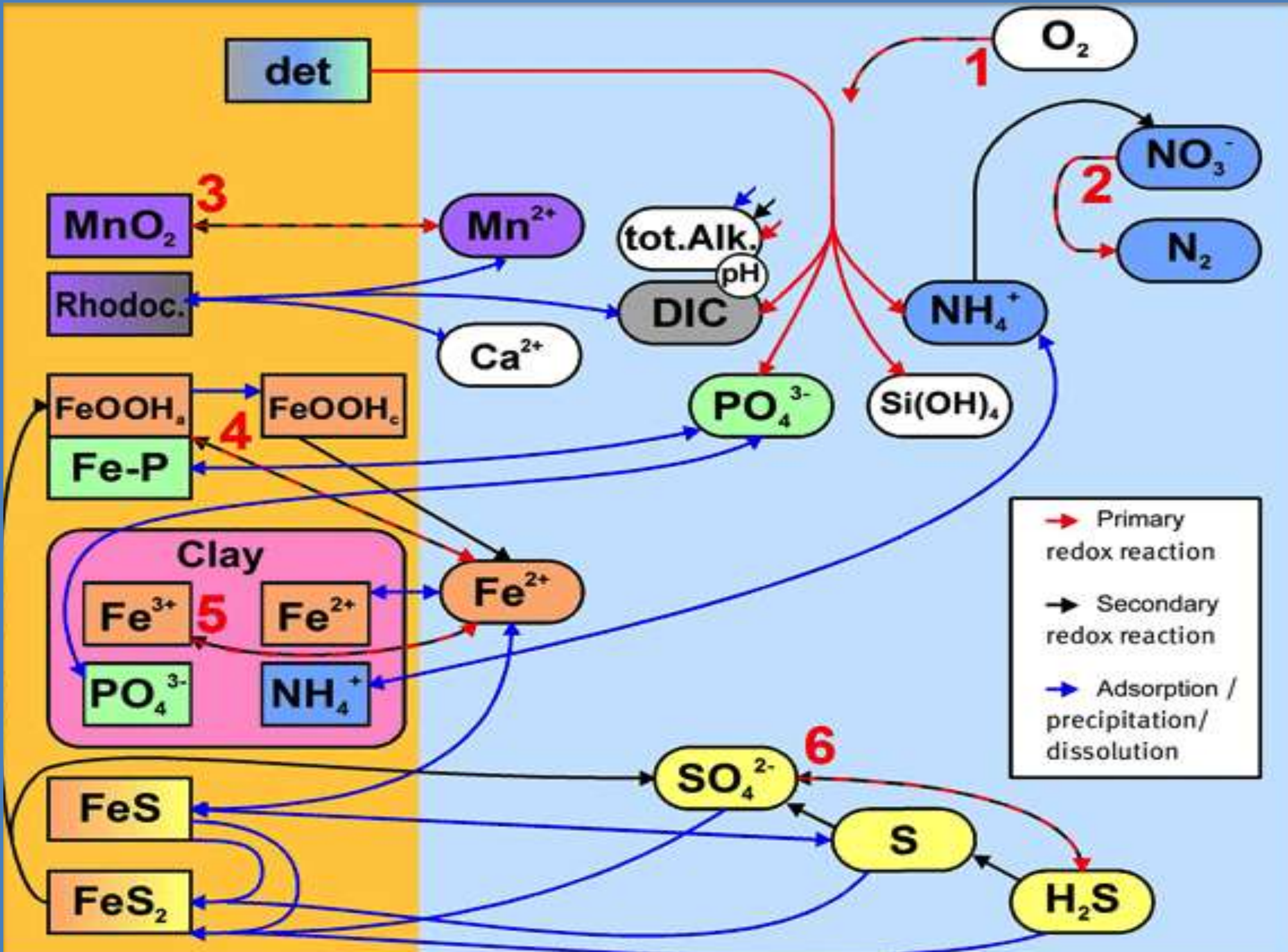

Fe2+
O2
S(-II)
ΣH2S
O2
Sx-
Polysulfides
FeHS+
Complexes
(FeS)x
Clusters
FeS
Nanoparticles
(Mackinawite)
Dissolved
Solid
Fe2+
FeS
Mackinawite
O2
Fe3S4
Greigite
FeS2
Pyrite


