"Possibilities and drawbacks of portable XRF instrumentation for characterization of metal contaminated sites"

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ICTJA

CSIC

International Atomic Agency Technical Meeting on In-situ Methods for Characterization of Contaminated Sites

5-9 July 2010, IAEA Headquarters, Vienna, Austria

Laboratory of X-ray Analytical Applications (LARX)

- **LARX was established in 1982**
- **It is located in the Institute of Earth Sciences "Jaume Almera", CSIC (Barcelona, Spain)**
- **Instrumentation:**
  - X-ray diffraction spectrometry (XRD)
  - X-ray fluorescence spectrometry (XRF): EDXRF, WDXRF, TXRF
- **Research projects: "Environmental issues"**
  - Dispersal of metal pollutants at different environmental compartments (water, air, soils and biota)
- **Collaborative links:**
  - CFAUL, Lisbon, Portugal
  - INETI, Lisbon, Portugal
  - MiTAC, Antwerp, Belgium
  - Atominstitut TW, Vienna, Austria
  - CENA, Sao Paulo, Brazil

Layout

- **Aims of the presentation**
- **Introduction**
  - Metal contamination / Legislation
  - Analytical techniques
  - Quality Assurance (QA)
- **Application cases**
  - As anomalies in floodplains (Handheld-EDXRF system)
  - Environmental impact of past-mining activities (portable EDXRF/TXRF systems)
  - Metal content in industrial waste waters effluents (portable EDXRF/TXRF systems)
- **Conclusions**

Aims of the presentation

The Technical Meeting will review the current status, developments, and trends in (i) nuclear *in-situ* techniques for contaminated site characterization, and (ii) both nuclear and non-nuclear *in-situ* techniques used at nuclear-related sites, including nuclear fuel cycle facilities. In particular, applications to be addressed in the Technical Meeting could include those used at sites contaminated due to:

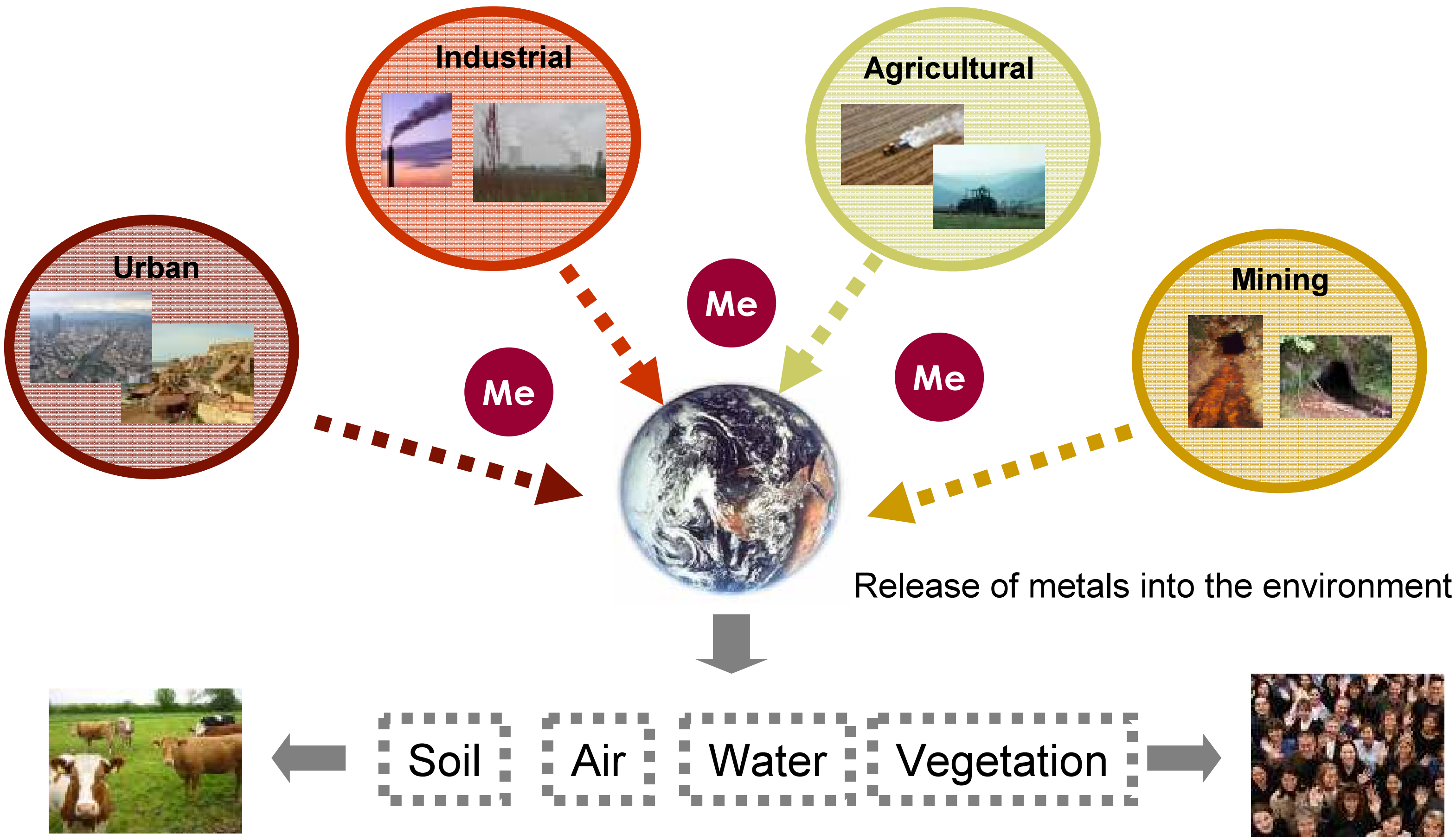
- Mineral exploration and mining (e.g. uranium mining)
- Nuclear power and nuclear processing facilities
- Industrial activities that produce Naturally Occurring Radioactive Materials (NORM)
- Industrial activities that produce metal contaminants (i.e. lead, zinc, copper, etc.)
- Military actions involving the utilization of nuclear material
- Accidents
- Terrorism actions

The following subjects of discussion are expected to be included in the programme:

- Selected *in-situ* applications at different kinds of contaminated sites
- Comparison of different techniques/methodologies for the characterization of contaminated sites
- Sampling approaches (i.e. choice of number and location of measurements)
- Mapping approaches of a contaminated site
- QC/QA of the in-situ analytical technique and interpretation of the results
- State of the art of the portable instrumentation for in-situ characterization. Current trends
- The role of the IAEA in the promotion and effective use of nuclear spectrometry instrumentation and of associated analytical methodologies for *in-situ* applications in developing Member States.

Introduction

- Metal contamination

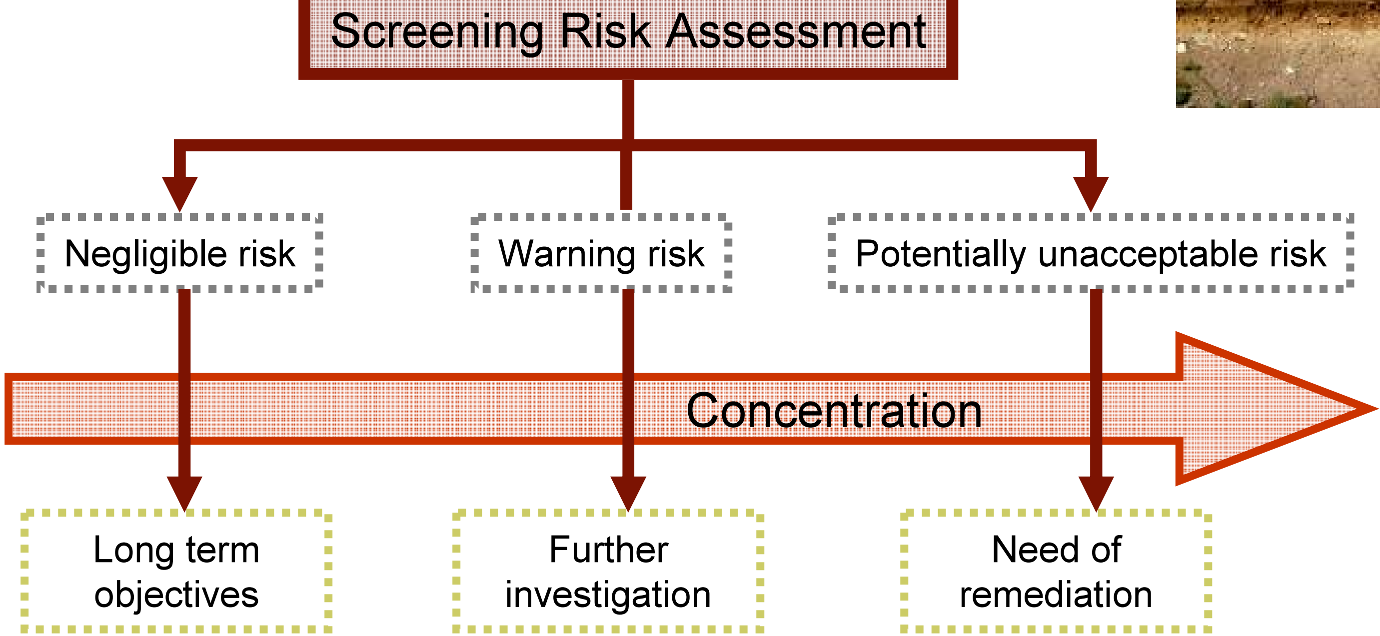


Metals are not biodegradable!
(Accumulation, environmental impact)

Introduction

- Legislation

  - **Soil screen values (SVs)**
    - Are quality standards that are used to regulate land contamination
    - Based on concentration thresholds (mg/kg soil-dry weight)
    - Are derived on the basis of the:



Derivation of screening values based on various risk levels and different screening values applications
(EUR 22805 EN-2007)

- **Soil screen values (SVs)** for metal and metalloids (mg/kg)

Negligible risk

	Belgium Wa	Czech Republic	Netherlands	Slovakia
As	12	30	29	29
Ba		600	160	500
Be		5	0.04	3
Cd	0.2	0.5	0.80	0.8
Co		25	0.38	20
Cr	34	130	100	130
Cr(VI)	2.5			
Cu	14	70	36	36
Hg	0.05	0.4	0.3	0.3
Pb	25	80	85	85
Mo		0.8	0.13	1
Ni	24	60	35	35
Sb			0.13	
V		180	42	120
Zn	67	150	140	140

Warning risk

	Austria	Belgium Fl*	Belgium Wa	Czech Rep.	Finland	Germany	Slovakia	Denmark	Sweden
As	20	110	40	65	5	50	30	20	15
Be				15			20		
Cd	2	6	3	10	1	20	5	0.5	1
Co				180	20		50		200
Cr	50		125	450	100	400	250	500	250
Cr(VI)			4.2					20	15
Cu	100	400	110	500	100		100	500	
Hg	2	15	9	2.5	0.5	20	2	1	5
Pb	100	700	195	250	60	400	150	40	300
Mo				50			40	5	
Ni	70	470	150	180	50	140	100	30	150
Sb	2			25	2				
Se							5		
Tl	2							1	
V				340	100		200		200
Zn		1000	230	1500	200		500	500	700

*For historical contaminants only

Potentially unacceptable risk

	AUT	BE(F)*	BE(B)	BE(W)	CZE	FIN	ITA	LTU	NLD	POL	SVK	UK	DNK
As	50	110	110	300	70	50	20	10	55	22.5	50	20	20
Ba					1000			600	625	285	2000		
Be					20		2	10	30		30		
Cd	10	6	6	30	20	10	2	3	12	5.5	20	2	5
Co					300	100	20	30	240	45	300		
Cr	250		300	520	500	200	150	100	380	170	800	130	1000
Cu	600	400	400	290	600	150	120	100	190	100	500		1000
Hg	10	15	15	56	10	2	1	1.5	10	4	10	8	3
Pb	500	700	700	700	300	200	100	100	530	150	600	450	400
Mo					100			5	200	25	200		
Ni	140	470	470	300	250	100	120	75	210	75	500		30
Sb	5				40	10	10	10	15				
Se							3	5	100		20	35	
Sn					300		1	10	900	40	300		
Te									600				
Tl	10						1		15				
V					450	150	90	150	250		500		
Zn		1000	1000	710	2500	250	150	300	720	325	3000		1000

