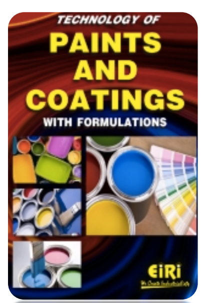
Des nanomatériaux pour étudier les processus de transformation en milieux complexes des nanoparticules minérales

Origins of nanoparticles (NPs)

1) **Natural.** Ex : volcanoes, deserts
2) **Anthropogenic.** Ex : industries, exhaust gas
3) **Manufactured.** Applications :

- Ag NPs : textiles (anti-bacterial, anti-odor) — *J.P Shastri et al. 2012*
- TiO_2 NPs : paints (anti-abrasive, anti-corrosion) — *L. Golanski et al. 2010*
- NPs de ZnO : sunscreen (UV protection) — *N.A.M. Riviere al. 2011*
- Quantum dots (QDs, ex : CdSe) : solar cells — *Ren et al. 2011*

QDs = *boîte quantique.* Semi-conductor nanocrystals. 2 - 10 nm.



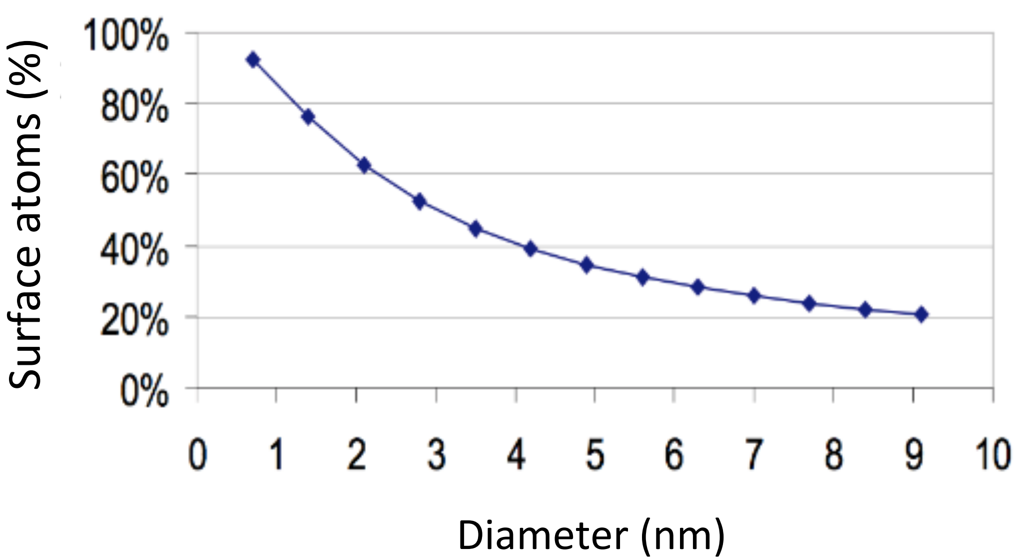
Images sources : Internet

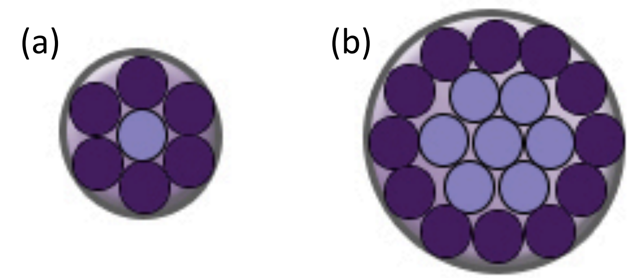
NPs specific properties

Why various applications of these NPs ?

Nano-size → **High specific surface** → High surface reactivity

(Nel A. et al. 2006)





$S_{specific}$ (a) **>** $S_{specific}$ (b)

NPs flow & concentration estimation in surface water

NPs flow prediction in surface water (US), originates from

production, manufacturing & consumption of NPs

- ZnO NPs : 15 tons/year
- TiO_2 NPs : 48 tons/year
- Ag NPs : 0.2 tons/year
- Quantum dots : ~ 10 tons/year (Europe)

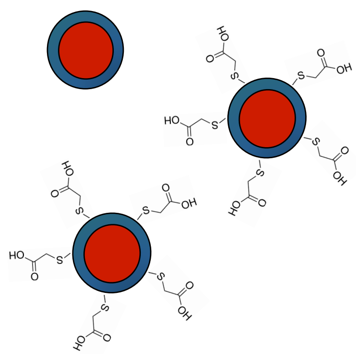
NPs concentration estimation in surface water (Europe)

- ZnO NPs : 10 ng/L ou ppt
- TiO_2 NPs : 15 ng/L
- Ag NPs : 0.76 ng/L
- Quantum dots : ~ ng/L

