The Loire river : Sediment and Geochemistry

The geochemistry of sediments at the catchment scale: the Loire basin as an example. ***Philippe Négrel***

Multi isotopic characterization (Pb-Zn-Cd-Hg) of the suspended sediments of the Loire River Basin, France. ***Romain Millot, Philippe Négrel, David Widory, Anne-Marie Desaulty, Julie Gattacceca, Christophe Innocent, Catherine Guerrot, Xavier Bourrain, Tom M. Johnson***

Geoscience for a sustainable Earth
brgm

Sediment quality – Geochemistry / environmental chemistry

- **Catchments and weathering: foundations of geochemistry,**
- **Basic knowledge on isotope(s),**
- **The geochemistry of sediments at the catchment scale: the Loire basin,**
- **Suspended matter and sediments,**
- **The erosion quantification,**
- **From the sediment to the labile fraction : how to characterize the anthopogenic environment,**
- **The labile fraction and the extension to the basin,**
- **And the future**

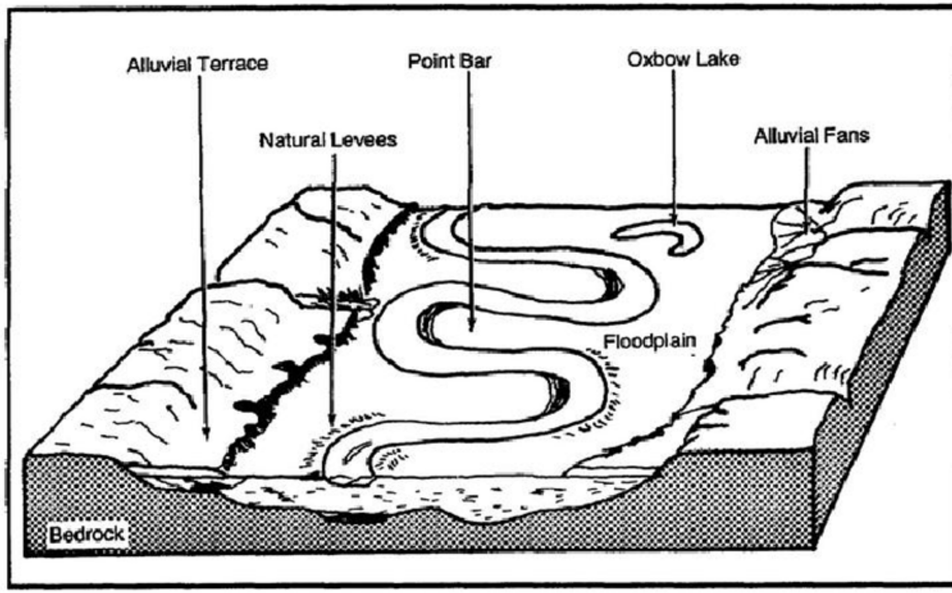
Geoscience for a sustainable Earth
brgm

Catchments and weathering: foundations of geochemistry

> **fluvial system and catchment**

- *water course is a continuum from rainwater towards the ocean*
- *through runoff, evapotranspiration, infiltration, flow in rivers, unsaturated zone and aquifers.*

> **therefore, the way to study hydrologic functioning of fluvial systems must be global.**



Geoscience for a sustainable Earth
brgm

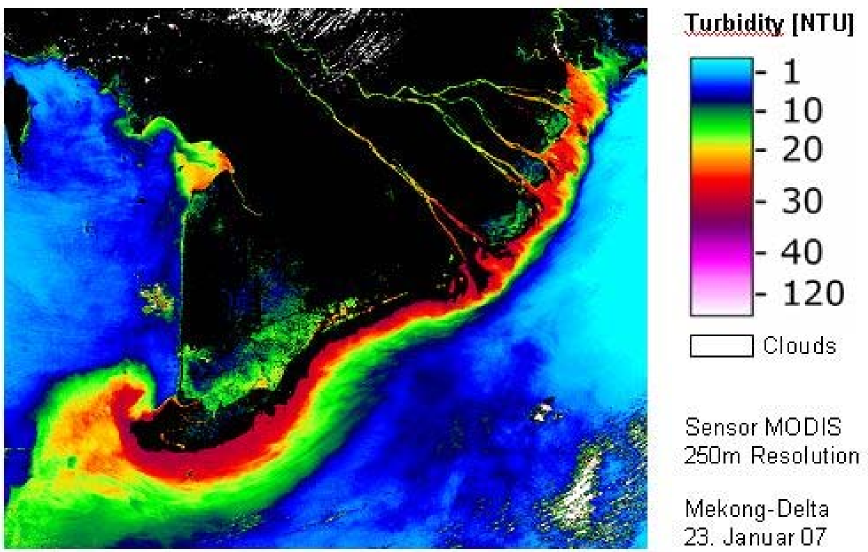
The foundations

- **knowledge of the different inputs to the dissolved and particulate loads carried by streams and rivers:**
  - study of the different natural and anthropogenic sources.
- **Identify and quantify the different inputs to the dissolved and particulate loads:**
  - to describes the spatial evolution of weathering and mechanical erosion rates
- **Identify particle sources and weathering mechanisms:**
  - to determine the temporal variations of chemical species bound to the suspended matter and sediments

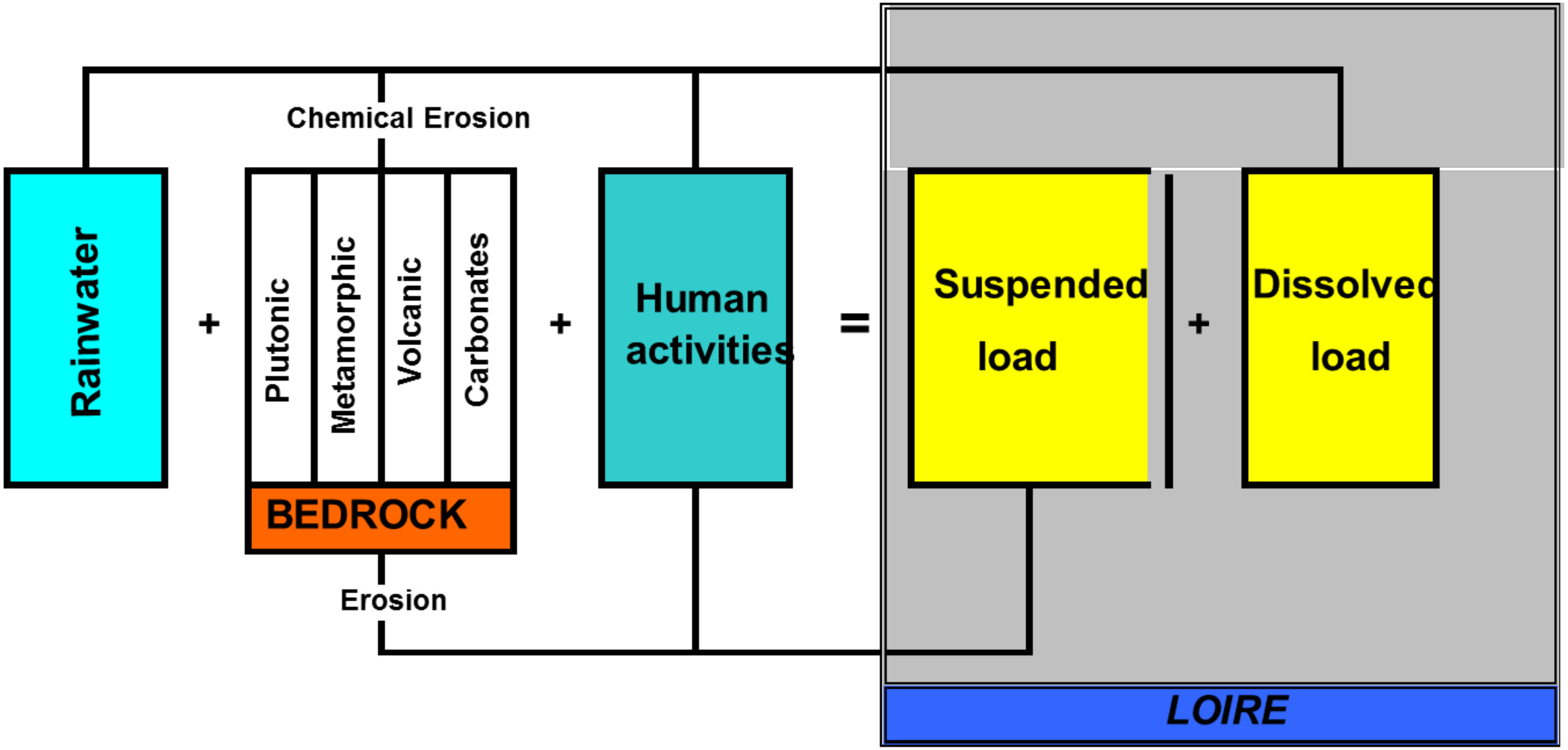
Geoscience for a sustainable Earth
brgm

The foundations: dissolved and suspended load

- Weathering processes initiate the dissolved and suspended loads of most of the world's major rivers.
- Chemical weathering of rocks and soils is one of the essential processes in the geochemical cycling of elements in rivers
- Residual products from chemical and mechanical weathering are carried by rivers and streams to the ocean:
  - as suspended load, typically smaller than a few microns in diameter,
  - and as bed load representing the coarser fraction

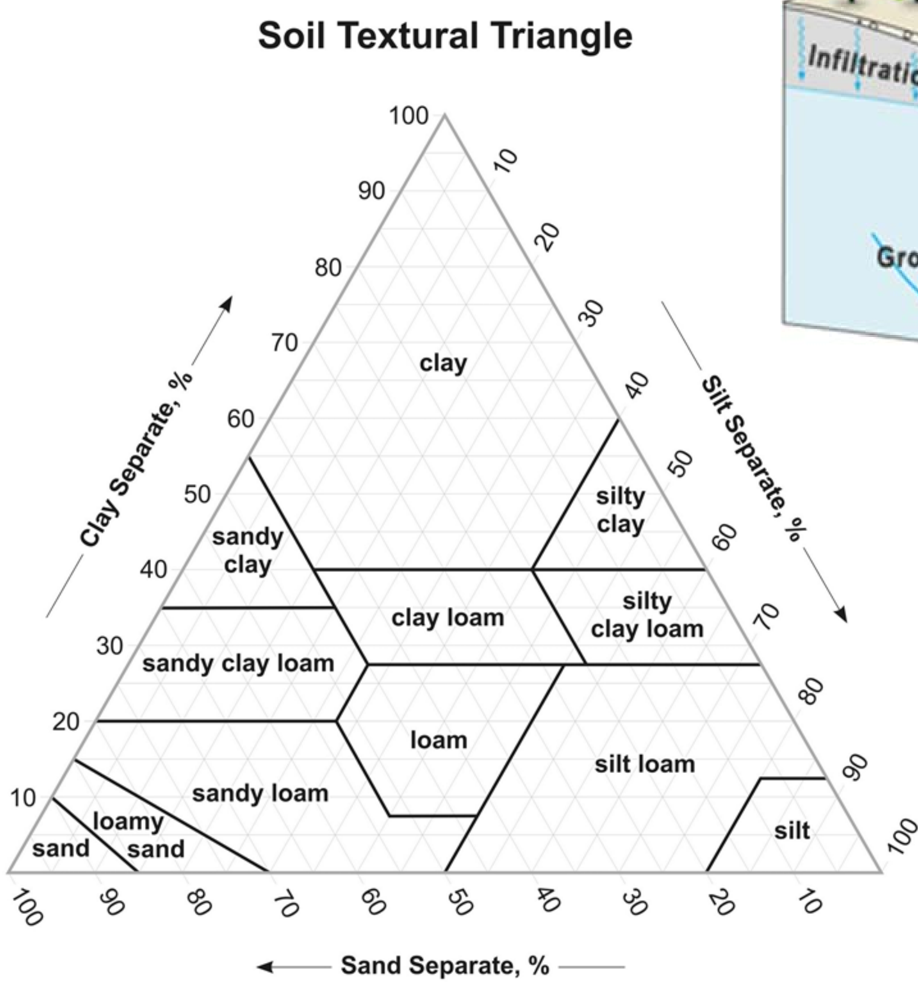


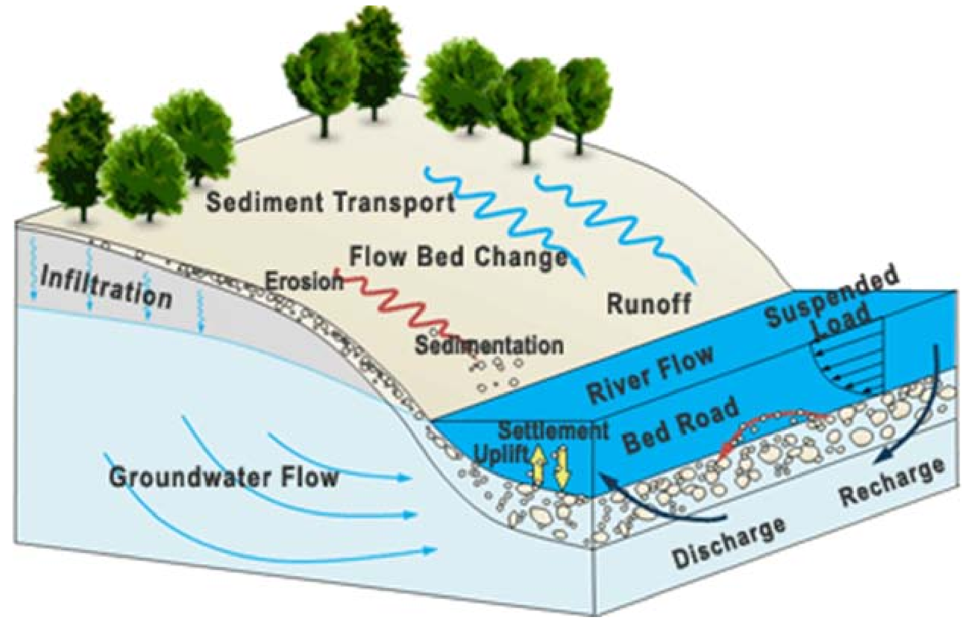
The foundations



brgm
Geoscience for a sustainable Earth

The foundations





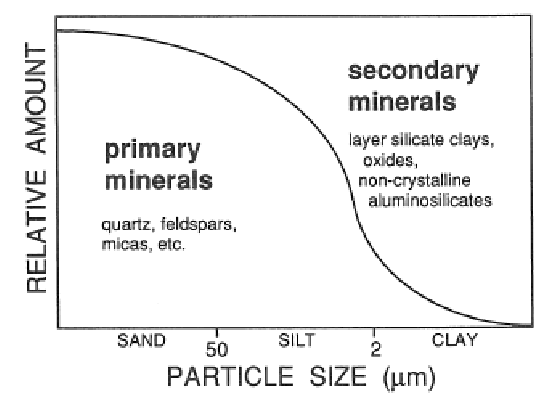
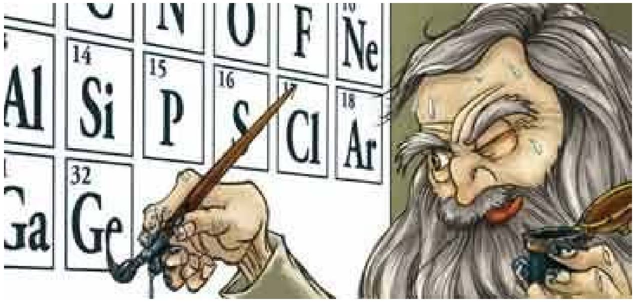


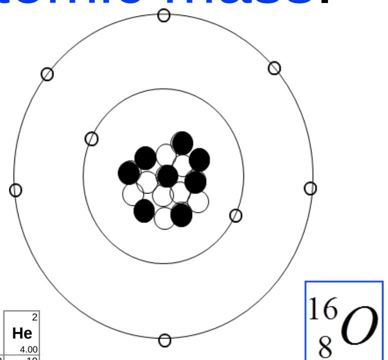
Figure 2.2. Typical abundance of primary and secondary minerals in different size fractions of the soil.