*For new contaminants only

Soil screen values (SVs) for metal and metalloids (mg/kg)

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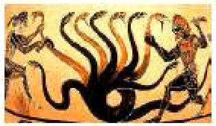
Cd	10	6	6	30	20	10	2	3	12	5.5	20	2	5
Co					300	100	20	30	240	45	300		
Cr	250		300	520	500	200	150	100	380	170	800	130	1000
Cu	600	400	400	290	600	150	120	100	190	100	500		1000
Hg	10	15	15	56	10	2	1	1.5	10	4	10	8	3
Pb	500	700	700	700	300	200	100	100	530	150	600	450	400
Mo					100			5	200	25	200		
Ni	140	470	470	300	250	100	120	75	210	75	500		30
Sb	5				40	10	10	10	15				
Se							3	5	100		20	35	
Sn					300		1	10	900	40	300		
Te									600				
Tl	10						1		15				
V					450	150	90	150	250		500		
Zn		1000	1000	710	2500	250	150	300	720	325	3000		1000

*For new contaminants only

Lack of harmonization among screening values used in EU Member States



THE HERACLES FRAMEWORK
HUMAN AND ECOLOGICAL RISK ASSESSMENT FOR CONTAMINATED LAND IN EUROPEAN MEMBER STATES
Towards the development of common references

Introduction

- Legislation

  - **Water Framework Directive (2008/105/CE)**
    - Settlement of the limits of concentration in surface waters of:
      - 33 priority substances (Hg, Pb, Cd, Ni and its compounds)
      - 8 other pollutants

ANNEX I

ENVIRONMENTAL QUALITY STANDARDS FOR PRIORITY SUBSTANCES AND CERTAIN OTHER POLLUTANTS

No	Name of substance	CAS number	AA-EQS Inland surface waters	AA-EQS Other surface waters	MAC-EQS Inland surface waters	MAC-EQS Other surface waters
(6)	Cadmium and its compounds	7440-43-9	≤0.08 (Class 1) 0.08 (Class 2) 0.09 (Class 3) 0.15 (Class 4) 0.25 (Class 5)	0.2	≤0.45 (Class 1) 0.45 (Class 2) 0.6 (Class 3) 0.9 (Class 4) 1.5 (Class 5)	≤0.45 (Class 1) 0.45 (Class 2) 0.6 (Class 3) 0.9 (Class 4) 1.5 (Class 5)
(20)	Lead and its compounds	7439-92-1	7.2	7.2	not applicable	not applicable
(21)	Mercury and its compounds	7439-97-6	0.05	0.05	0.07	0.07
(23)	Niquel and its compounds	7440-02-0	20	20	not applicable	not applicable

Concentrations are expressed as μg/L
AA: annual average value, MAC: maximum allowable concentration
Cd: Values are depending on the hardness of the water (Class 1: <40mg/L $CaCO_3$, Class 2: 40 to <50mg/L $CaCO_3$, Class 3: 50 to <100mg/L $CaCO_3$, Class 4: 100 to <200mg/L $CaCO_3$, Class 5: ≥200mg/L $CaCO_3$

Introduction

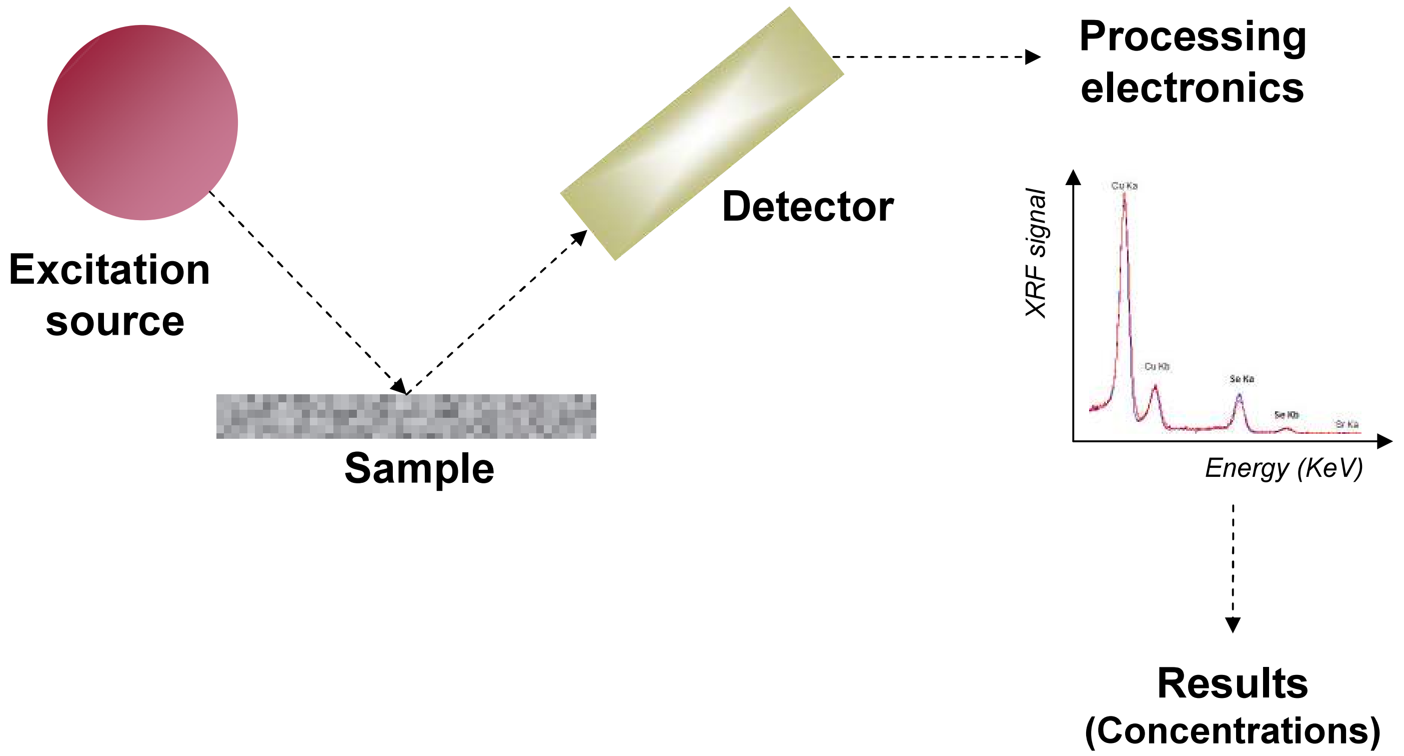
- Analytical techniques
  - **Qualitative/Quantitative measurements of the amounts and distribution of metals in the contaminated areas**

  ⇓

  - **Necessity of appropriate analytical methodologies**
    - Multi-elemental capability
    - Simple sample preparation (Non-destructive)
    - Wide dynamic range
    - High throughput
    - Relatively low investment and operational costs
    - Adequate instrumental sensitivity, accuracy and precision of the obtained results (legislation)
  - **In-situ techniques?**

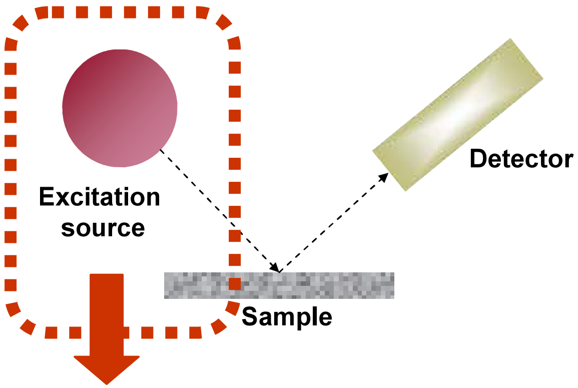
Introduction

- Analytical techniques
  - **Field portable X-ray fluorescence spectrometry systems (FPXRF)**



Introduction

- Analytical techniques
  - **Field portable X-ray fluorescence spectrometry systems (FPXRF)**



- Radioisotope source
- Miniaturized X-ray tubes

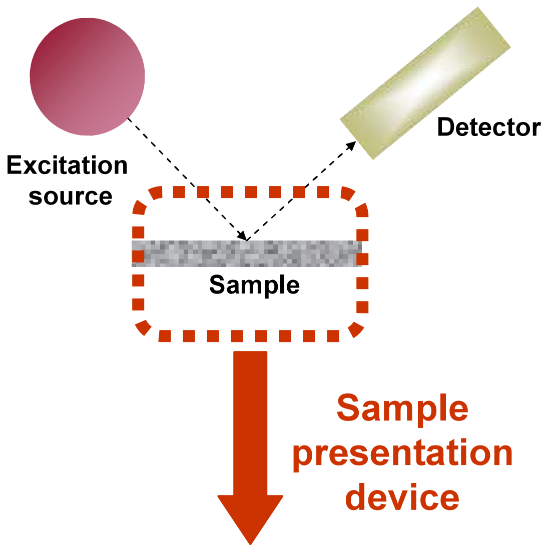
- Radioisotope sources:

Isotope	Half-life	Useful radiation	E (keV)
Fe-55	2.7 years	Mn K X-rays	5.9
Co-57	270 days	Fe K X-rays	6.4
Cd-109	1.3 years	Ag K X-rays	22.2
Am-241	470 days	Np L X-rays	14-21
Cm-244	17.8 years	Pu L X-rays	14-22

- X-ray tubes:
  - Wider range of excitation energies
  - Higher X-ray flux
  - Use of filters to reduce the continuum radiation

Introduction

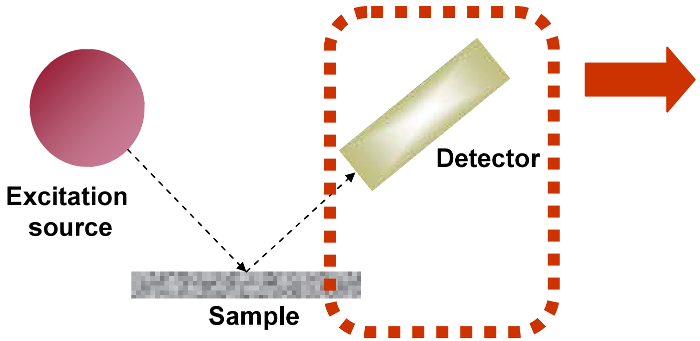
- Analytical techniques
  - **Field portable X-ray fluorescence spectrometry systems (FPXRF)**



- In situ mode
- Intrusive mode

Introduction

- Analytical techniques
  - **Field portable X-ray fluorescence spectrometry systems (FPXRF)**



- Gas flow proportional detector
- Scintillation detector
- **Solid-state semiconductors**
  - Best resolution
  - Cooling necessary
    (liquid nitrogen or electronic cooling)

Introduction

- Analytical techniques
  - **Field portable X-ray fluorescence spectrometry systems (FPXRF): "Available Instrumentation"**

"Handheld" systems

- Weight: **0.8-1.5 kg**
- Changeable batteries
- Sample analysis:
  - In situ mode
  - Intrusive mode

"Bench top" systems

- Weight: **30-40 kg**
- No cooling media
- No gas consumption
- Plug in (220V)
- Sample analysis:
  - Intrusive mode

Layout

- Aims of the presentation
- Introduction
  - Metal contamination / Legislation
  - Analytical techniques
  - **Quality Assurance (QA)**
- Application cases
  - As anomalies in floodplains (Handheld-EDXRF system)
  - Environmental impact of past-mining activities (portable EDXRF/TXRF systems)
  - Metal content in industrial waste waters effluents (portable EDXRF/TXRF systems)
- Conclusions

Introduction

- Quality Assurance (QA)

  - **Method 6200 US-EPA: "Field portable X-ray fluorescence spectrometry for the determination of elemental concentrations in soil and sediment" (revision 2007)**

  … Be aware of :

  - **Sample preparation**
  - **Calibration/Quantification**
  - **Limits of detection**
  - **QA/QC Considerations**

Introduction

- Quality Assurance (QA)

Sample preparation

- Considerations:
  - Representative samples
  - Sample moisture (<20%)
  - Sample placement and prove geometry
  - Physical matrix effects: particle size, heterogeneity, surface condition

Introduction

- Quality Assurance (QA)

Sample preparation

- **In-situ analysis**
  - Without sample preparation
  - Minimal sample preparation

