Observatoire des Sédiments du Rhône

Multi-decadal records of PCBs and PCDD/F in Rhône River sediment cores

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GRESE Groupement de Recherche Eau Sol Environnement · USGS science for a changing world · LEHNA · ENTPE · Université de Montréal · irstea

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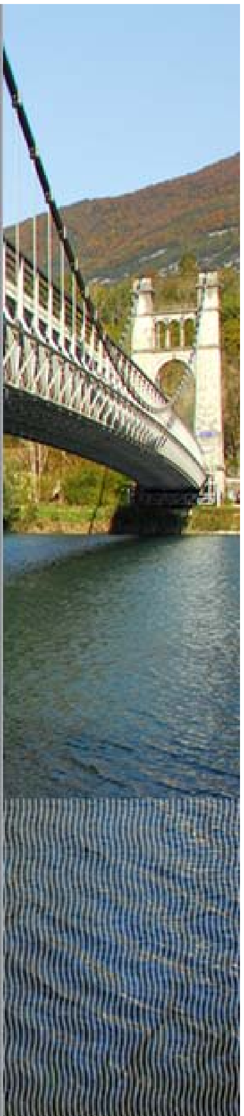
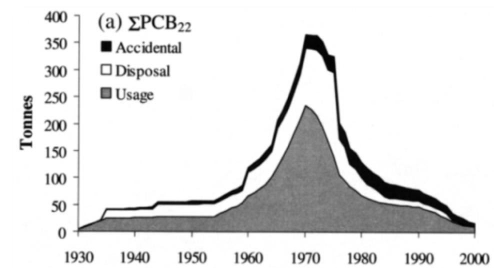
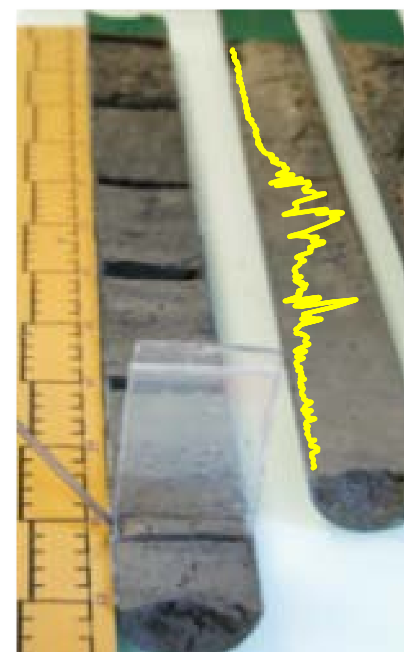
Context







- Since few decades, the human impact on the natural environment has accelerated : the degradation of the water quality is one of the consequences.

- Identification of historical trends in contaminant concentrations in rivers can contribute to improve risk assessment

  → Not available for most large rivers

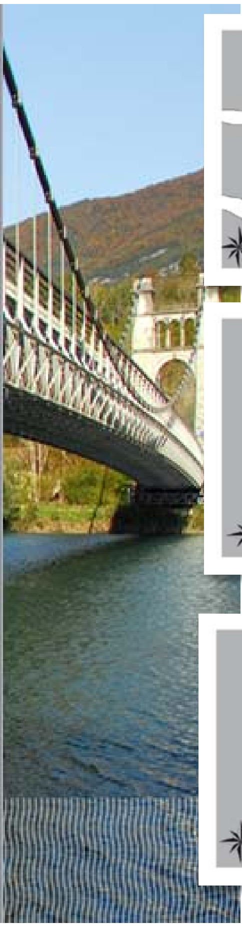
- **Sediment cores** constitute excellent witnesses of the functioning of river systems and human impacts over decenal time scale:

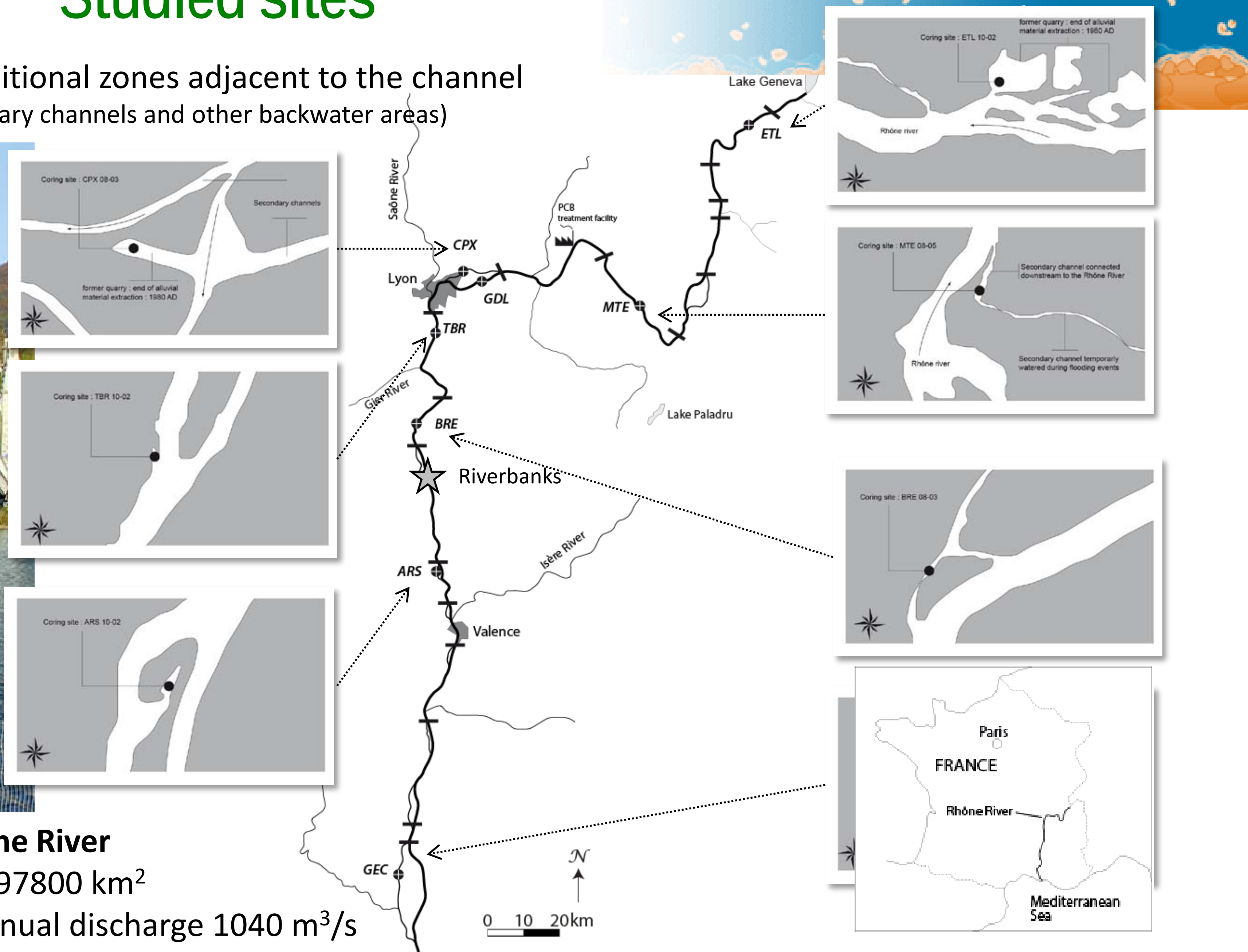
  - document hydro-sedimentary dynamics,
  - assess historical and spatial trends,
  - evaluate the effectiveness of environmental policies.

