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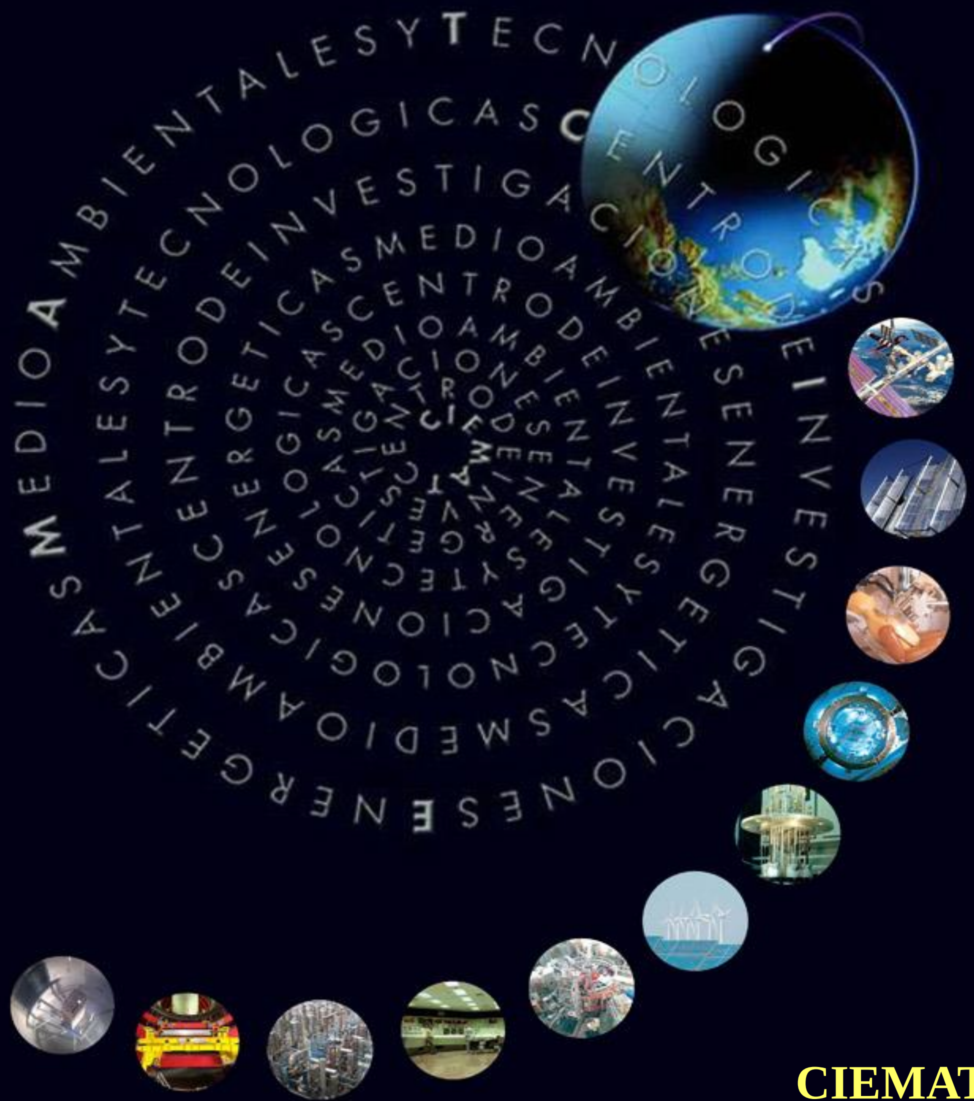

Environmental studies for mercury monitoring

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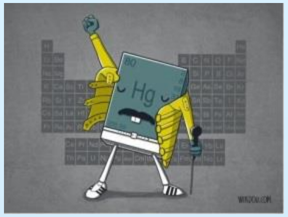
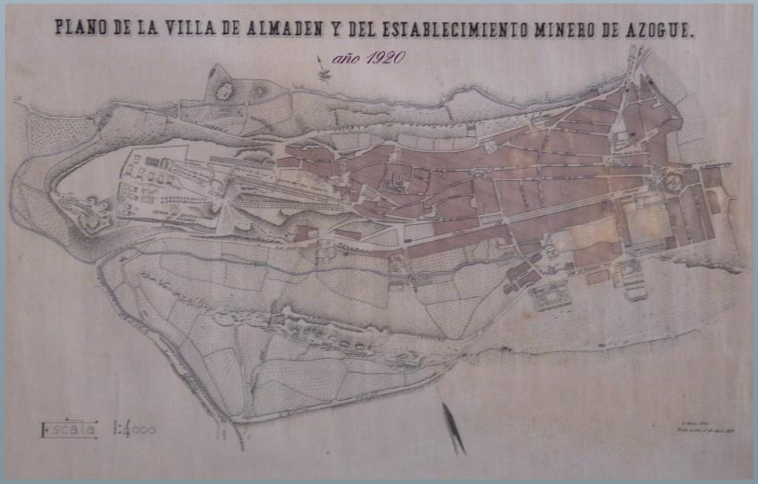
2016