Improved accuracy →

- **Ex-situ analysis**
  - Sample cubs
  - Core sampling

- Avoid physical matrix effects
  - Homogenization
  - Sieve (<2mm)
- Moisture content<20%
  - Drying (few hours)
- Flat smooth (packing the soil)

- Composite sample
- Homogenization
- Drying
- Sieve
- Sample cups (3-5g)

Introduction

- Quality Assurance (QA)

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Introduction

- Quality Assurance (QA)

Calibration / Quantification

- **Quantification depends on:**
  - Detector resolution (spectral interferences)
  - Sample matrix effects (suitable calibration standards)
  - Sample preparation (particle size, homogeneity…)
- **Calibration methods (XRF signal →Concentration)**
  - Fundamental parameters (standard less calibration)
  - Empirical calibration (site-typical standards)
  - Compton peak (normalization method)
- **FPXRF results are quantitative when:**

$$\%D=((C_S-C_k)/C_k)x100$$

$$\%D= \pm 20\%$$

%D= Percent difference
C_k= Certified concentration of standard sample
C_S= Measured concentration of standard sample

Introduction

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Introduction

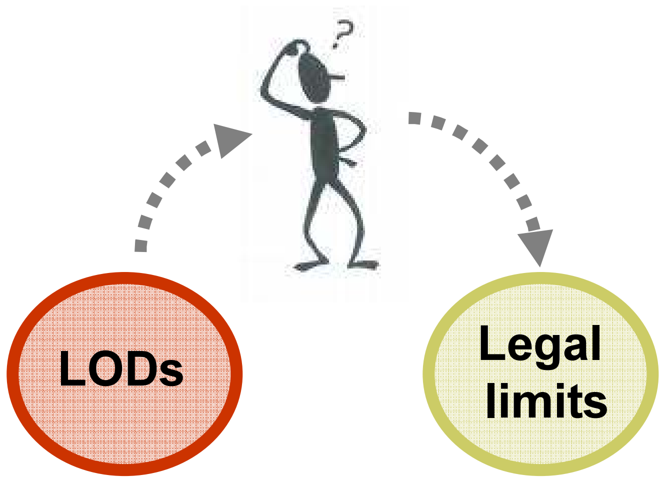
- Quality Assurance (QA)

Limits of Detection (LODs)

- LODs depend on:
  - Instrumental characteristics (Excitation source, type of detector…)
  - Sample matrix
  - Element itself (fluorescent yield)
  - Measuring time

Element	Sand matrix		Soil matrix	
	60s	120s	60s	120s
Mn	130	80	250	175
Fe	100	75	250	175
Co	75	50	200	150
Ni	75	50	120	90
Cu	75	50	100	60

XLt 700 Series Analyzer (X-ray tube excitation)



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  … Be aware of :

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  - **Limits of detection**
  - **QA/QC Considerations**

Introduction

- Quality Assurance (QA)

QA/QC Considerations

- **Precision:** Assess variation in the reported values
  - Relative standard deviation (RSD)

RSD=(SD/Mean concentration)x100

RSD= ±20% (n=2)

  - Total variation:

$$\sigma^2_{total} = \sigma^2_{\substack{sample\\representation}} + \sigma^2_{\substack{sample\\collection}} + \sigma^2_{\substack{sample\\preparation}} + \sigma^2_{analysis}$$

Negligible!

Introduction

- Quality Assurance (QA)

QA/QC Considerations

- **Accuracy:**
  - Internal calibration → Gain correction
    - Instrumental stability
    - Energy calibration
  - Calibration checks at several concentrations
    - Certified reference materials
    - Well characterized site samples
- **Comparability:**
  - Comparison field-method with laboratory data (in-situ / ex-situ comparison)
  - Usually: 10% of total samples

Introduction

- Quality Assurance (QA)

QA/QC Considerations

Data quality level	Requirements
Qualitative Screening (Q1)	RSD>20% R^2 < 0.70 Inferential statistics indicate two data sets are statistically different
Quantitative Screening (Q2)	RSD<20% R^2 =0.70-1.0 Inferential statistics indicate two data sets are statistically different
Definitive (Q3)	RSD≤10% R^2 =0.85-1.0 Inferential statistics indicate two data sets are statistically similar (slope=1, intercept=0)

US EPA, QA/QC Guidance for Removal Program Activities, 1998

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- Application cases
  - As anomalies in floodplains
    (Handheld-EDXRF system)

    C.Parsons, E.Pili, E.Margui, G.Roman-Ross, L.Charlet.
    "*Physical and chemical controls on Arsenic distribution on the Saone Flood plain: A statistical assessment of As liberation risks*". Applied Geochemistry, submitted (2010)
  - Environmental impact of past-mining activities
    (portable EDXRF/TXRF systems)
  - Metal content in industrial waste waters effluents
    (portable EDXRF/TXRF systems)
- Conclusions and future perspectives

Application cases

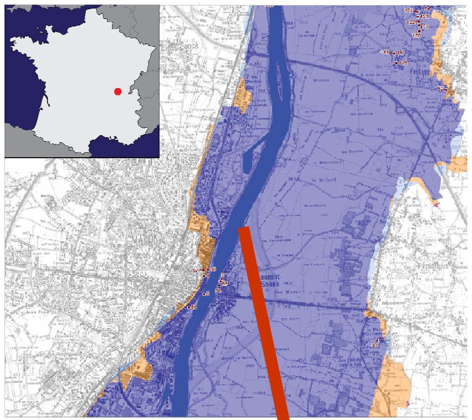
- As anomalies in flood plains

Introduction and motivation

- Area characterized by flooding events which lead to reducing conditions and As liberation in soils

- Motivation: what is the spatial heterogeneity of As concentrations in soil on the floodplain and which factors control As distribution?

Analysis of a high amount of soil samples (n=119)
In-situ analysis?



Application cases

- As anomalies in flood plains

Instrumentation

NITON XLt Handheld-XRF (Thermo Scientific)

Weight	**1.4 Kg**
Dimensions	**248x273x95 mm**
Excitation source	**Miniature X-ray tube (Ag anode, 40kV/50μA)**
X-ray detector	**High-performance Si-PIN detector (Peltier cooled)**
Batteries	**Rechargeable Lithium-ion battery packs**
Analysis range	**Ti (Z=22) to Pu (Z=94), 25 elements**

"point and shoot"

Application cases

- As anomalies in flood plains

Sample preparation

Loose the soil to a depth of 1.5-2.5cm

Homogenization
Drying
Sieving

Mix the loose soil and pack

Handheld XRF analysis

Remove any debris (leaves, stones…)

20 samples/day

Application cases

- As anomalies in flood plains

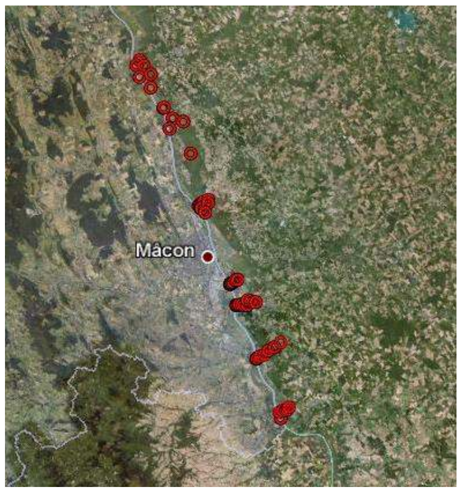
Results

- Measuring time: 120s → **LOD (As)~6mg/kg**
- Quantization purposes: Compton normalization (eliminates need for time-consuming specific calibrations)

N=119	**As (mg/kg)**
Min.	**6.9**
Max.	**45**
Average	**22**

	As (mg/kg)
European average (soils)	**6**
Guideline value agricultural soils	**20**

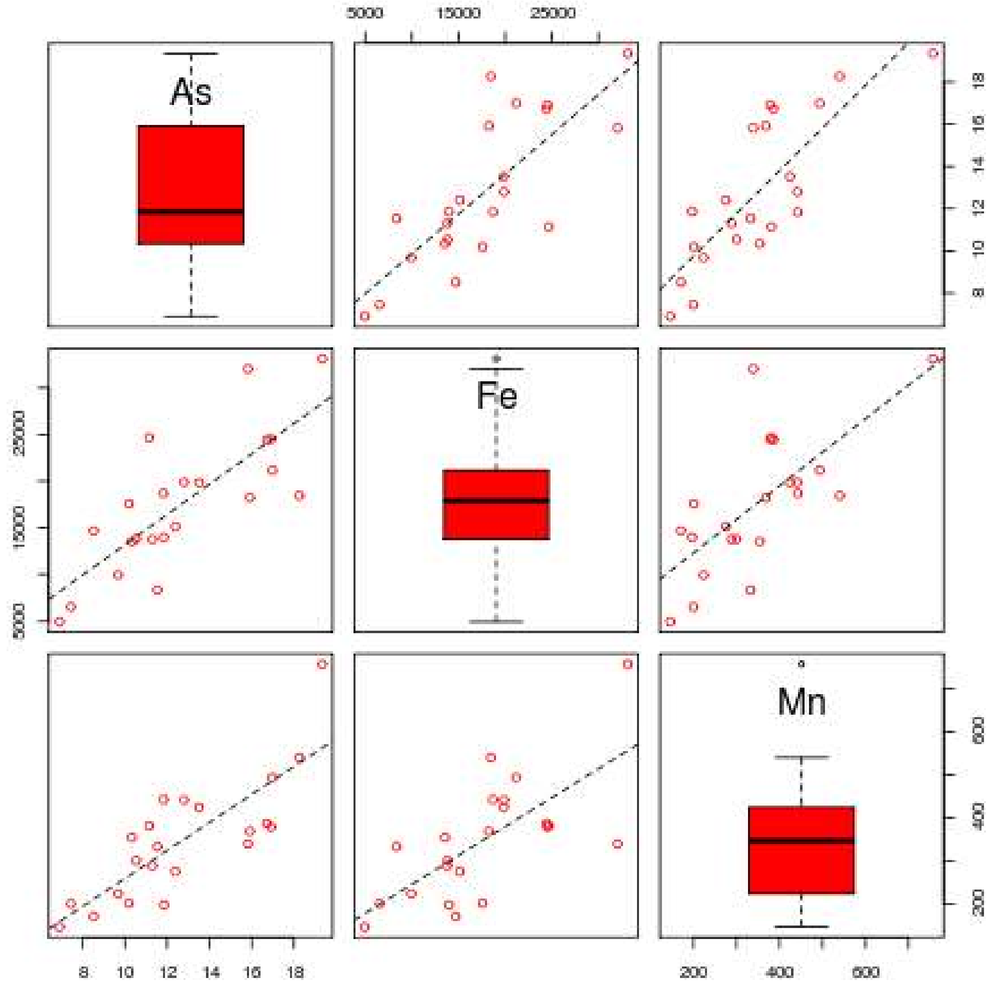
Determination of "hot-spots"



Application cases

- As anomalies in flood plains

Multielemental information!