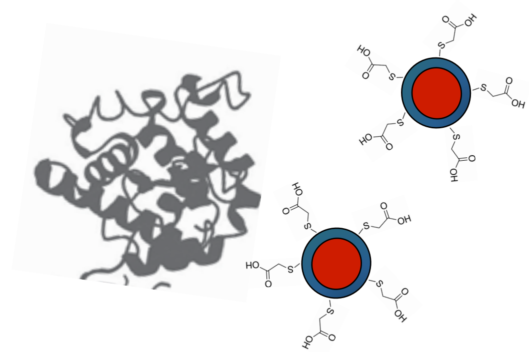
Ref: Gottschalk et al. ES&T, 2009. Piccinno et al. J Nano Res, 2012

NPs behavior in natural environment

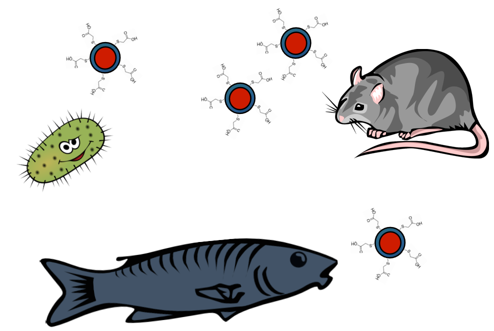
Physico-chemical characterizations :
Size, form, composition, structure, specific surface, solubility, coating



Transformation / Interaction with other phases :
Adsorption, aggregation, complexation with les organic/ mineral matters



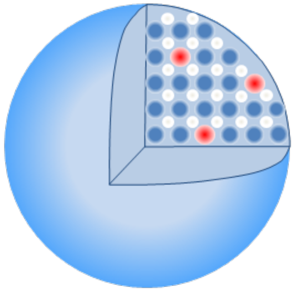
Interaction with living organisms :
Bio-availability
Ecotoxicity



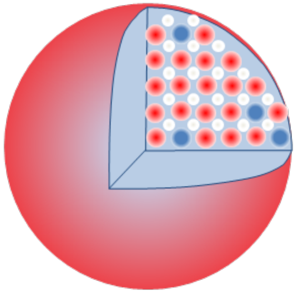
- **Dispersion and degradation in natural environment ?**
- **Understand their impact on biogeochemical cycles ?**
- Indispensable to understand their transformations in the environment
- BUT : study at **realistic concentrations – mg/L → ng/L**
- Problems : **Environmental background noise** et **detection limit**
- Innovative analytical tools ? **STABLE ISOTOPES !**

Isotopically modified NPs (spiked)

