DEVELOPMENT OF ELECTROCHEMICAL METHODS FOR FIELD DETECTION OF TRACE METALS IN SEDIMENTS

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Trace metals and electrochemistry

Electrochemical methods are widely used for the detection of trace metals in the different environmental matrixes, with the possibility of assessment the trace metal speciation.

It offers a simple alternative to traditional analytical methods, with a high degree of sensitivity for lower cost.

Great challenge in the area of trace metal detection is the development of electrochemical techniques and working electrode materials which are

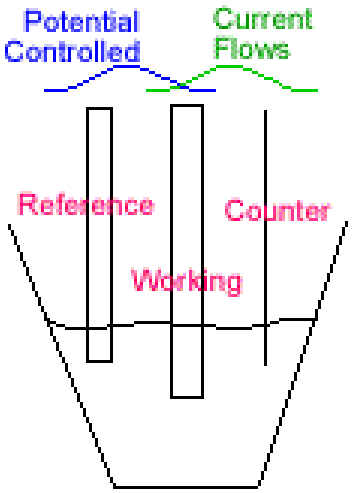
- selective
- have a low detection limit e.g. sensitivity
- stability and renewability of the working electrode surface

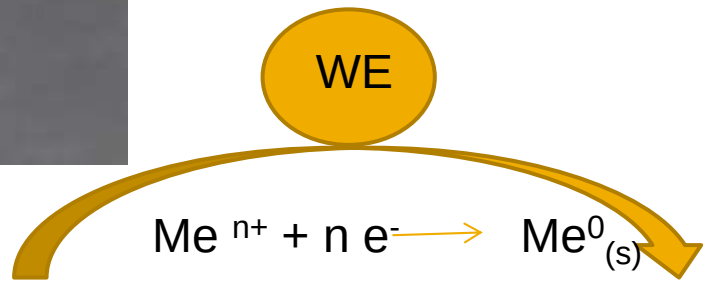
One of the advantages is the device miniaturization that opens the possibility of developing a real time field detection system to overcome possible artefacts due to sample collection and handling and to provide immediate results for decision.

The modern electrochemistry is focused on the finding the different strategies dedicated to improving the analytical performances and minimizing the impact of the techniques on the environment.

Electrochemistry

- is the branch of chemistry concerned with the interrelation of electrical and chemical changes that are caused by the passage of current.
- for detection of the trace metals the anodic stripping voltammetric techniques are applied as they offer possibility to preconcentrate the electroactive trace metals in the potential range of the working electrode.