a = RX
b= olefin
c= FeOOH, MnO2
d= Mn2+, Fe2+
e = O2/Fe2+ or Mn2+
f= CO/CO2 + H2
Inorganic Pool
REDUCED
OXIDIZED
S8
Sx2-
S2O32-
H2S/HS
O2, c, e
SO32-
FeSaq ↔ FeS(s)
FeS2
SxO62-
H2S
SO32-
SO42-
RSx-
RSH
RS2O3-
RSR
RSSR
RSO3H
RO4S-
R3S+
R2SO
R2SO2
Organic Pool


SO42-
Organic matter
Bacterial sulfate reduction
H2S
Fe2+
polysulfides
Sx-
FeHS+ complexes
(FeS)x clusters
+Fe2+
?
Nucleation on biological surfaces
FeS2 pyrite
'amorphous FeS' (poorly ordered mackinawite)
FeS mackinawite
+O2
Fe3S4 greigite

A DEEP GLANCE TO THE AVS PROBLEM

- FeS and Fe_3S_4 minerals have rarely been reported from marine sediments
- The measurement of AVS-S cannot be related directly to any particular sulfide component in a sediment
- Analytical protocols for AVS-S vary considerably and are entirely empirical. Different protocols leach different amount of AVS materials
- AVS-S is not equivalent to FeS-S
- Pore water analyses will include filter-passing, nanoparticulate solids as well as clusters and complexes
- Pyrite-S contributes to AVS-S and analytical protocols cannot be assumed to separate S(-II) components from pyrite-S
- The effects of sample handling on measurements of AVS-S have not been quantified


det
O2
1
NO3-
2
N2
3
MnO2
Mn2+
tot.Alk.
pH
Rhodoc.
DIC
NH4+
Ca2+
FeOOHa
FeOOHc
4
PO4 3-
Si(OH)4
Fe-P
Clay
Fe3+
5
Fe2+
Fe2+
PO4 3-
NH4+
Primary redox reaction
Secondary redox reaction
Adsorption / precipitation/ dissolution
6
SO4 2-
FeS
S
FeS2
H2S