Almadén

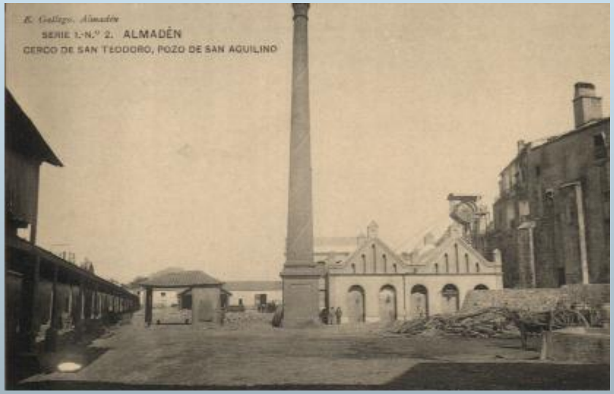


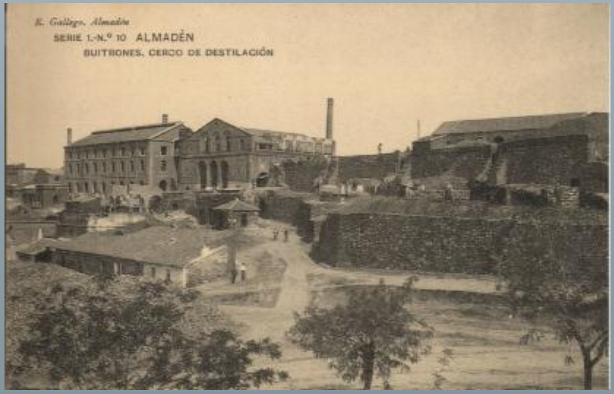
Almadén is located 300 km (SW) from Madrid, in the Province of Ciudad Real.

The mercury ores in this area are the main Hg concentration in the World. It was the oldest and biggest Mercury mine.



Almadén…a life around the Hg mine





Almadén, Idrija and Monte Amiata produced 99% of the primary mercury mined in Europe.

The Almadén mercury mine has been exploited over the past two millenniums. Well know during the Roman times.

Almadén provided nearly a third of the total known mercury produced in the world.

But… at present

Working staff reduced from >1200 to < 100

Population decreased:

1950: 12375

2000: 7152

2006: 6406

2014: 5861

The unemployment rate increased

OBJECTIVES

Study the soil parameters (physical, chemical and biological) that influence the Hg behaviour in soil; rhizosphere; soil-plant system (natural vegetation and crops); water and sediments.

Development of environmental restoration proposals including socio-economical alternatives (land uses) and environmental monitoring for the Almadén area in collaboration with MAYASA and MAGRAMA.

R&D and knowledge transfer and implementation mainly in Central and South America (Bolivia, Mexico, Brasil, Cuba…) and also, Indonesia.