$Me^{n+} + n\,e^- \rightarrow Me^0_{(s)}$

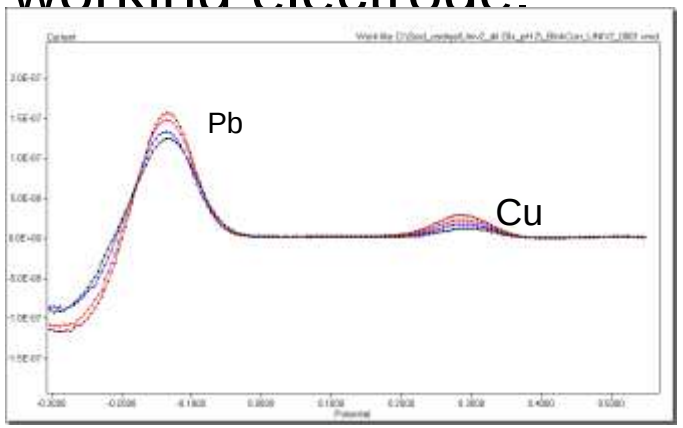
Reduction

Me^{n+}

Preconcentration

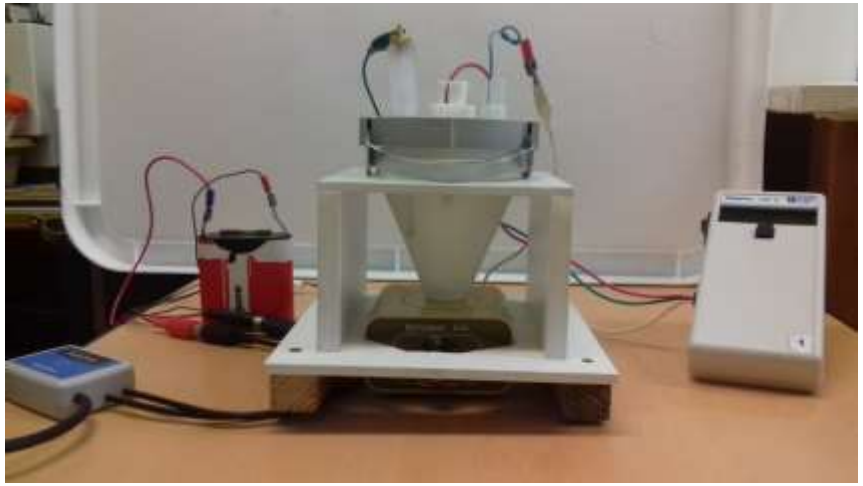
$Me^0(s) \rightarrow Me^{n+} + n\,e^-$

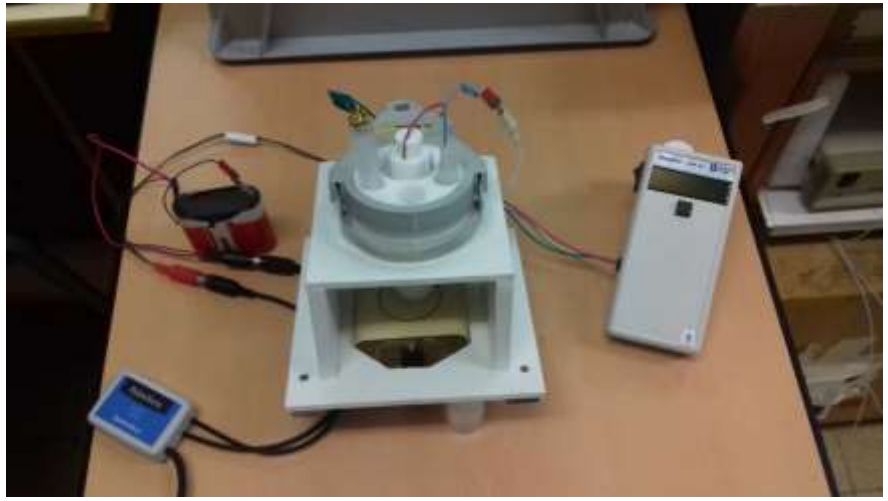
Stripping (oxidation)



Methodology

- in our work, we focused on the detection: Pb, Cu, Cd and Zn which are expected to have elevated concentrations in the samples.
- the aim was to develop and to test Bi modified glassy carbon electrode (Bi-GC) and the Au microwire electrode
- all the samples were acidified to pH 2 before measurements

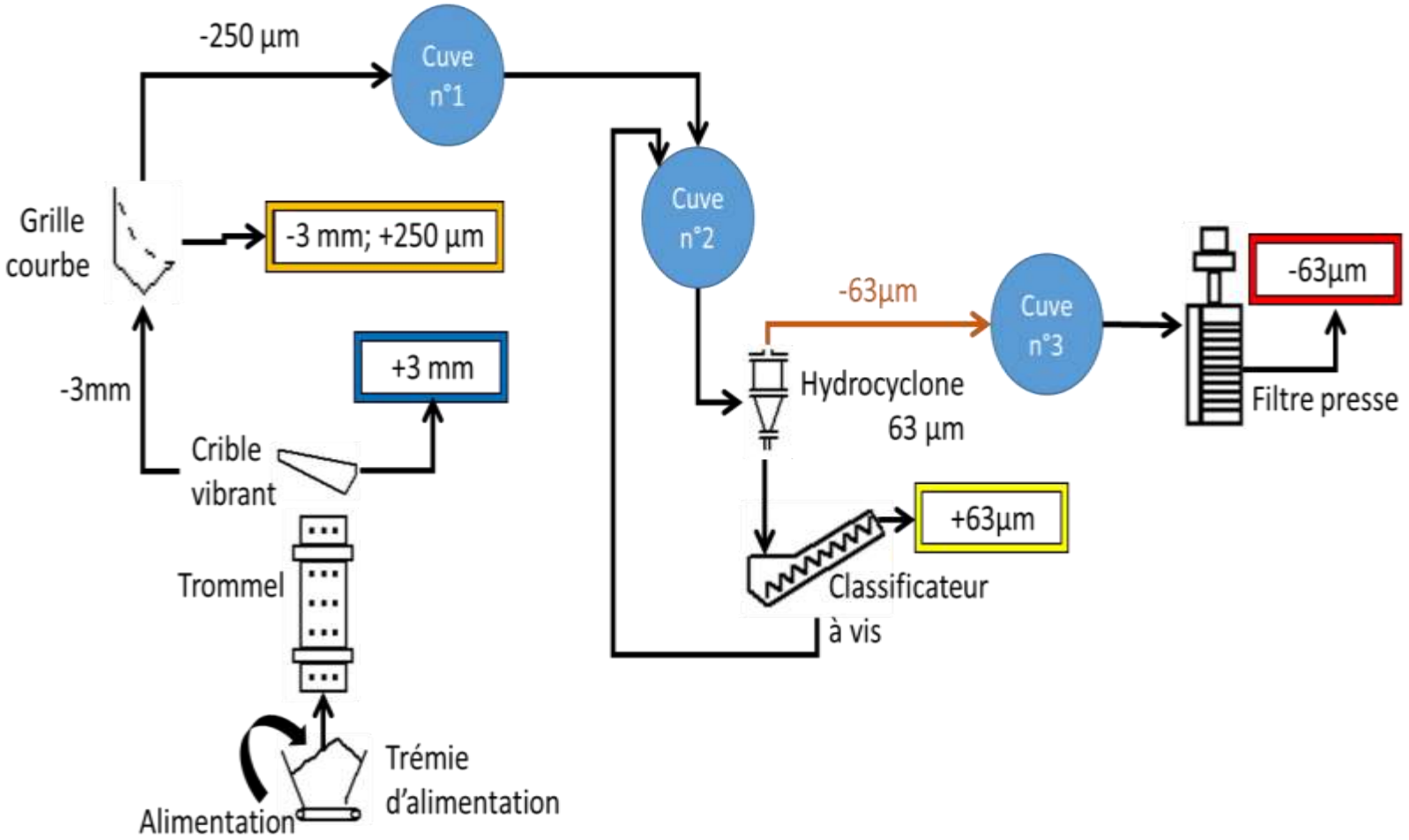




Water sampling at the CTP

- Water samples were also taken and filtered during a granulometric treatment process of sediment at the CTP