Nanoparticle

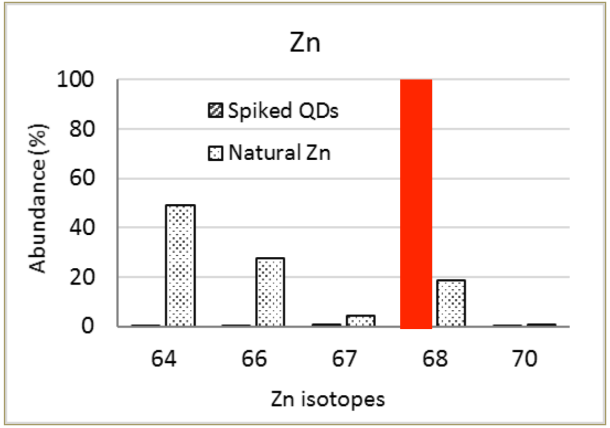


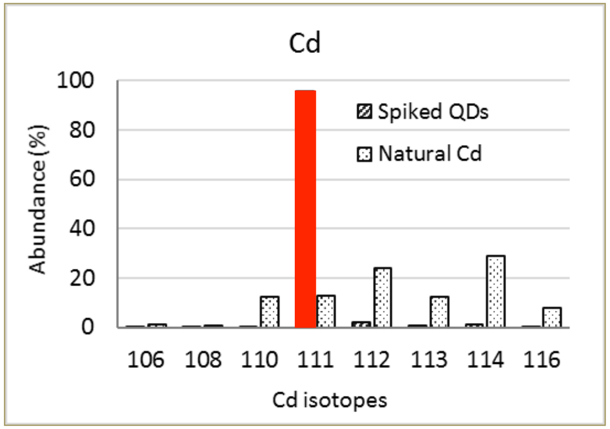
Heavy isotope-enriched NP

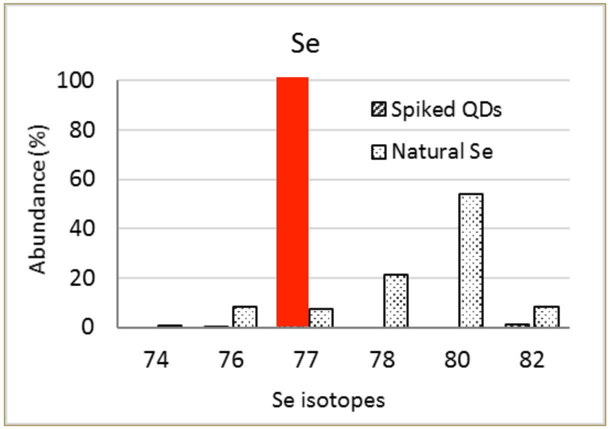


Light isotopes : ^{64}Zn

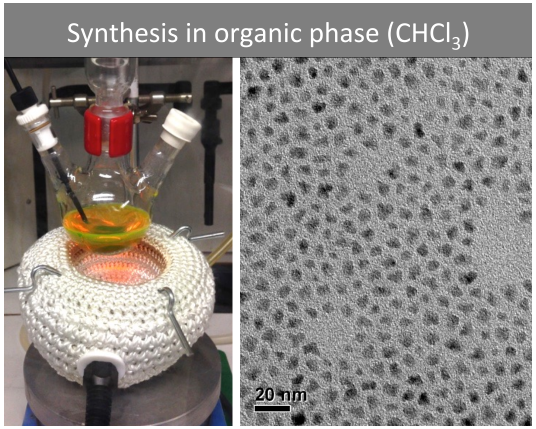
Heavy isotopes : ^{68}Zn

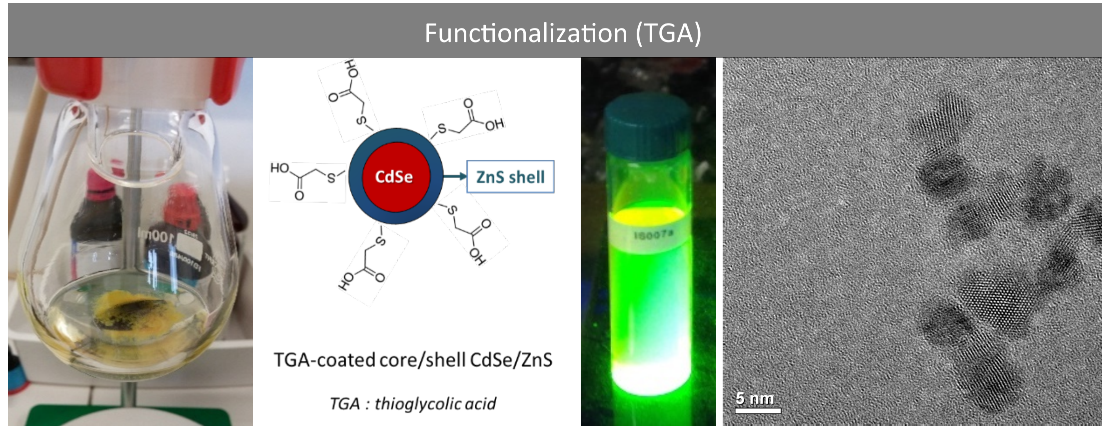






Isotopically modified NPs (spiked)



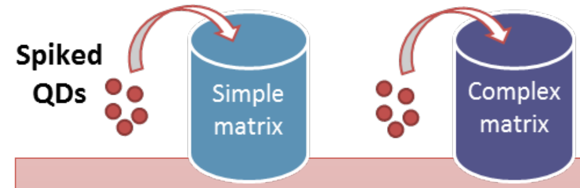


- Synthesis of multi-isotopically labelled core/shell CdSe/ZnS quantum dots
  - Protocol: adapted from Bae et al. 2008
  - Functionalization: thioglycolic acid (TGA)

- Characterization
  - Green luminescent under UV light (312 nm)
  - DLS: 7-8 nm ; HR-TEM: 7 nm, rounded shape (some are slightly oval)
  - ICP-OES: [Zn] = 101.1 mg/L ; [Cd] = 31.8 mg/L ; [Se] = 19.2 mg/L
  - HR-ICP-MS: determination of QDs isotopic composition

QDs dissemination in simple and complex matrices

- Simple matrices
  - HNO_3 2%
  - $NaNO_3$ 0.01N
- Natural matrices
  - Seine river water *(0.22 µm)*
  - Seawater *(artificial ; recipe from ASTM International)*
  - Estuaries *(Seine river water + artificial seawater)*
- **Biological matrices**
  - **Saliva** *(artificial ; West et al. 2002)*
  - **Urine** *(artificial ; Shiotsuki et al. 2012)*
  - **Plasma** *(Sprague Dawley ; from Janvier-Labs France)*
  - **Growth media** *(DPBS ; Dulbecco and Vogt, 1954)*



QDs dissemination in these matrices at concentrations ranging from

$[Zn]_{QDs}$ = 0.1 - 5000 ng/L

resulting in :