Application cases

- As anomalies in flood plains

Quality assurance of the field measurements

Precision

- Relative standard deviation (RSD)
- N=2

RSD=6-20%

Comparability

- Comparison with laboratory data
- N=10 (10% total samples)

Application cases

- As anomalies in flood plains

Comparability: Microwave digestion + ICP-MS

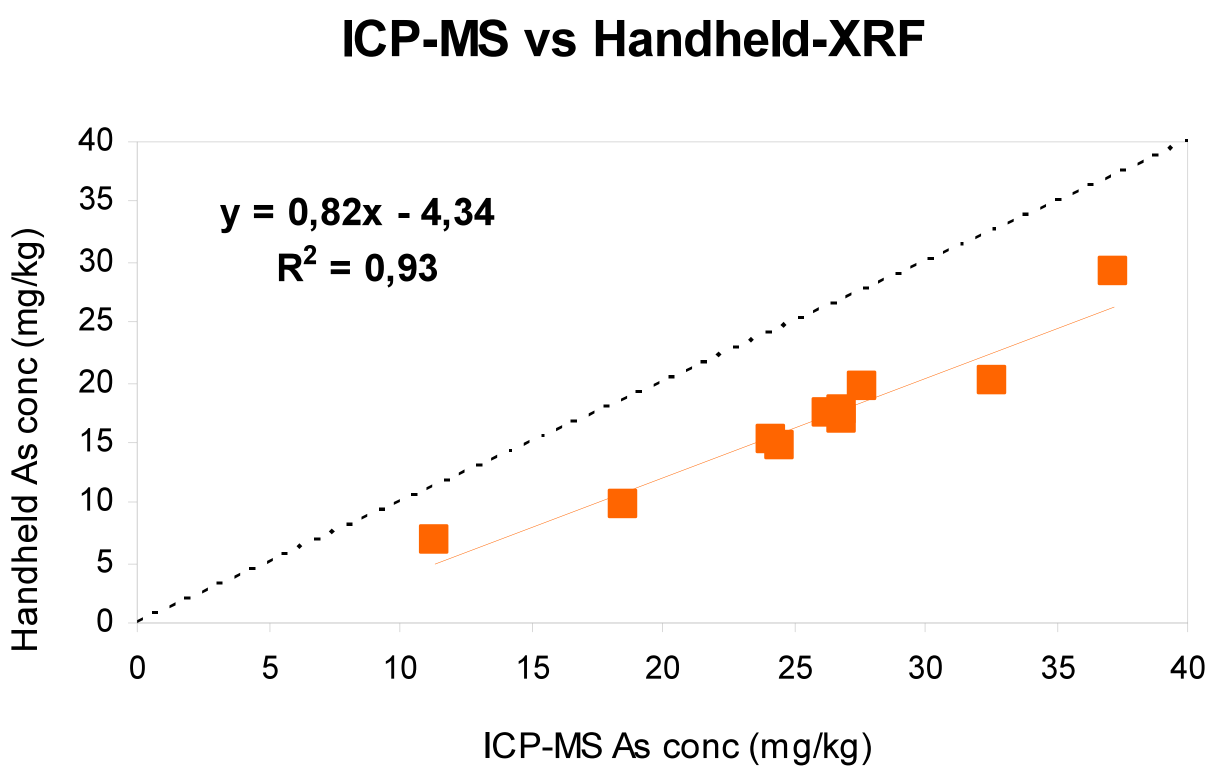
- **Microwave digestion**: EPA method 3052
- Soil amount: 0.1g
- Acid mixture:
  - Step-1 (9mL HNO_3 65% + 1.5mL HF 40% + 1mL H_2O_2 33%)
  - Step-2 (5mL H_3BO_3 5% + 1mL HF 40%)

- Quadrupole-based **ICP-MS system** (Agilent 7500c)
- Octapole collision/reaction cell
- Analytical conditions: ^{75}As, Internal standard: Rh
- Cell conditions: 3.0mL/min (Reaction gas:H_2) + 0.5mL/min (Collision gas: He)

Application cases

- As anomalies in flood plains

Comparability: Microwave digestion + ICP-MS



Regression analysis: LR model, Handheld=A+B (ICP-MS)

Application cases

- As anomalies in flood plains

Quality assurance of the field measurements

Precision

- Relative standard deviation (RSD)
- N=2

Comparability

- Comparison with laboratory data
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Quantitative screening (Q2)

- RSD<20%
- R^2=0.70-1.0

Criteria for characterizing data quality

Data quality level	Requirements
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Application cases

- As anomalies in flood plains

Conclusions

- Handheld instrumentation prove to be a powerful tool for in-situ determination of As in flood plains (determination of “hot-spots”).
- Simple sample preparation in the field
- Speed of data acquisition compared to other methods.
- Multielemental information.
- Qualitative / Quantitative information
- Cost effective compared to traditional ICP-MS analysis.

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    O.González-Fernández, I.Queralt. "*Fast element screening of soil and sediment profiles using small-spot energy dispersive X-ray fluorescence: Application to mine sediments geochemistry*". Applied Spectroscopy 64(2010), in press.

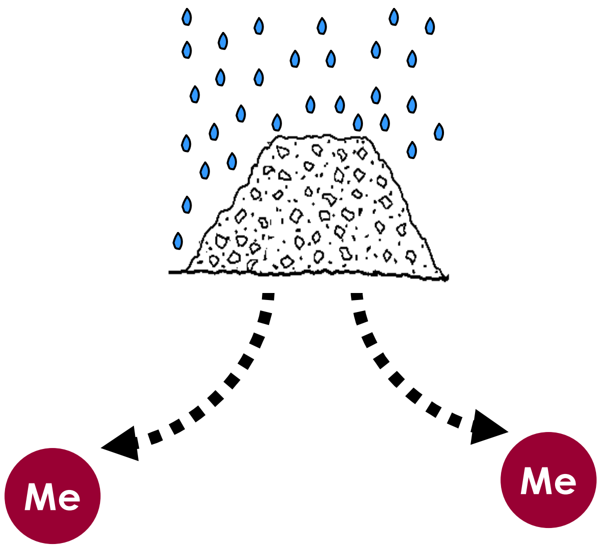
    E.Margui,A.Jurado, M.Hidalgo, G.Pardini, M.Gispert, I.Queralt. "*Application of small-spot energy dispersive X-ray fluorescence instrumentation in phytoremediation activities around metal mines*". Applied Spectroscopy 63(2009)1396.
  - Metal content in industrial waste waters effluents (portable EDXRF/TXRF systems)
- Conclusions

Application cases

- Past mining activities

Introduction and motivation

Mining wastes dumped indiscriminately



The current problem of abandoned mining areas…

Metals are not biodegradable! (Environmental impact / accumulation)

- Chemical weathering of sulphide minerals: release of metals into the environment !

Application cases

- Past mining activities

Introduction and motivation

Evaluation of metal contamination

Remediation of the abandoned areas

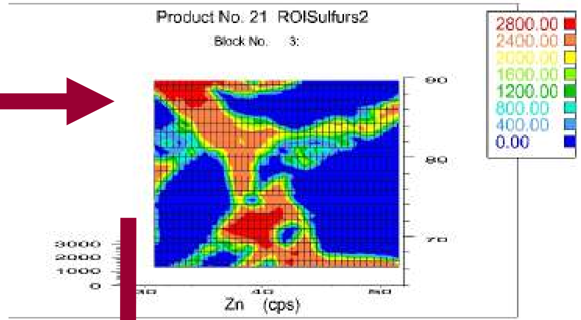
Determination and distribution of metals in soils and ores

Phytoremediation treatments

Application cases

- Past mining activities

- Distribution of regulated pollutants among different mineral phase ore veins:



Benchtop EDXRF system

Calibration: Standard free

No	ZnS 1 ...	CaCO...	Fe 1 [...	Mn 1 [...	Cu 1 [...	Cd 1 [...	Pb 1 [...	Prüfer	
287	64.2	28.3	6.40	0.682	0.100	0.392	-0.057	vr	1
288	27.1	55.1	16.0	1.75	-0.124	0.273	-0.110	vr	1
289	1.19	77.3	19.8	1.84	-0.108	0.109	-0.034	vr	1
290	2.28	70.6	24.7	2.40	-0.099	0.130	-0.069	vr	1
291	1.80	70.4	25.0	2.88	-0.090	0.080	-0.037	vr	1
292	1.97	71.9	23.2	2.87	-0.017	0.089	-0.068	vr	1
293	61.1	27.2	10.7	0.636	0.153	0.352	-0.041	vr	1
294	90.2	0.988	8.21	-0.008	0.083	0.568	-0.016	vr	1
295	91.6	0.241	7.54	0.008	0.080	0.517	-0.015	vr	1
296	90.5	0.356	8.62	0.021	0.114	0.452	-0.012	vr	1
297	91.0	0.129	8.16	0.009	0.146	0.548	0.016	vr	1
298	91.8	0.256	7.43	0.002	0.076	0.496	-0.032	vr	1

Application cases

- Past mining activities

- Evaluation of the effects of metal pollution in soils/sediments:

Core sampling of metal polluted soils (depth:30cm)

Drying (room temperature)

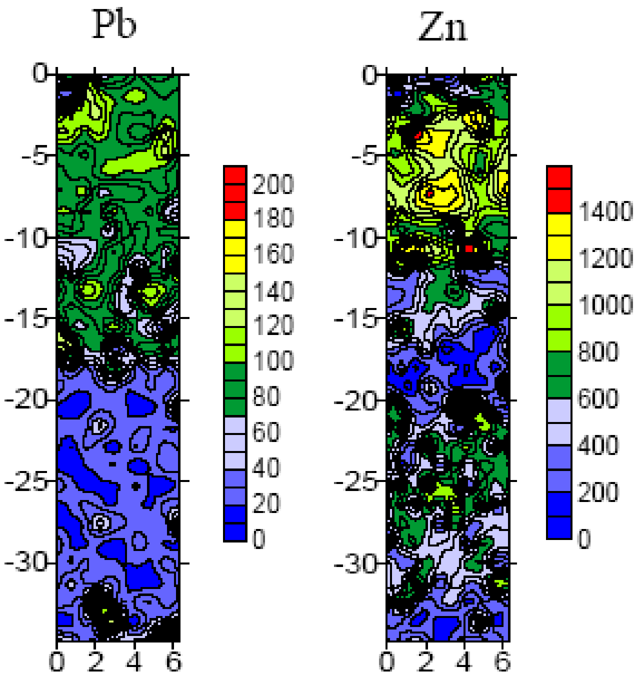
Metal distribution by EDXRF

- 50kV, 1mA, W-tube
- Measuring time: 50s
- Spot area: 600μm
- Mapping: 18x48 (864 points)

Application cases

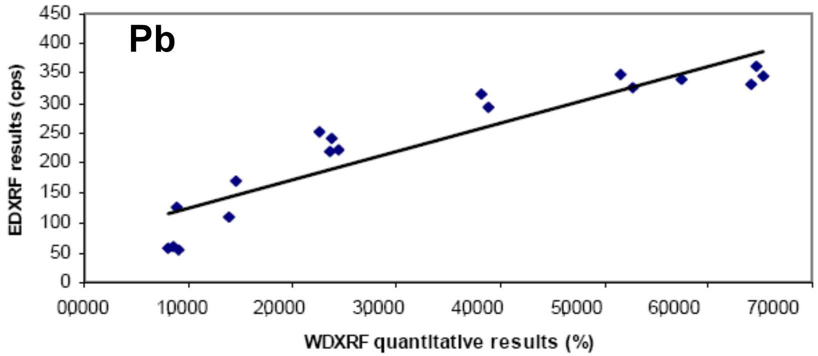
- Past mining activities

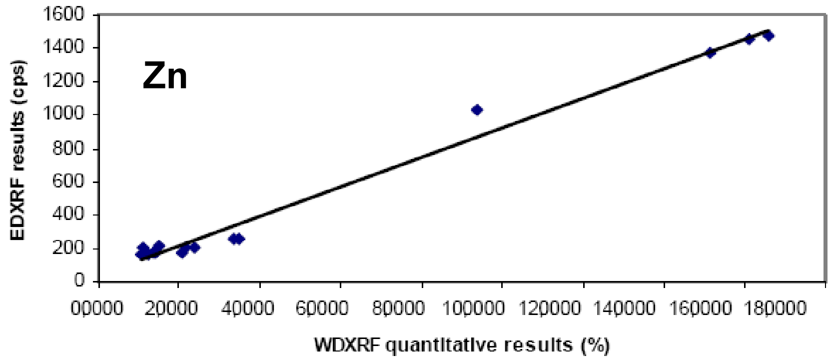
"Qualitative information"



Cores were split in slices of 2cm

"Quantitative information"