Water sampling at the CTP



M7647 sediment form Wallonie

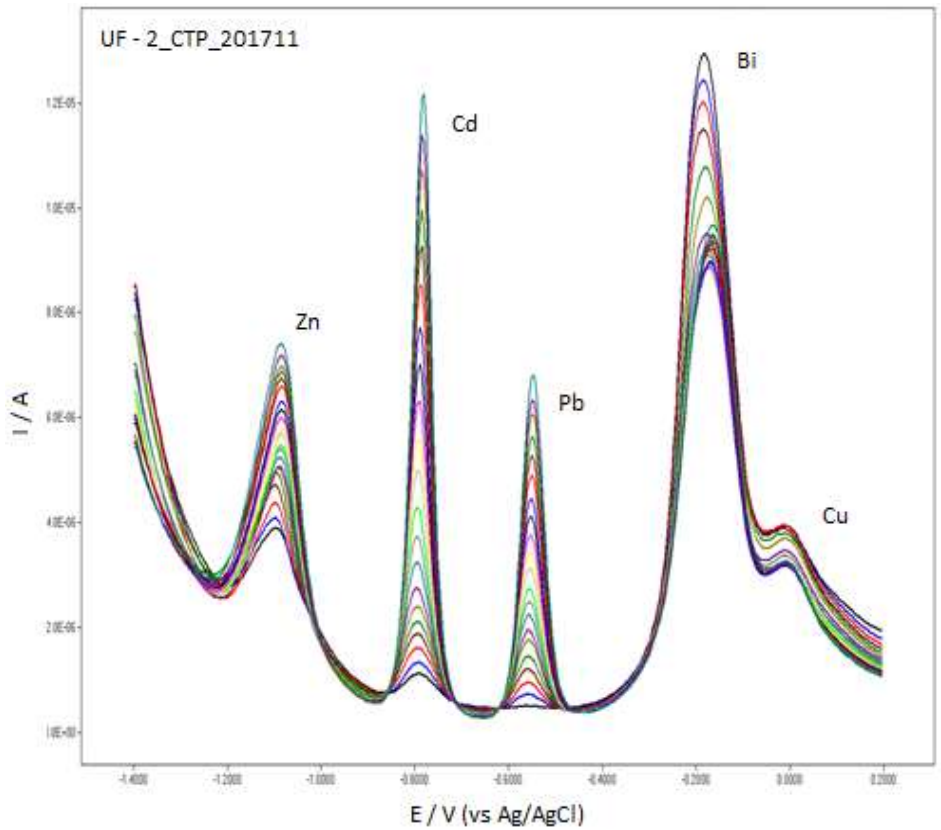
Cd, Zn and Cu, Pb

M7993 sediment from France

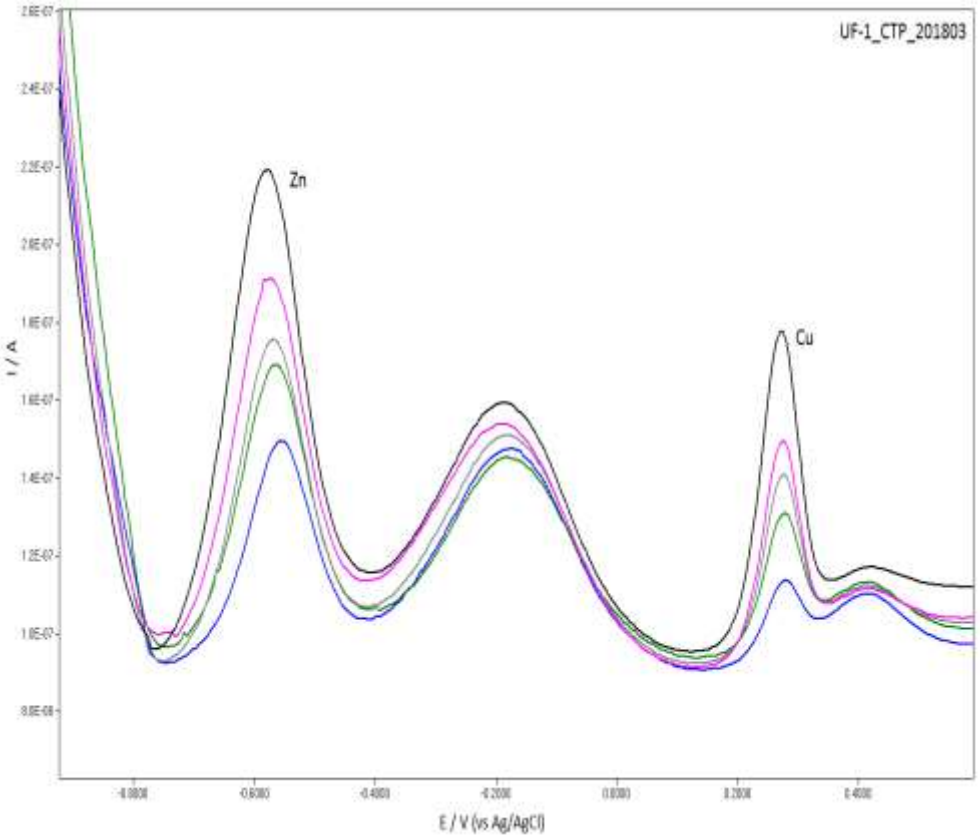
Cu and Hg, Pb, Zn

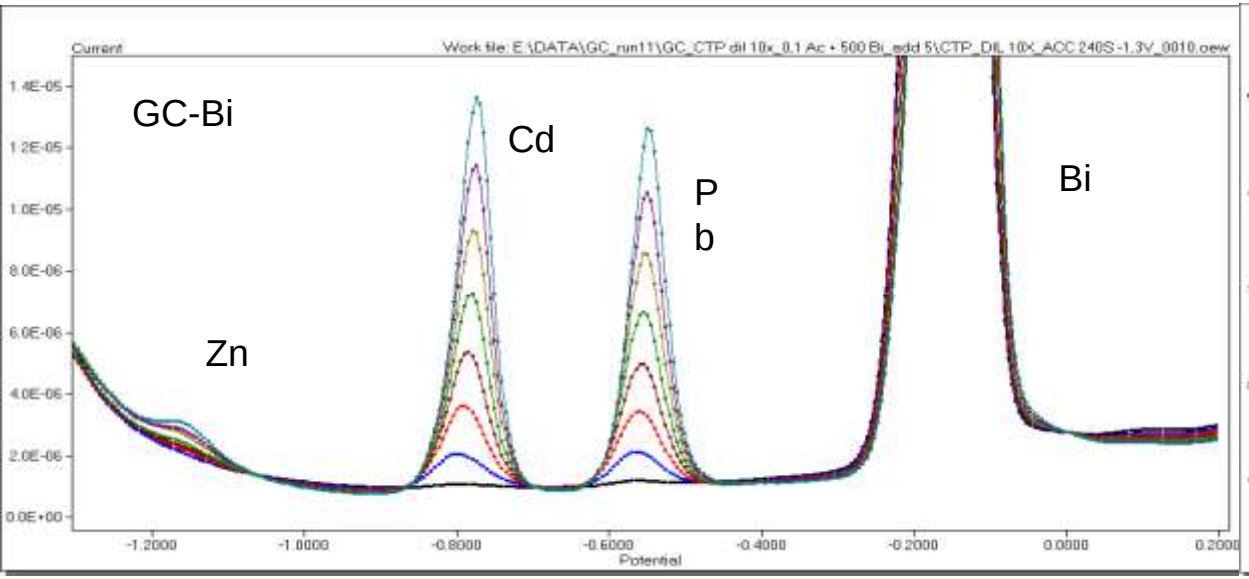
Characterization of sediment was done by CTP