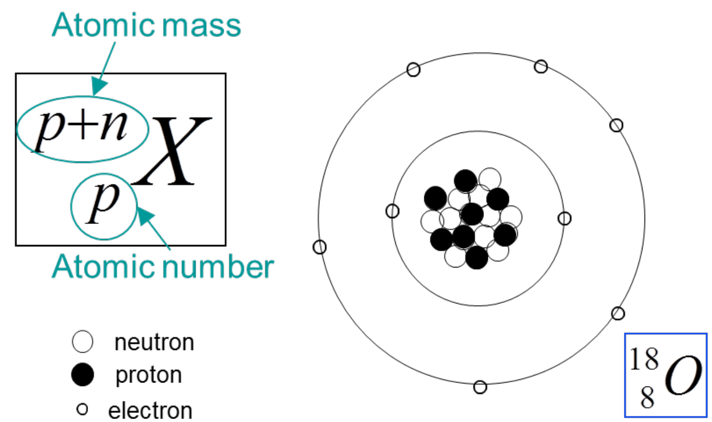
Geoscience for a sustainable Earth
brgm



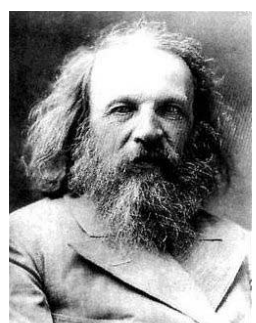
BASIC KNOWLEDGE OF ISOTOPES

- Isotope : Chemical elements with the same atomic number (same name and same position in the Mendeleiev table) but which differ by their atomic mass.





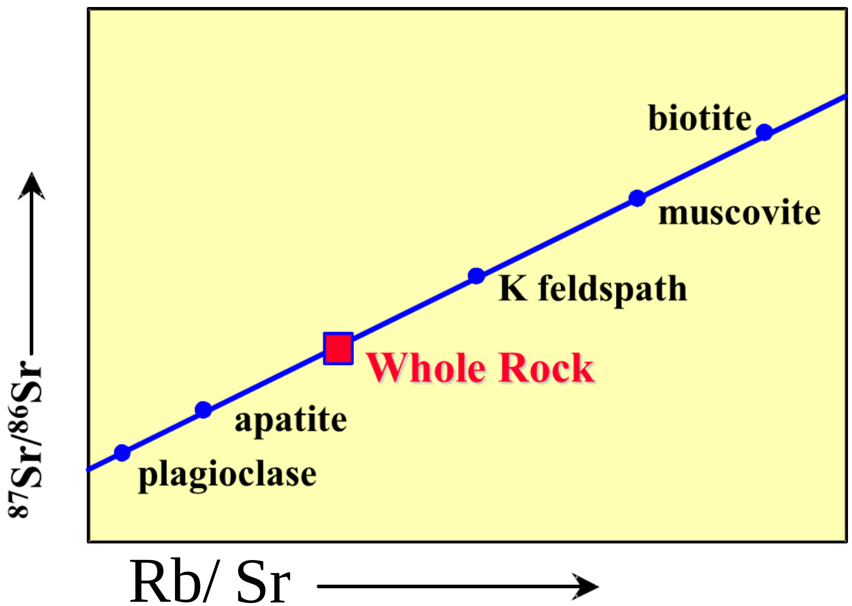
1 H 1.008																	2 He 4.00
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 23.00	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.71	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc 98.91	44 Ru 101.07	45 Rh 102.90	46 Pd 106.40	47 Ag 107.90	48 Cd 112.40	49 In 114.80	50 Sn 118.70	51 Sb 121.80	52 Te 127.60	53 I 126.90	54 Xe 131.30
55 Cs 132.90	56 Ba 137.30	57 La* 138.90	72 Hf 178.50	73 Ta 181.00	74 W 183.90	75 Re 186.20	76 Os 190.20	77 Ir 192.20	78 Pt 195.10	79 Au 197.00	80 Hg 200.60	81 Tl 204.40	82 Pb 207.20	83 Bi 209.00	84 Po (210)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac** (227)	104 Ku (258)	105 Ha (260)													
***Lanthanides**				58 Ce 140.10	59 Pr 140.90	60 Nd 144.20	61 Pm (145)	62 Sm 150.40	63 Eu 152.00	64 Gd 157.30	65 Tb 158.90	66 Dy 162.50	67 Ho 164.90	68 Er 167.30	69 Tm 168.90	70 Yb 173.00	71 Lu 175.00
****Actinides**				90 Th 232.00	91 Pa 231.00	92 U 238.00	93 Np 237.00	94 Pu 239.10	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (254)	100 Fm (257)	101 Md (256)	102 No (254)	103 Lr (258)

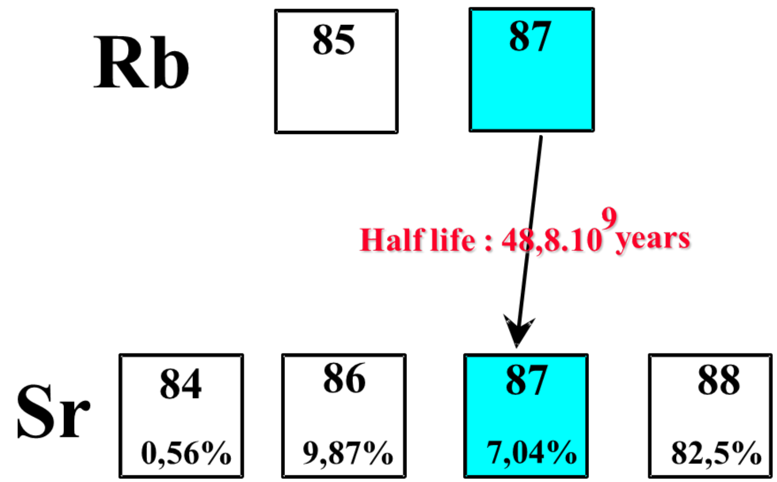


Dimitri I. Mendeleïev
So friendly

Geoscience for a sustainable Earth
brgm

The radiogenic isotopes





Decay constant

time

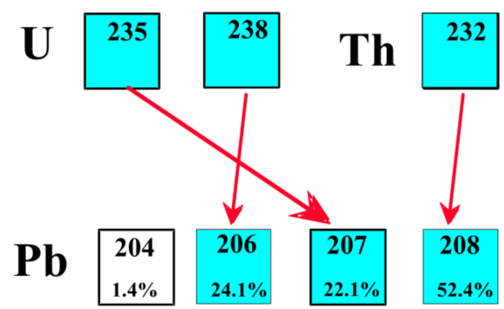
$$^{87}Sr = {}^{87}Sr_0 + {}^{87}Rb(e^{\lambda t} - 1)$$

daughter

initial

parent

$$\frac{^{87}Sr}{^{86}Sr} = \left(\frac{^{87}Sr}{^{86}Sr}\right)_0 + \frac{^{87}Rb}{^{86}Sr}\left(e^{\lambda t} - 1\right)$$

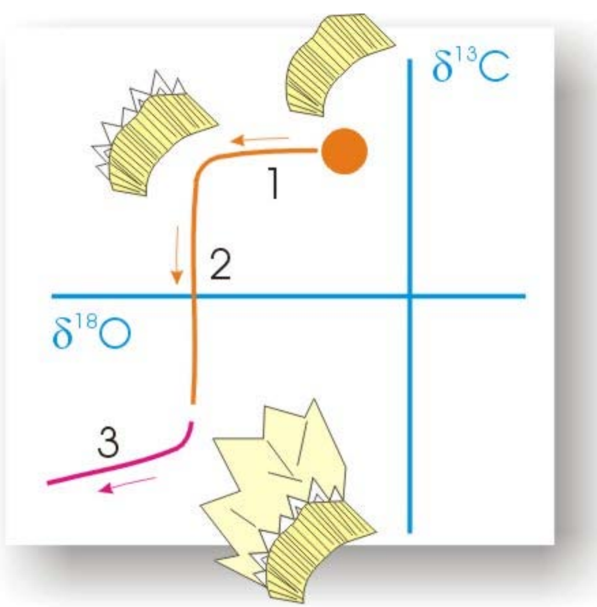


Geoscience for a sustainable Earth
brgm

The stable isotopes

Table 9.1. Isotope Ratios of Stable Isotopes

Element	Notation	Ratio	Standard	Absolute Ratio
Hydrogen	δD	D/H ($^2H/^1H$)	SMOW	1.557×10^{-4}
Lithium	δ^7Li	$^7Li/^6Li$	NIST 8545 (L-SVEC)	12.285
Boron	$\delta^{11}B$	$^{11}B/^{10}B$	NIST 951	4.044
Carbon	$\delta^{13}C$	$^{13}C/^{12}C$	PDB	1.122×10^{-2}
Nitrogen	$\delta^{15}N$	$^{15}N/^{14}N$	atmosphere	3.613×10^{-3}
Oxygen	$\delta^{18}O$	$^{18}O/^{16}O$	SMOW, PDB	2.0052×10^{-3}
	$\delta^{17}O$	$^{17}O/^{16}O$	SMOW	3.76×10^{-4}
Sulfur	$\delta^{34}S$	$^{34}S/^{32}S$	CDT	4.43×10^{-2}

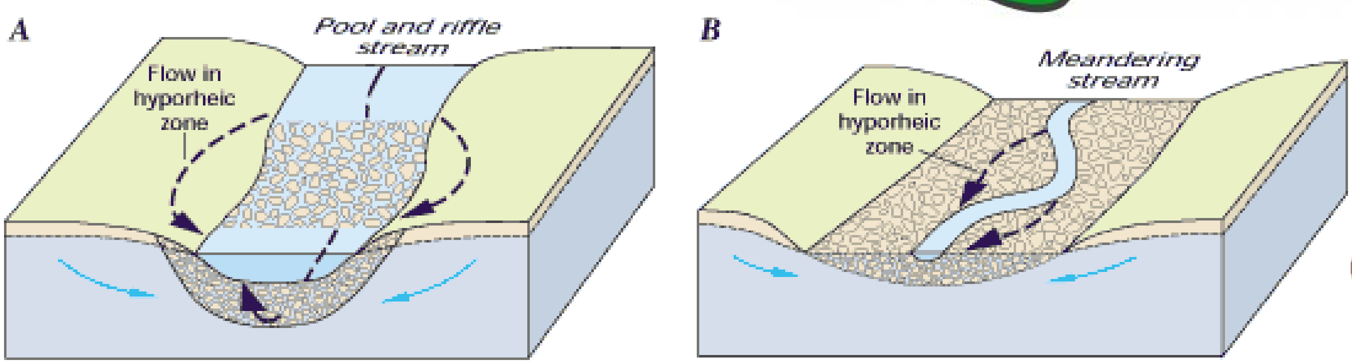


$$\delta^{18}O = \left[\frac{(^{18}O/^{16}O)_{sam} - (^{18}O/^{16}O)_{SMOW}}{(^{18}O/^{16}O)_{SMOW}}\right] \times 10^3$$

The *fractionation factor*, α, is the ratio of isotope ratios in two phases:

$$\alpha_{A-B} \equiv \frac{R_A}{R_B}$$

THE GEOCHEMISTRY OF SEDIMENTS AT THE CATCHMENT SCALE: THE LOIRE BASIN



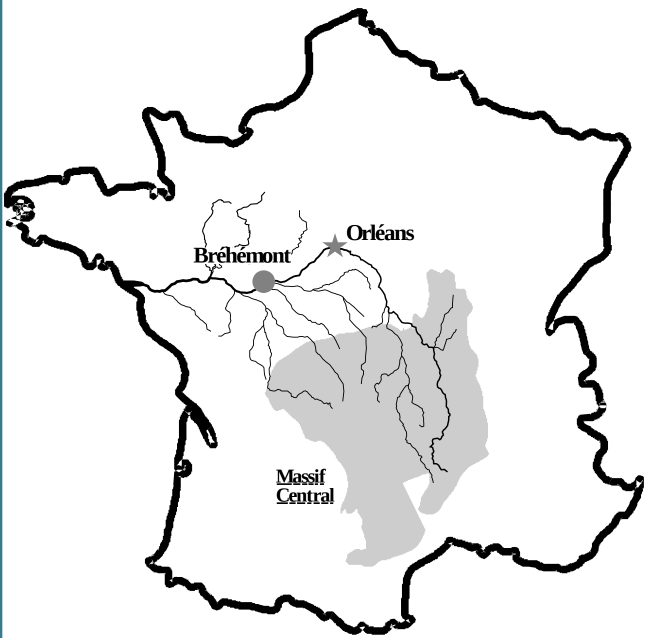
Geoscience for a sustainable Earth
brgm

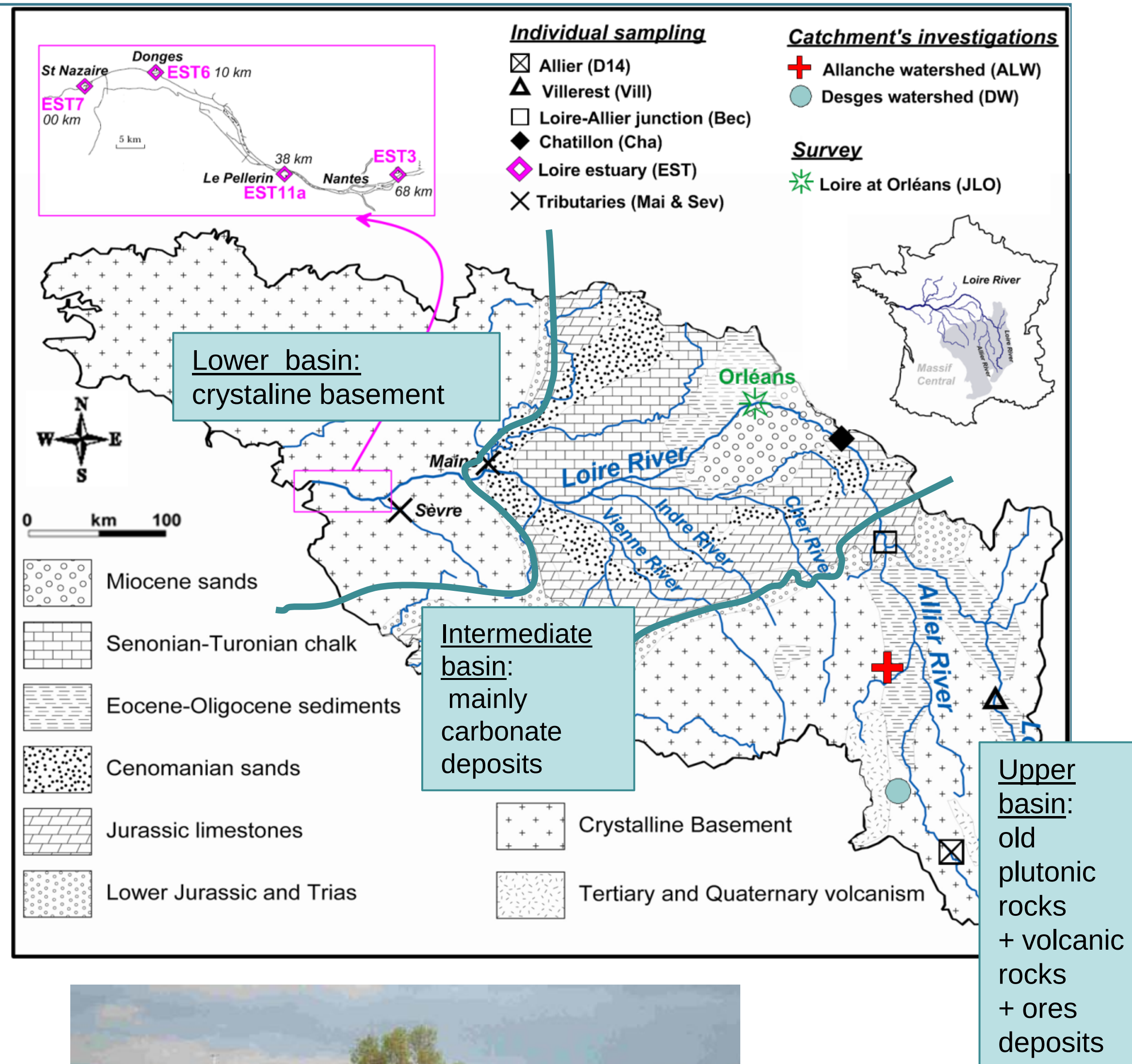
The Loire

> **The surface waters of the Loire drainage basin offer unusual opportunities for selected geochemical studies because:**