$[Cd]_{QDs}$ = 0.03 - 1500 ng/L

$[Se]_{QDs}$ = 0.02 - 1000 ng/L

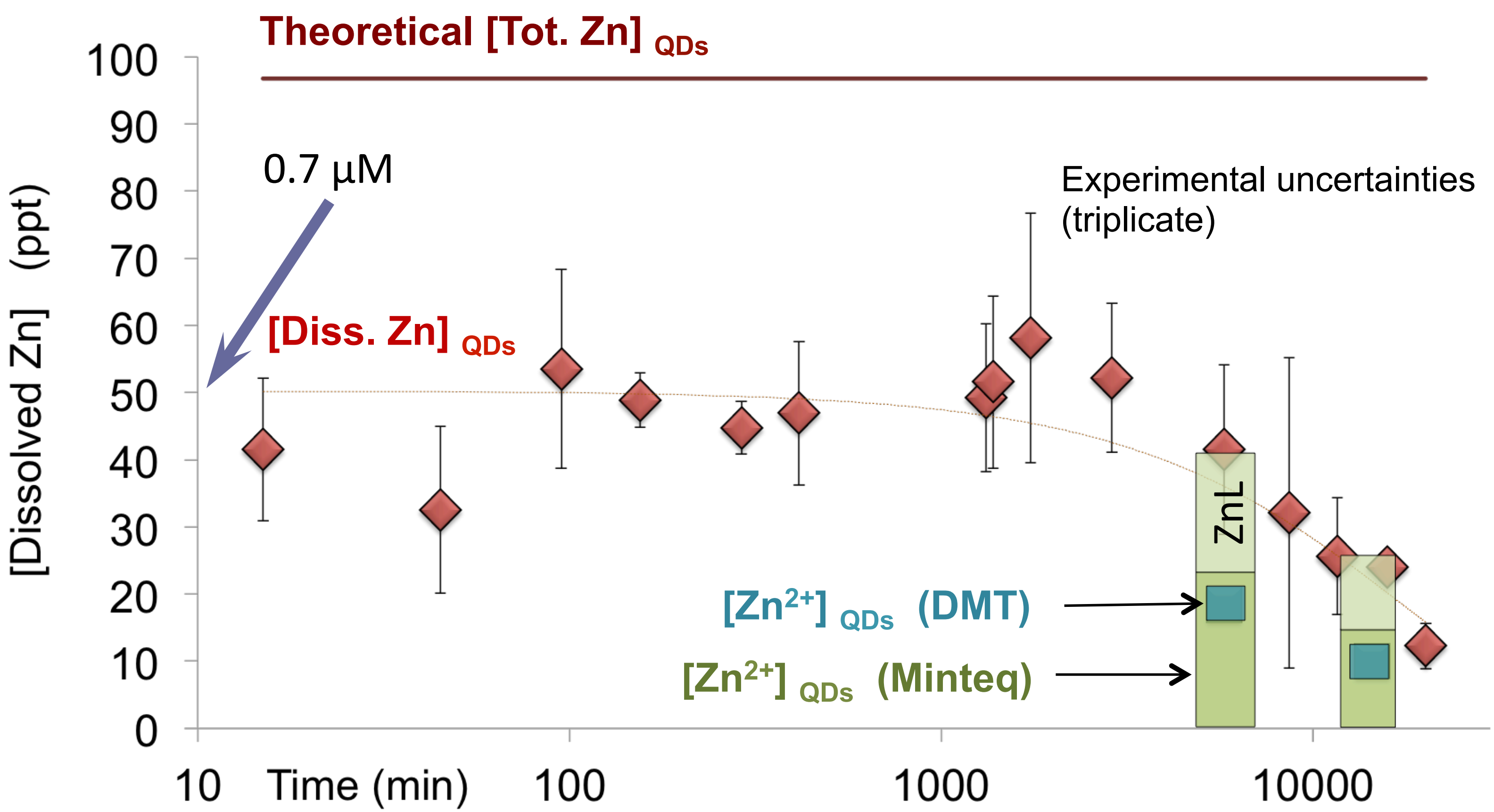
Samples analyses (HR-ICP-MS)

- ^{64}Zn, ^{66}Zn, ^{67}Zn, ^{68}Zn, ^{70}Zn
- ^{74}Se, ^{76}Se, ^{77}Se, ^{78}Se, ^{80}Se, ^{82}Se,
- ^{106}Cd, ^{108}Cd, ^{110}Cd, ^{111}Cd, ^{112}Cd, ^{113}Cd, ^{114}Cd, ^{116}Cd
- ^{60}Ni, ^{72}Ge, ^{103}Rh (internal standard), ^{105}Pd, ^{115}In, ^{118}Sn

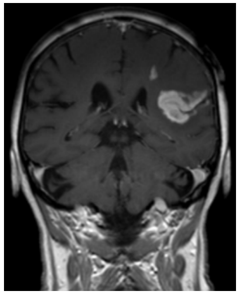
QDs dissolution in Seine river water

Kinetics of dissolution of Zn-spiked CdSe/ZnS QDs in Seine river water sample

([Diss. Zn] $_{Seine}$ = 2000 ppt)



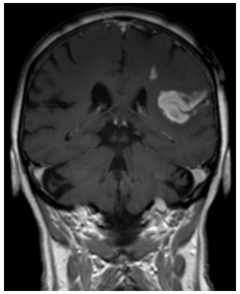
Destinée de nanoparticules manufacturées en milieu complexe

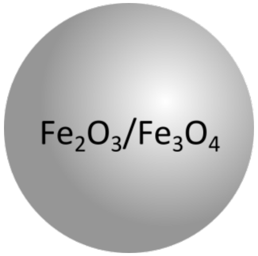


Projet NanoDestinée (DIM NanoK),

Destinée de nanoparticules manufacturées en milieu complexe Traçage isotopique *in Vivo*

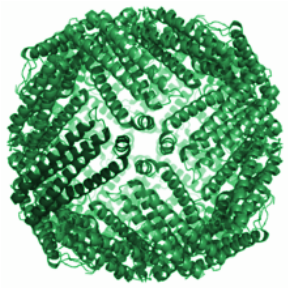
- NPs d'oxyde de Fer en tant qu'agents de contraste pour l'IRM



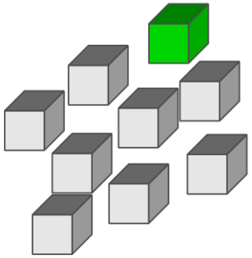


Devenir:
rate, foie, reins, ...