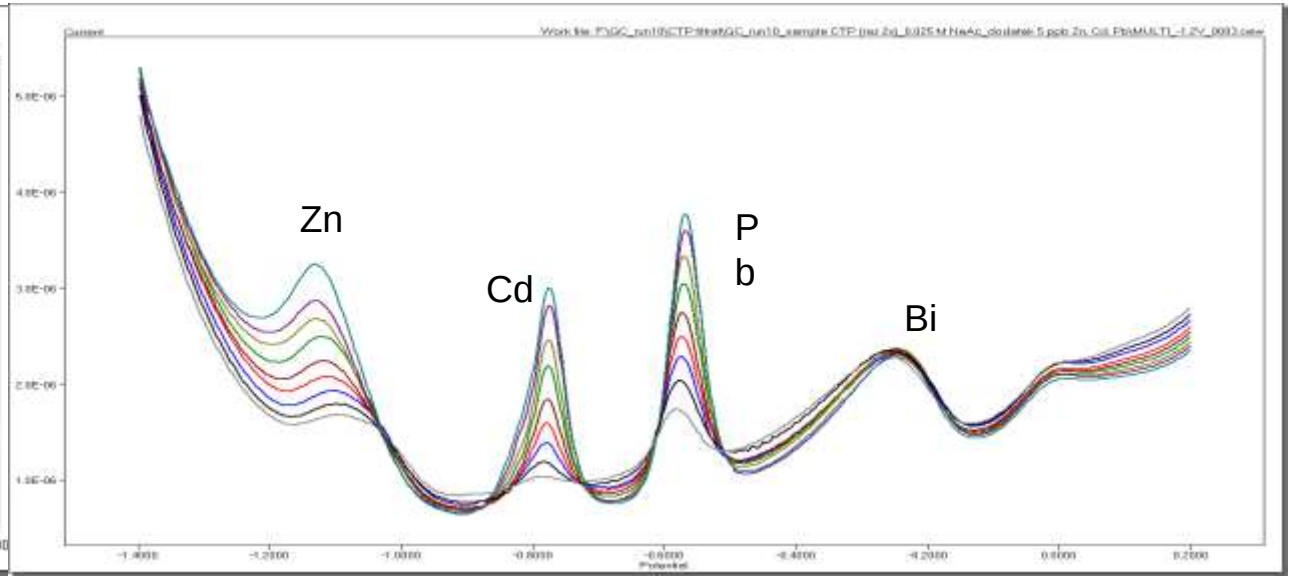
Electrode : GC- Bi

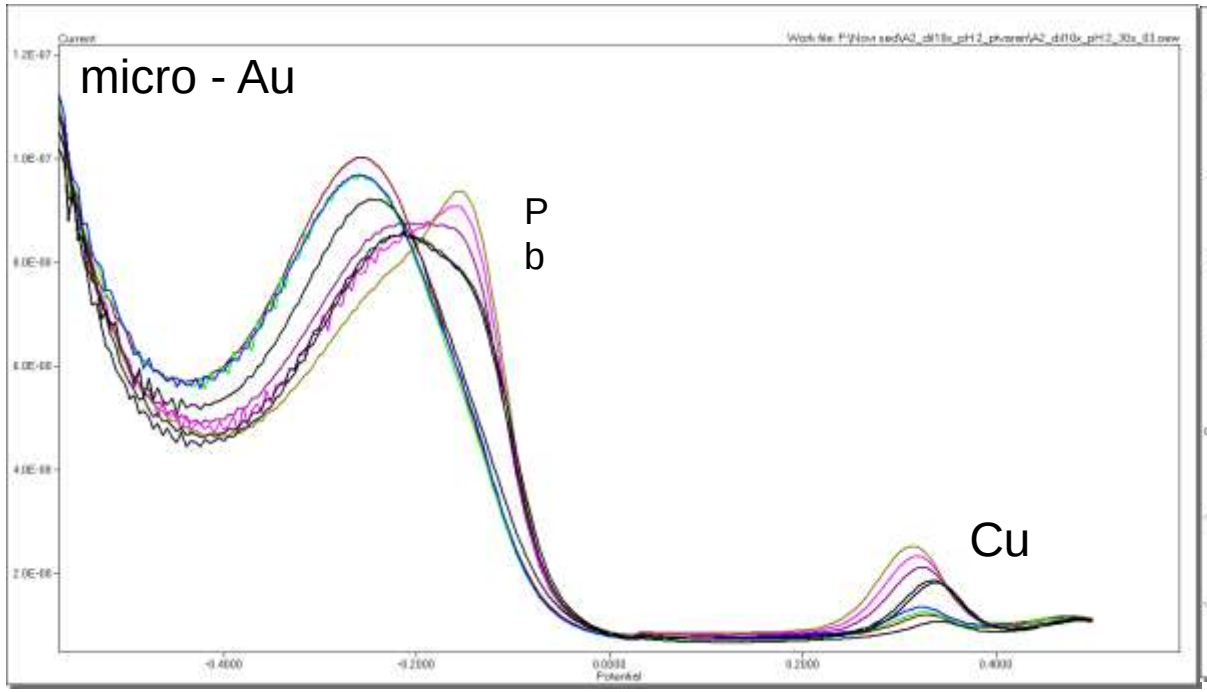


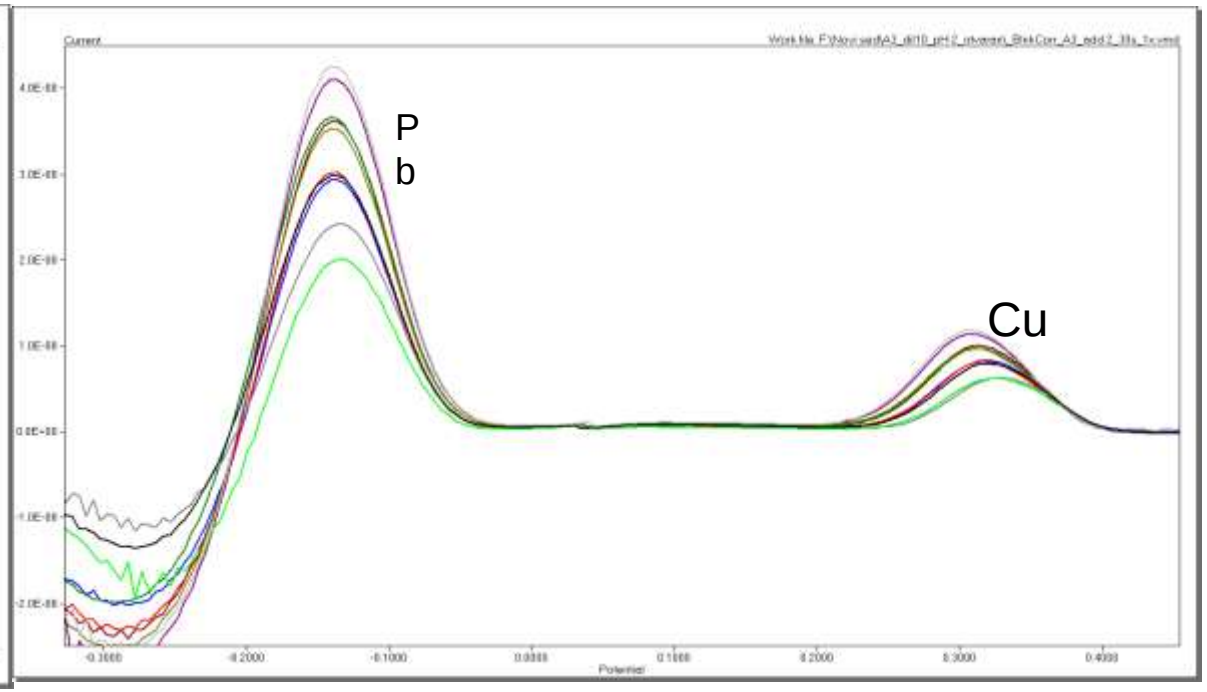
Electrode : uAu




GC-Bi
Zn
Cd
P
b
Bi
Potential


Zn
Cd
P
b
Bi


micro - Au
P
b
Cu
Potential


P
b
Cu
Potential

Results obtained on the GC-Bi electrode in the samples collected at CTP 10/2017

Cd (ppb)