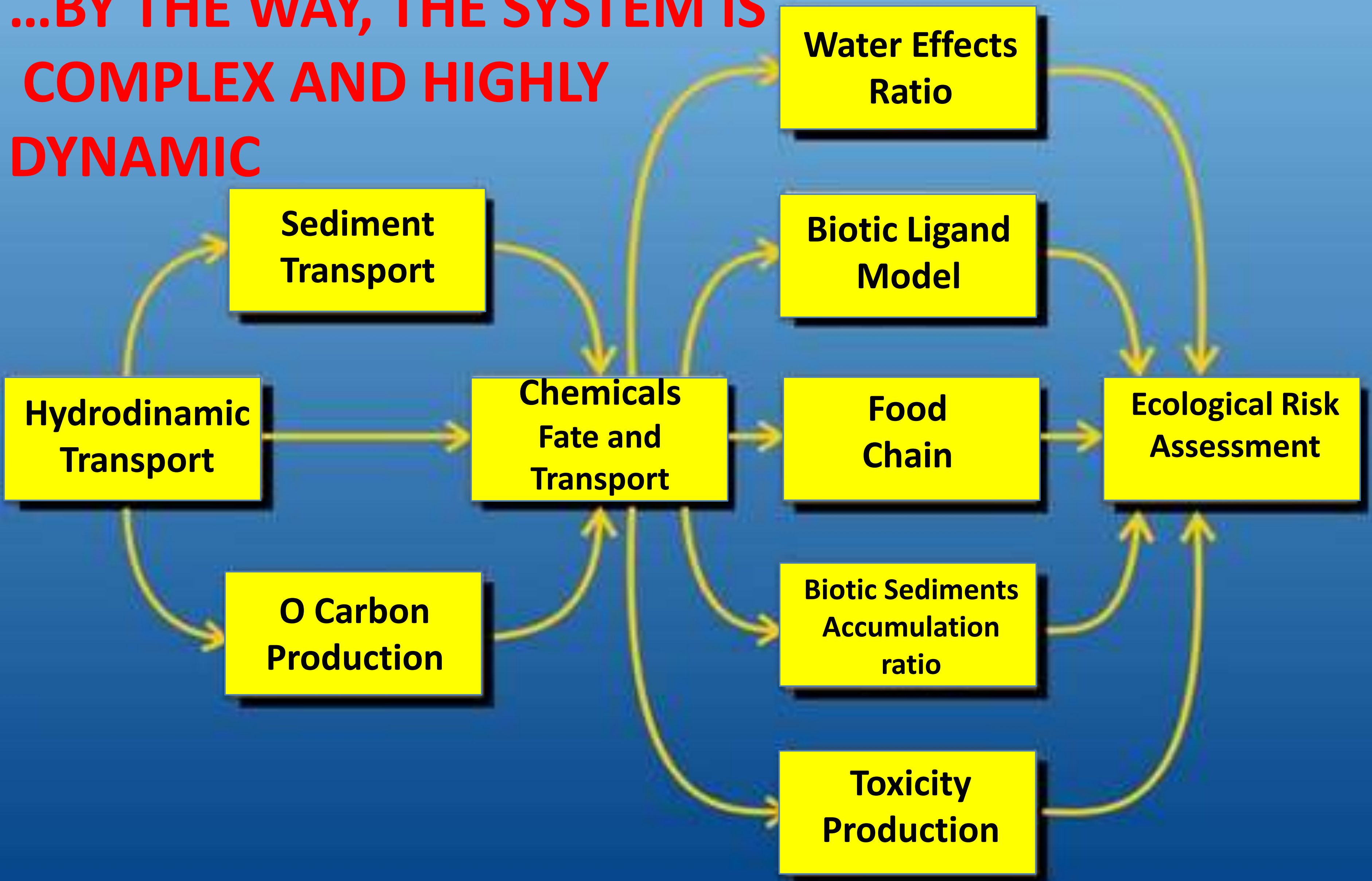
$$\text{SEM} = \text{FeS} + F_{OC}K_{OC}C_W + K_d(a+b[\text{FeO}_x+\text{MnO}_x])$$

POPs

$$\underbrace{[\text{MeHg}] + \text{N-SEM}}_{\text{EXTRA-M}}$$

$$\text{BIOAVAIL.} = \text{SEM} + \Sigma_i\, f_{OC}\, K_{i,OC}\, FCV_i + \text{EXTRA-M}$$

…BY THE WAY, THE SYSTEM IS COMPLEX AND HIGHLY DYNAMIC



Ecotoxicology (mainly bioassays) under pressure…

- ❑ An integrated view of processes…no system understanding
- ❑ A static view of sediments: **(thermo)dynamics vs kinetics**
- ❑ A **black-box of responses**: limited understanding of dynamic chemical processes at the sediment interfaces
- ❑ Only a “linear” exploration of **COMPLEXITY**
- ❑ **False positives and negatives** obscure/hide complexity

NEED OF A MUCH MORE DEEPER LEARNING

- Improved **biogeochemistry** and system non-linear responses
- **Dynamics** vs Stable conditions
- Improved scientific **handling of environmental variables**
- An **integrated** view of processes
- **Complexity** vs linearity

COMPLEX SYSTEM AND EMERGENT PROPERTIES

- From a linear and/or combined view of pollutants behaviour, multiple physical parameters of sediments and aquatic/biotic interfaces to… a systemic approach

- Analysis of emergent properties of the whole chemical-physical and ecological system rather than of any or a simple addition of its components