- the Loire drains 2 main types of bedrock – the silicate basement (Massif Central) and the sedimentary area of the southern Paris Basin
- inland basin, main European riverine inputs to the Atlantic Ocean, 1/3 of France,
- parts of the watershed are industrialized and parts are agricultural, where anthropogenic activities may contribute in varying degrees to the dissolved load. 50% of cereal cultivations, 40% of food processing industries

Geoscience for a sustainable Earth
brgm



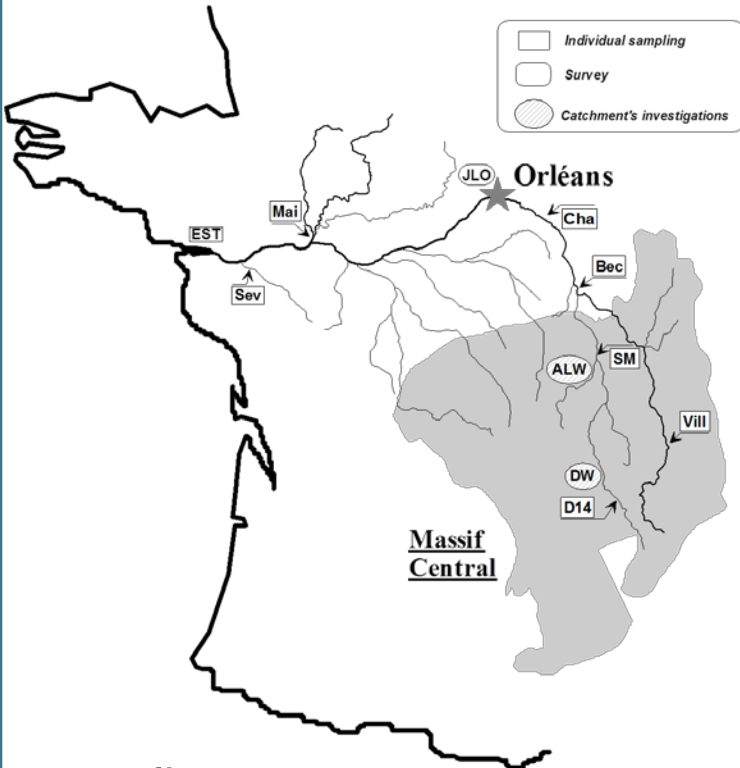


1010 km long, drainage area of 117,800 km^2:
Orleans (34% of the total basin surface)
Brehemont, 150 km downstream, draining 50% of the total basin surface.

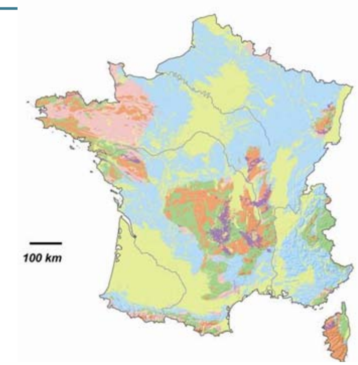
plutonic rocks volcanic area represent 46%