	ICP-AES	Electrochemistry
T2-1	9.012	4.13
T2-2	9.301	4.502
T2-3	8.877	2.312
OF2	9.238	4.046
OF3		2.422
UF1	8.855	2.302
UF2	9.267	3.626
UF3	8.998	1.536

Zn (ppb)

T2-1	70.334	24.5133501
T2-2	69.792	10.9374878
T2-3	70.686	17.7895356
OF2	70.65	11.253559
OF3		23.832778
UF1	72.446	23.9574828
UF2	73.218	20.8447791
UF3	72.729	20.4690488

Results obtained on the micro-Au electrode in the samples collected at CTP 03/2018

Zn (ppb)

	ICP-AES	Electrochemistry pH = 2	Electrochemistry pH =3.5
T2-1	261	202.04	300
T2-2	102		110
T2-3	< 50	5.1	40
OF-1	78	10.08	
OF-2	50	26.94	50.14
OF-3	< 50		51.565
UF-1	103	14.66	100
UF-2	55	13.72	50
UF-3	53	4.56	48
RC-1	259	119.98	
RC-2	215	144.02	221.94
RC-3	52		53.65

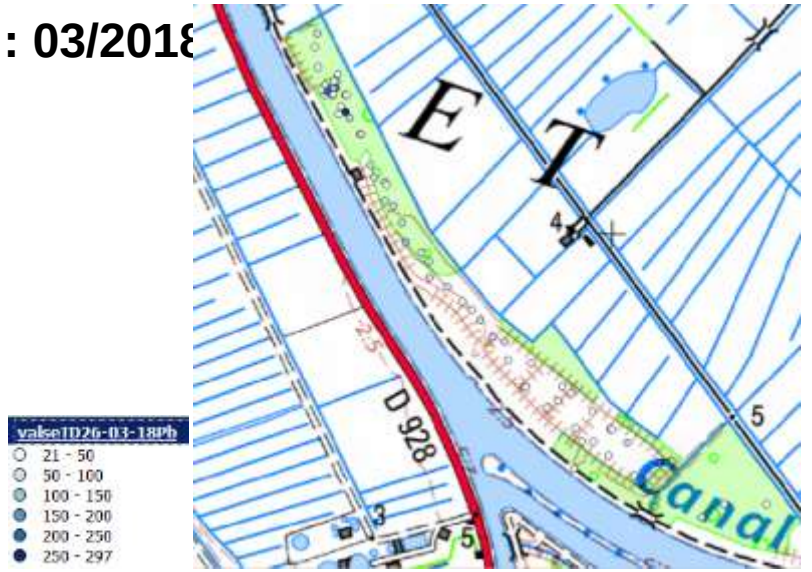
Cu (ppb)

	ICP-AES	Electrochemistry pH = 2
T2-1	35	21.04
T2-2	28	35.86
T2-3	25	23.63
OF-1	27	34.86
OF-2	25	23.9
OF-3	25	21.64
UF-1	37	27.8
UF-2	26	26.04
UF-3	27	22.48
RC-1	33	24.32
RC-2	26	16.38
RC-3	25	25.76

Sediment sampling

- TD 26 disposal site near St. Omer (northern France)
- the concentration of the metals in the surface samples was measured with the pXRF
- The electrochemical measurements and AVS were performed on the surface samples and one sediment column profile

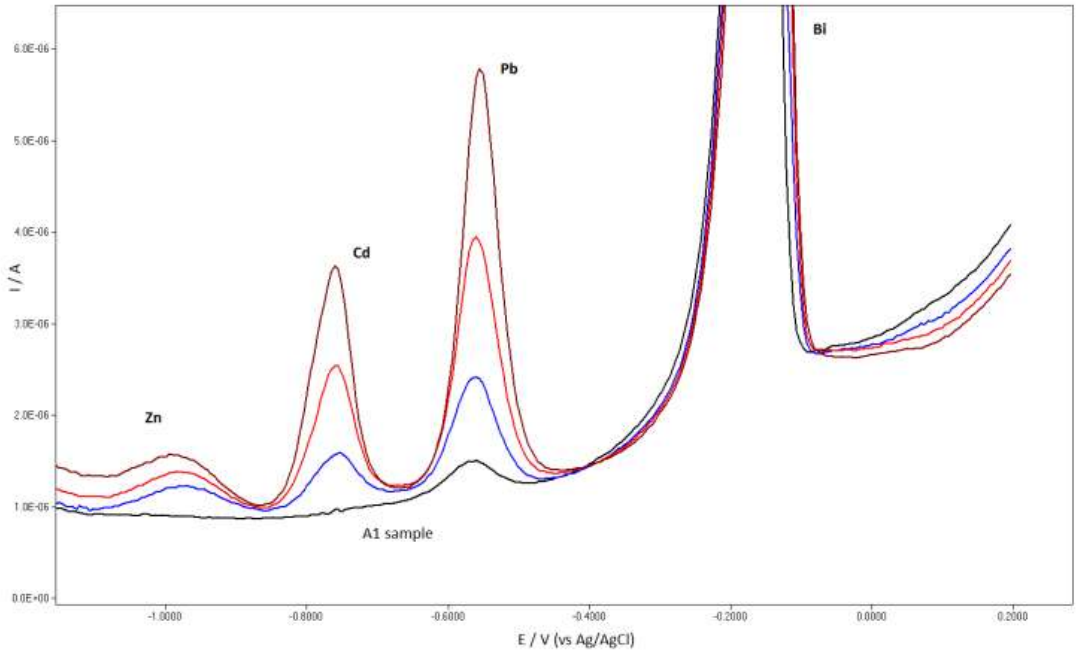
TD 26 : 03/2018



On site analysis of the sediment samples

The samples digestion was done with 1 M HCl for 1h and after filtration voltammetric measurements at Bi modified GC electrode were preformed on site.