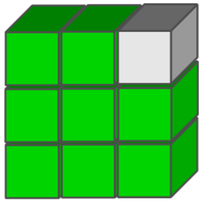
- Corps humain riche en Fer endogène : globules rouges, ferritine



composition isotopique naturelle

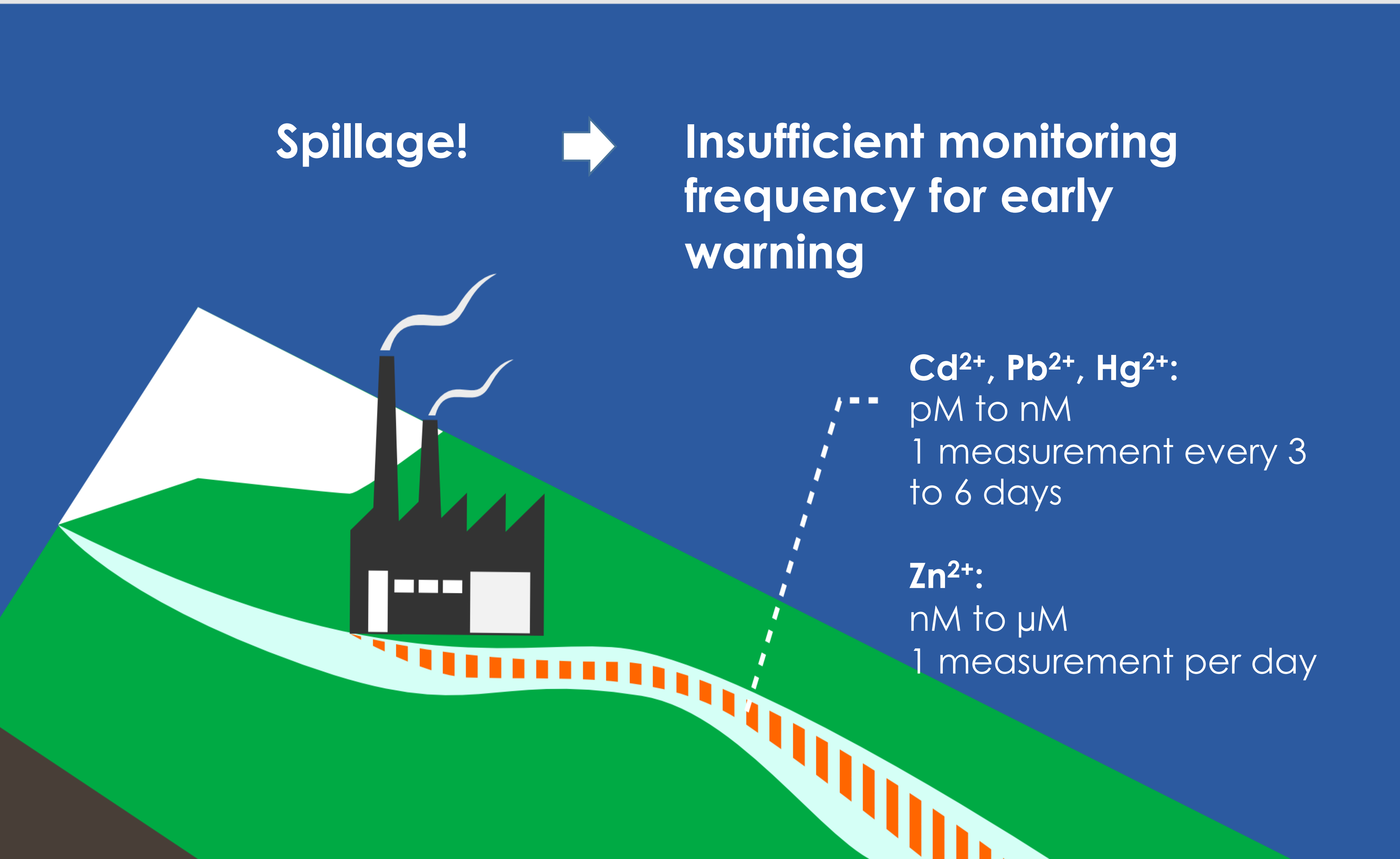


NPs marquées, enrichies en ^{57}Fe



Isotope du Fe	54	56	57	58