PCBs, PCDD/F

Studied sites

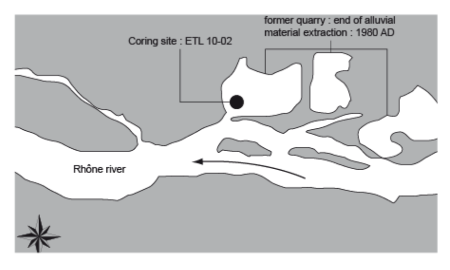
Depositional zones adjacent to the channel
(secondary channels and other backwater areas)



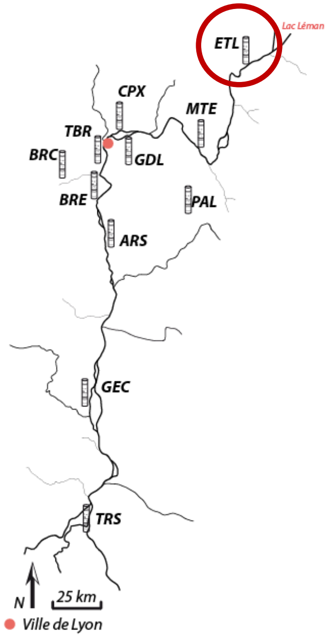


The Rhône River
Basin of 97800 km^2
Mean annual discharge 1040 m^3/s

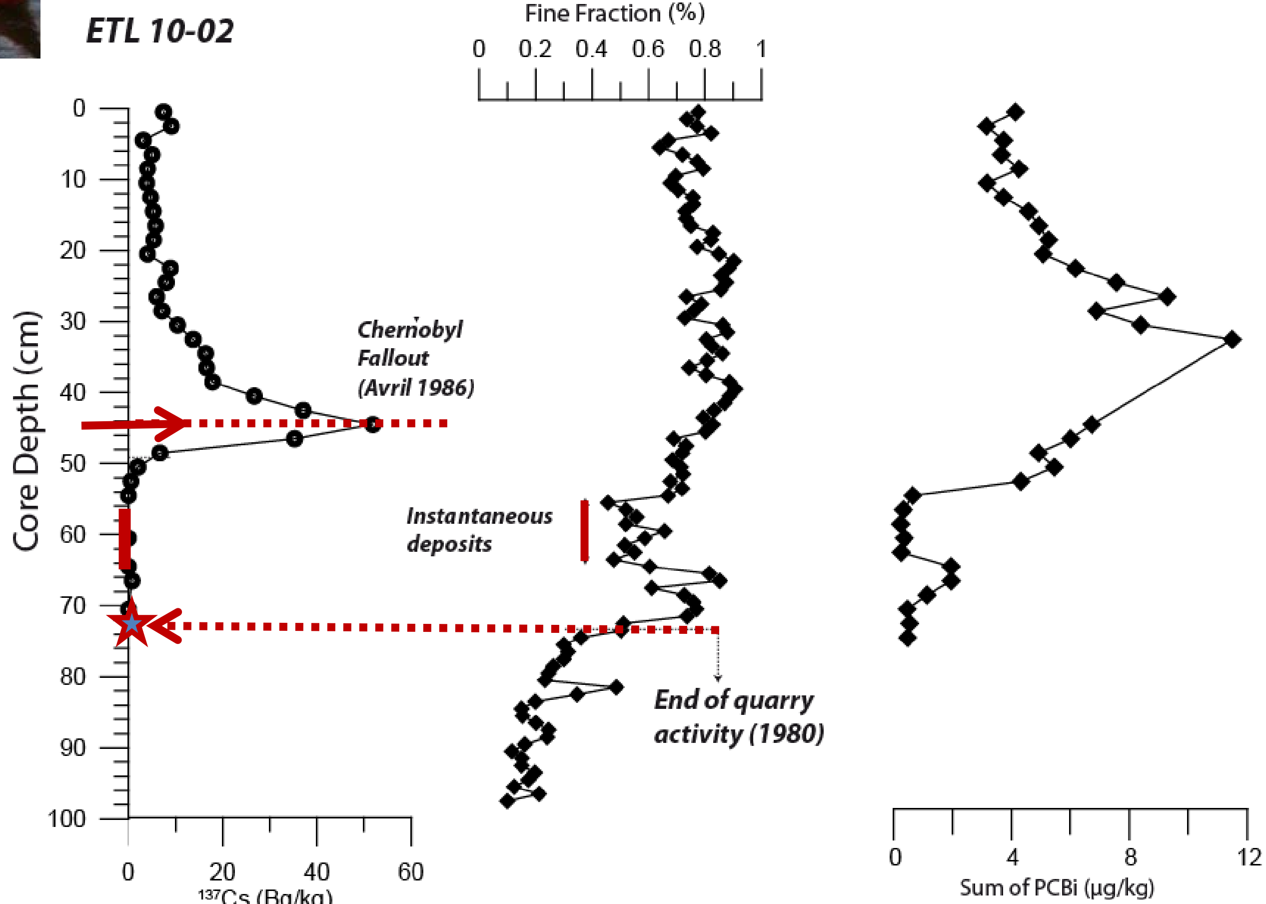
Methods



Coring site : ETL 10-02
former quarry : end of alluvial material extraction : 1980 AD
Rhône river