In the samples with the applied procedure the Pb was detected. All the samples will be analyzed at laboratory to optimize the measurement procedures and sample preparation protocols.



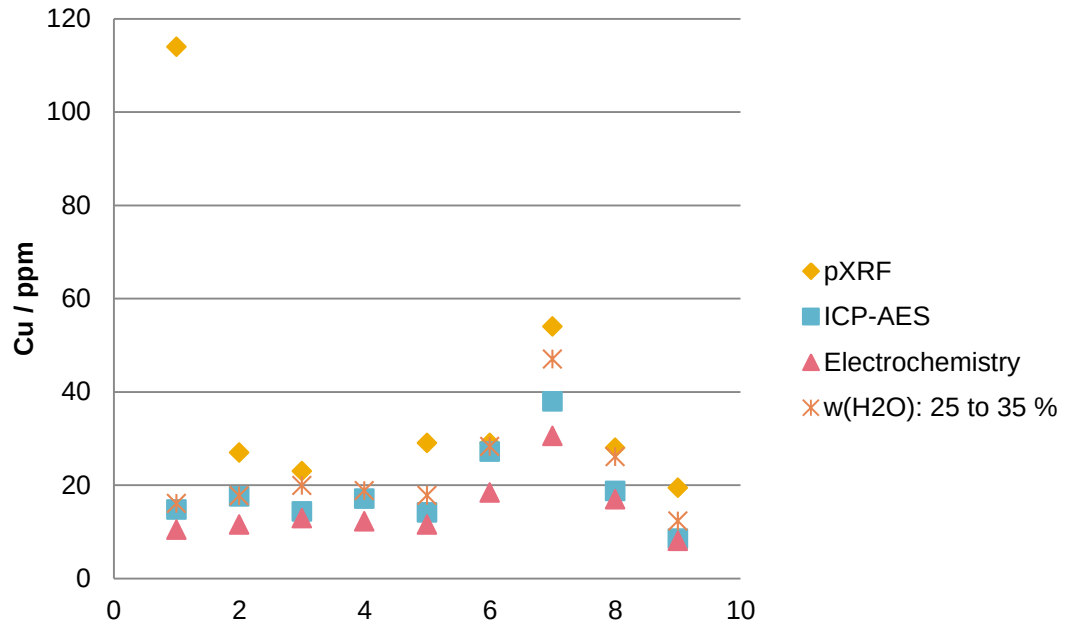
Results

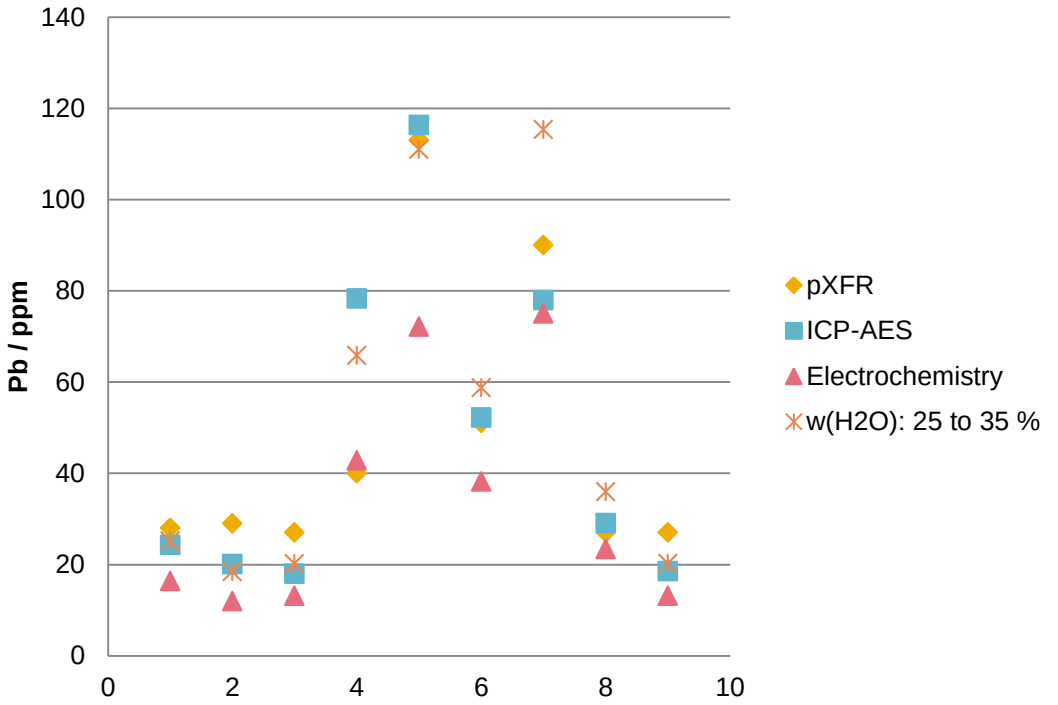
Cu / ppm

	pXRF	ICP-AES	Electrochemistry
A0	114	14.7495933	10.45029809
A2	27	17.5872629	11.51094935
A3	23	14.3236589	12.92608617
A4		17.0688751	12.23899861
A5	29	14.1607896	11.53430274
B	29	27.1989961	18.39075102
C	54	37.9320088	30.55294499
D	28	18.7585204	16.964416
E	19.45	8.5028432	8.003726441