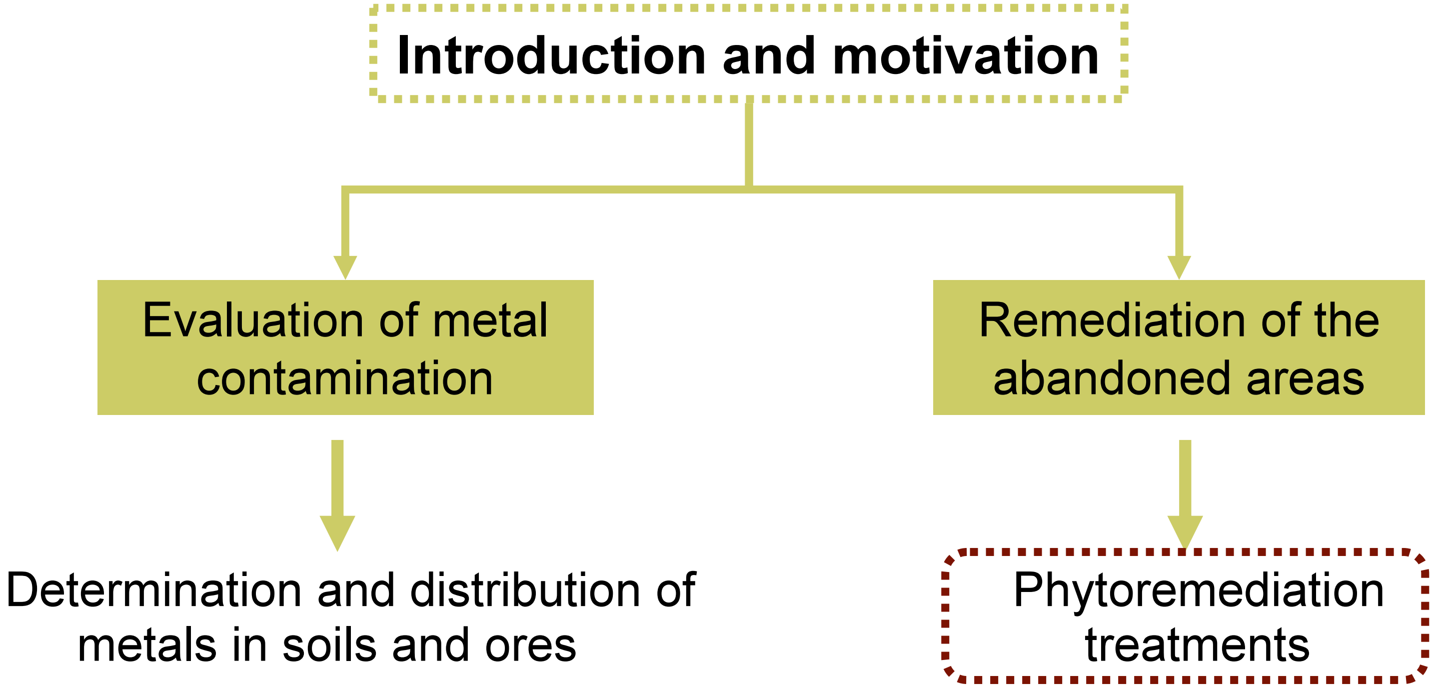


WDXRF analysis

Pellets (5g sample + 0.4g Elvacite)

Application cases

- Past mining activities

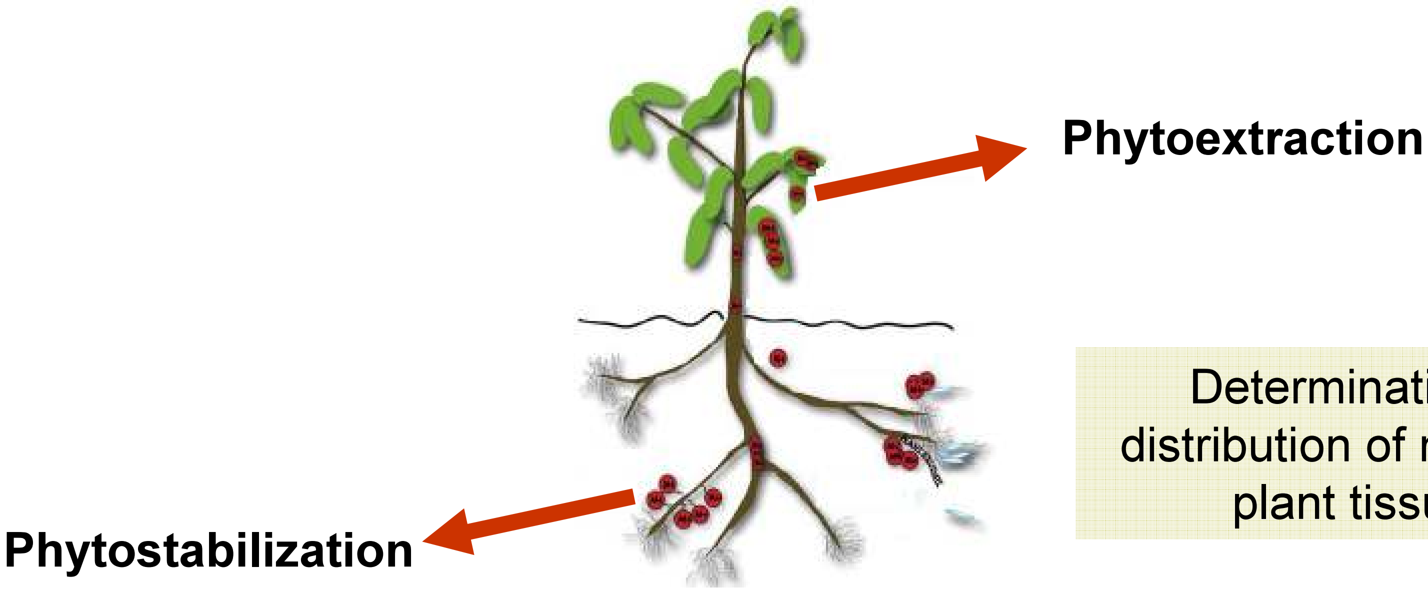


Application cases

- Past mining activities

  - <u>Phytoremediation Technology:</u>

    - The use of plants for the remediation of metal contaminated environments
    - Complementary cost-effective non-invasive technology to the engineering based remediation methods



Determination of distribution of metals in plant tissues

Application cases

- Past mining activities

Potential use of sunflower (Helianthus annuus) for phytoremediation of an abandoned Pb/Zn mining area

Experimental land plots

Zone A (mining dump)

Zone B (mining dump)