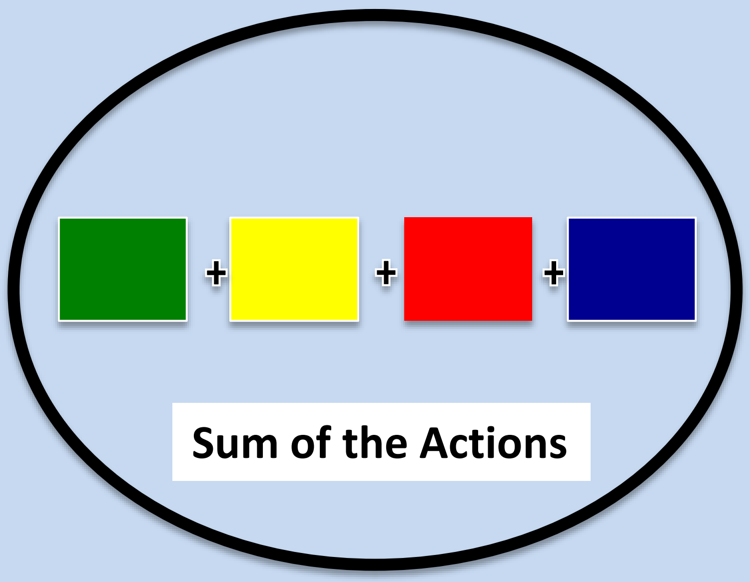
EMERGENT PROPERTIES

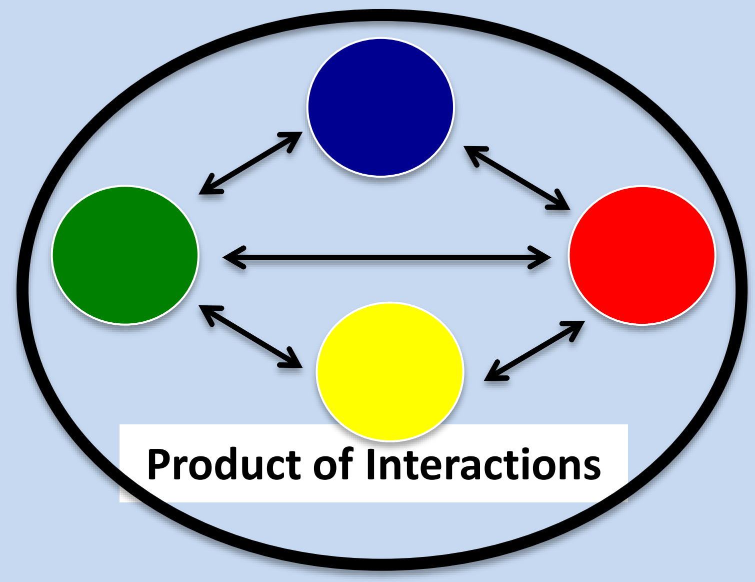
- Properties of the system **as a whole** rather than properties that can be derived from the properties of components of a system
- Emergent properties are a consequence of the relationships between system components
- They can therefore only be assessed and measured once the components have been integrated into a system

BIOAVAILABILITY/TOXICITY

EMERGENT PROPERTY OF A COMPLEX SYSTEM

Properties of the Whole vs. Properties of the Parts





MINERALOGY AND DYNAMICS OF PHYSICAL AND CHEMICAL PARAMETERS

GEOCHEMISTRY AT WORK

A FIRST EXAMPLE OF AN APPROACH IN TERMS OF A COMPLEX/DYNAMIC SYSTEM

BASIC SYSTEM OF EQUATIONS

- $Fe(OH)_3 + 3H^+ = Fe^{2+} + 3H_2O$
- $Fe^{2+} + \frac{1}{4} O_2 + 2OH^- + 1/2\ H_2O = Fe(OH)_3$
- $FeS + H_2S = FeS_2 + H_2$
- $FeS_2 + H^+ = Fe^{2+} + HS^- + S^0$
- $FeS_2 + 8H_2O + 14Fe^{3+} = 15Fe^{2+} + 2SO_4^{2-} + 16H^+$
- $FeS_2 + H_2O + 7/2O_2 = Fe^{2+} + 2SO_4^{2-} + 4H^+$
- *$Fe^{2+} + HS^- = FeSH^+$*
- *$Fe^{2+} + H_2S = FeS + 2H^+$*
- $FeS + 2\ H^+ = Fe^{2+} + H_2S$
- *$FeS + H^+ = Fe^{2+} + HS^-$*