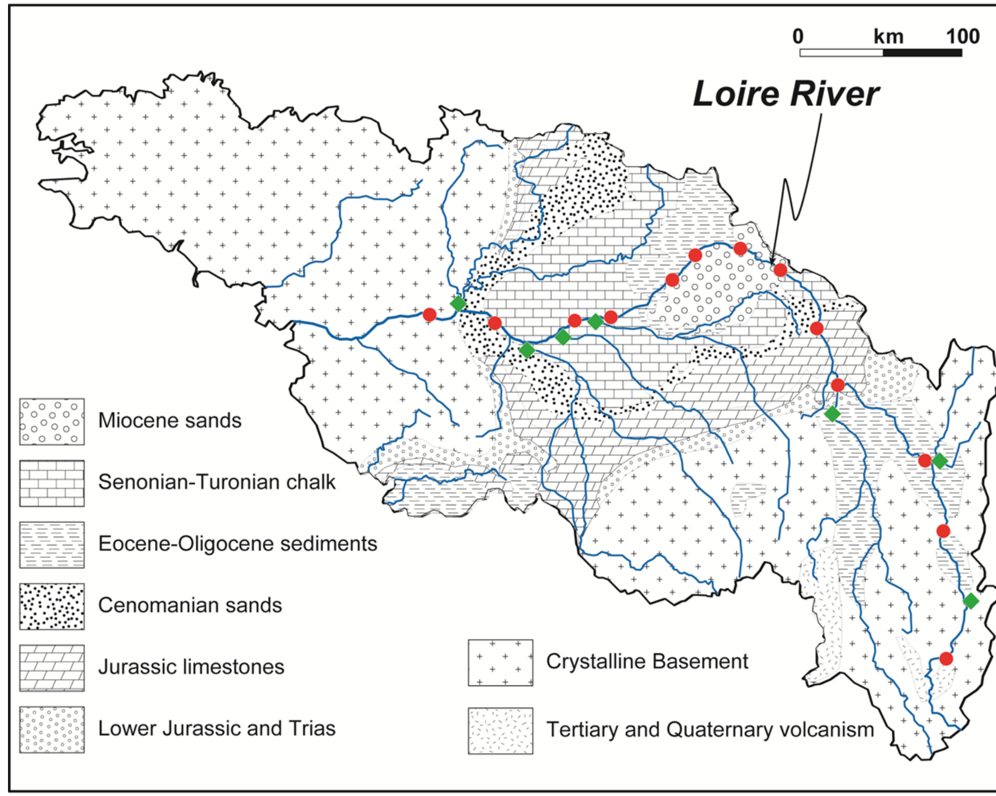
Geoscience for a sustainable Earth
brgm

Sampling



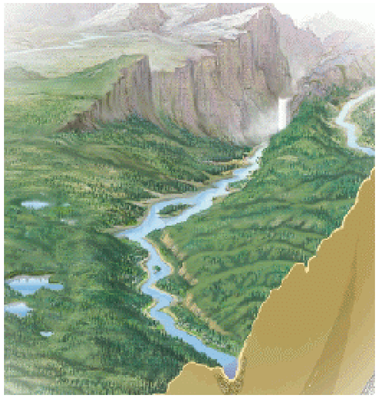
Sampling 1994-2008

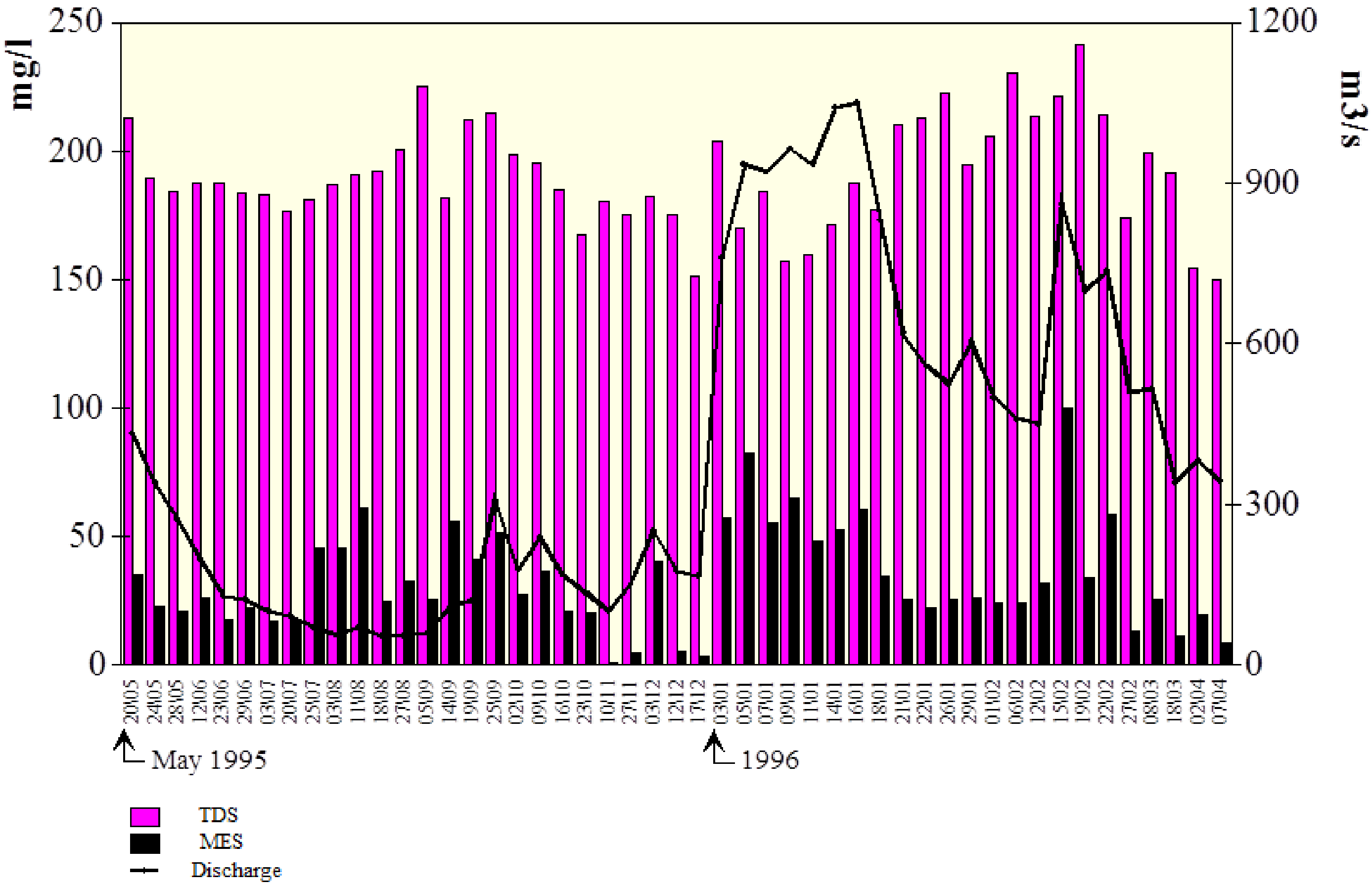




Sampling 2011-present

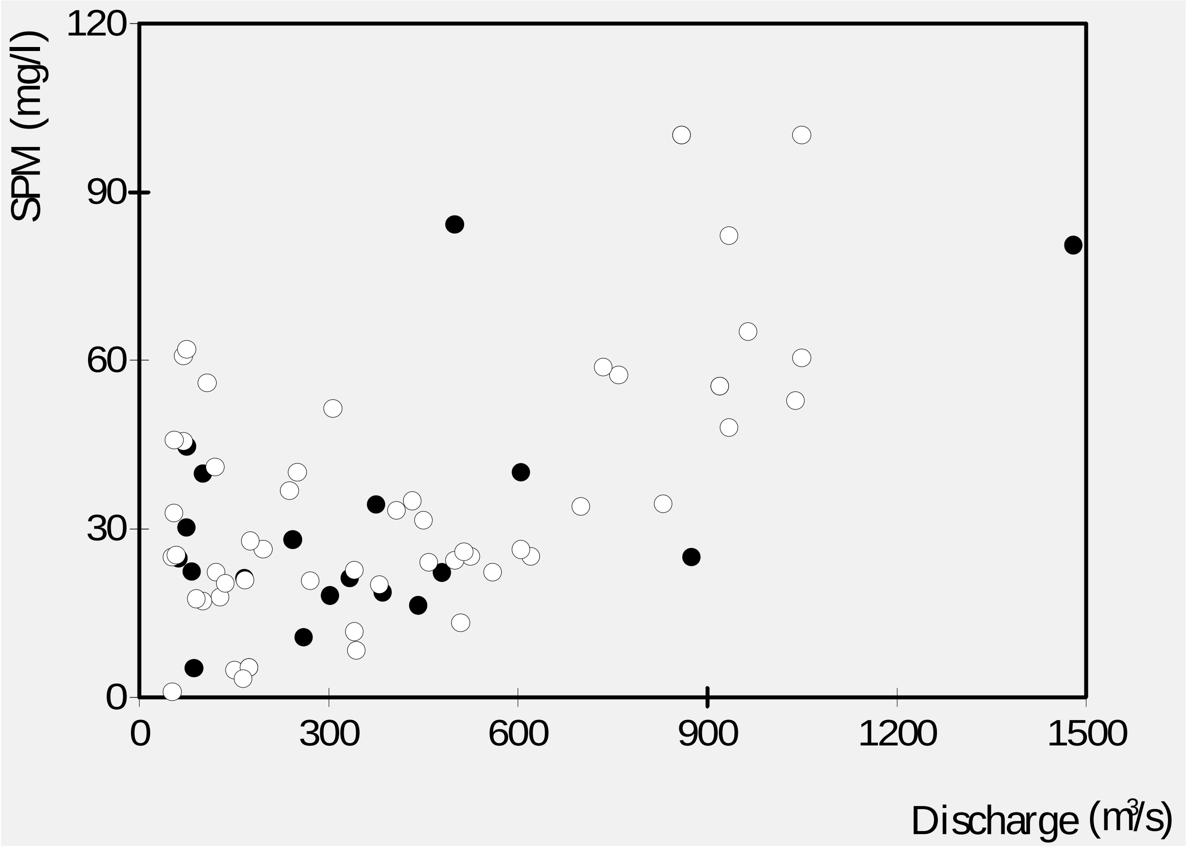
SUSPENDED MATTER AND SEDIMENTS





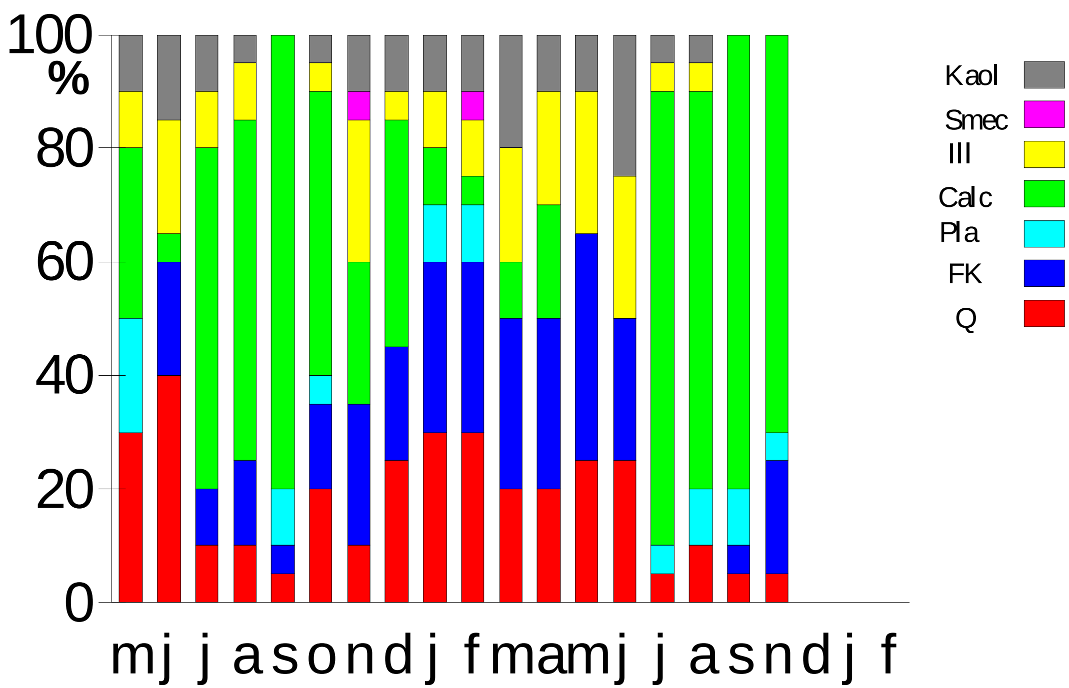
Geoscience for a sustainable Earth
brgm

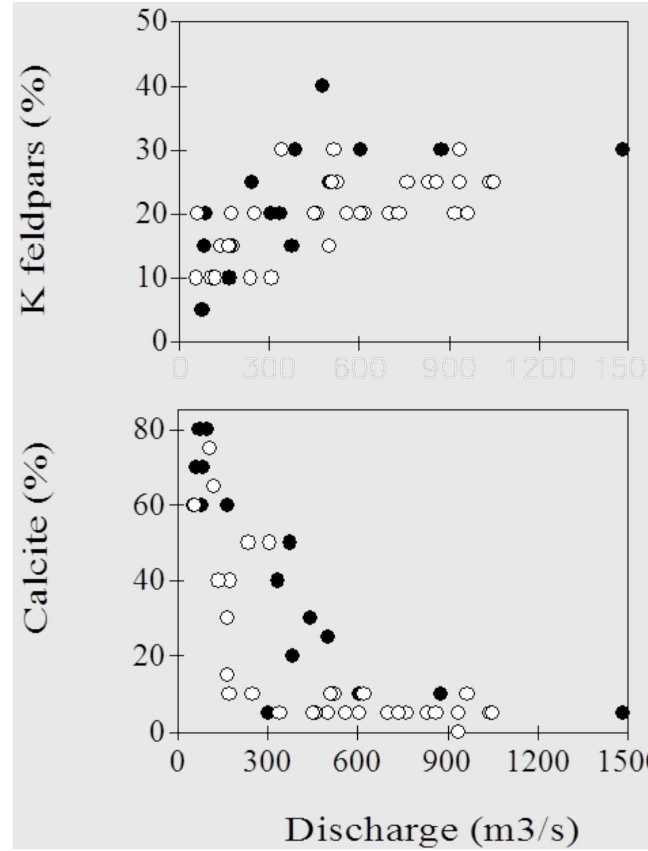
Evolution of SPM concentration with discharge for daily (open circles) and monthly (filled circles) samples



- ✓ weak correlation of increasing SPM concentration with increasing discharge
  - no cyclical relationship with river flow.
- ✓ The existence of dams along the river implies that, suspended load could be controlled by non-natural processes.

Mineralogical composition of the SPM

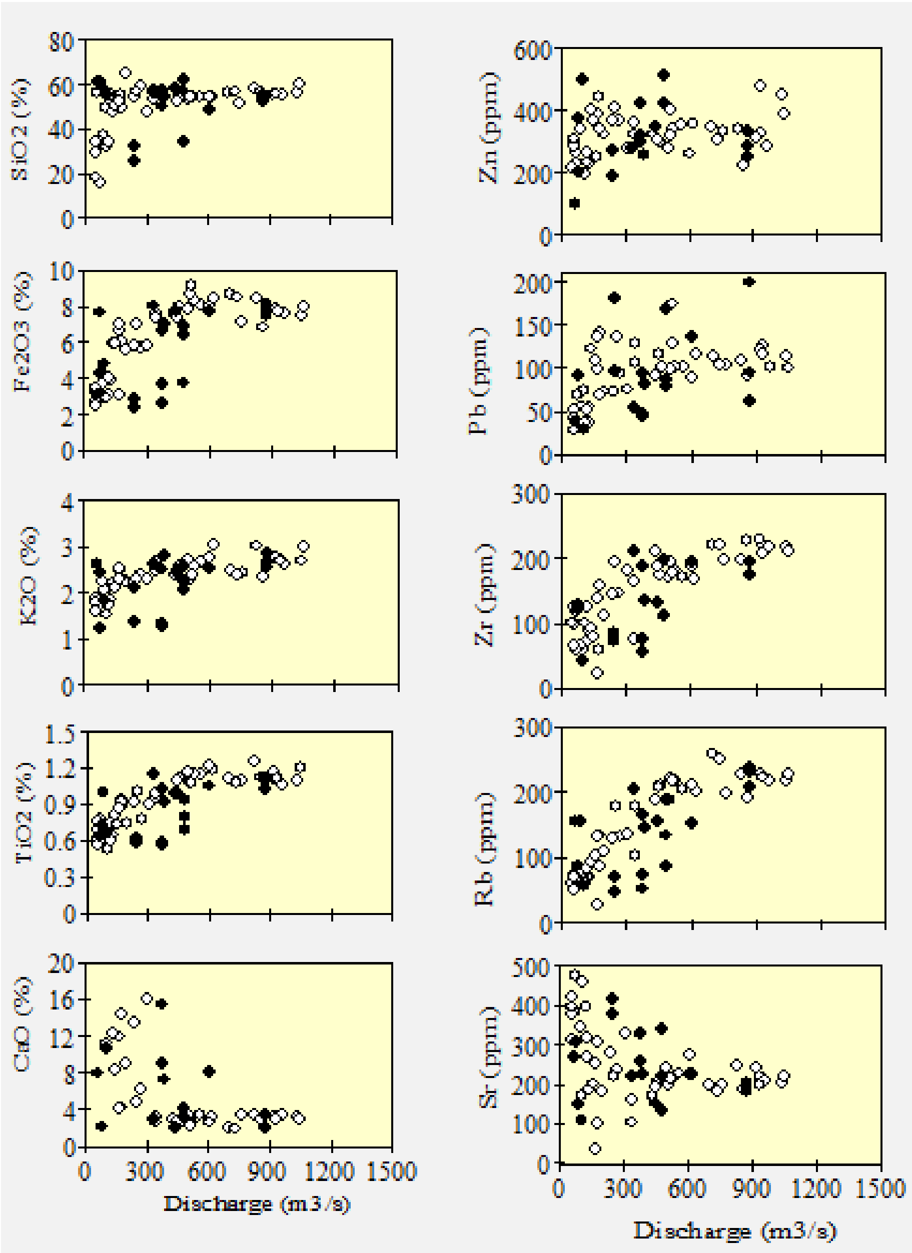




> **Evolution of calcite and K-feldspar abundances with river discharge**

- The quartz and K-feldspar contents increase, calcite contents decrease with increasing discharge

Geoscience for a sustainable Earth
brgm



Evolution of major-and trace element concentrations

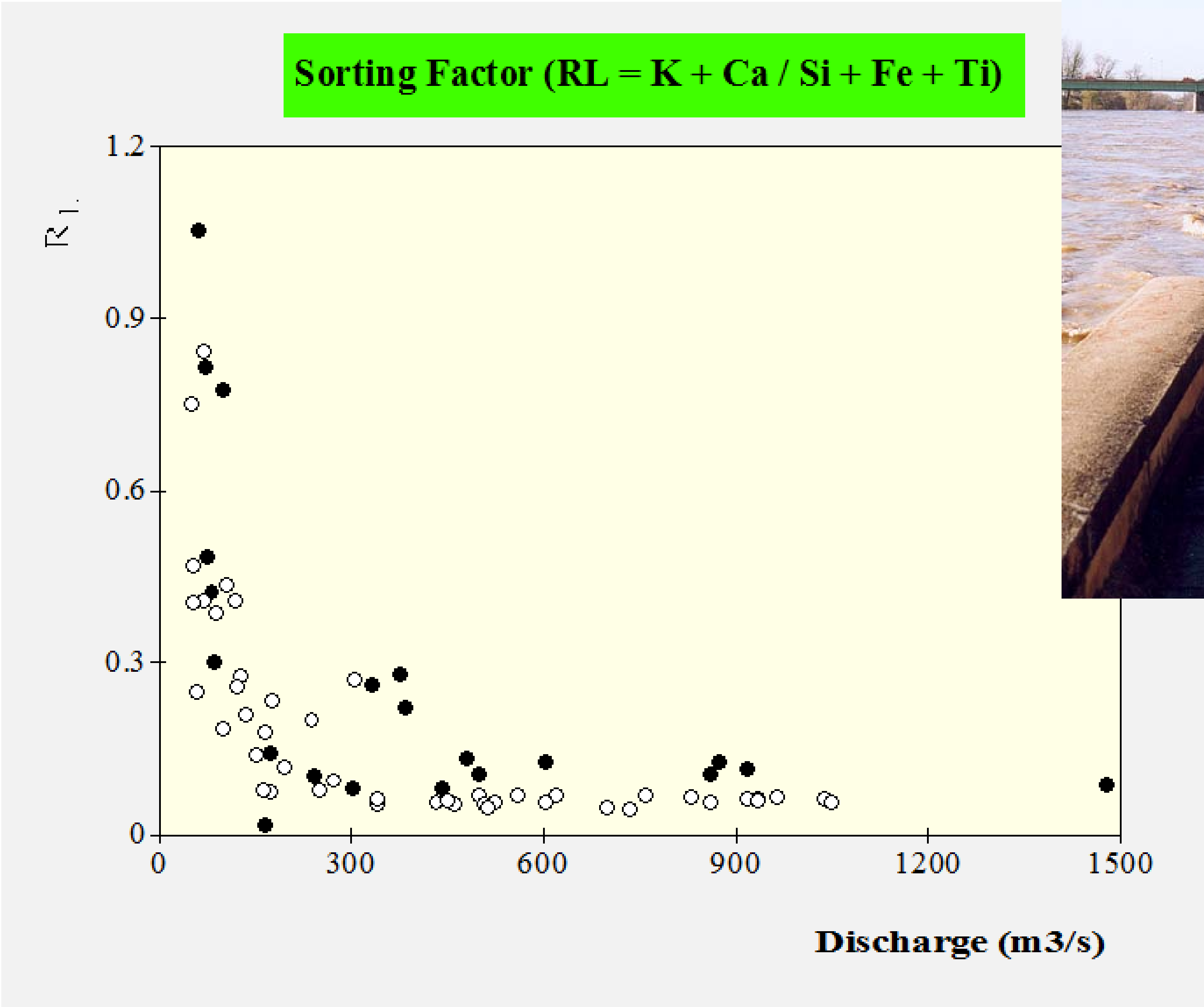
- in suspended matter
- with river discharge

Concentrations of chemical species can be related to fluctuations in the mineralogical assemblages:

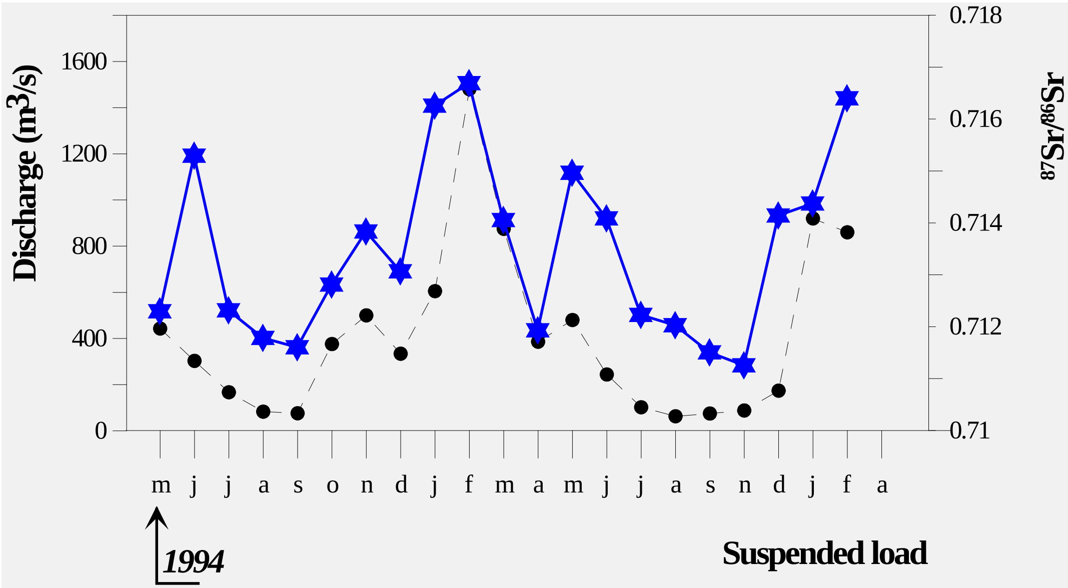
- abundance of illite and K-feldspar for K, Si, Fe, Zr, Rb and Ti,
- abundance of calcite and plagioclase for Ca and Sr

Geoscience for a sustainable Earth
brgm

Sorting Factor



Suspended matter: characterisation of natural and anthropogenic fluxes



Fluctuations in $^{87}Sr/^{86}Sr$ in the suspended load (✸) discharge of the Loire river (●) as a function of months

Mixing model with two signatures:

⌧ high flow, highest $^{87}Sr/^{86}Sr$, agree with the geochemical signature of the weathered silicate bedrock of the Massif Central,