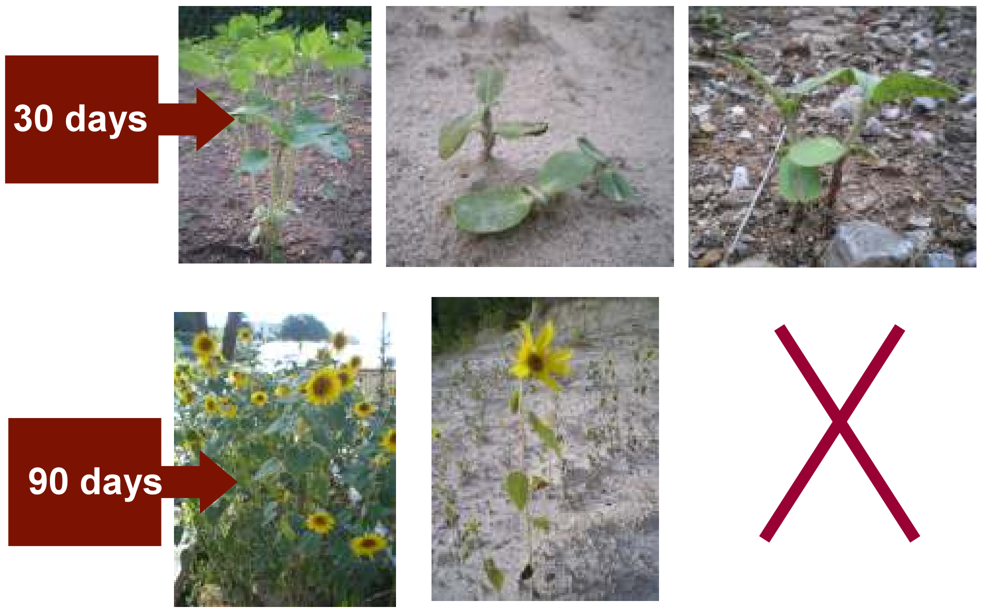
Control soil

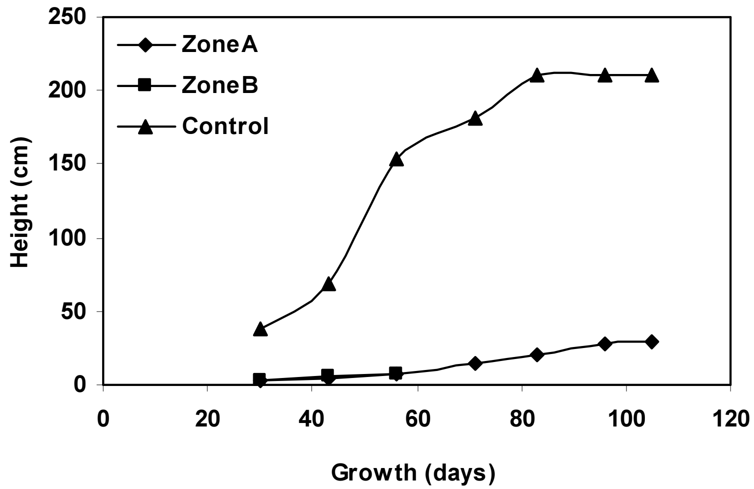
Application cases

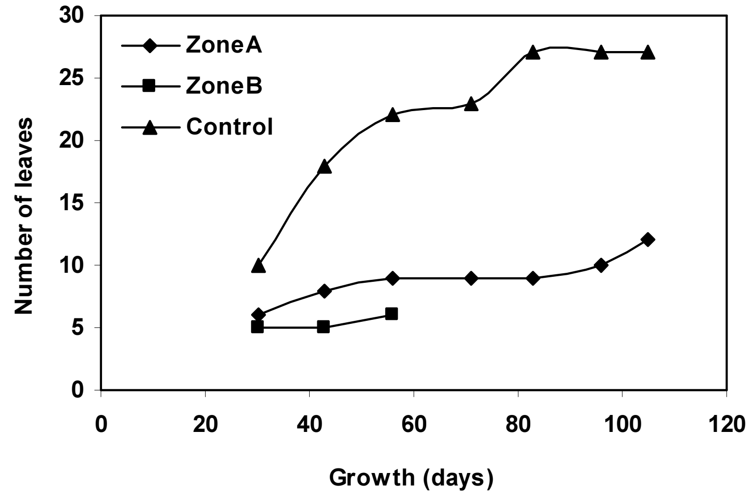
- Past mining activities

Sunflowers development

Control **Zone B** **Zone A**



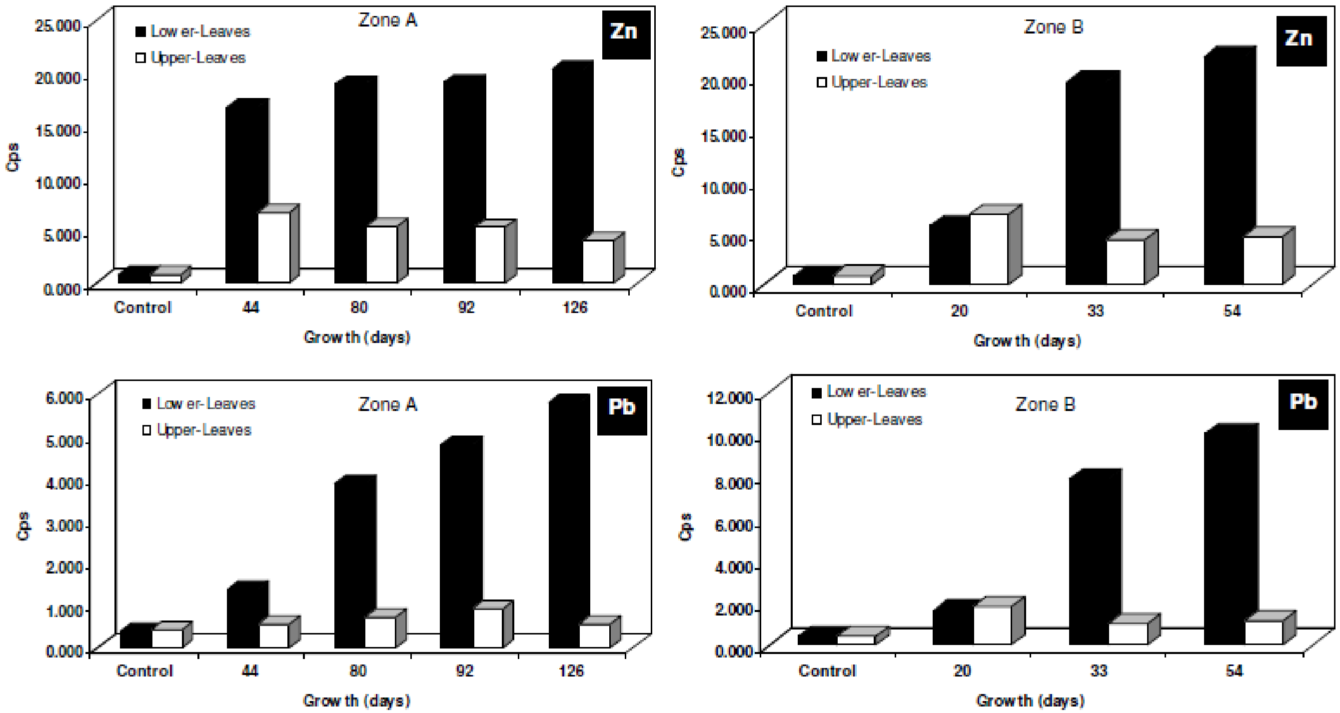


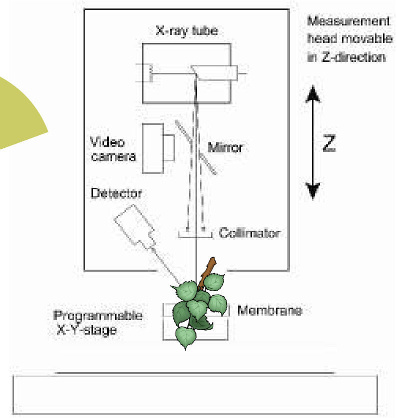


Application cases

- Past mining activities

Metal distribution over time

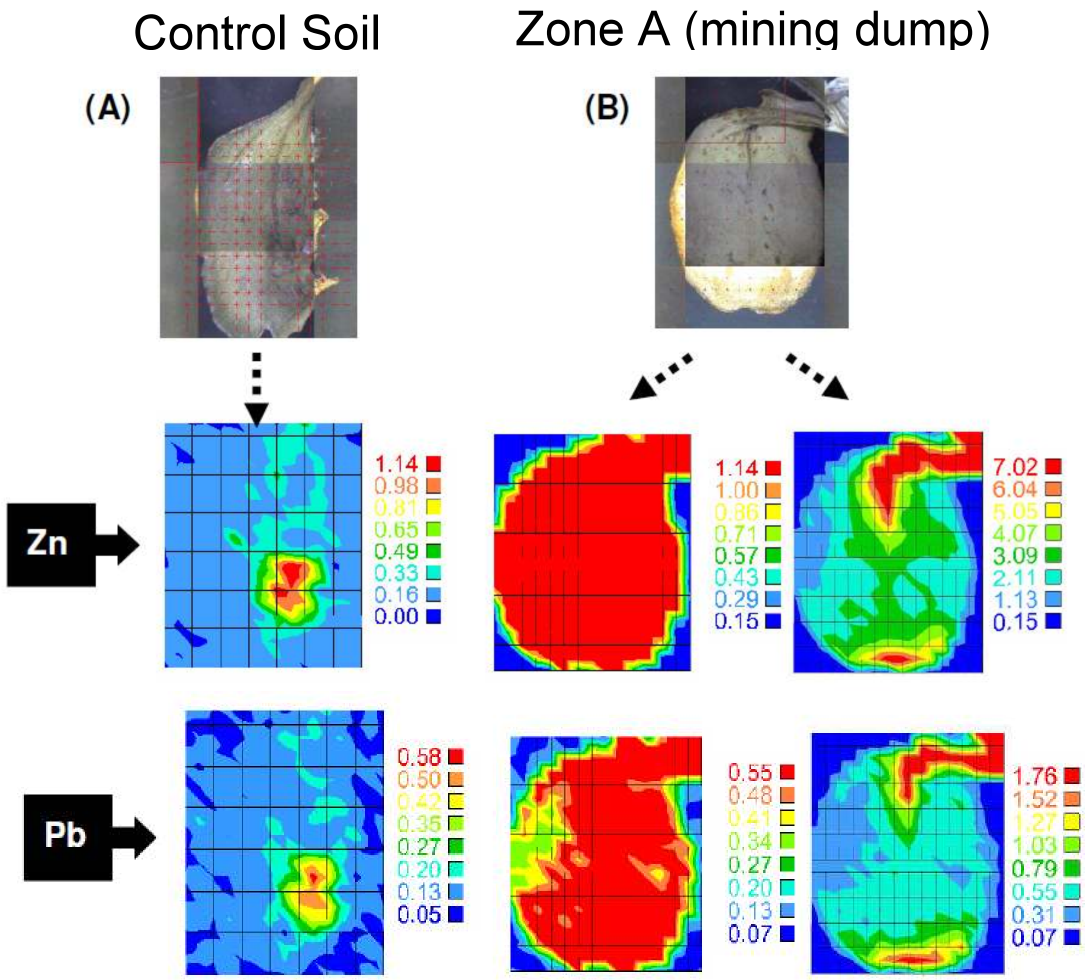




Application cases

- Past mining activities

Two-dimensional Pb and Zn mapping of sunflower leaves by EDXRF spectrometry



Instrument conditions:

- **Spot size (200μm)**
- **Measuring time (200s/spot)**
- **Gridding (15 x 20 points)**

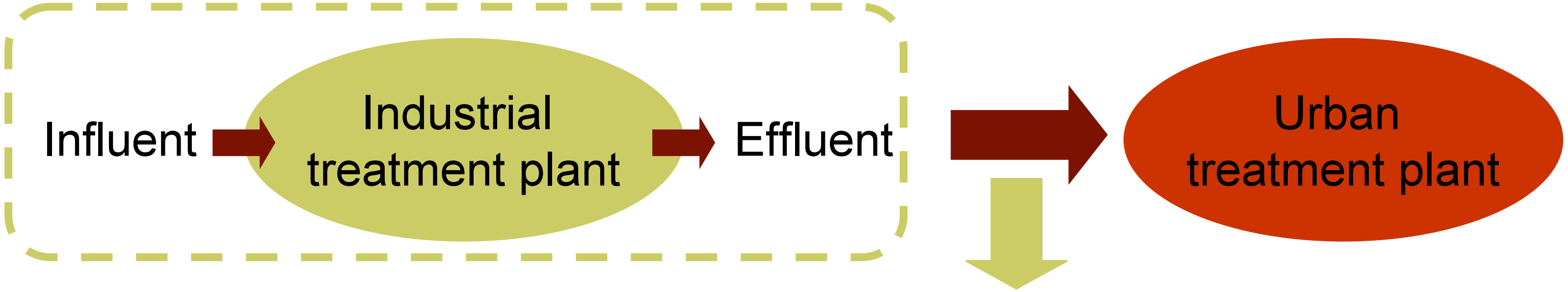
Layout

- Aims of the presentation
- Introduction
  - Metal contamination / Legislation
  - Analytical techniques
  - Quality Assurance (QA)
- Application cases
  - As anomalies in floodplains (Handheld-EDXRF system)
  - Environmental impact of past-mining activities (portable EDXRF/TXRF systems)
  - Metal content in industrial waste waters effluents (portable EDXRF/TXRF systems)

    E.Margui, J.C.Tapias, A.Casas, M.Hidalgo, I.Queralt. "*Analysis of inlet and outlet industrial waste water effluents by means of benchtop total reflection X-ray fluorescence spectrometry*". Chemosphere 80(2010)2630.
- Conclusions

Application cases

- Industrial waste water effluents



Analytical troubles

- Influents:
  - -High organic matter content
  - -Viscosity of samples
- Effluents:
  - -High "Ca" content (chemical treatment)

Element	Limit (mg/L)
Ba	10
Cd	0.5
Cu	3
Cr	3
Sn	5
Fe	5
Mn	2
Ni	5
Pb	1
Se	0.5
Zn	10

Limits for waste water spill (Garrotxa, Spain, 2006)

Application cases

- Industrial waste water effluents

Determination of metals in waste waters

Conventional XRF (EDXRF)

Analysis of liquid samples after preconcentration (thin films)

Total reflection X-ray spectrometry (TXRF)

"Direct" analysis of the liquid samples

Field portable XRF systems

Application cases

- Industrial waste water effluents

Analysis of liquid samples after preconcentration

PRECONCENTRATION
Thin layer organic material

Commercial solid phase chelating disks (3M ™ Empore)

- Sorbent: polystyrene divinylbenzene
- Functional group: sodium salt of iminodiacetic acid

+

Benchtop EDXRF system

Characteristics:
- X-ray tube (W): 50kV, 1mA
- Collimator (Focal spot): 0.1-3mm
- Silicon Drift Detector (>190eV Mn)
- No vacuum

Application cases

- Industrial waste water effluents

Experimental Procedure

Chelating disk + **Aqueous sample** Metals

Sample volume=1L

Chelating disk Metals

Aqueous sample

EDXRF

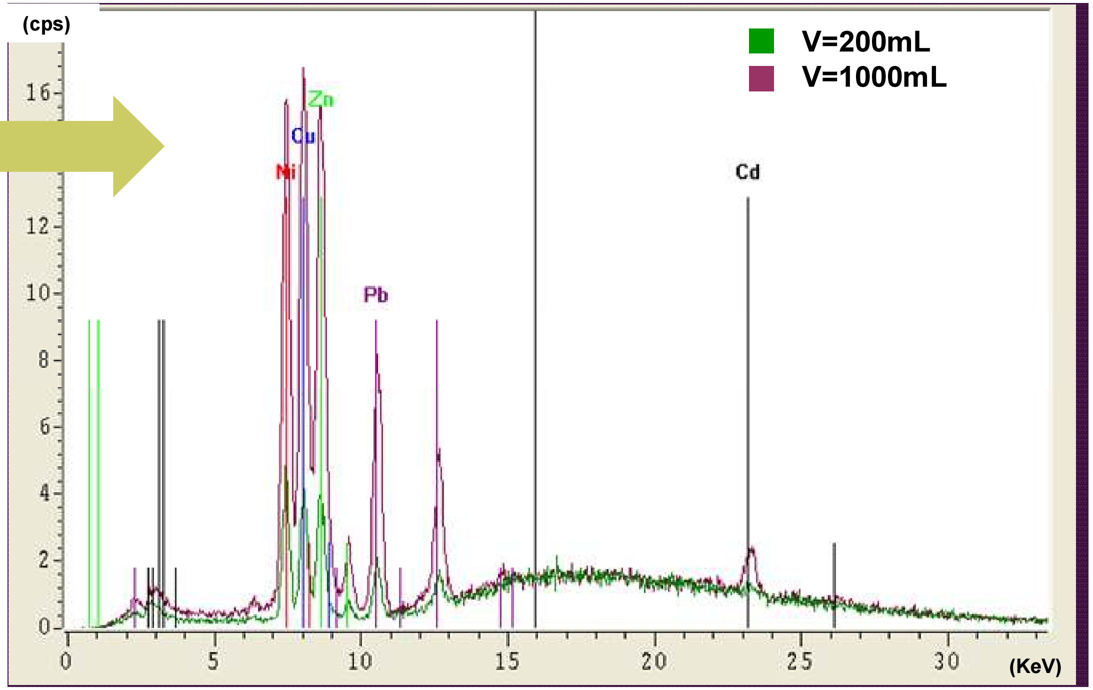
Application cases

- Industrial waste water effluents

Analysis of liquid samples after preconcentration

Instrumental parameters	
Anode X-Ray tube	W
Voltage	50 kV
Current	1 mA
Filter	Ti300
Collimator	3 mm
Acquisition time	100 s
Measures	5