BASIC SYSTEM OF EQUATIONS

1) $SO_4^{2-} + 10H^+ \xrightarrow{k_a} H_2S + 4H_2O$ **k = 10^{40}**

2) $SO_4^{2-} + 9H^+ \xrightarrow{k_b} HS^- + 4H_2O$ **k = 10^{33}**

3) $HS^- + H^+ \xrightarrow{k_c} H_2S$ **k = 10^{7}**

4) $Fe^{2+} + \frac{1}{4}O_2 + 2OH^- + \frac{1}{2}H_2O \xrightarrow{k_1} Fe(OH)_3$ ***k_{cin} = 1.5*10^{13} l^2 mol^{-2} atm^{-1} min^{-1}***

5) $FeS + H_2S \xrightarrow{k_2} FeS_2 + H_2$ **k = $10^{6.1}$** ***K_{cin} = 1.03 * 10^{-4} l $mol^{-1}s^{-1}$***

6) $FeS_2 + H^+ \xrightarrow{k_3} Fe^{2+} + HS^- + S_0$ **K_{sp} = $10^{-16.4}$** ***K_{cin} = 1 * $10^{-7.52}$ mol m^{-2} s^{-1}***

7) $FeS_2 + H_2O + \frac{7}{2}O_2 \xrightarrow{k_4} Fe^{2+} + 2SO_4^{2-} + 4H^+$ ***k_{cin} = 10^{-10} mol m^{-2} s^{-1}***

8) $Fe^{2+} + H_2S \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} FeS + 2H^+$ **K =$10^{-3.7}$** ***k_{cin}= 7 l mol^{-1} s^{-1}***