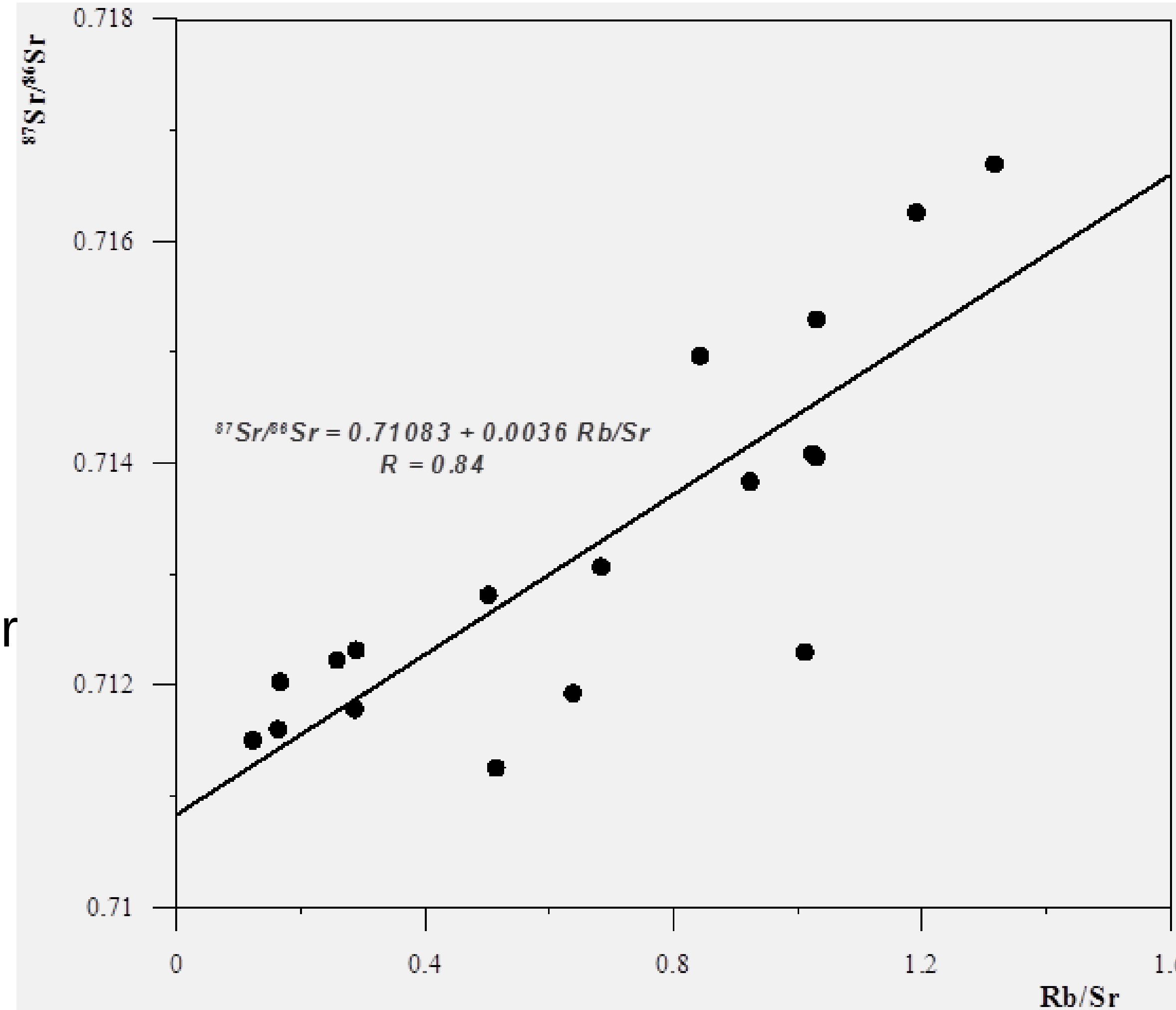
⌧ low flow, lowest $^{87}Sr/^{86}Sr$, agree with the geochemical signature of weathered carbonate bedrock, groundwaters and fertilizers inputs

✓ Increase of the $^{87}Sr/^{86}Sr$ ratio with increasing K-feldspar abundance and, conversely, a decrease in the $^{87}Sr/^{86}Sr$ ratio with increasing calcite abundance

Geoscience for a sustainable Earth
brgm

Sr isotope systematics

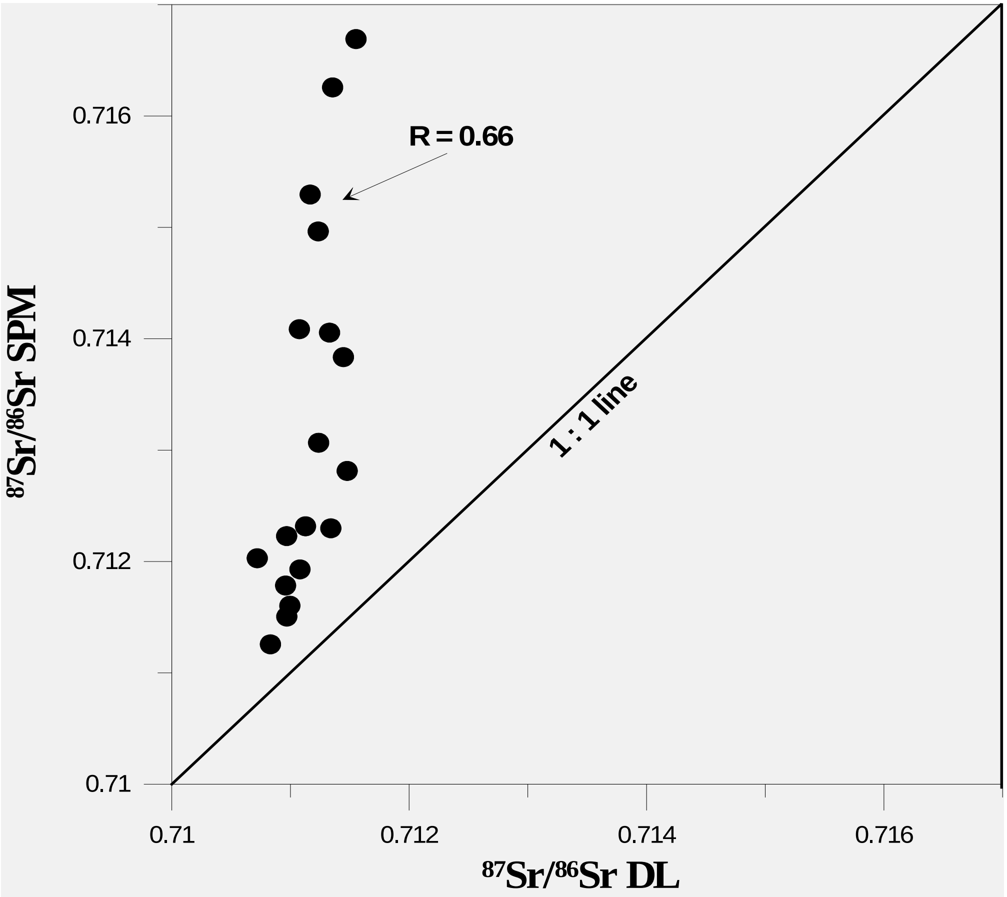
- ✓ The $^{87}Sr/^{86}Sr$ ratio fluctuates accordingly to the inverse fluctuation of calcite and K-feldspar with river discharge.
- ✓ The relationship between the $^{87}Sr/^{86}Sr$ and Rb/Sr ratios indicates binary mixing between calcite and K-feldspar end-members.



Suspended matter: characterisation of natural and anthropogenic fluxes

Similarities between the $^{87}Sr/^{86}Sr$ ratios near the 1:1 line confirm the existence of authigenic calcite, imply the considerable abundance of this phase primarily during low river flow.

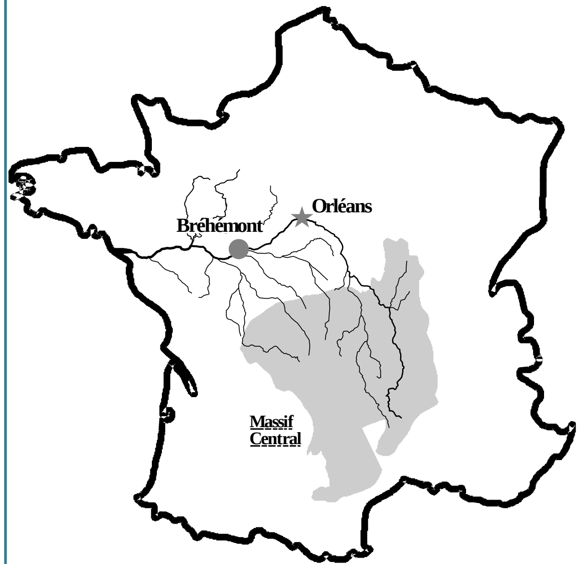
The increase in $^{87}Sr/^{86}Sr$ ratios in the SPM is linked to the corresponding increase in K-feldspar abundance.



Relationship between the $^{87}Sr/^{86}Sr$ ratios of the suspended particulate matter and of the dissolved load.

Geoscience for a sustainable Earth
brgm

The erosion rates



> **The detrital and authigenic exportation fluxes were calculated at the two sampling sites.**

- At Orleans, the total annual flux is calculated to be 370 10^3 T/y including 16% of authigenic carbonates.
- At Brehemont, the flux is calculated to be 525 10^3 T/y with a percentage of authigenic carbonate ranging between 10% and 25%.

> **An homogeneous specific erosion rate of 8 t/y/km^2 has been determined at Orleans and Brehemont**

Geoscience for a sustainable Earth
brgm

FROM THE SEDIMENT TO THE LABILE FRACTION : HOW TO CHARACTERIZE THE ANTHOPOGENIC ENVIRONMENT

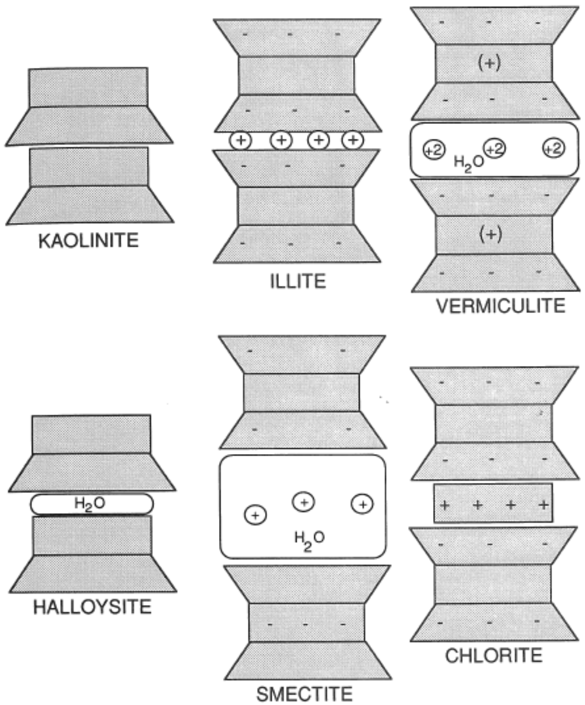
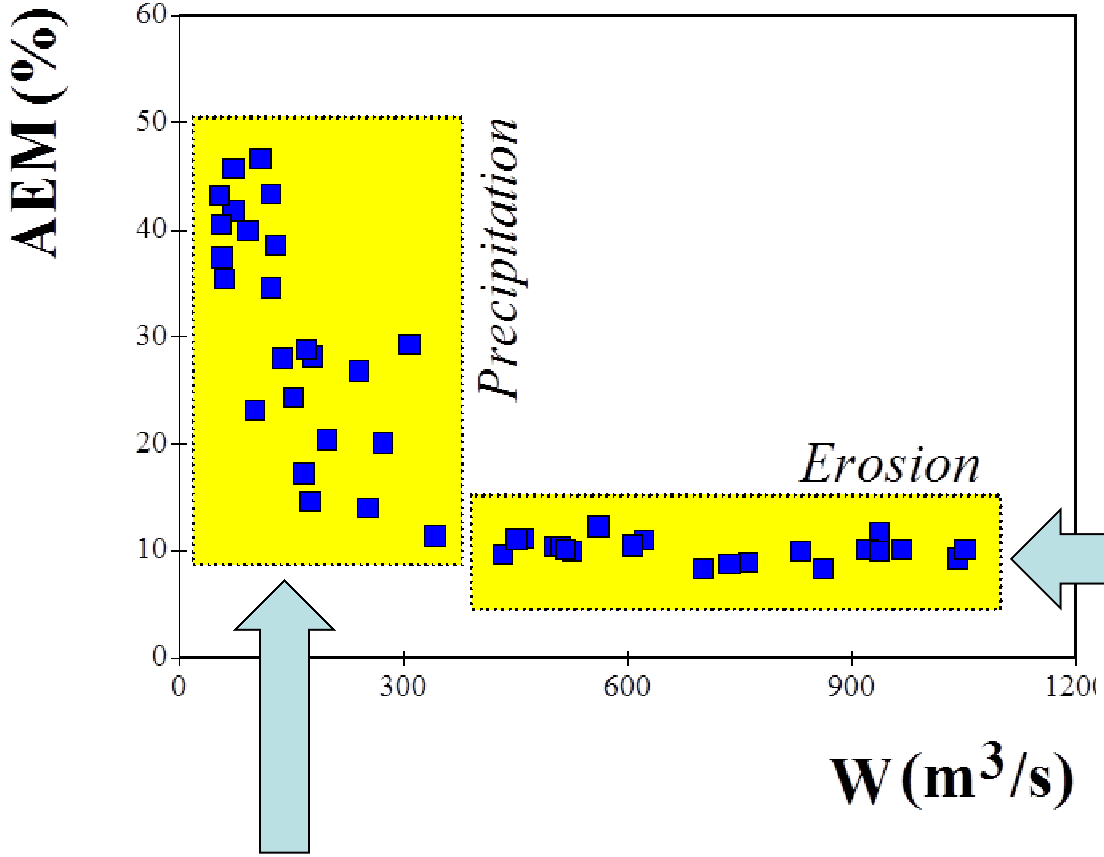


Figure 2.16. Common groups of layer silicate clay structures found in soils, pictured in terms of their tetrahedral (▬) and octahedral (■) sheets. The usual locations of structural charge and exchange cations are indicated by − and + signs.