Determination of:
Ni, Cu, Zn, Pb and Cd

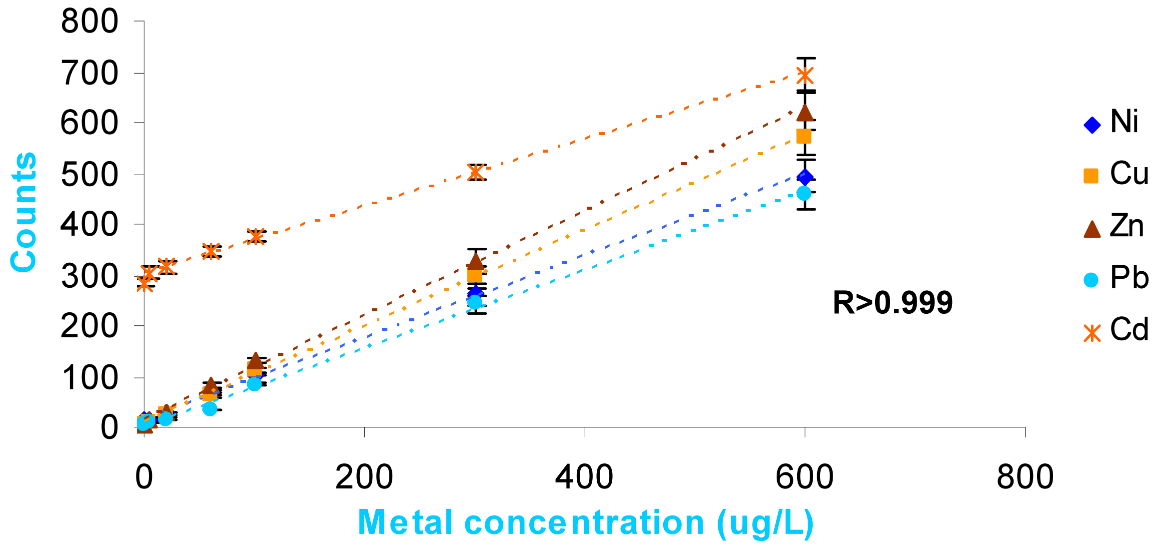


EDXRF spectra (standard solution at 600 $\mu g/L$ level)

Application cases

- Industrial waste water effluents

Calibration (5-600μg/L)



Detection Limits

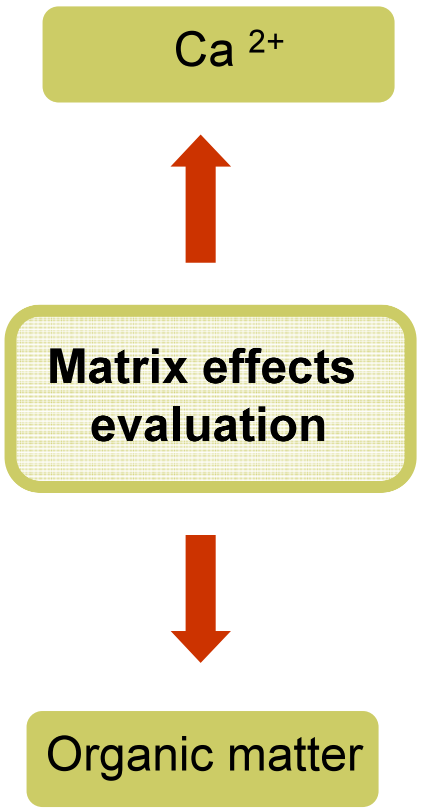
Metal	LOD (μg/L)
Ni	1.2
Cu	2.4
Zn	1.7
Pb	1.4
Cd	16

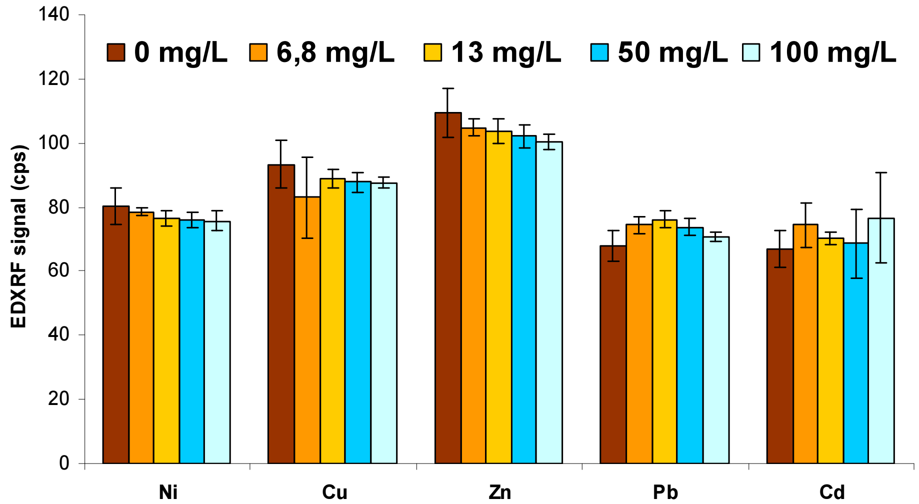
Accuracy

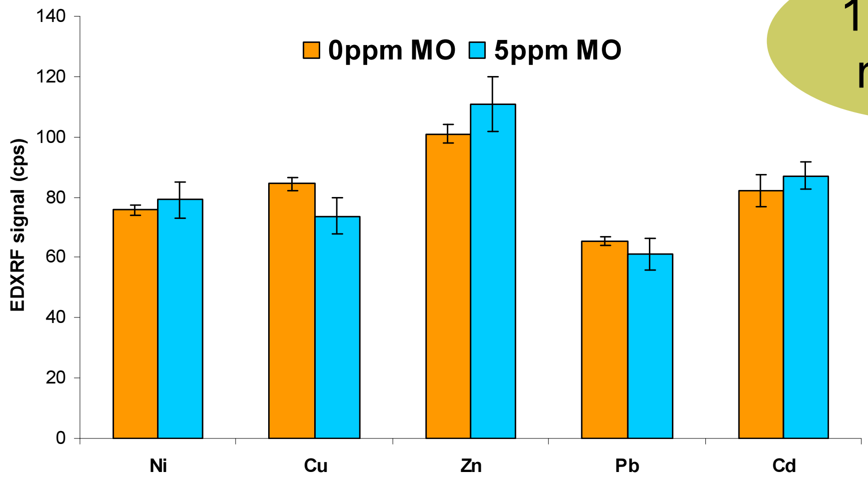
Fortified tap water (100 μg/L)	Ni	Cu	Zn	Pb	Cd
Recovery (%)	101.0	100.5	98.8	99.4	90.8

Application cases

- Industrial waste water effluents







100µg/L metals

Application cases

- Industrial waste water effluents

Comparability: Benchtop EDXRF / ICP-MS

μg/L	EDXRF method		ICP-MS	
	Mean	Std.Dev	Mean	Std.Dev
Ni	351	9	351	7
Cu	114	3	130	3
Zn	350	5	400	8
Pb	n.d	*	n.d	*
Cd	n.d	*	n.d	*

Application to real samples

↓

Waste water

Application cases

- Industrial waste water effluents

Comparability: Benchtop EDXRF / HE-P-EDXRF

X-ray tube (Gd)
Acquisition time:100s
Measures:3

Element	Conditions	Secondary target	Analytical line
Ni, Cu, Zn	65kV-6mA	Ge	K_α
Pb	100kV-6mA	Zr	L_α
Cd	100kV-6mA	CsI	K_α
Cd	100kV-6mA	Al_2O_3	K_α

LOD (μg/L)	Benchtop EDXRF	HE-P-EDXRF
Ni	1.2	0.1
Cu	2.4	0.1
Zn	1.7	0.1
Pb	1.4	0.2
Cd	16	0.3 (CsI target) 0.6 (Al_2O_3 target)

Application cases

- Industrial waste water effluents

Determination of metals in waste waters

Conventional XRF (EDXRF)

Analysis of liquid samples after preconcentration (thin films)

Total reflection X-ray spectrometry (TXRF)

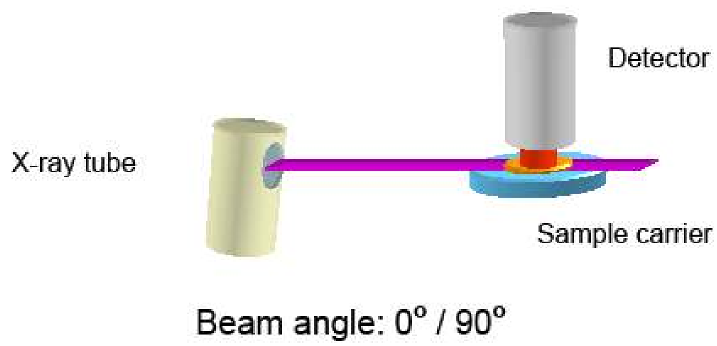
"Direct" analysis of the liquid samples

Field portable XRF systems

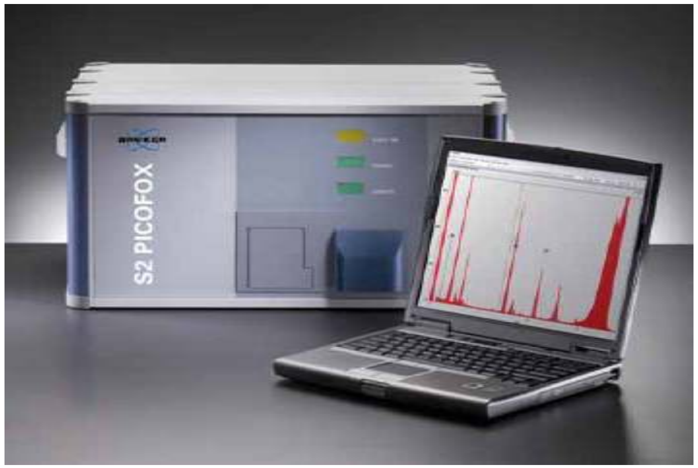
Application cases

- Industrial waste water effluents

Total reflection X-ray fluorescence spectroscopy (TXRF)



- **Analysis of liquid samples (μL)**
- Matrix effects are negligible
- Quantification:
  - Internal standardization (external calibration is not needed!!!)



Benchtop TXRF

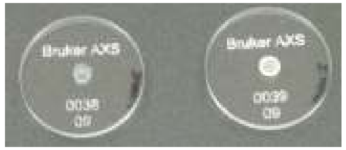
- Metal ceramic X-ray tube (W). 50kV, 1mA (heavy elements determination: Cd)
- Multilayer monochromator
- X-Flash Silicon Drift Detector (>149eV Mn)

Application cases

- Industrial waste water effluents

Sample preparation

Add internal standard



Pipette on a carrier (5-100µL) and dry

Pipette sample in a tube (1-5mL)

TXRF analysis

(Measuring time:500s)

Application cases

- Industrial waste water effluents

Limits of Detection

Element	Limit Value (mg/L)	Limits of detection (TXRF)	
		Raw sample	MW digestion
Cr	3	0.24	0.24
Mn	2	0.17	0.12
Fe	5	0.09	0.07
Ni	5	0.11	0.07
Cu	3	0.10	0.06
Zn	10	0.08	0.05
As	1	0.03	0.02
Se	0.5	0.02	0.09
Cd	0.5	0.009	0.003
Sn	5	0.04	0.03
Ba	10	0.49	0.48
Pb	1	0.01	0.01

Limit values: according to the regulation from the Catalonia Water Agency (Spain)

Application cases

- Industrial waste water effluents

Accuracy and Precision

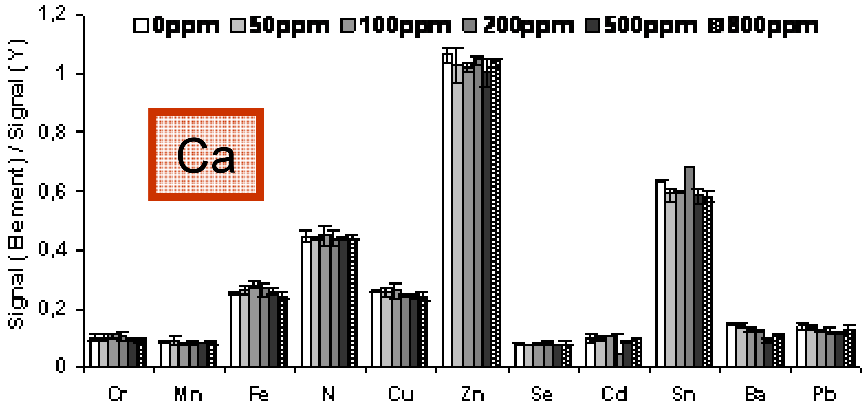
Element	Certified		Raw sample		MW digestion	
	Value	SD	Mean	SD	Mean	SD
Cr	1	0.005	1.244	0.245	0.993	0.035
Mn	2	0.01	2.014	0.001	2.199	0.602
Fe	5	0.025	4.858	0.041	4.339	0.101
Cu	0.3	0.002	0.385	0.031	0.399	0.072
Ni	5	0.025	4.928	0.192	4.522	0.341
Cu	2	0.01	1.997	0.146	1.918	0.063
Zn	3	0.015	3.062	0.060	2.831	0.146
As	0.5	0.003	0.442	0.076	0.409	0.087
Se	0.5	*	0.440	0.025	0.075	0.005
Cd	0.1	0.0005	0.276	0.039	0.321	0.022
Sn	5	*	4.496	0.228	4.657	0.008
Ba	10	*	11.249	0.748	11.778	0.001
Pb	0.5	0.003	0.830	0.066	0.746	0.001