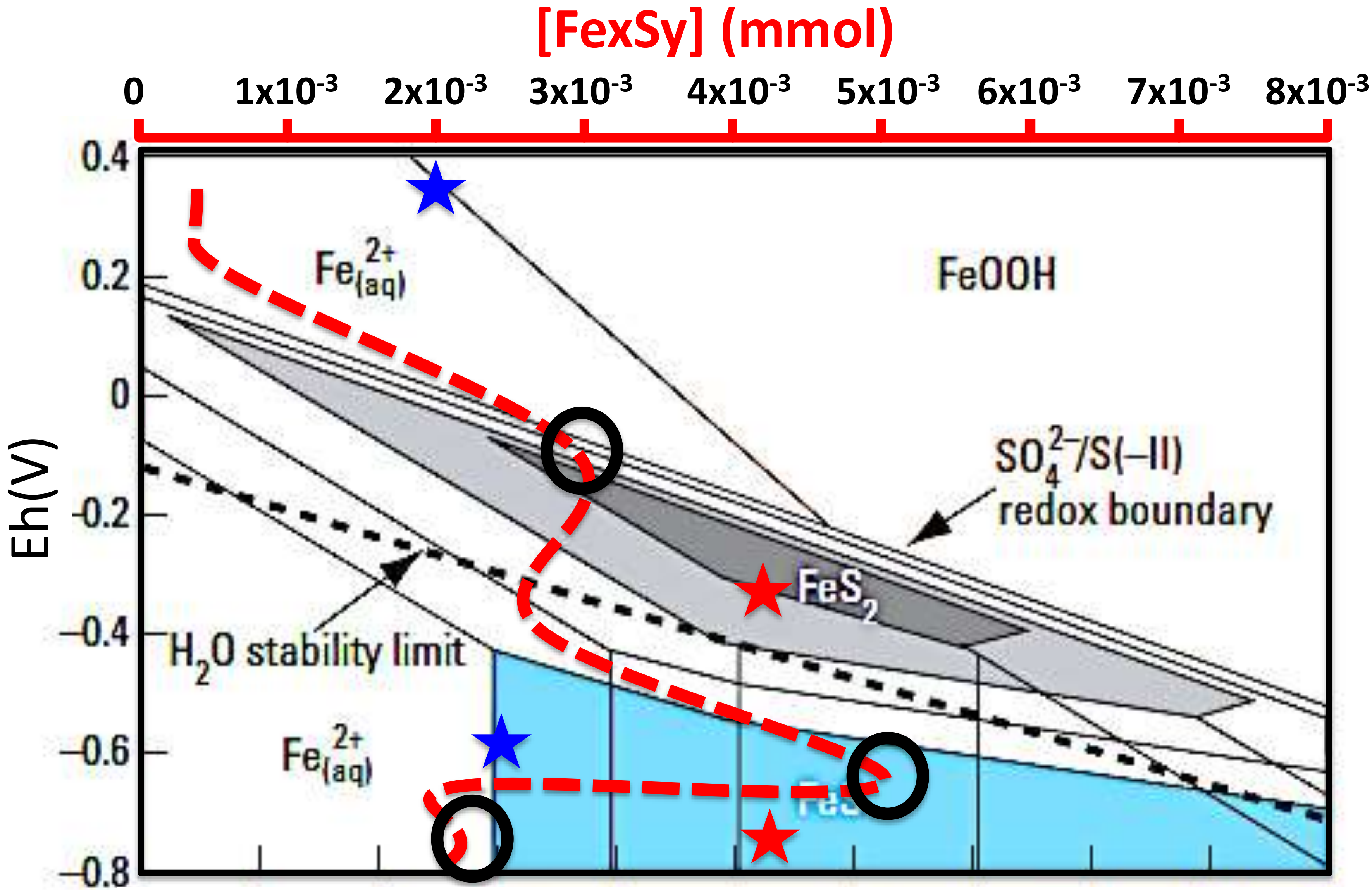
DYNAMICAL SYSTEM

$x_1(t) = [Fe^{2+}]$ $x_2(t) = [FeS]$ $x_3(t) = [FeS_2]$
$x_4(t) = [H_2S]$ $x_5(t) = [HS^-]$

$$\begin{cases} \dfrac{dx_1}{dt} = C - k_1 \dfrac{A}{[H^+]^2}[O_2]^{1/4}[H_2O]^{1/2}x_1 + k_{-5}[H^+]^2 x_2 + k_4[H_2O][O_2]^{7/2}x_3 \\ \qquad -k_5 x_1 x_4 - k_3[S^0]\,x_1 x_5, \\ \dfrac{dx_2}{dt} = -k_2 x_2 x_4 + k_5 x_1 x_4 - k_{-5}[H^+]^2\,x_2 \\ \dfrac{dx_3}{dt} = k_2 x_2 x_4 + k_3[S^0]\,x_1 x_5 - k_4[H_2O][O_2]^{7/2}\,x_3 \\ \dfrac{dx_4}{dt} = -k_2 x_2 x_4 - k_5 x_1 x_4 + k_{-5}[H^+]^2\,x_2 + k_c[H^+]\,x_5 + k_a[SO_4^{2-}]\,[H^+]^{10} \\ \dfrac{dx_5}{dt} = -k_3[S^0]\,x_1 x_5 - k_c[H^+]\,x_5 + k_b[H^+]^9\,[SO_4^{2-}] \end{cases}$$