Abondance naturelle, en %	5.80	91.72	2.20	0.28

Nanoparticles for monitoring heavy metal ions in freshwaters



Criteria for sensing in fresh waters

Sensitive — no preconcentration step needed

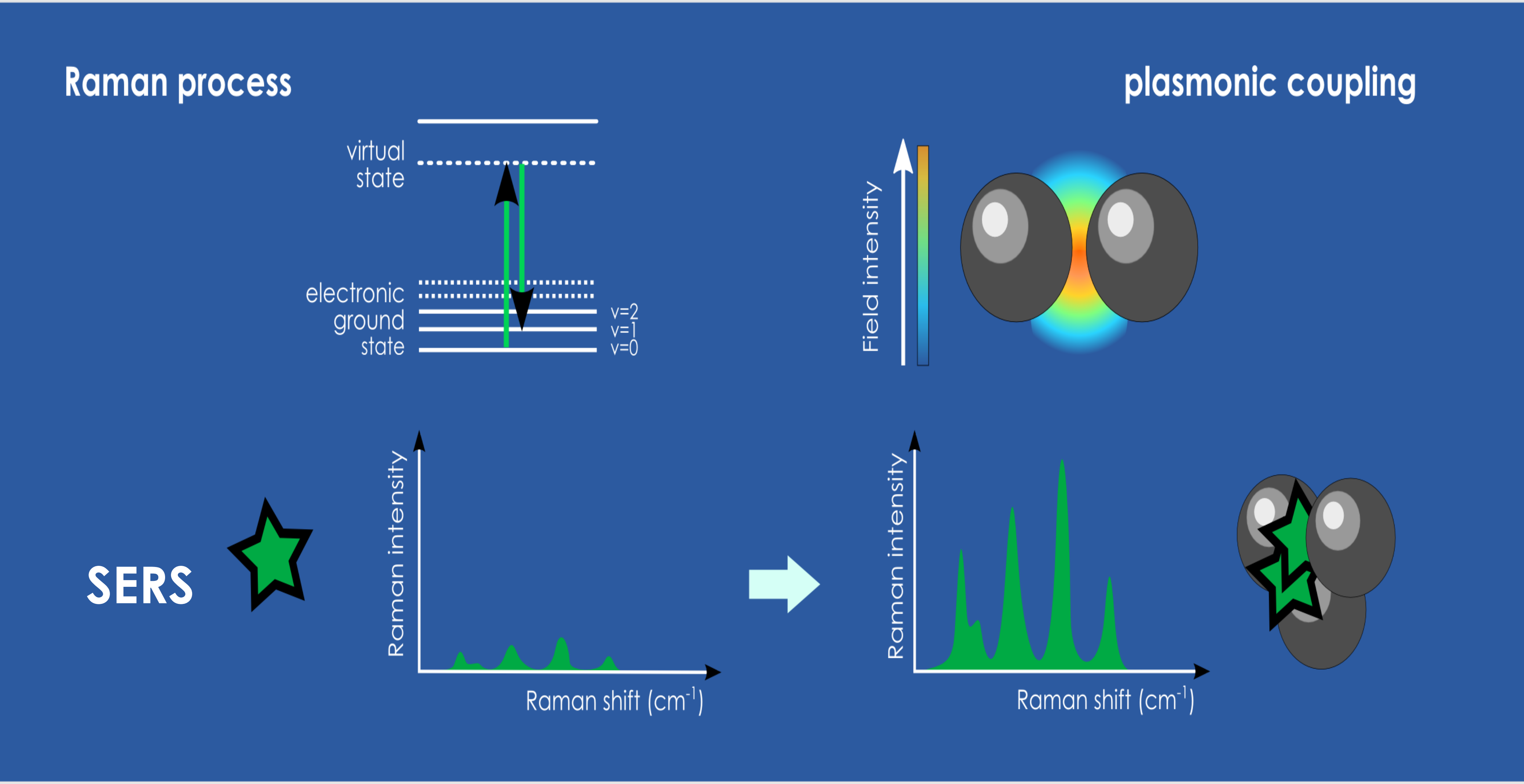
Specific — no mistaking the analyte for another