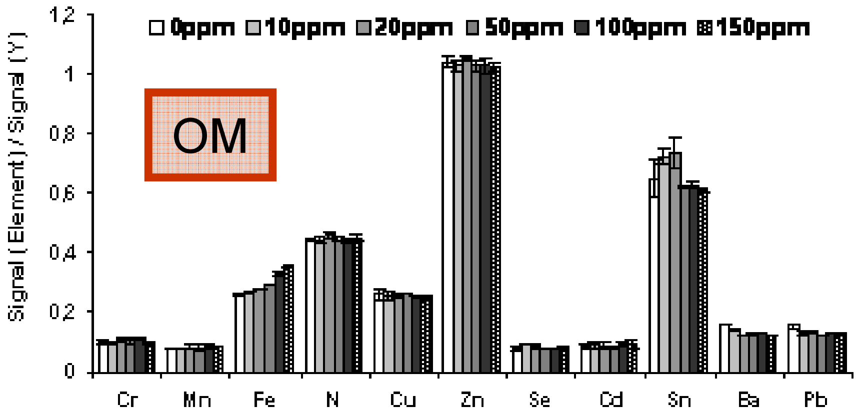
Element concentrations (mg/L) for the direct TXRF analysis of the reference material SPS-WW2" (elements in wastewaters) and after a microwave digestion (sample volume: 20μL, 1000s, n=3)

Application cases

- Industrial waste water effluents

Evaluation of matrix effects





Analytical troubles

- Influents:
  - -High organic matter content
  - -Viscosity of samples
- Effluents:
  - -High "Ca" content (chemical treatment)

Application cases

- Industrial waste water effluents

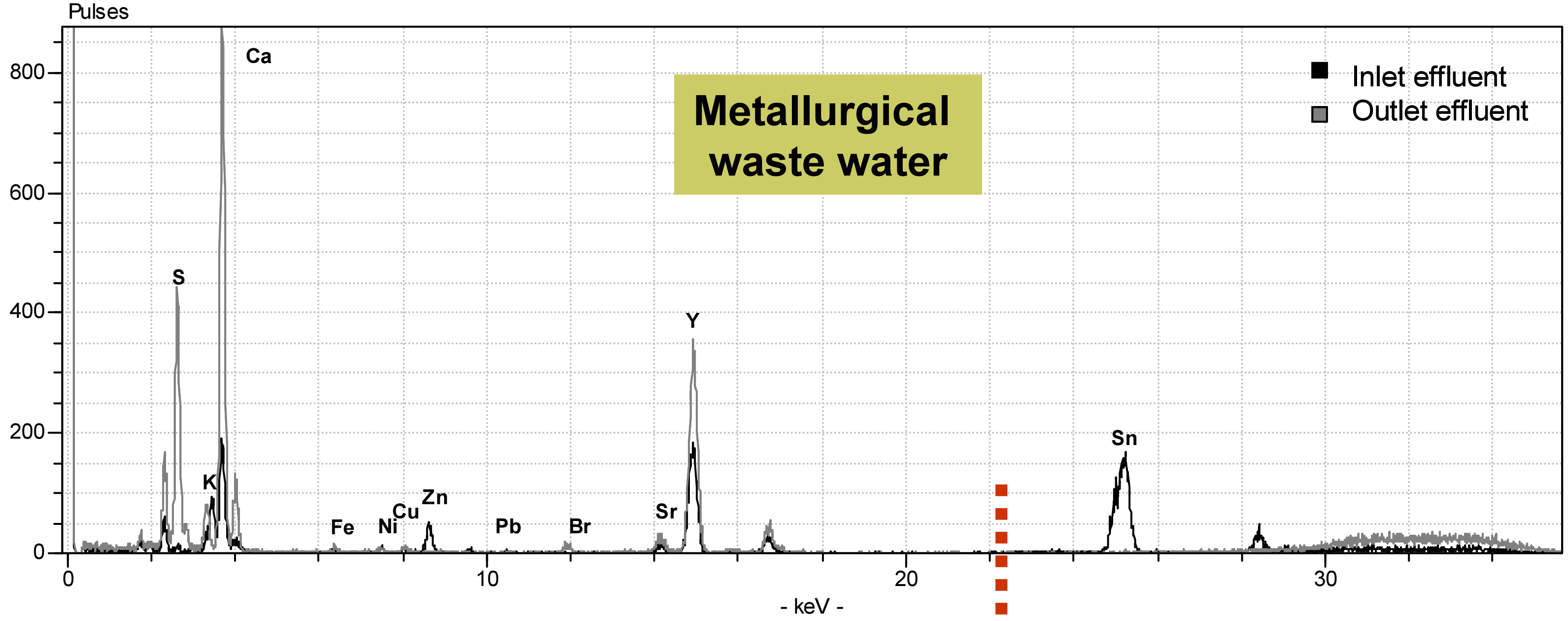
Application to real samples

	Inlet effluent			Outlet effluent		
	TXRF		ICP-MS/ICP-OES	TXRF		ICP-MS/ICP-OES
	Direct analysis	MW digestion	MW digestion	Direct analysis	MW digestion	MW digestion
	Mean/SD	Mean/SD	Mean/SD	Mean/SD	Mean/SD	Mean/SD
Metallurgical waste water						
Cr	12.5 / 0.3	14.2 / 0.6	12.6 / 1.0	n.d	n.d	n.m
Fe	88.9 / 0.9	87.0 / 1.0	99.0 / 2.0	n.d	n.d	n.m
Ni	93.8 / 0.8	88.8 / 0.9	82.0 / 3.0	0.22 / 0.02	0.19 / 0.02	0.17 / 0.04
Cu	27.1 / 0.3	27.8 / 0.5	27.9 / 0.8	n.d	n.d	n.m
Zn	453.3 / 3.1	409.0 / 2.0	389.0 / 2.0	0.62 / 0.03	0.67 / 0.04	0.59 / 0.02
Pb	0.93 / 0.03	1.36 / 0.09	n.m	n.d	n.d	n.m
Tanning waste water						
Cr	5.1 / 0.3	3.6 / 0.3	4.00 / 0.05	n.d	0.23 / 0.06	0.156 / 0.002
Fe	0.77 / 0.02	1.2 / 0.3	1.50 / 0.02	3.0 / 0.1	3.07 / 0.09	3.65 / 0.01
Ni	0.11 / 0.01	0.12 / 0.04	0.093 / 0.001	n.d	n.d	n.m
Cu	0.25 / 0.03	0.29 / 0.06	0.279 / 0.001	0.37 / 0.08	0.28 / 0.05	0.261 / 0.006
Zn	0.21 / 0.01	0.22 / 0.01	0.19 / 0.02	n.d	n.d	n.m
Pb	0.93 / 0.01	0.93 / 0.06	0.768 / 0.005	n.d	n.d	n.m

Application cases

- Industrial waste water effluents

Application to real samples

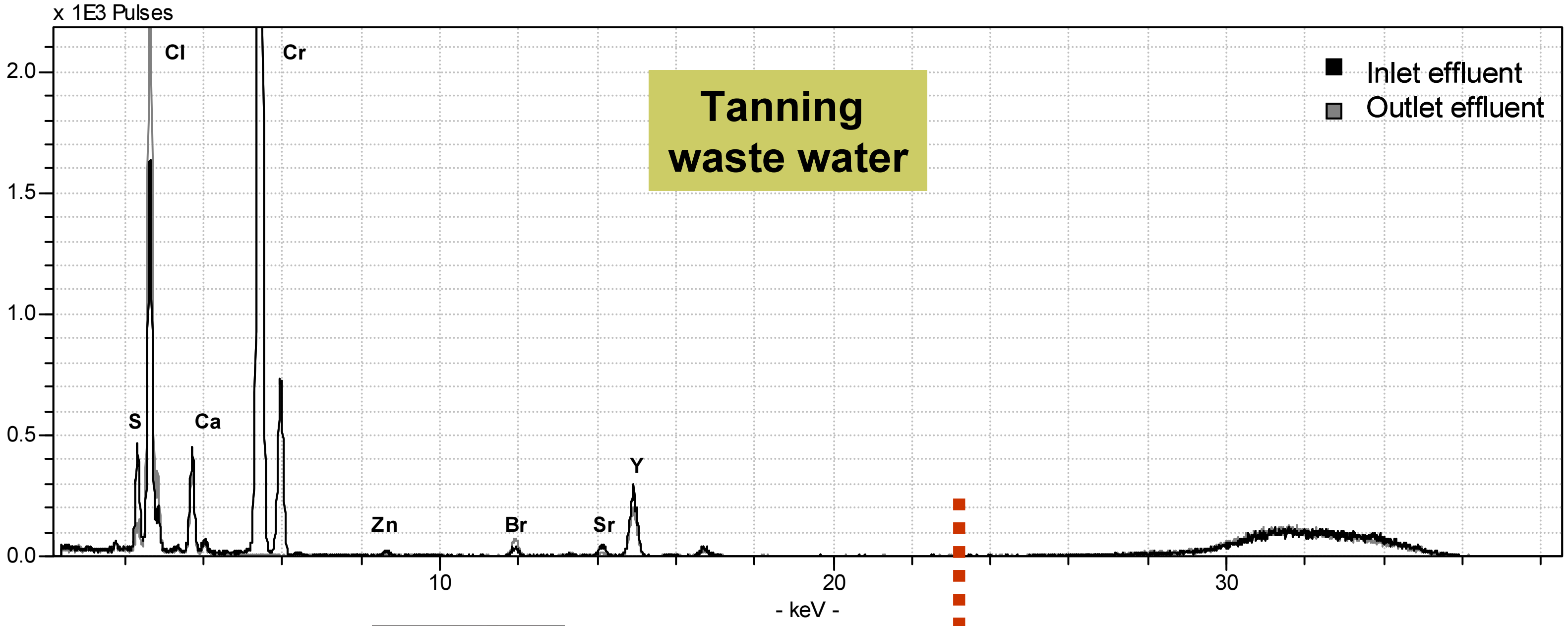


- **High Ca content**
- **Appreciable amounts of: Fe, Cu, Zn, Sn, Ni, Pb**

Application cases

- Industrial waste water effluents

Application to real samples



- **High density and organic matter**
- **Appreciable amounts of: Cr**

Application cases

- Industrial waste water effluents

Conclusions

- Routine and screening analysis of industrial inlet and outlet effluents: direct TXRF analysis depositing 20μL of the internal standardized sample on a quartz reflector
- Adequate detection limits according to current legislation
- TXRF can be performed directly on the raw waste water sample
- Multielemental information
- Easy quantification (internal standardization)
- Low operating costs (simple sample treatment, no gas consumption)

Layout

- Aims of the presentation
- Introduction
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- Application cases
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  - Metal content in industrial waste waters effluents (portable EDXRF/TXRF systems)
- **Conclusions**

Conclusions…

Field portable X-ray fluorescence spectrometry systems (FPXRF)

Advantages ☺	Limitations ☹
• Screening tool to design a targeted sampling strategy • Multielemental characterization • Minimal sample preparation • On-site decision (remediation stages) • Allows prioritization of sample analysis • Relatively low investment and operational costs • Solid, liquid samples	• Need for laboratory analysis check • Detection limits require careful consideration • More reliable for some metals than others • Heterogeneity of sample may affect the results

Acknowledgments

- Laboratory of X-ray Analytical Applications (ICTJA-CSIC), Barcelona, Spain
- Department of Chemistry. University of Girona, Spain.
- Micro and Trace Analysis Centre. University of Antwerp (Belgium)
- Département Analyse Surveillance Environment (CEA), Bruyères-le-Chatel, France.
- Laboratoire de Géophysique Interne et Tectonophysique (LGIT-OSUG). University of Grenoble I, Grenoble, France.

and to you all, for your kind attention…