The labile fraction

Relationship between the abundance of acid extracted matter (AEM) in the suspended particulate matter and the discharge of the Loire river



These two fields correspond to time-related processes within the river and thus reflect two end-member inputs

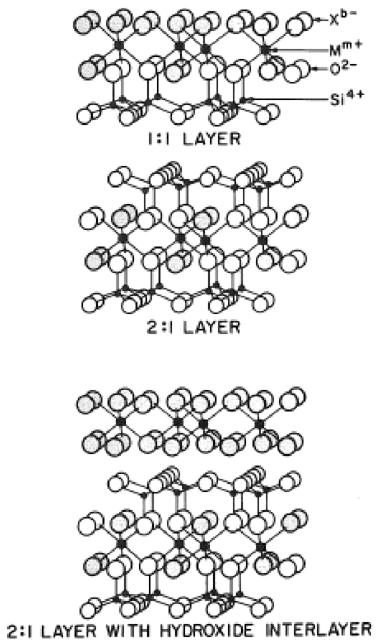
hydrous Fe-Mn oxides or adsorbed onto clays during high flow

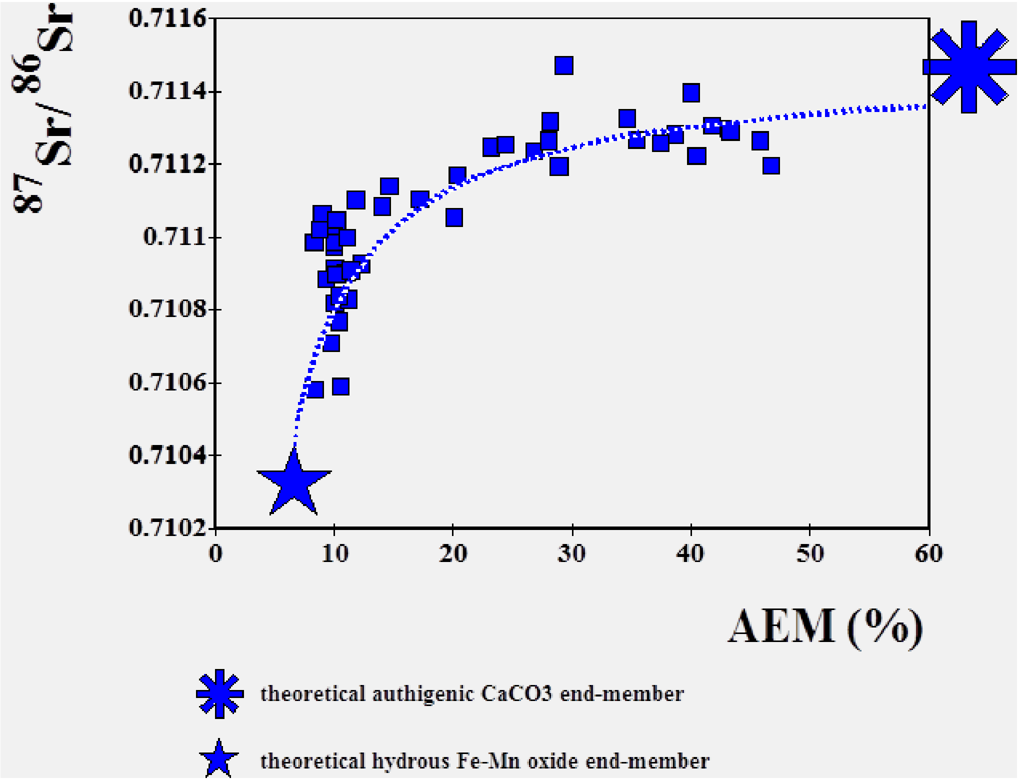
$CaCO_3$ precipitation during low flow in summer

Sr isotopes in the labile fraction

$^{87}Sr/^{86}Sr$ ratios plotted against the abundance (%) of acid extracted matter (AEM) in the suspended particulate matter of the Loire river

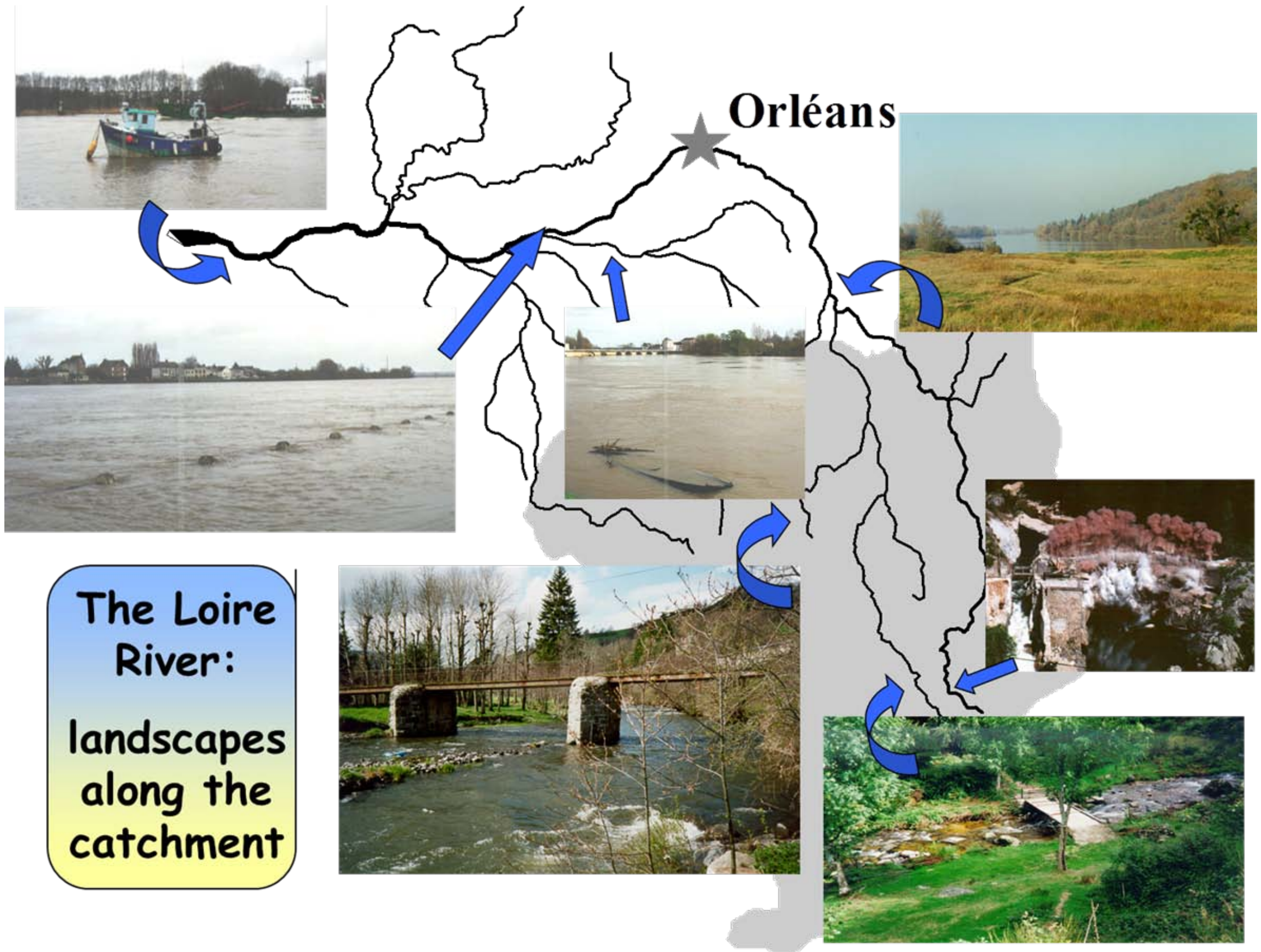
FIG. 2.4 The three layer types of clay minerals (Table 2.3). (Reprinted with permission from G. Sposito, *The Surface Chemistry of Soils*, Oxford Univ. Press, New York, 1984.)



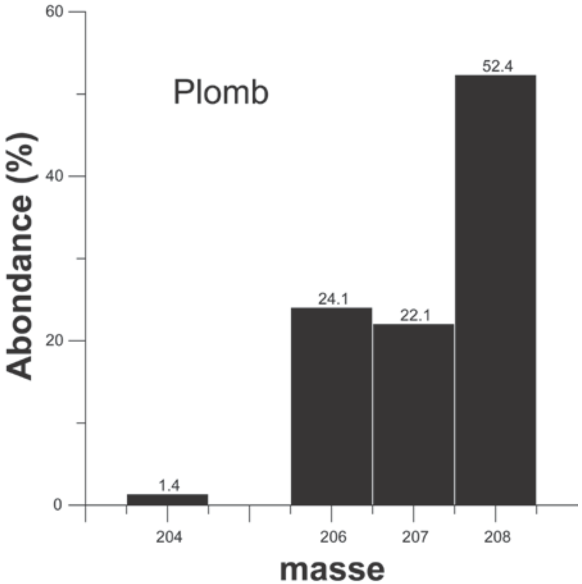


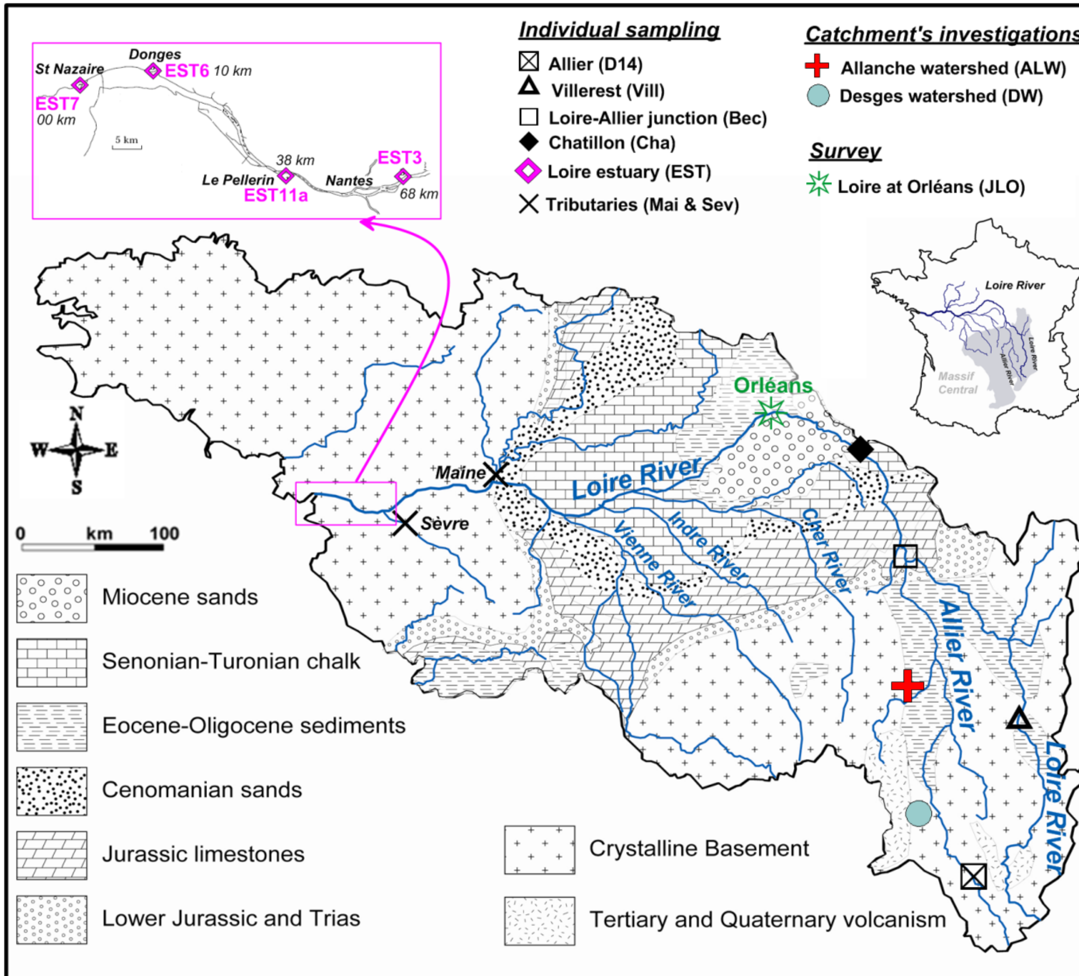
- Sr integrated into neoformed calcites is directly derived from the local dissolved load.
- Fe and Mn hydroxides may have precipitated in waters similar to those found in the upstream part of the basin (crystalline basement of the Massif Central).

THE LABILE FRACTION AND THE EXTENSION TO THE BASIN



Loire sediment and Pb





Applied Geochemistry 27 (2012) 2019–2030

Contents lists available at SciVerse ScienceDirect

Applied Geochemistry

journal homepage: www.elsevier.com/locate/apgeochem

ELSEVIER

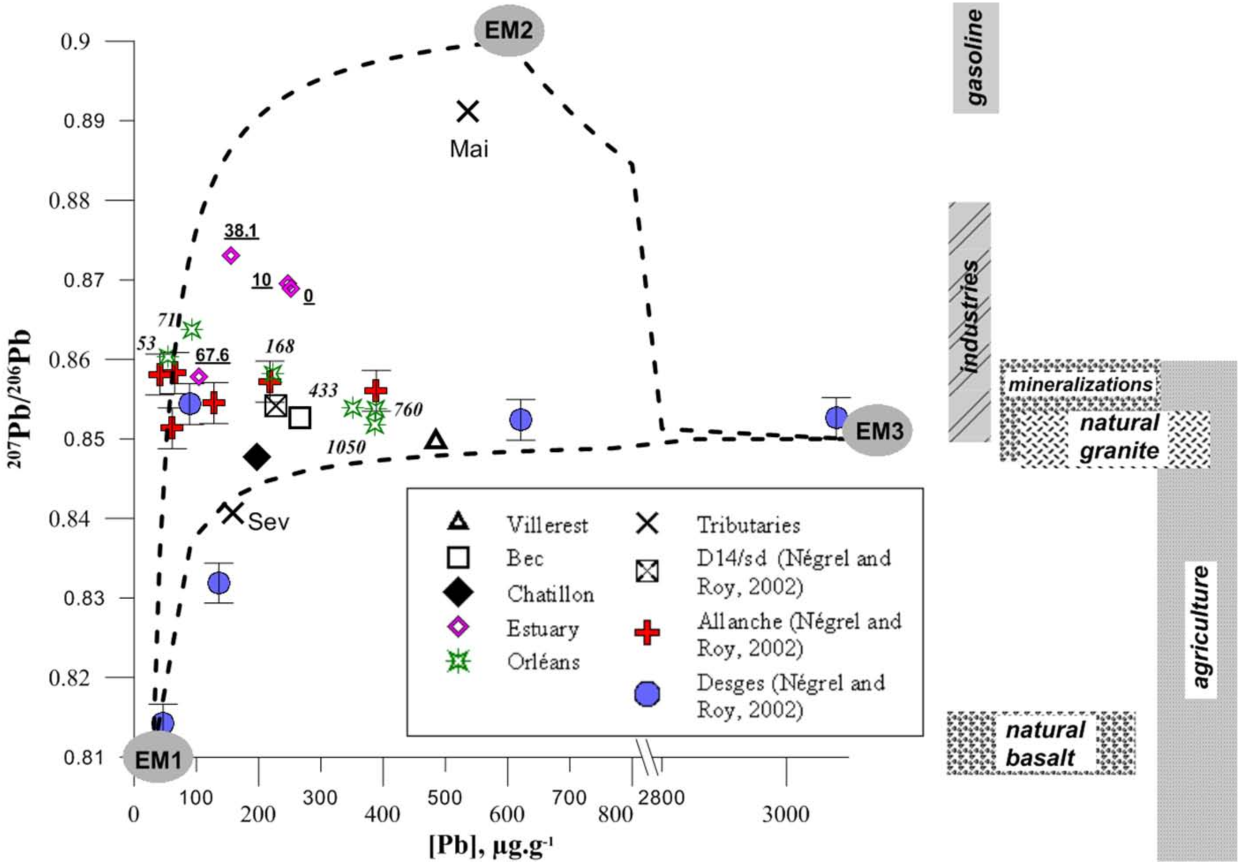
Isotopic evidence of lead sources in Loire River sediment