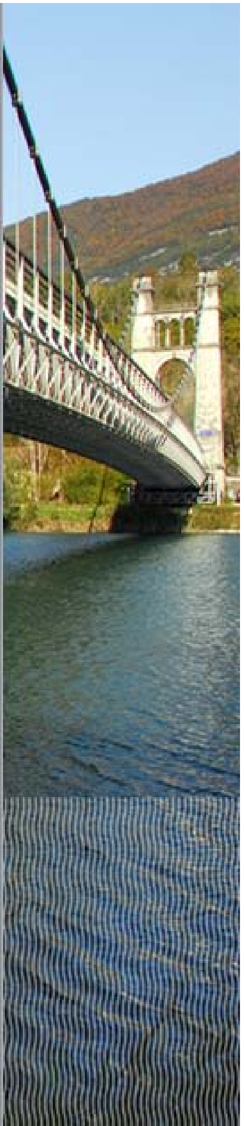


ETL
Lac Léman
CPX
MTE
TBR
BRC
GDL
BRE
PAL
ARS
GEC
TRS
N
25 km
Ville de Lyon

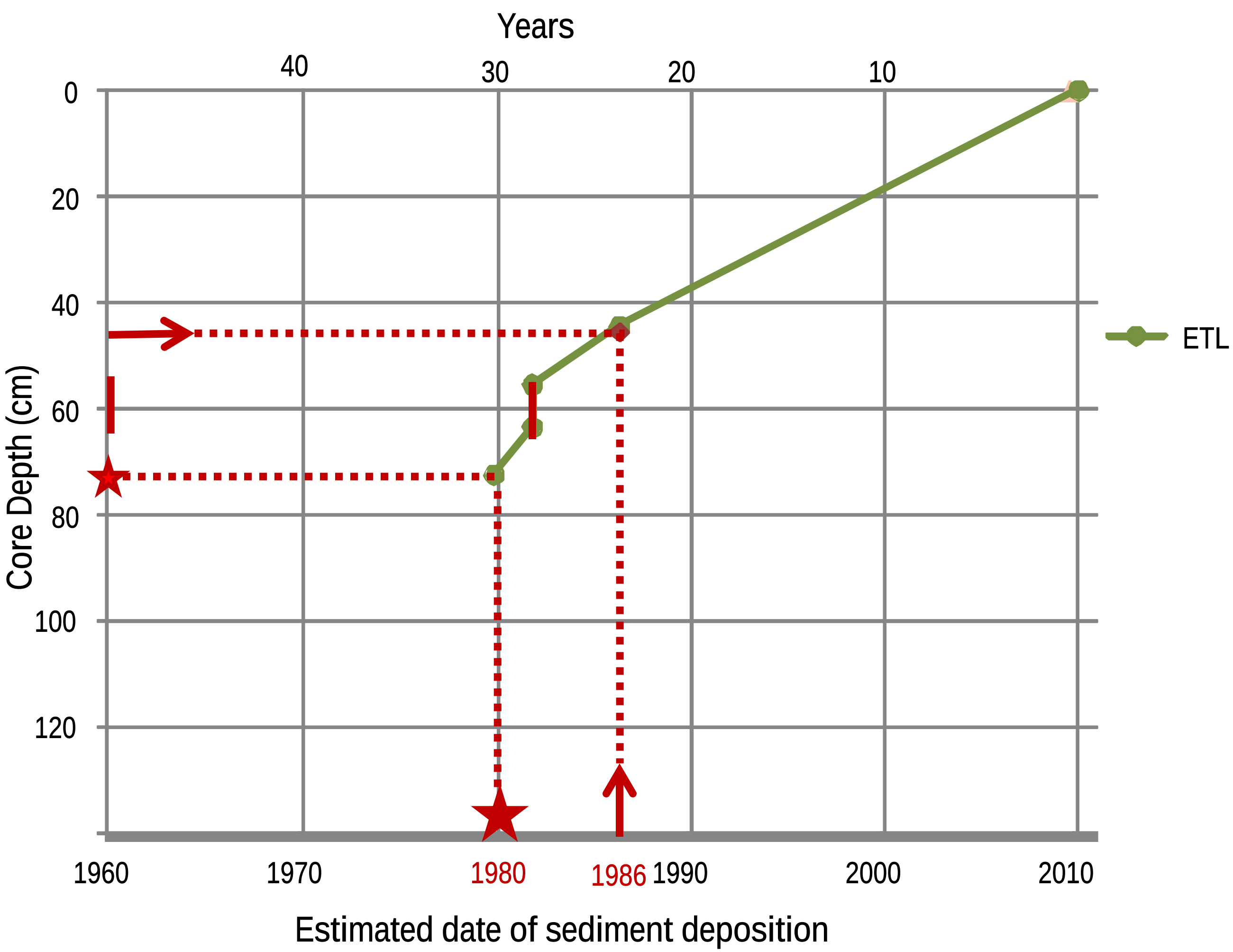


ETL 10-02
Fine Fraction (%)
0 0.2 0.4 0.6 0.8 1
Core Depth (cm)
0 10 20 30 40 50 60 70 80 90 100
Chernobyl Fallout (Avril 1986)
Instantaneous deposits
End of quarry activity (1980)
0 20 40 60
137Cs (Bq/kg)
0 4 8 12
Sum of PCBi (µg/kg)