Speedy — monitoring with $hour^{-1}$ or min^{-1} frequency

Deployable on field — Light, handy, cost effective

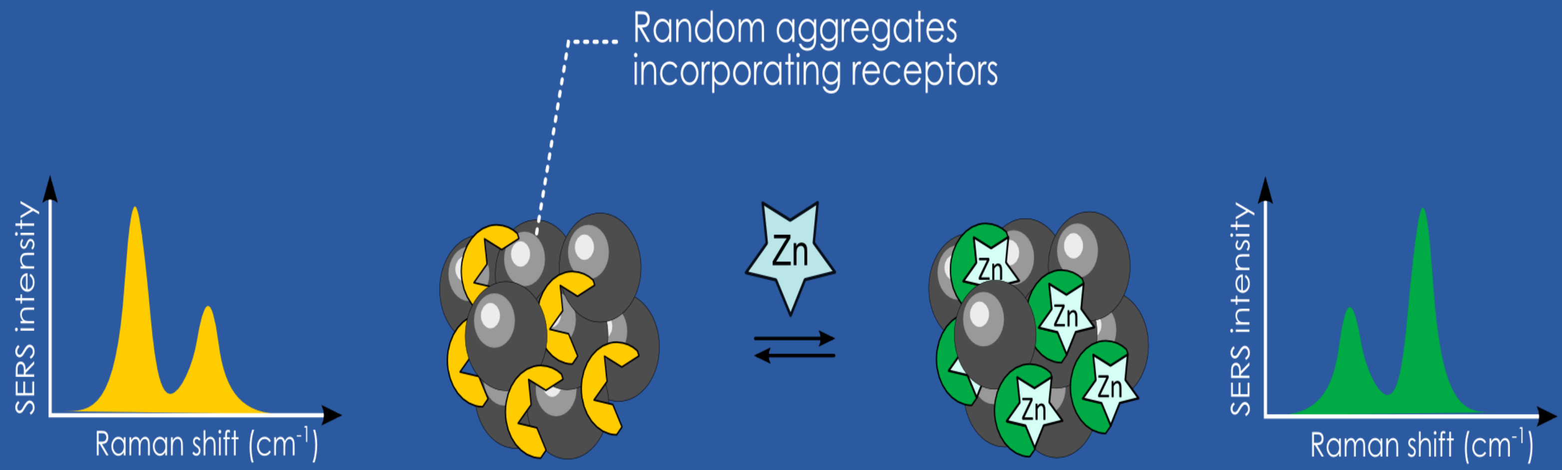
➡ **SERS: the ideal sensor ?**

Principle of SERS



Raman Intensity X 10^4 to 10^6 for random aggregates

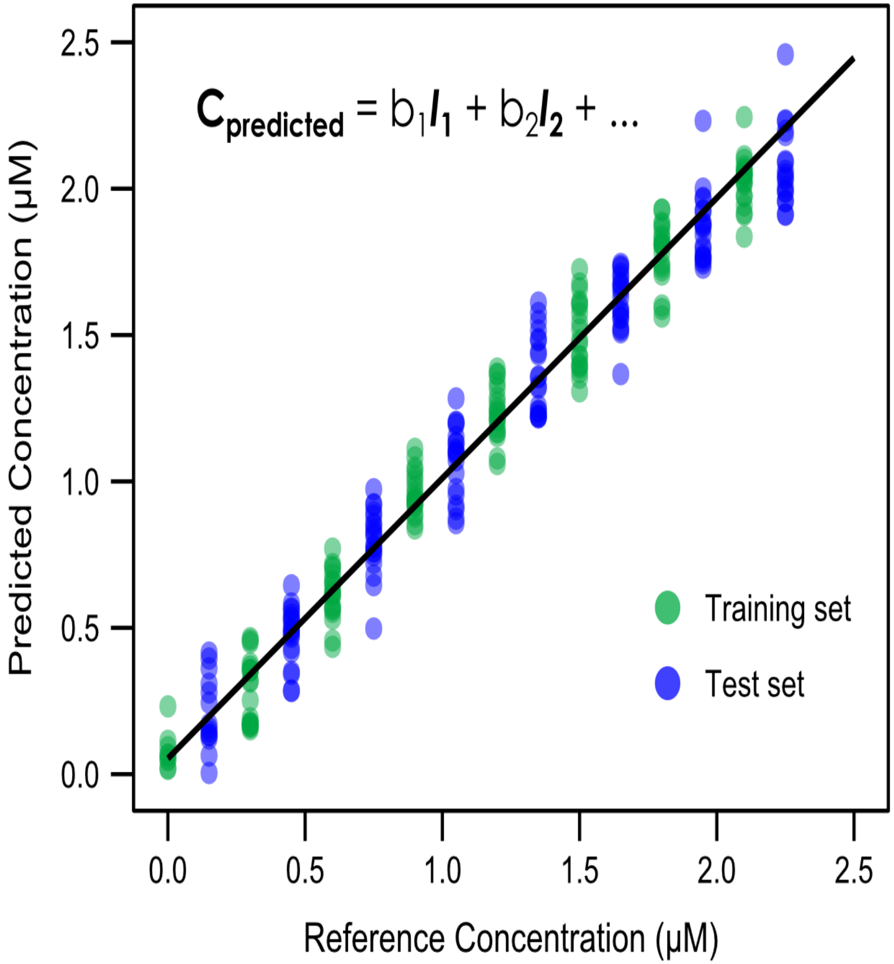
SERS sensing of atomic ions



Analytical performances ?

Useful in fresh waters ?