Philippe Négrel *, Emmanuelle Petelet-Giraud

BRGM, BP 6009, 45060 Orléans Cedex 2, France

Geoscience for a sustainable Earth

Pb and its isotopes



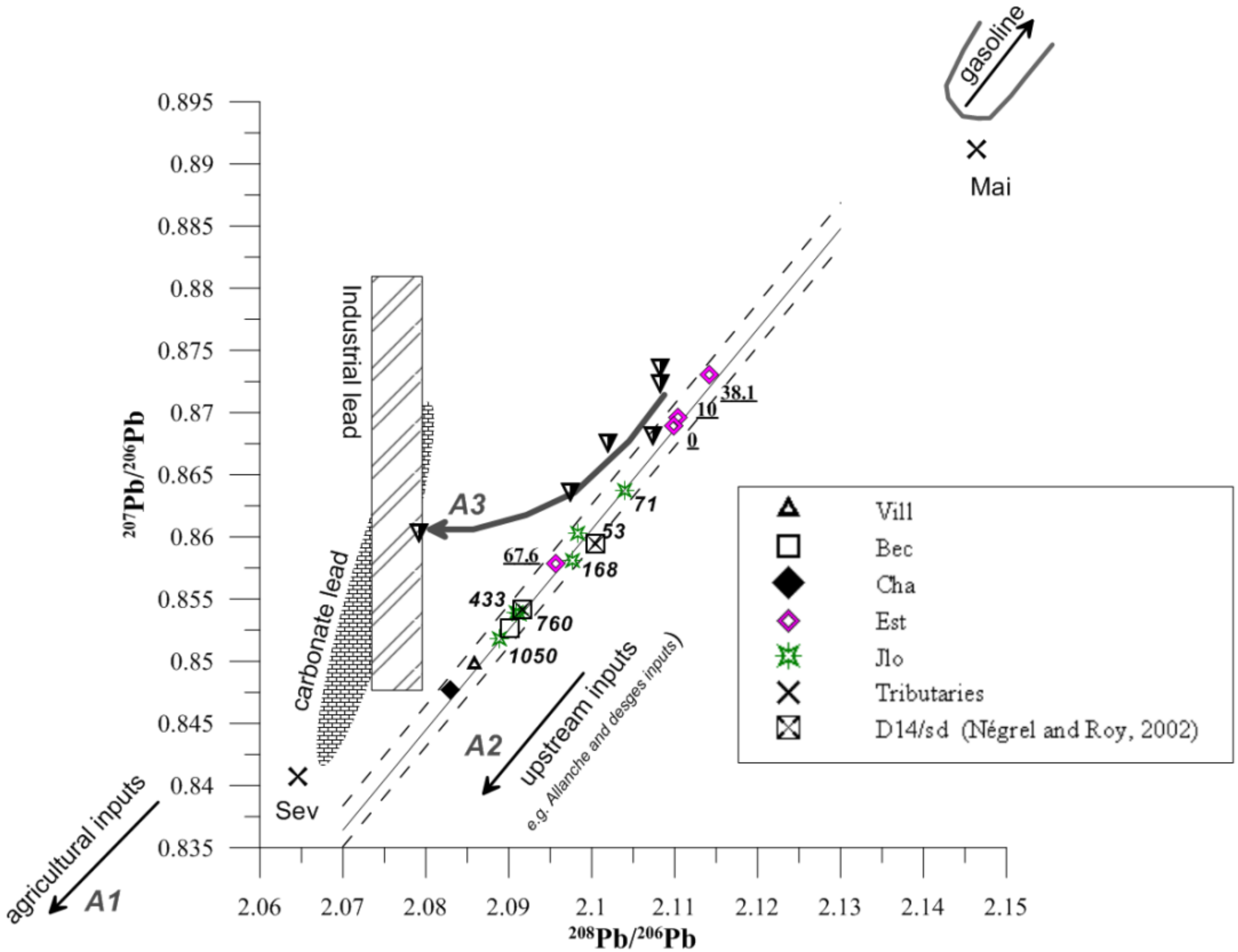
The relationship in AEM between ^{207}Pb/^{206}Pb and Pb content, the latter shown as a broken axis for easier viewing (800 – 2800). several linear mixing curves can be calculated between end-members as Pb sources.

The different Pb sources are

- natural Pb from weathering processes,
- Pb derived from industrial activities,
- Pb from gasoline,
- Pb from agricultural activities (fertilizers and amendments),
- and Pb from past mining activities.

Geoscience for a sustainable Earth
brgm

Lead isotope systematics in sediments at catchment scale



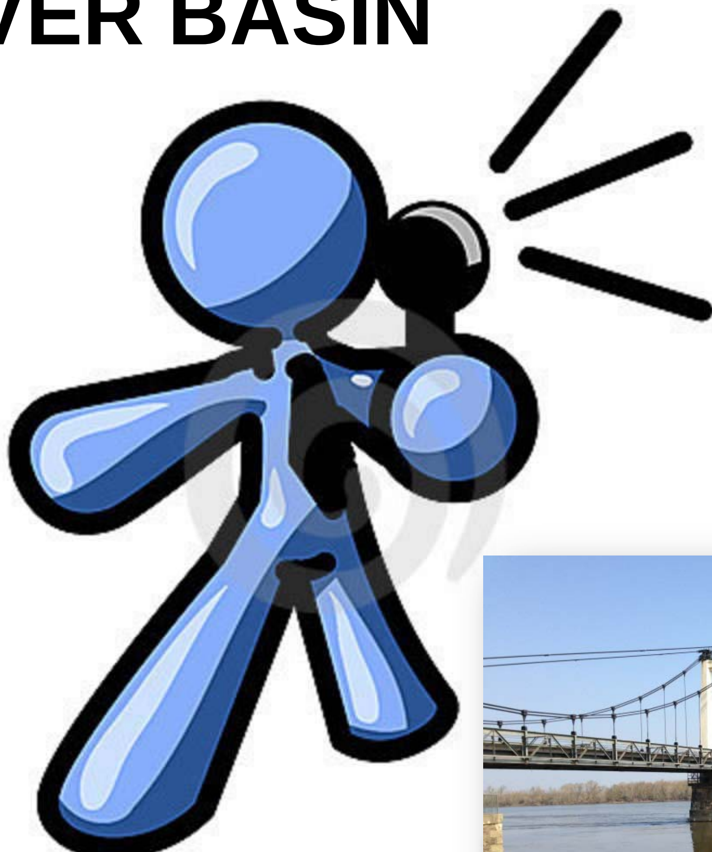
- ✓ Pb-isotopic compositions of AEM and various potential sources plotted as $^{207}Pb/^{206}Pb$ vs. $^{208}Pb/^{206}Pb$ define a linear relationship.
- ✓ Two of the tributaries plot outside:
  - Maine River sample probably derived mainly from gasoline
  - Sèvre River show an influence of agricultural-lead inputs.

From the Loire-Allier junction up to the estuary data define a strong linear trend between:

- the gasoline field (higher Pb-isotope)
- the upstream catchment inputs (lower Pb-isotope)

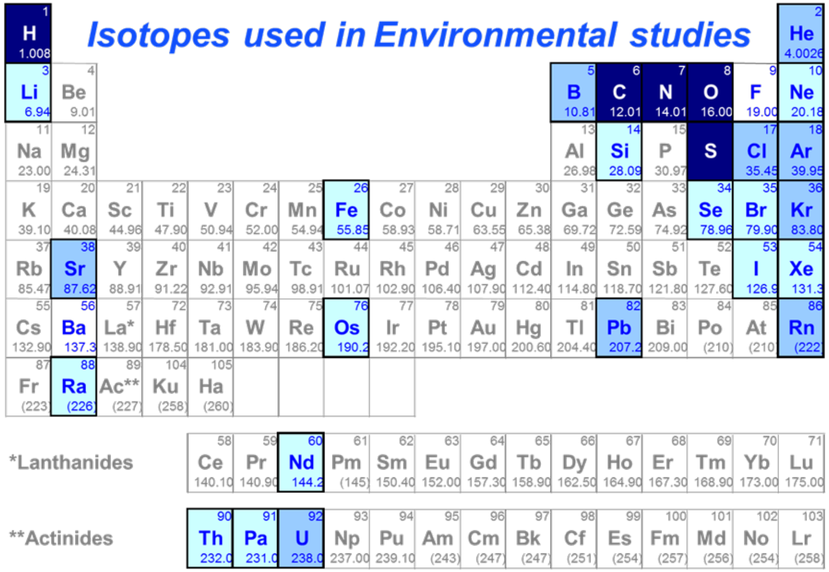
Geoscience for a sustainable Earth brgm

Pb-Zn MULTI ISOTOPIC CHARACTERIZATION OF THE LOIRE RIVER BASIN

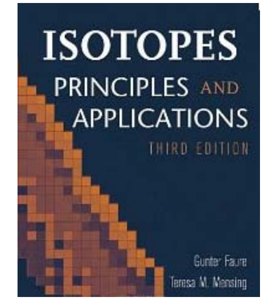


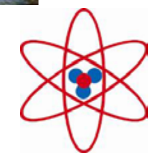
brgm
Geoscience for a sustainable Earth

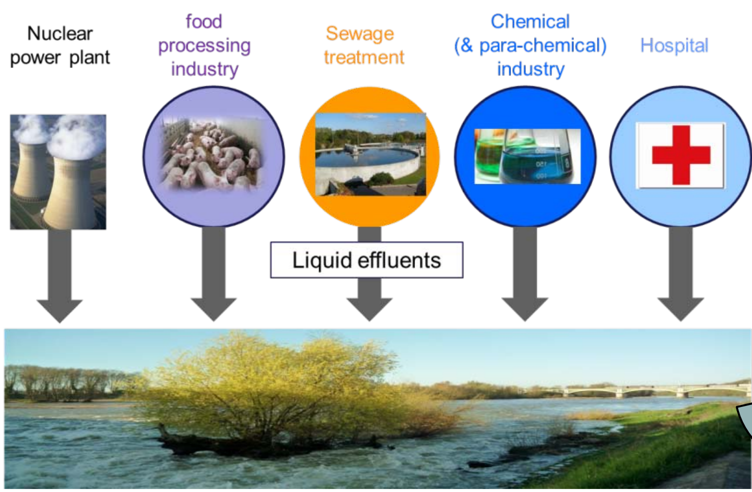
AND THE FUTURE

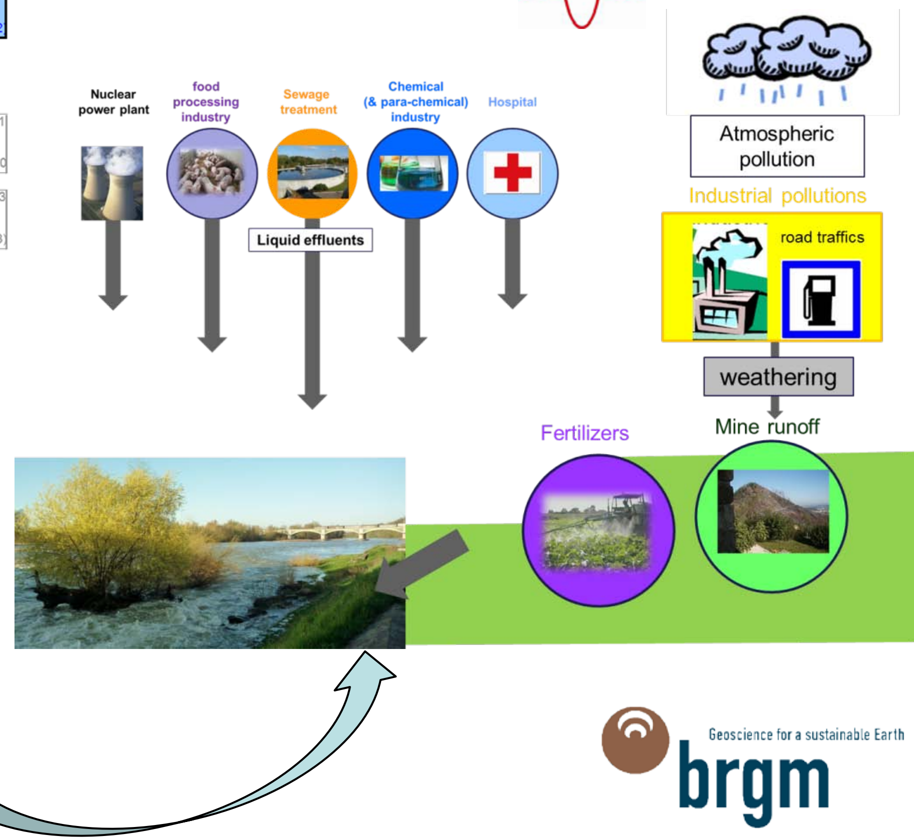


C *Classically used in hydrogeology*
U *Research, some applications in hydrogeology*
Fe *Ongoing research*

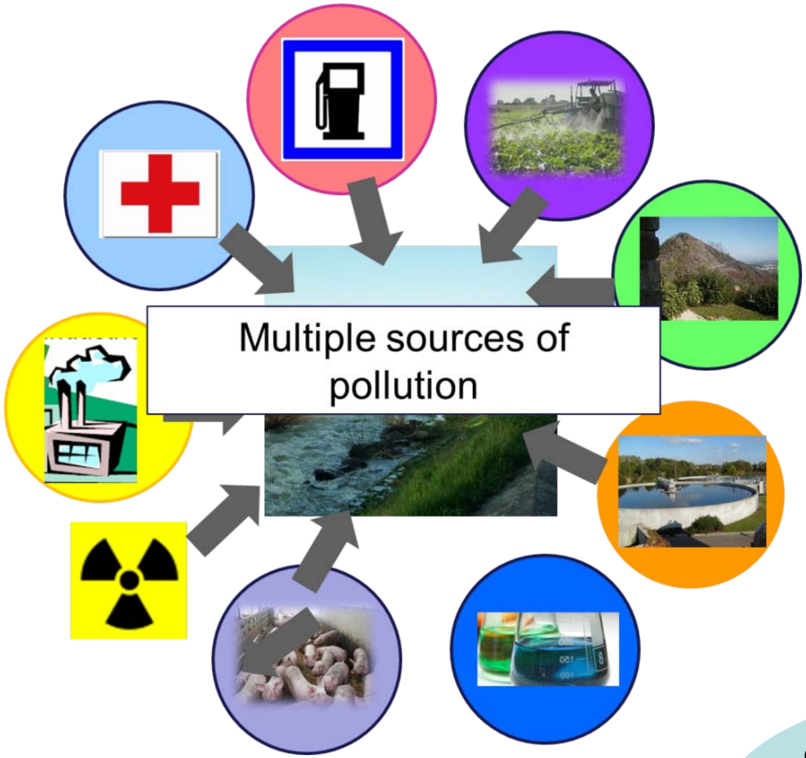


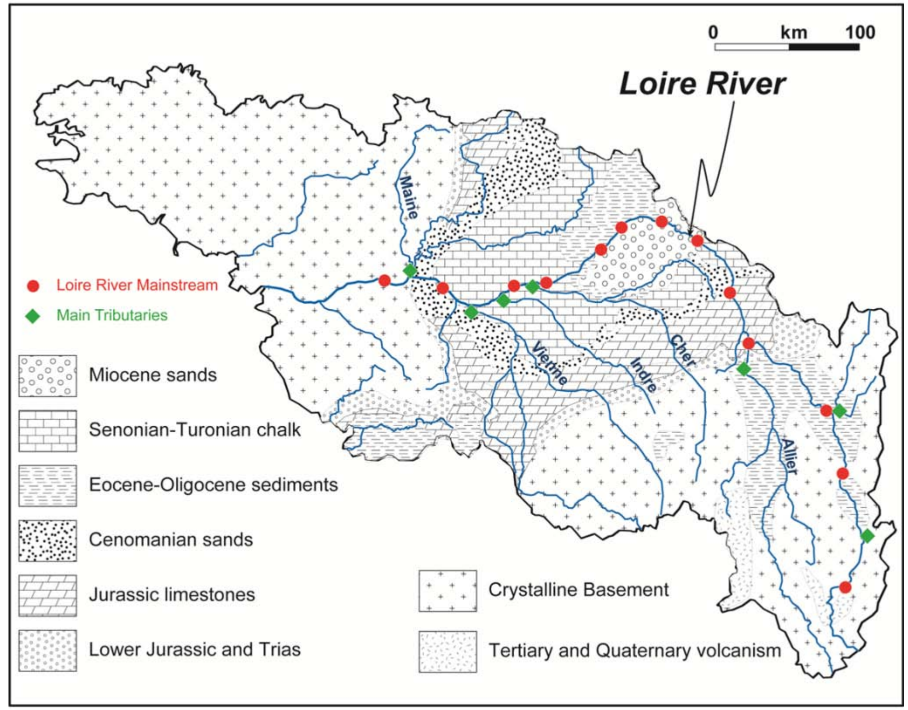






BACK TO THE FUTURE





track the sources of pollution in Loire river

$\delta^{66}Zn/^{64}Zn$

$^{206}Pb/^{204}Pb$

$^{207}Pb/^{204}Pb$

$^{208}Pb/^{204}Pb$

Geoscience for a sustainable Earth
brgm

METHODOLOGY

Sampling

Liquid effluents

Sampled and provided by water agency

Dissolved load

Two campaigns of sampling (September and April)

High/low flow stage

Suspended matter

monitoring in Montjean

Chemical characterization

Major et trace elements analyses by Q-ICPMS, ICP-AES

Isotopic characterization

Sample preparation
In clean lab.