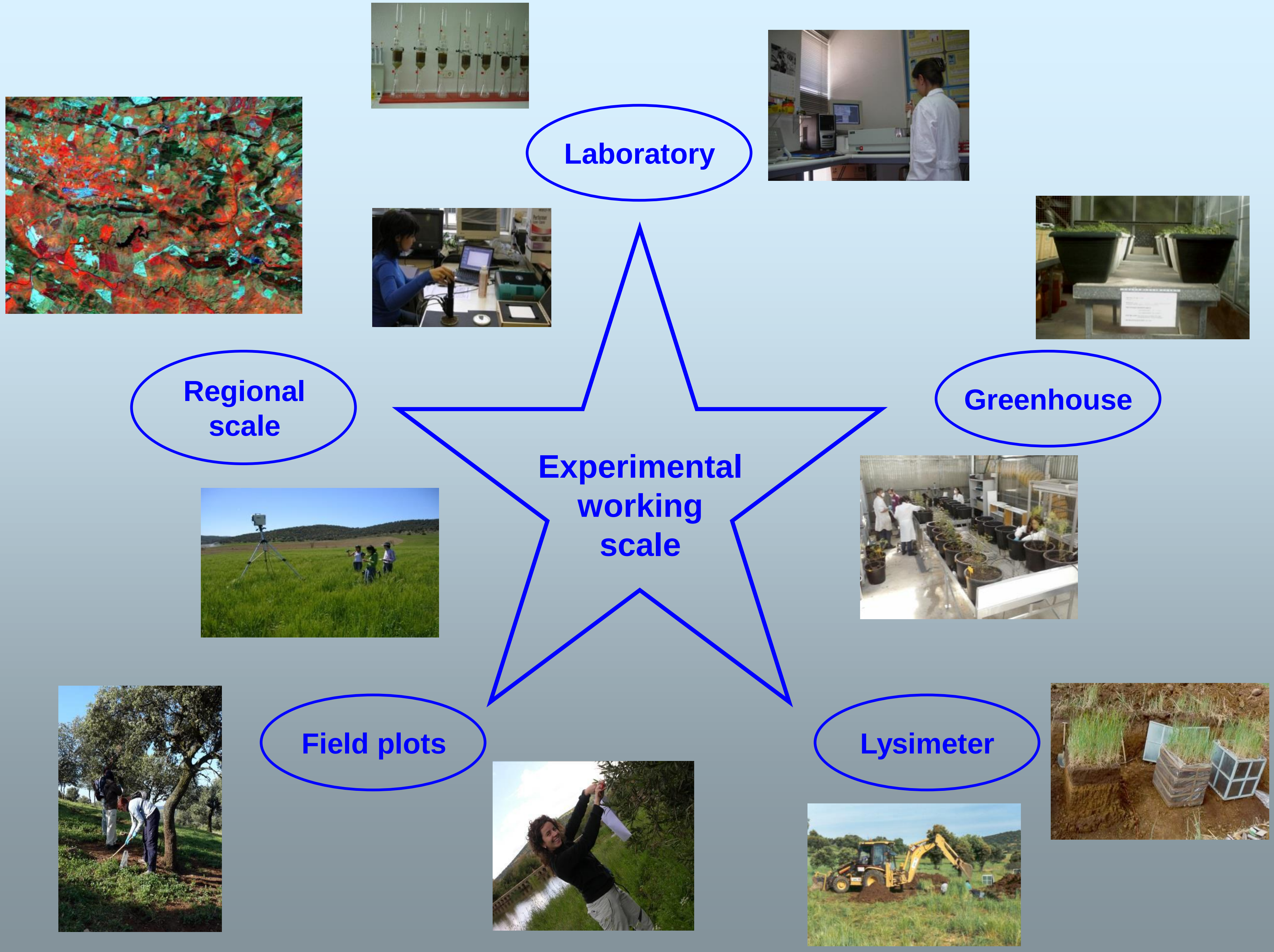
To collaborate with institutions, research groups and companies for environmental restoration and monitoring and sites decontamination.

To collaborate in areas where there are ASGM.

Environmental restoration

- Identification of mine structures and problems
- Selection of the most adequate techniques (barriers, bioremediation, phytecnologies, soil amendments, etc).
- Feasibility study and effectiveness of selected technique.
- Monitoring and control of conditions.
- Recommended strategies.

“El Entredicho” open pit

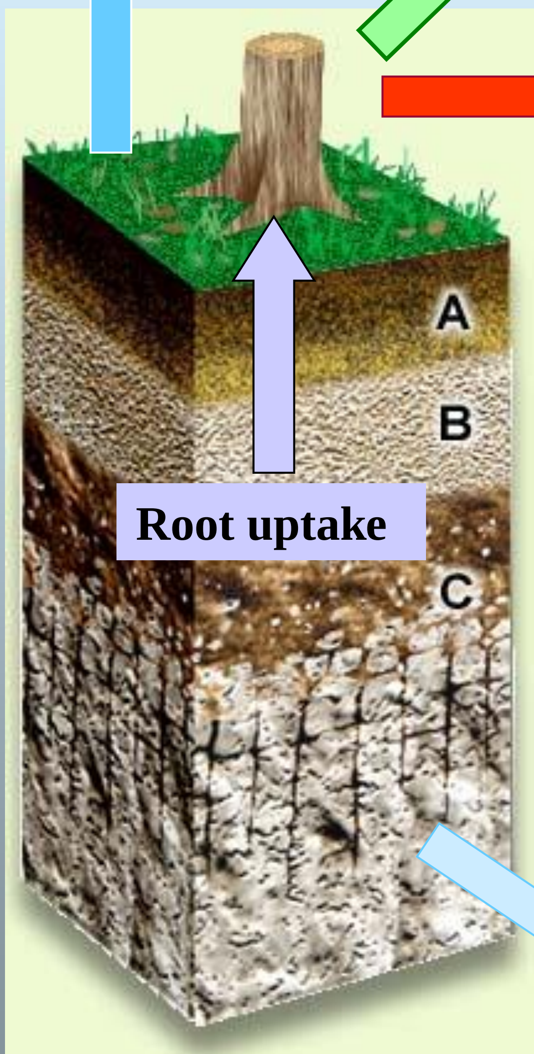

Laboratory
Regional scale
Greenhouse
Experimental working scale
Field plots
Lysimeter

SOIL: Organic matter content, pH, CEC, texture and soil depth, are the main influence parameters related with mercury behaviour. Relevant differences are observed depending of the soil type and the parent material (lithology).