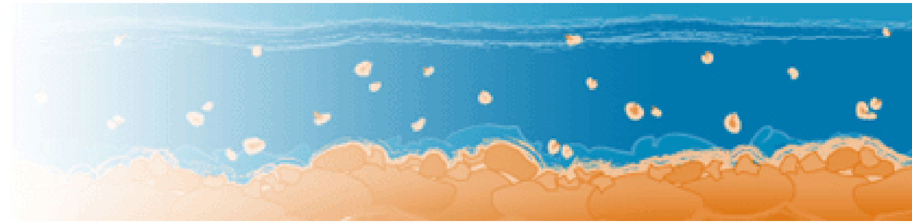
Methods

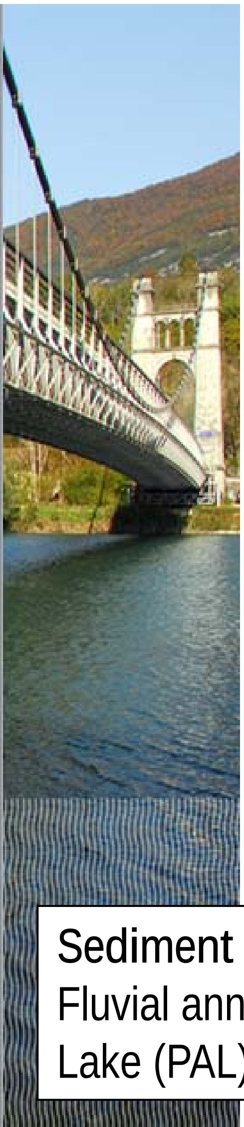


Age-depth model for ETL core

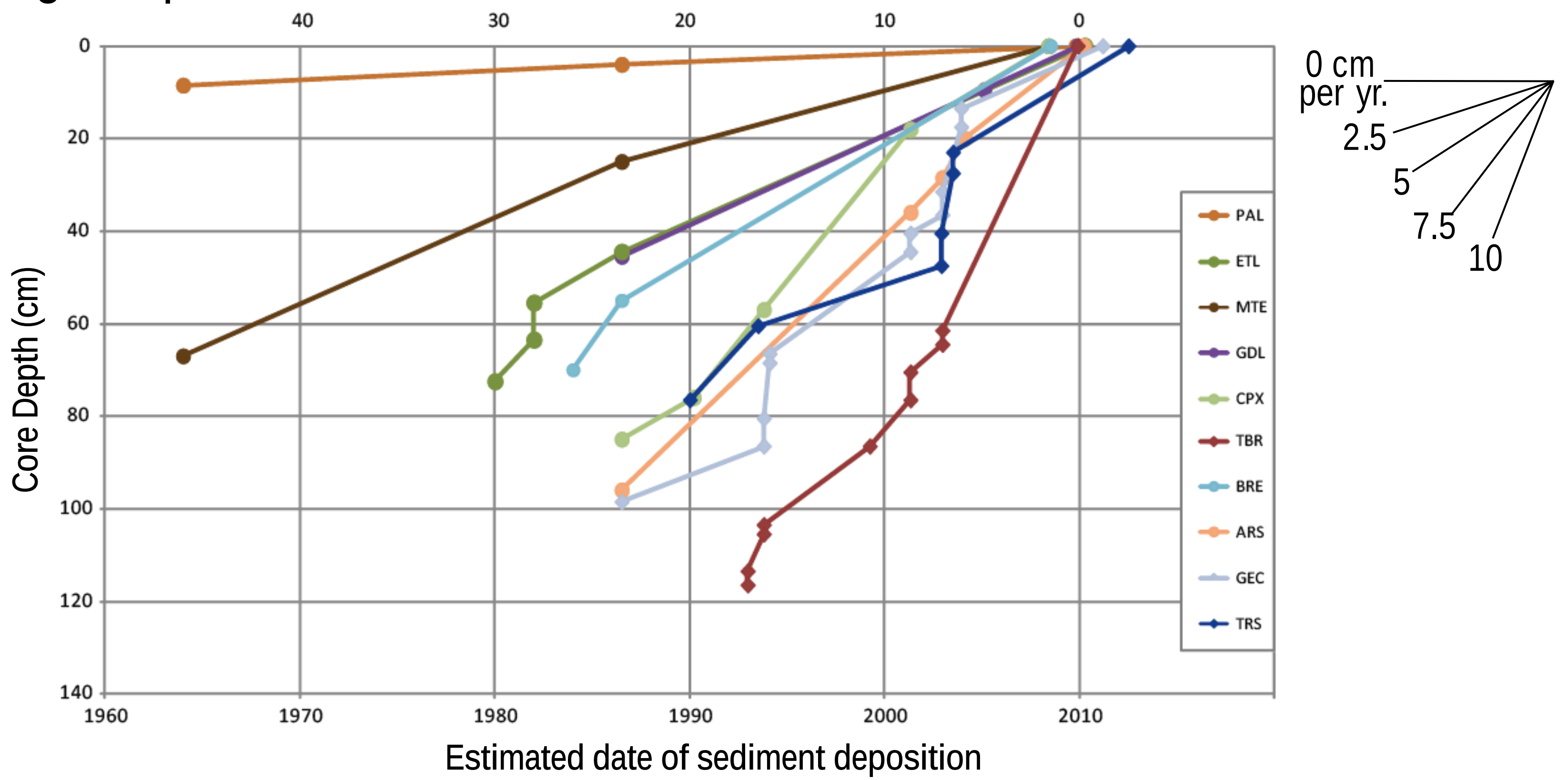


Hydro-sedimentary dynamics



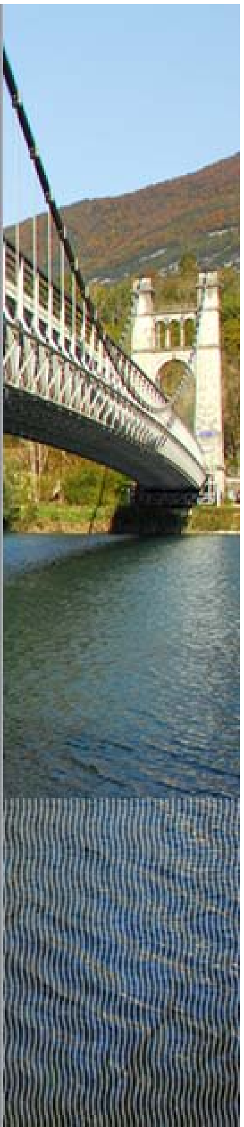


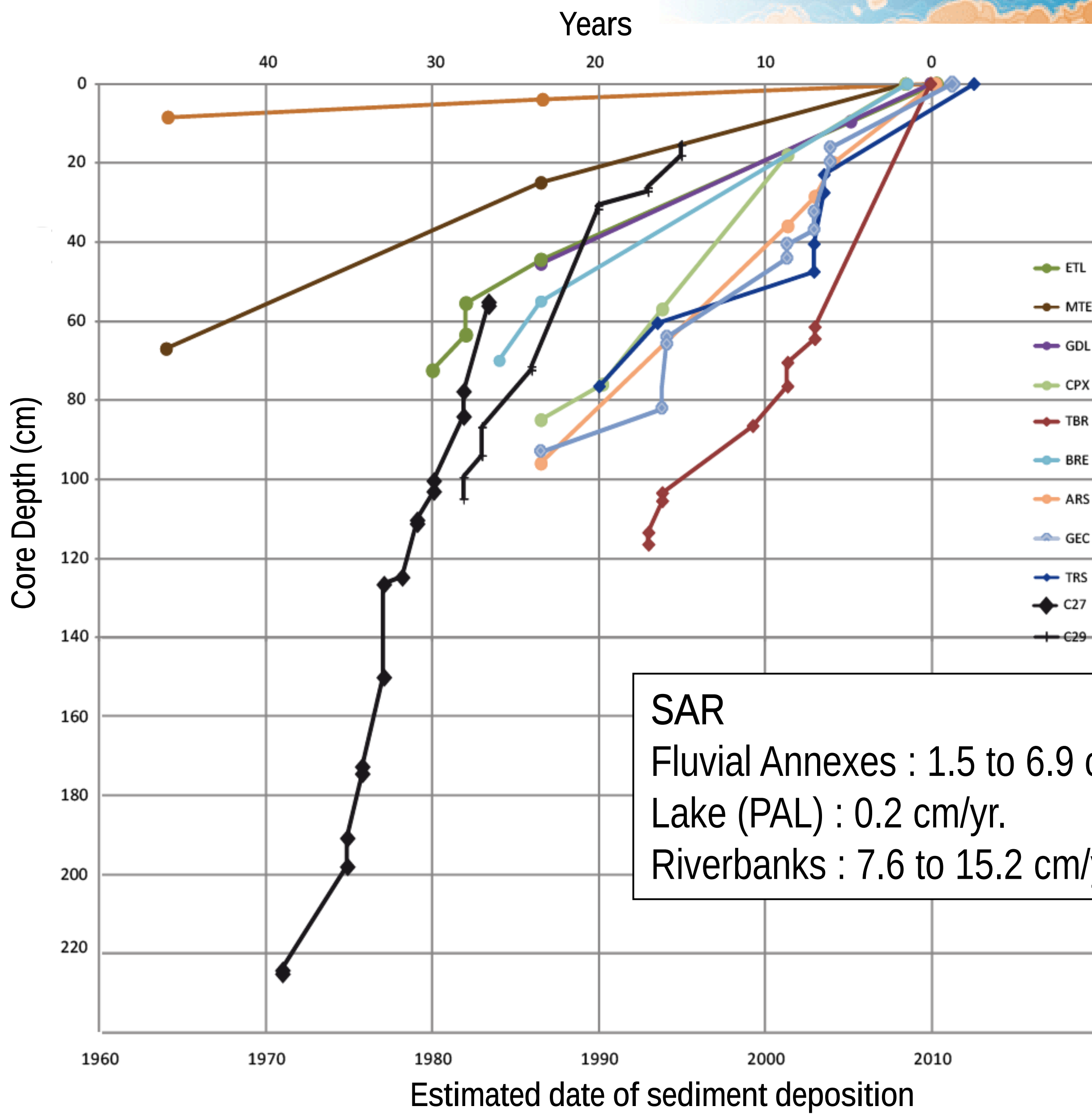
Age-depth models

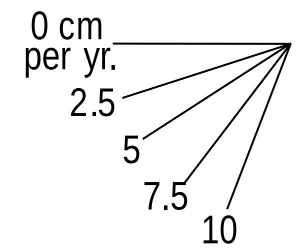


Sediment accumulation rate (SAR)
Fluvial annexes : from 1.5 to 6.9 cm/yr (3.6 cm/yr)
Lake (PAL) : 0.2 cm/yr

Hydro-sedimentary dynamics







SAR

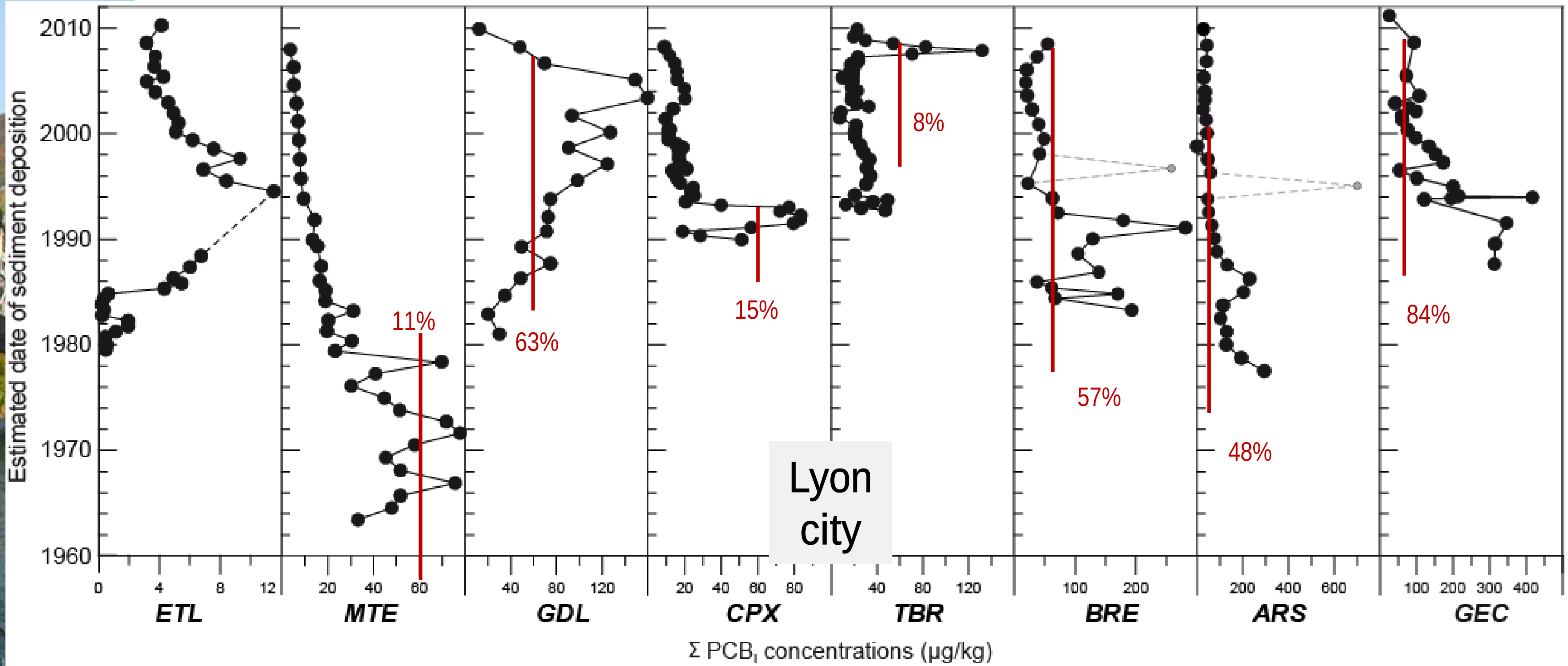
Fluvial Annexes : 1.5 to 6.9 cm/yr. (3.6 cm/yr.)

Lake (PAL) : 0.2 cm/yr.

Riverbanks : 7.6 to 15.2 cm/yr.