Calcination, dissolution, chemical purification…

Isotopic analyses

Pb
Zn

Neptune
MC-ICP-MS

Granitic rocks domain
Michard-Vitrac et al., 1981
Downes et al., 1997
Négrel & Roy, 2002
Négrel & Petelet-Giraud, 2012

Basaltic rocks domain
Négrel & Roy, 2002
Négrel & Petelet-Giraud, 2012

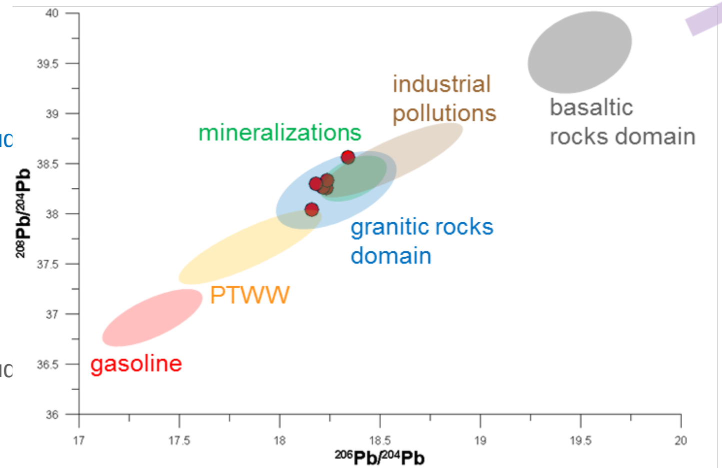
Mineralizations
Marcoux, 1986

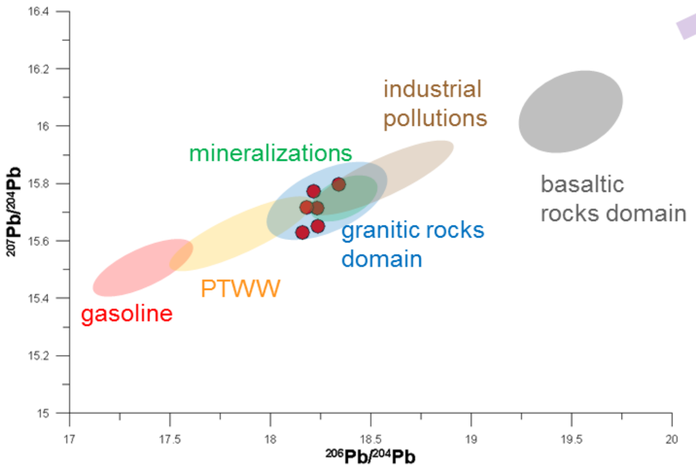
Fertilizers
Roy & Négrel, 2001
Négrel & Roy, 2002

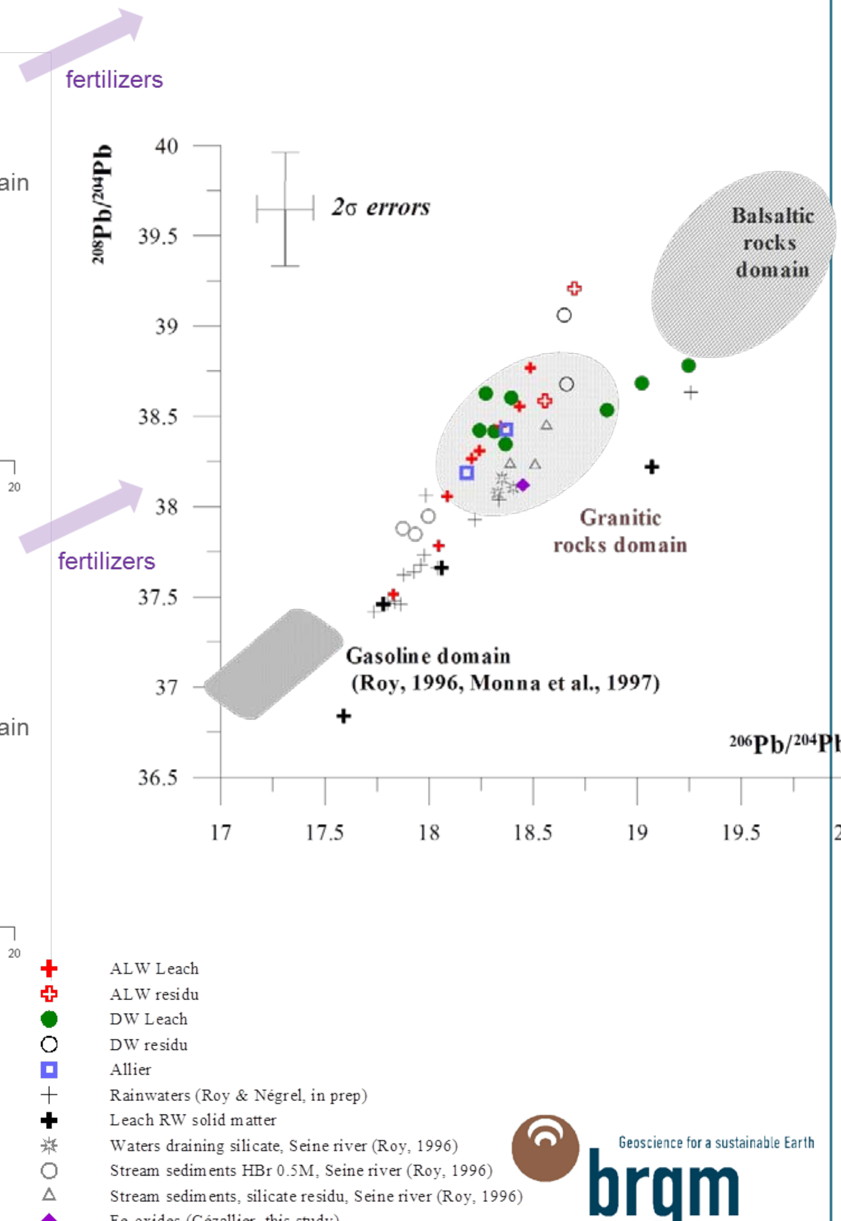
Industrial pollutions
this study
Petit, 1977
Elbaz-Poulichet et al., 1986
Monna et al., 1997

PTWW
Plant Treatment Waste waters
this study

Gasoline
Roy, 1996
Monna et al., 1997

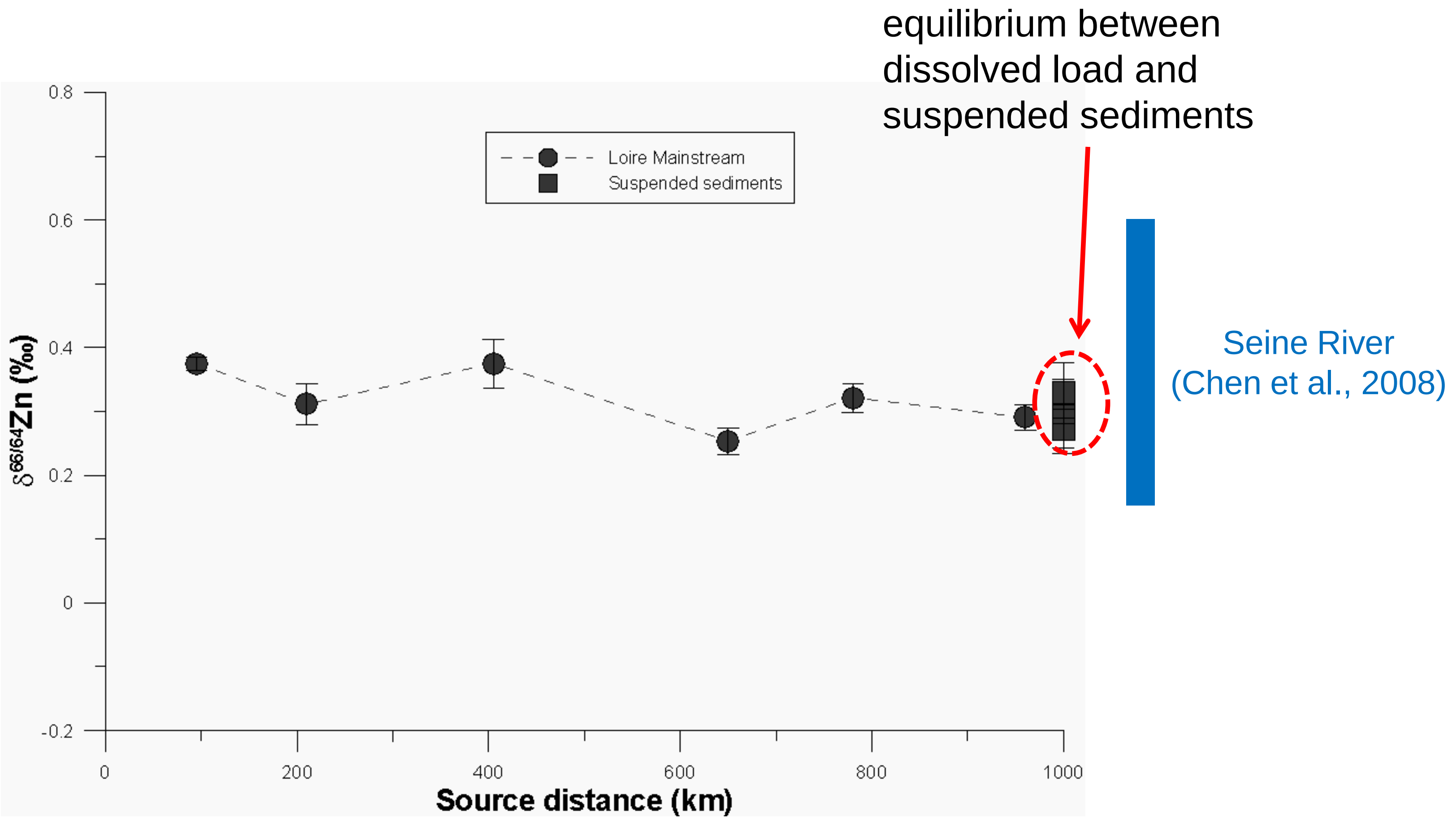




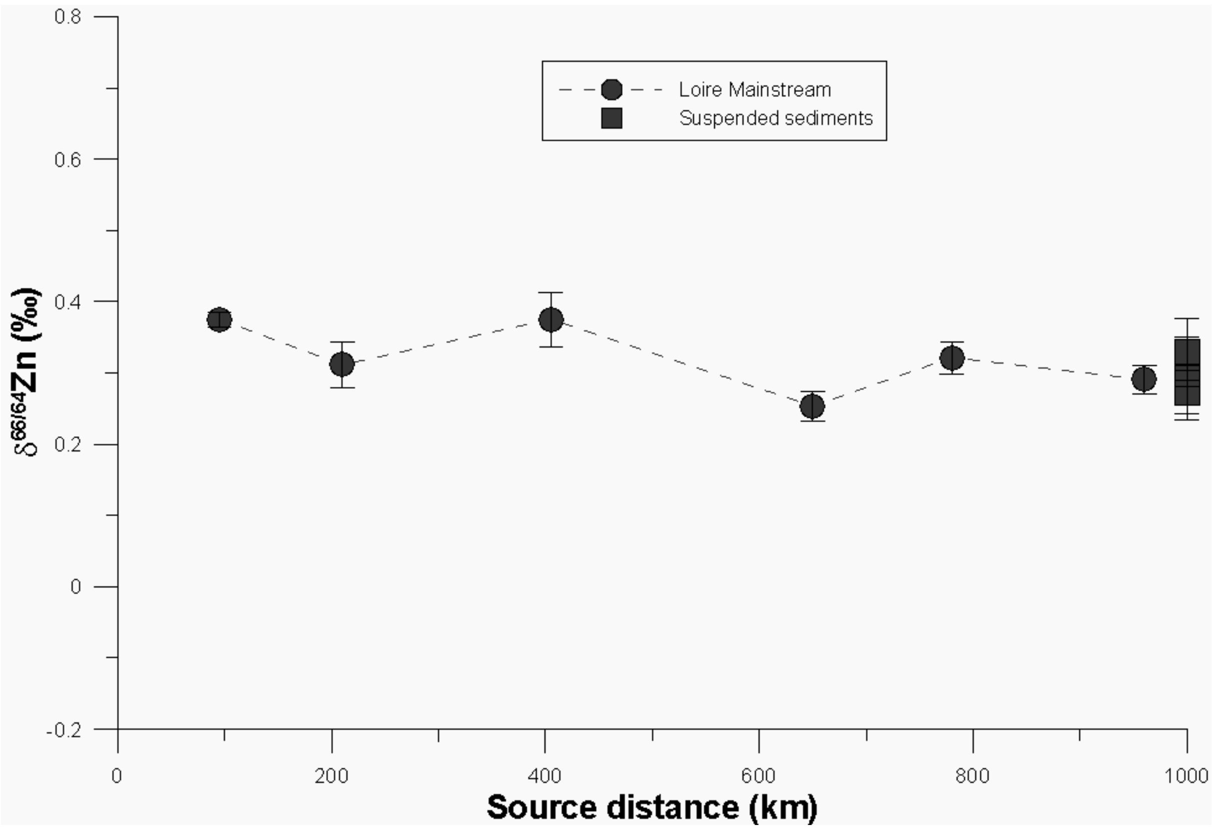


Geoscience for a sustainable Earth
brgm

Zinc isotopes



Zinc isotopes



natural source ?

fertilizers

industrial pollutions

roof streaming & leached of zinc roof

$\delta^{66}Zn/^{64}Zn$ weakly decrease ⇨ liquid effluents ? roof streaming?

⇨ better knowledge of geological background required

Geoscience for a sustainable Earth
brgm

To conclude (I) present work

- A very homogenous Pb and Zn signatures from the upstream to the downstream
- Pb isotopic signature close to geogenic domain

low anthropic pollution

- Complementary analyses in progress

$\delta^{66}Zn/^{64}Zn$	dissolved load
$^{206, 207, 208}Pb/^{204}Pb$	geological background suspended sediments dissolved load during

$\delta^{66}Zn/^{64}Zn$
$^{206, 207, 208}Pb/^{204}Pb$ → sediment cores in dams and estuary

Geoscience for a sustainable Earth
brgm

TO CONCLUDE (II)
ABOUT GEOCHEMISTRY

Whatever the size of the river is

- Think about tools to be used
- Bulk includes mainly geogenic
- Leach concerns anthropic
- Use multi tools approach

Geoscience for a sustainable Earth
brgm