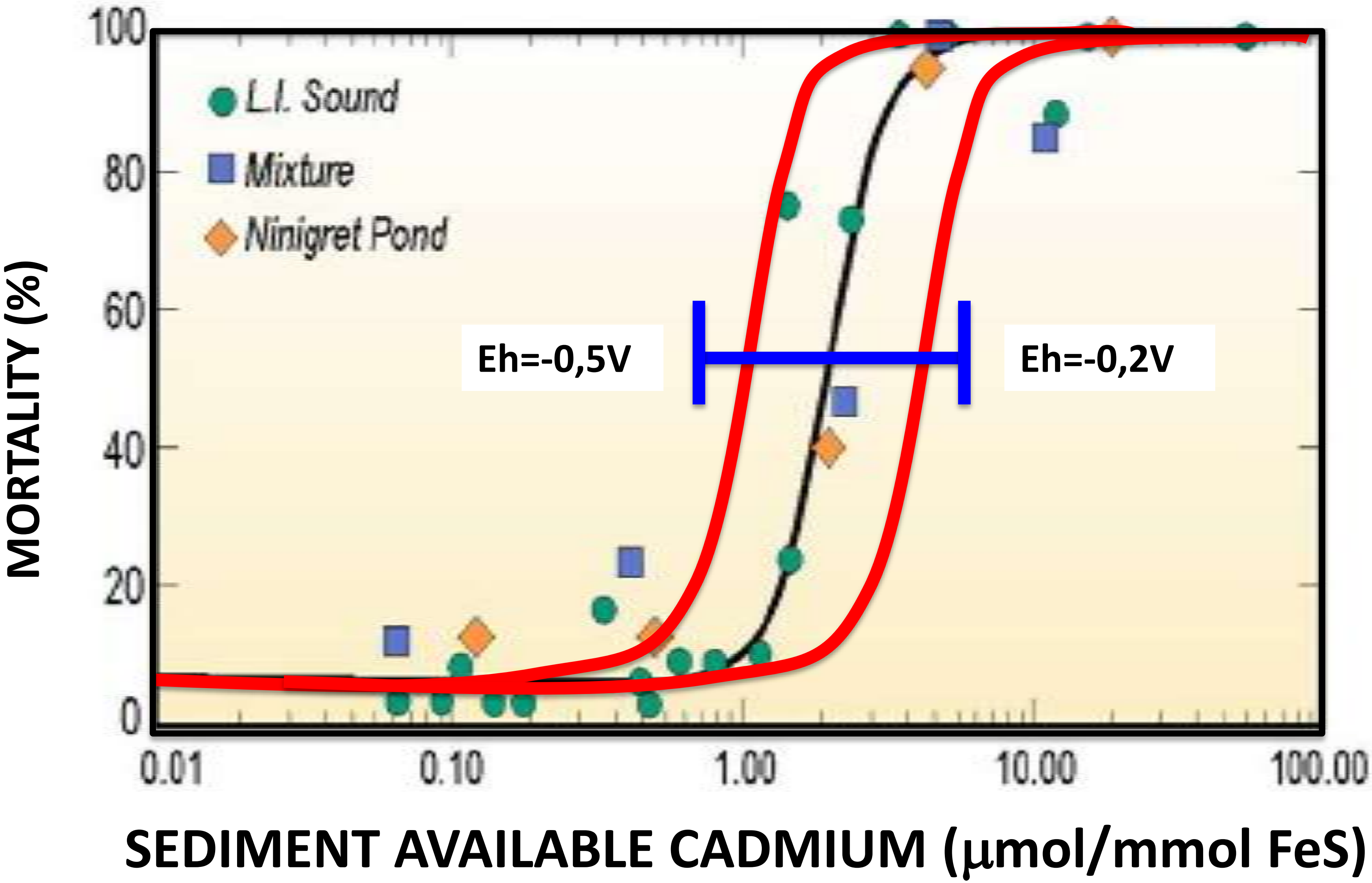
SPECIFIC FEATURES OF THE SYSTEM

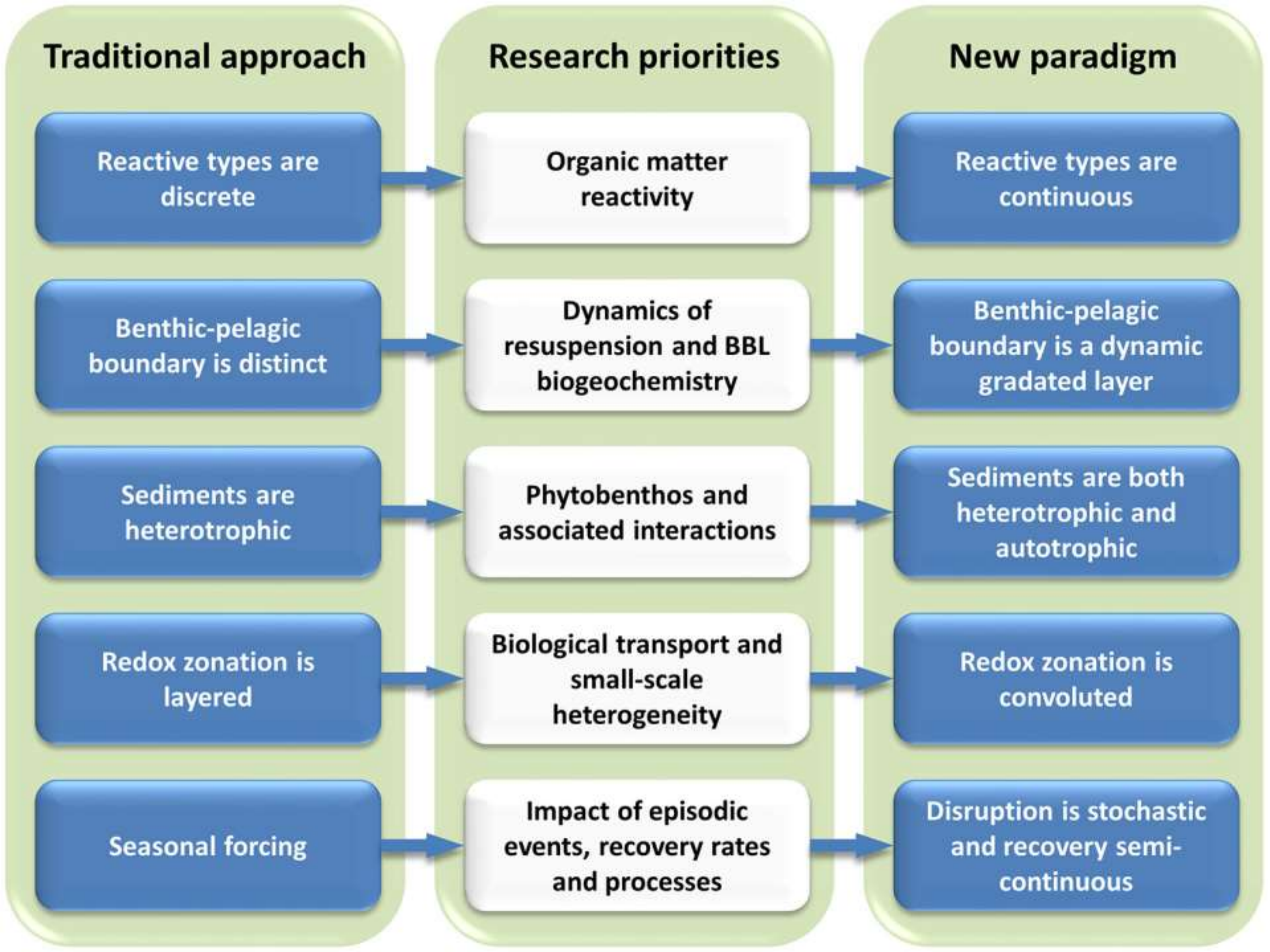
- Non-linear system, continuous and converging towards attractors. System stable at various conditions
- Trajectories of the different species in the Eh-pH stability field are well-described and quantified
- We can calculate the buffer (complexing) capacity of the Fe_xS_y system
- Need of field-tests to verify theory


[FexSy] (mmol)
0
1x10-3
2x10-3
3x10-3
4x10-3
5x10-3
6x10-3
7x10-3
8x10-3
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
Eh(V)
$Fe^{2+}_{(aq)}$
FeOOH
$SO_4^{2-}/S(-II)$
redox boundary
FeS_2
H_2O stability limit
$Fe^{2+}_{(aq)}$

Av. Metals

FE_XS_Y NORMALIZATION




Traditional approach
Research priorities
New paradigm
Reactive types are discrete
Organic matter reactivity
Reactive types are continuous
Benthic-pelagic boundary is distinct
Dynamics of resuspension and BBL biogeochemistry
Benthic-pelagic boundary is a dynamic gradated layer
Sediments are heterotrophic
Phytobenthos and associated interactions
Sediments are both heterotrophic and autotrophic
Redox zonation is layered
Biological transport and small-scale heterogeneity
Redox zonation is convoluted
Seasonal forcing
Impact of episodic events, recovery rates and processes
Disruption is stochastic and recovery semi-continuous

…MY TAKE HOME MESSAGE…

- We must re-think our approach to evaluation of sediments bioavailability/toxicity in terms of complex system and biogeochemical dynamics. Non linear addition of “pieces” but approaches to emergent properties
- Eh, pH, O_2 (physics) dominate dynamics of [Fe, S, OC,FE/Mn hydroxides] chemistry in sediments: we need new and more “conservative” sampling methods
- Dynamics dominate stable conditions…this is complexity at work
- Ecotoxicity needs a deeper understanding of biogeochemical dynamics of pollutants in seds

Thanks for your attention!