Profils of PCBi concentrations

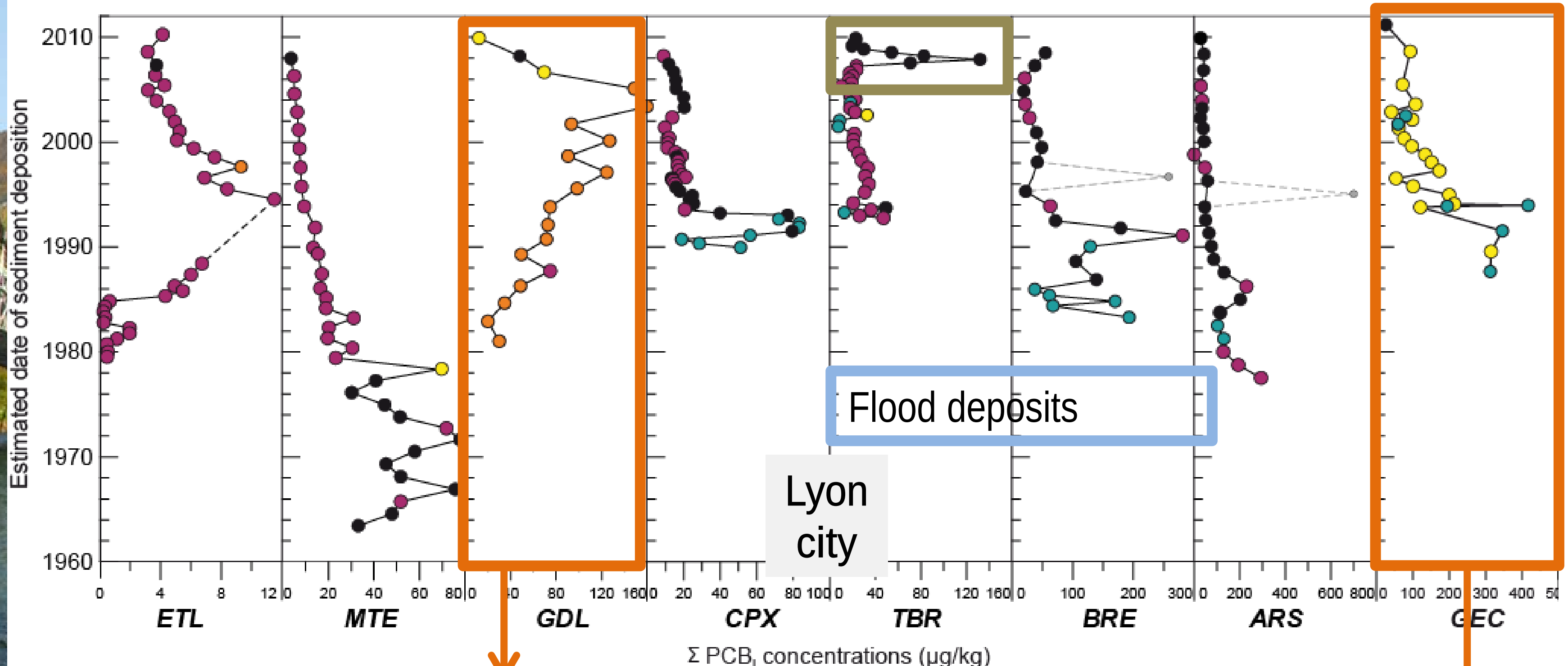
Desmet et al., 2012 (STOTEN)
Mourier et al., 2014 (STOTEN)



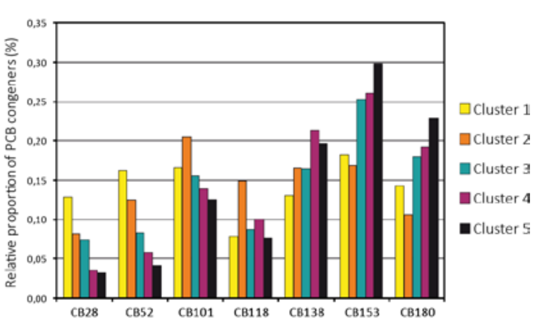
- PCBI concentrations and profiles varied considerably within and between the sites
- Maximum PCBI concentrations were lowest upstream and increased downstream to a concentration of 417.1 µg/kg at GEC.
- Sedimentary layers exceeding the recommended threshold (60 µg/kg) for dredging are larger downstream

PCB congener profiles as an indicator of sources ?

Punctual source

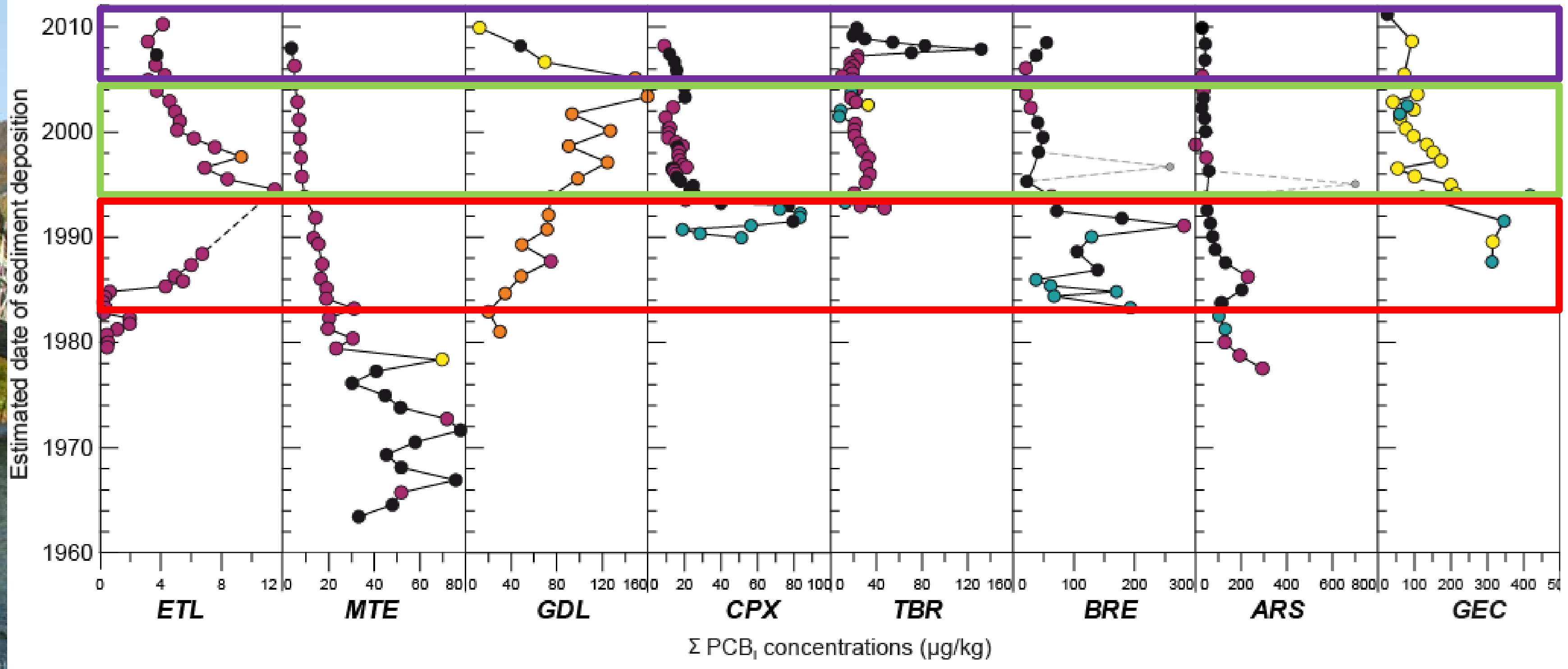


Other Tributary (Bourbre), Punctual source?



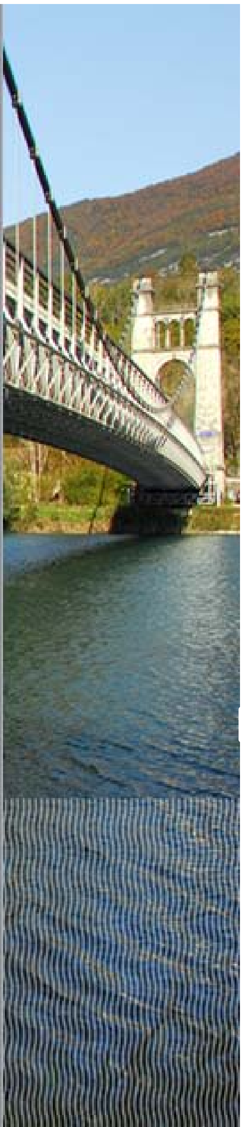
Other Tributary (Isère), Punctual source?