Calibration using chemometrics



Detection of Zn^{2+} by SERS:

- LOD ~ 190 nM
- High predictive power in the [0.2 – 2.5 μM] range

Typical concentration range of Combined Sewers Overflows (CSOs)

Zn^{2+} sensing in the presence of interferents - chemometric calibration

Typical combined sewer concentrations:

Zn^{2+}~ 1 µM

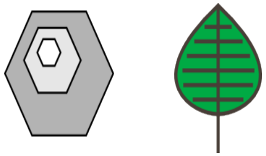
Ca^{2+} ~ 1.44 mM

Na^{+} ~ 1.35 mM

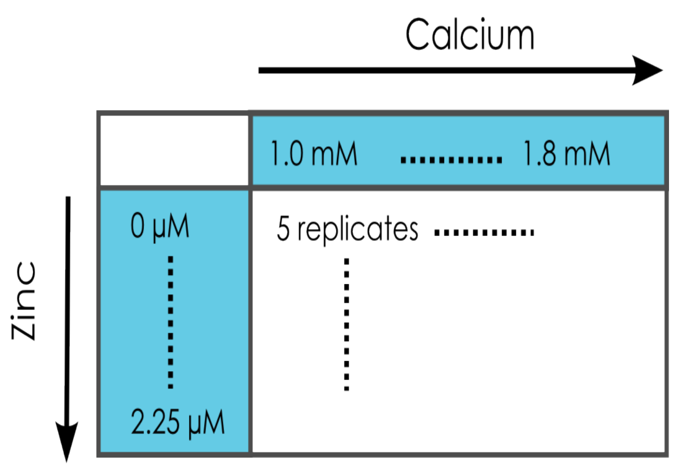
Mg^{2+} ~ 288 µM

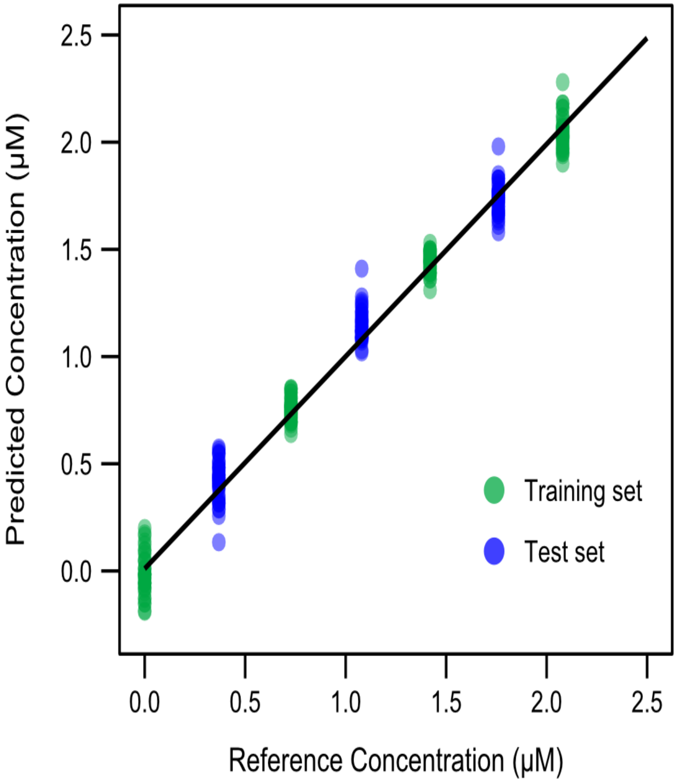
K^{+} ~ 264 µM

Suspended colloids:



Clays, decomposing plants





High predictive power, **regardless of the exact level of Ca interferent**

Journée Institut de Physique du Globe & Laboratoire Matière et Systèmes Complexes de l'Université Paris Diderot

* présentation des deux laboratoires : Laurent Limat (MSC) / Claude Jaupart (IPGP)
* exposés scientifiques (15 minutes)
    - dunes : Clément Narteau (IPGP) / Sylvain Courrech (MSC)
    - erosion et dissolution: Michael Berhanu (MSC) / Eric Lajeunesse (IPGP)
    - vagues, ondes et bruits sismisque : Éléonore Stutzmann (IPGP) / Eric Falcon (MSC)
    - nanoparticules, eau et environnement : Gaelle Charron ou Florence Gazeau (MSC) / Marc Benedetti ou Yann Sivry (IPGP)
    - méandrages : Adrian Daerr (MSC) / François Métivier (IPGP)
    - interface vie/physique/géologie : Bénédicte Ménez (IPGP), Florence Elias (MSC),
    - cyanobacteries et environnement : Julien Dervaux (MSC) / Alexandre Gélabert (IPGP)
    - milieux stratifiés : Angela Limare (IPGP) / Jean Rajchenbach (MSC) (ou à défaut Vincent Fleury, ou Cyprien Gay qui font des instabilités mécaniques)
    - intrusion et vortexs : Chloé Michaut (IPGP) / Matthieu Roché (MSC)
    - singularités et ruptures : Laurent Limat (MSC) / Pascal Bernard ou J.P. Vilotte (IPGP)
    - matériaux : verres, transition de structures, changements de phase : J. Siebert et/ou D. Neuville (IPGP) / Laurent Royon et/ou Bérangère Abou (MSC)
    - méthodes physico chimiques pour les diagnostiques médicaux : F. Moynier (IPGP) / Florence Gazeau et/ou Claire Wilhelm (MSC)