Pb / ppm

	pXFR	ICP-AES	Electrochemistry
A0	28	24.2481131	16.32352941
A2	29	20.0553364	11.93181818
A3	27	17.9864938	13.10502283
A4	40	78.2692181	42.78186275
A5	113	116.318361	72.11805556
B	51	52.2045729	38.175
C	90	77.9307369	74.97577519
D	27	29.0704448	23.36956522
E	27	18.5633643	13.11904762





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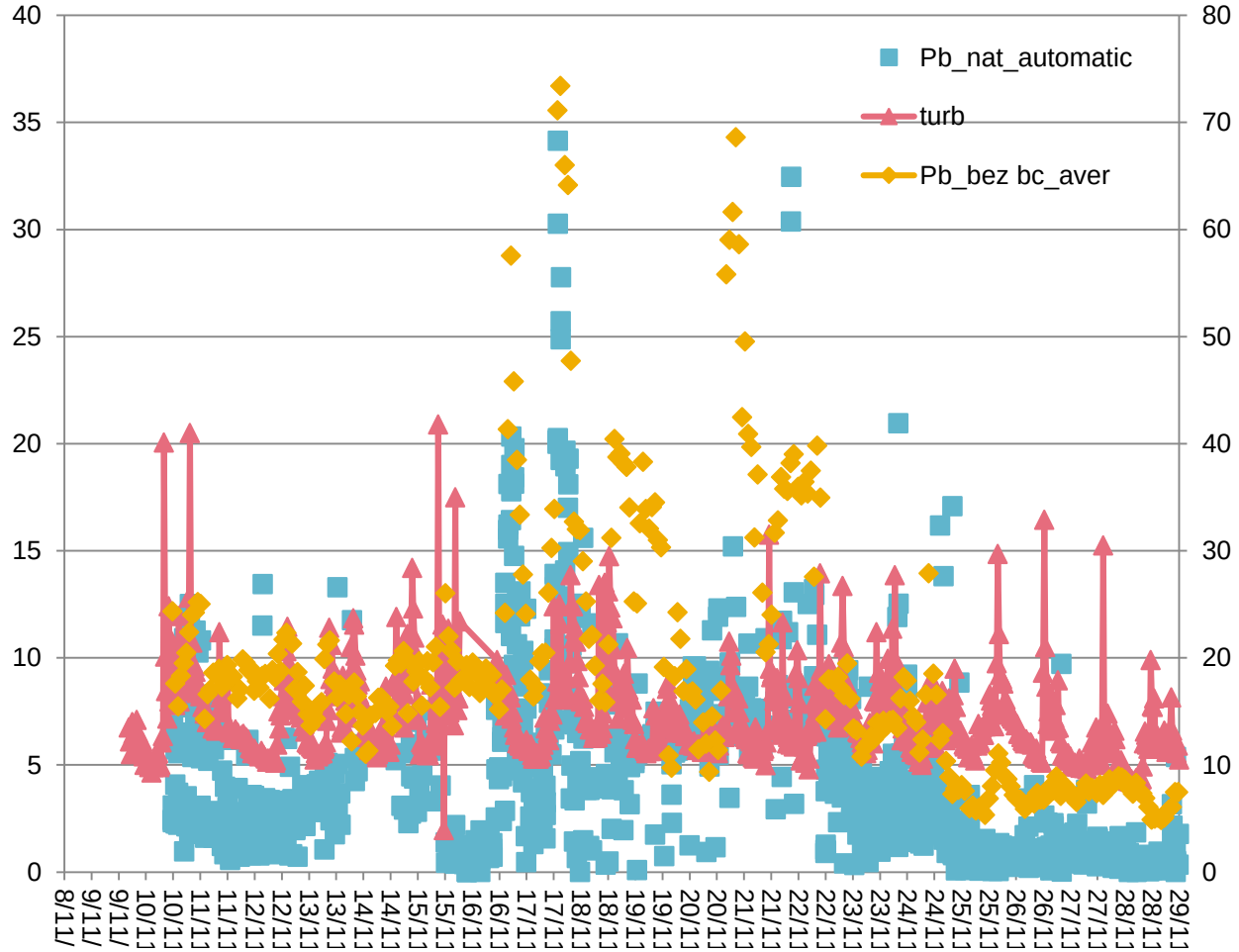
In situ analysis of the trace metals in river Deûle River (northern France) – further development and testing of the micro-Au for analysis of the trace metals connected with sediment resuspension



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Conclusion

- Electrochemistry has potential for the application in the field measurements
- Detection of the trace metals is possible, but the further development is necessary for development of procedures for specific trace metals

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