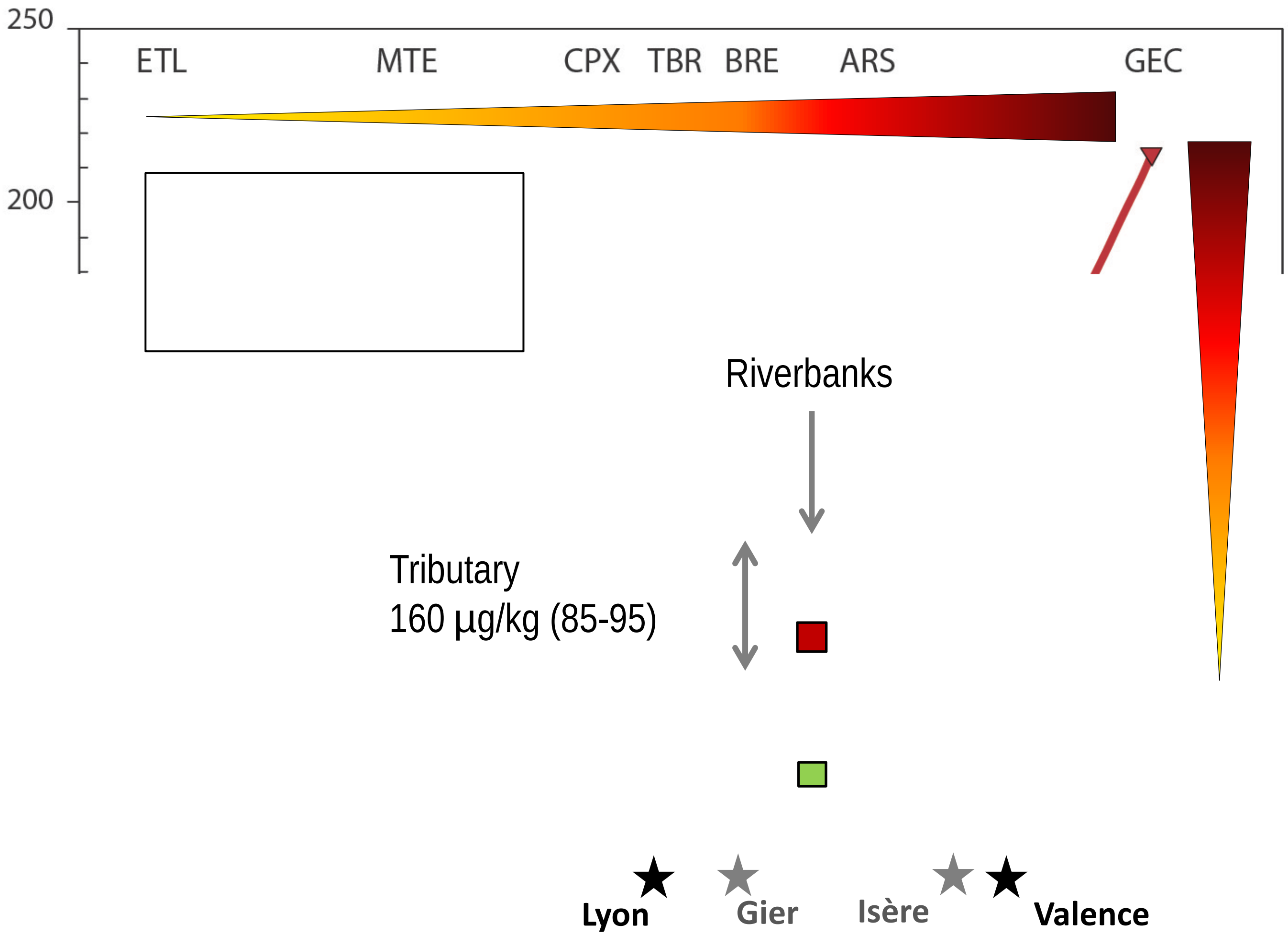
Spatial trends in PCBs at the scale of the Rhône River and changes through time



Separation in time windows (TW):
Before 1985 // 1986-1995 // 1996-2005 // After 2005

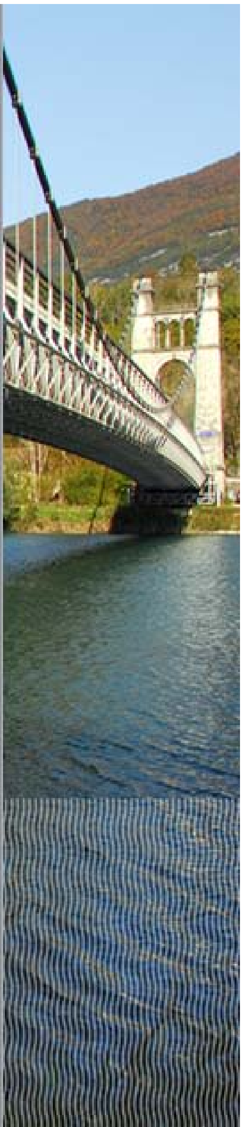
Spatial trends in PCBs at the scale of the Rhône River and changes through time





Mourier et al. 2014, STOTEN

Spatial trends in PCBs at the scale of the Rhône River and changes through time

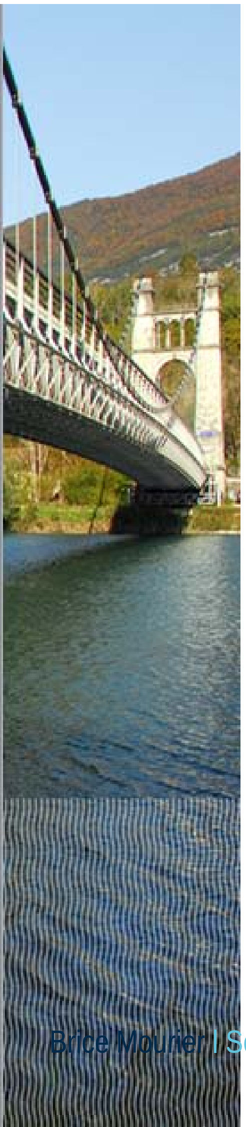


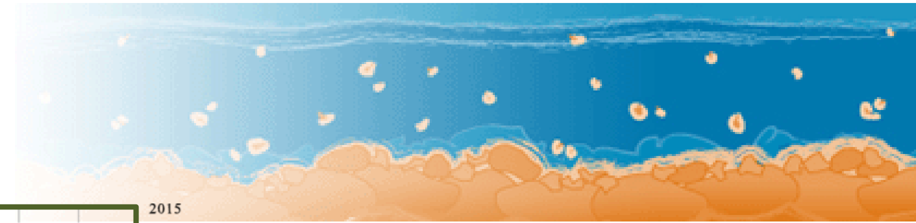
Environmental regulation of **point sources** enacted since 1975 and 1986 reduced the PCB burden recorded in sediments.

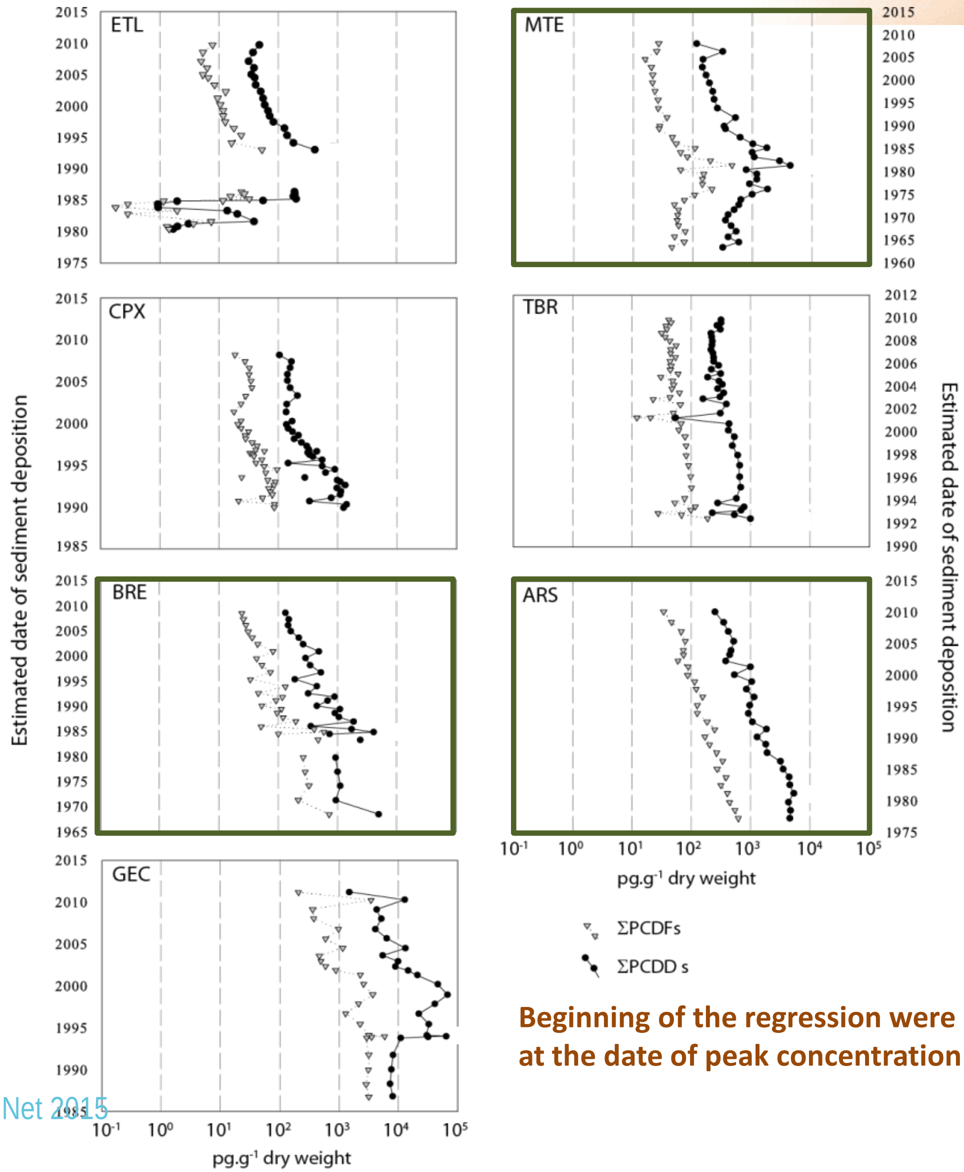
Recent concentrations (> 2005) are stable and correlated with the cumulated population of the basin :

→ Diffuse contribution of urban areas and associated industrial zones

Are PCDFs and PCDDs still a concern in the Rhône River?







PCCD/Fs in the list of priority substances - WFD (2013)

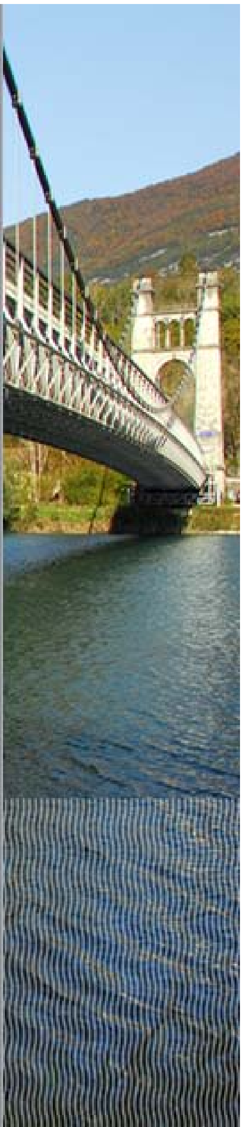
- Maxima concentrations peak between 1980 and 1985
- Rapid and substantial decreases in dioxin concentrations

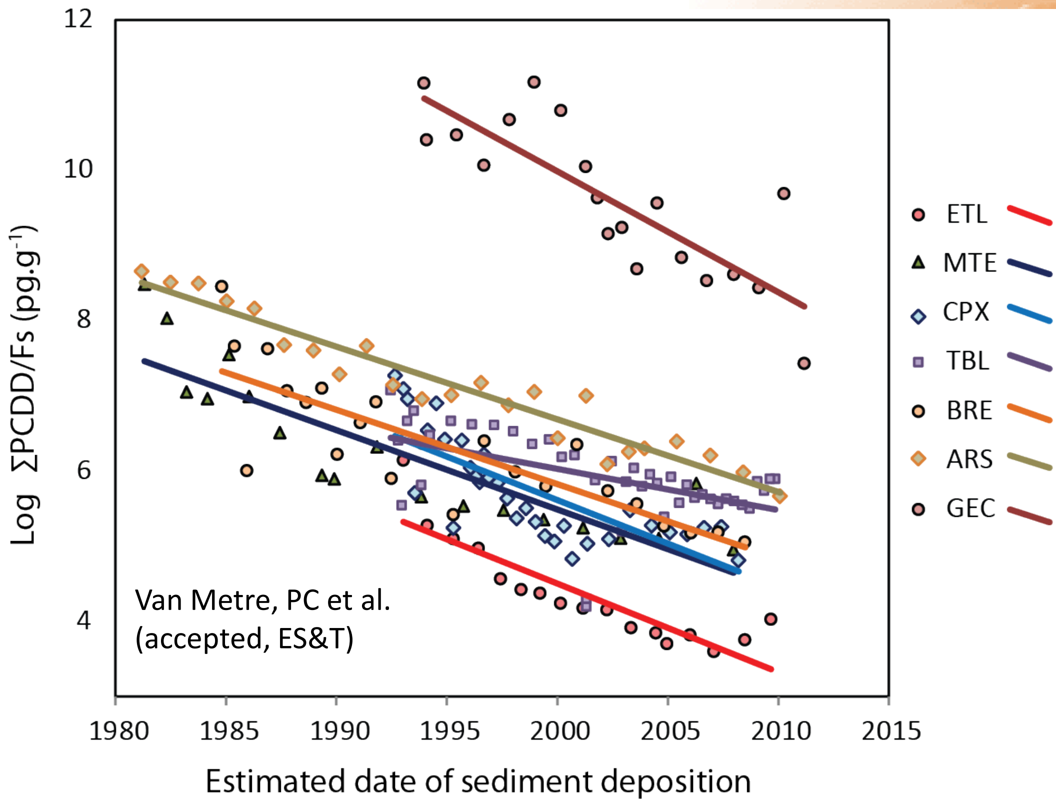
To evaluate the rate of change in concentrations, PCDD/F concentrations were regressed against date in each core.

Beginning of the regression were chosen at the date of peak concentration

Van Metre, PC et al. (accepted, ES&T)

Are PCDFs and PCDDs still a concern in the Rhône River?



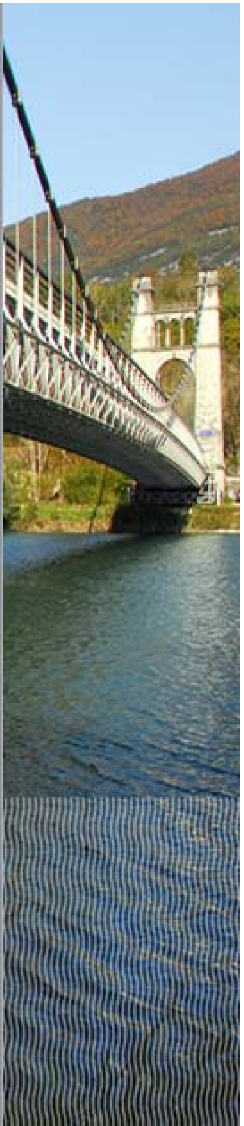


All of the trends were downward and significant ($p<0.005$)

Reductions in the cores from 1992-2010 for SPCDD/Fs average **83%**

- The rapid decreases in dioxin concentrations coincide with EU target, which aimed to achieve a 90% reduction by 2005, compared to the 1985 level.
- Risks caused by dioxins in biota have been greatly reduced (<10% TEQ),
- Continued trend monitoring at a few sites in the watershed will be a sufficient management response.

Conclusions



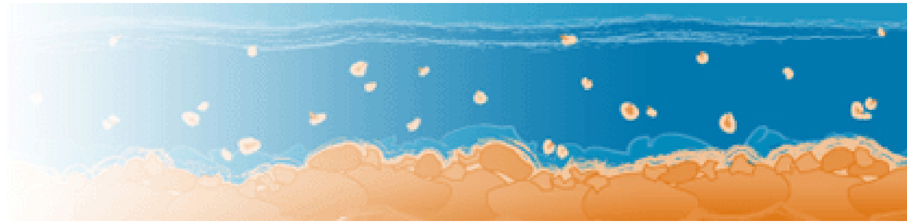
→ **Sediment core:** document current and past evolution of the fluvial environment

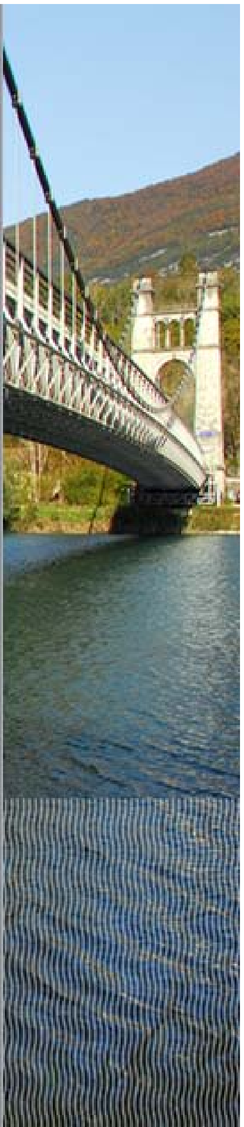
→ Better knowledge of the spatio-temporal release of PCBs and PCDD/F at the River scale

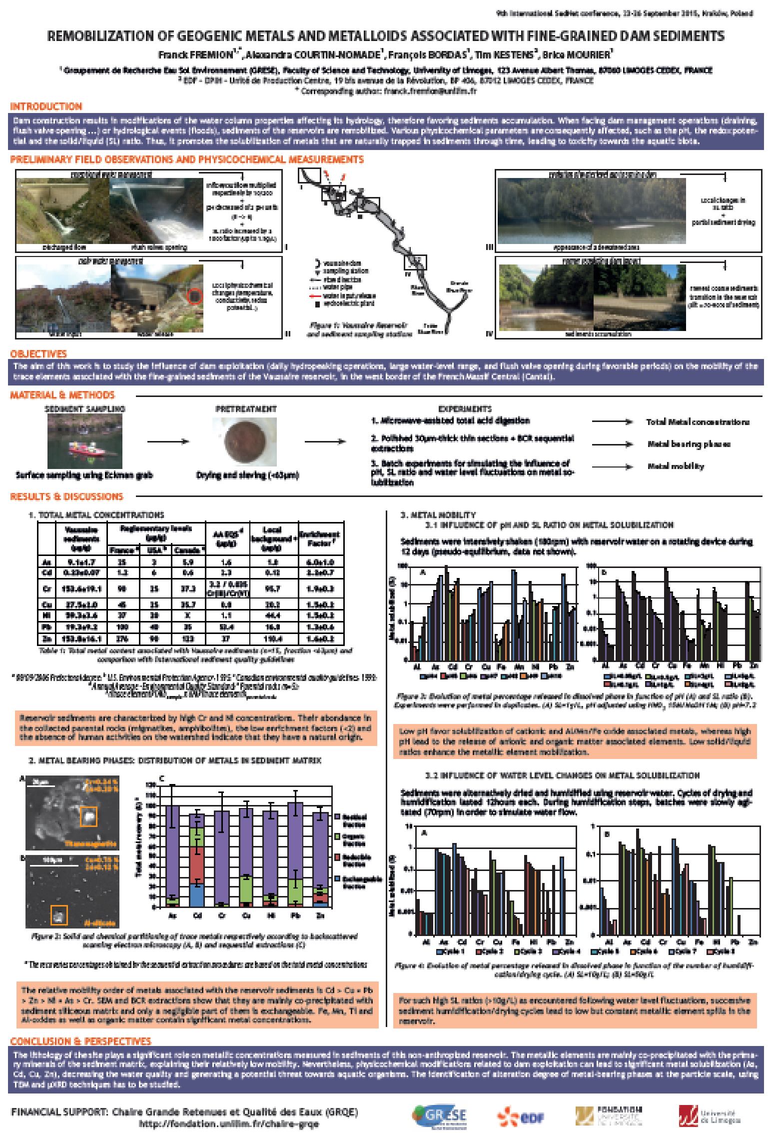
→ Evaluation of the effects of environmental policies

→ Recommendations for management operations on sediment stocks

Contaminant mobility in dam sediments







9th International SedNet conference, 23-26 September 2015, Kraków, Poland

REMOBILIZATION OF GEOGENIC METALS AND METALLOIDS ASSOCIATED WITH FINE-GRAINED DAM SEDIMENTS

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INTRODUCTION

Dam construction results in modifications of the water column properties affecting its hydrology, therefore favoring sediments accumulation. When facing dam management operations (draining, flush valve opening …) or hydrological events (floods), sediments of the reservoirs are remobilized. Various physicochemical parameters are consequently affected, such as the pH, the redox potential and the solid/liquid (SL) ratio. Thus, it promotes the solubilization of metals that are naturally trapped in sediments through time, leading to toxicity towards the aquatic biota.

PRELIMINARY FIELD OBSERVATIONS AND PHYSICOCHEMICAL MEASUREMENTS

Figure 1: Vassivière Reservoir and sediment sampling stations

OBJECTIVES

The aim of this work is to study the influence of dam exploitation (daily hydropeaking operations, large water-level range, and flush valve opening during favorable periods) on the mobility of the trace elements associated with the fine-grained sediments of the Vassivière reservoir, in the west border of the French Massif Central (Cantal).

MATERIAL & METHODS

SEDIMENT SAMPLING — Surface sampling using Eckman grab

PRETREATMENT — Drying and sieving (<63µm)

EXPERIMENTS

1. Microwave-assisted total acid digestion → Total Metal concentrations
2. Polished 30µm-thick thin sections + BCR sequential extractions → Metal bearing phases
3. Batch experiments for simulating the influence of pH, SL ratio and water level fluctuations on metal solubilization → Metal mobility

RESULTS & DISCUSSIONS

1. TOTAL METAL CONCENTRATIONS

Table 1: Total metal content associated with Vassivière sediments (n=15, fraction <63µm) and comparison with international sediment quality guidelines

Reservoir sediments are characterized by high Cr and Ni concentrations. Their abundance in the collected parental rocks (migmatites, amphibolites), the low enrichment factors (<2) and the absence of human activities on the watershed indicate that they have a natural origin.

2. METAL BEARING PHASES: DISTRIBUTION OF METALS IN SEDIMENT MATRIX

Figure 2: Solid and chemical partitioning of trace metals respectively according to backscattered scanning electron microscopy (A, B) and sequential extractions (C)

The relative mobility order of metals associated with the reservoir sediments is Cd > Cu > Pb > Zn > Ni > As > Cr. SEM and BCR extractions show that they are mainly co-precipitated with sediment siliceous matrix and only a negligible part of them is exchangeable. Fe, Mn, Ti and Al-oxides as well as organic matter contain significant metal concentrations.

3. METAL MOBILITY

3.1 INFLUENCE OF pH AND SL RATIO ON METAL SOLUBILIZATION

Sediments were intensively shaken (180rpm) with reservoir water on a rotating device during 12 days (pseudo-equilibrium, data not shown).

Figure 3: Evolution of metal percentage released in dissolved phase in function of pH (A) and SL ratio (B).

Low pH favor solubilization of cationic and Al/Mn/Fe oxide associated metals, whereas high pH lead to the release of anionic and organic matter associated elements. Low solid/liquid ratios enhance the metallic element mobilization.

3.2 INFLUENCE OF WATER LEVEL CHANGES ON METAL SOLUBILIZATION

Sediments were alternatively dried and humidified using reservoir water. Cycles of drying and humidification lasted 12hours each. During humidification steps, batches were slowly agitated (70rpm) in order to simulate water flow.

Figure 4: Evolution of metal percentage released in dissolved phase in function of the number of humidification/drying cycle.

For such high SL ratios (>10g/L) as encountered following water level fluctuations, successive sediment humidification/drying cycles lead to low but constant metallic element spills in the reservoir.

CONCLUSION & PERSPECTIVES

The lithology of the site plays a significant role on metallic concentrations measured in sediments of this non-anthropized reservoir. The metallic elements are mainly co-precipitated with the primary minerals of the sediment matrix, explaining their relatively low mobility. Nevertheless, physicochemical modifications related to dam exploitation can lead to significant metal solubilization (As, Cd, Cu, Zn), decreasing the water quality and generating a potential threat towards aquatic organisms. The identification of alteration degree of metal-bearing phases at the particle scale, using TEM and µXRD techniques has to be studied.

FINANCIAL SUPPORT: Chaire Grande Retenues et Qualité des Eaux (GRQE) http://fondation.unilim.fr/chaire-grqe

Poster of Franck Frémion

Thank you !