Volatilization

Food chain

Erosion /Run-off



Precipitation

Complexation (organic ligands, anions…)

Soluble / available in soil solution

Adsorption in a non-reversible form

Exchangeable / reversible adsorption (OM, Clay)

Mineral forms

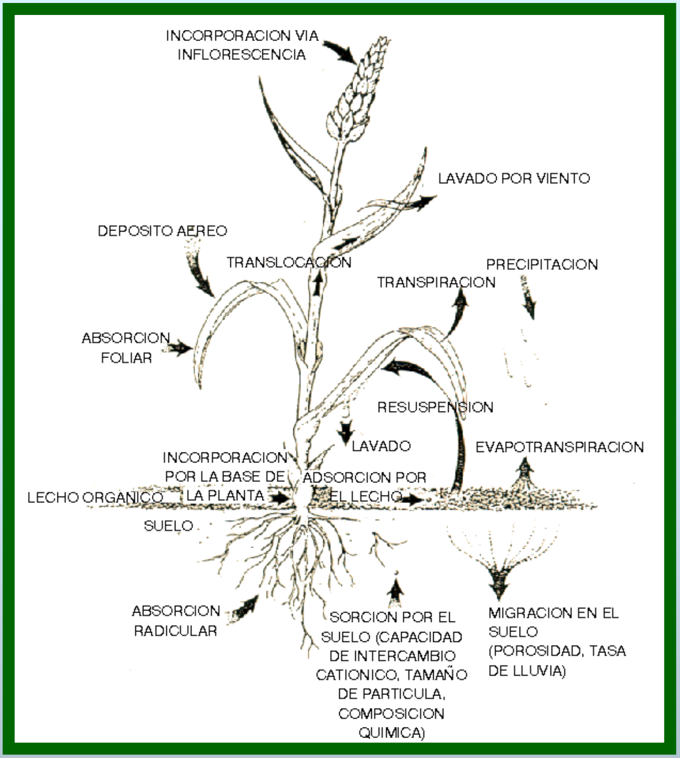
Lixiviation / migration to ground water table

VEGETATION

Incorporation (root / leaves)

Translocation and distribution in plant

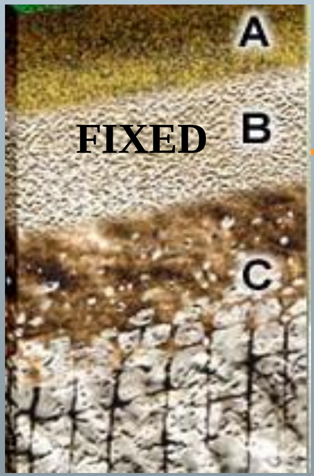
Crops: Hg content in the edible part



SOIL

VEGETATION

Solid phase



FIXED

Aqueous phase

SOLUBLE

EXCHANGEABLE

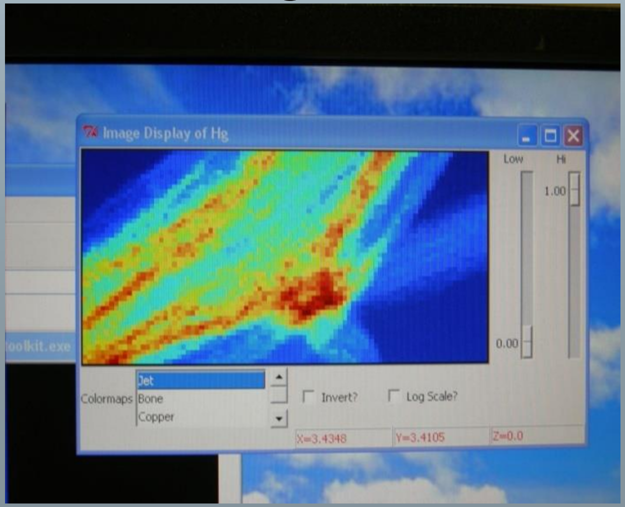
Adsorption in a reversible form

Available

Non-available form (Adsorbed in non-reversible form)

RHIZOSPHERE

SSRL. Stanford Synchrotron Radiation Light source Lab

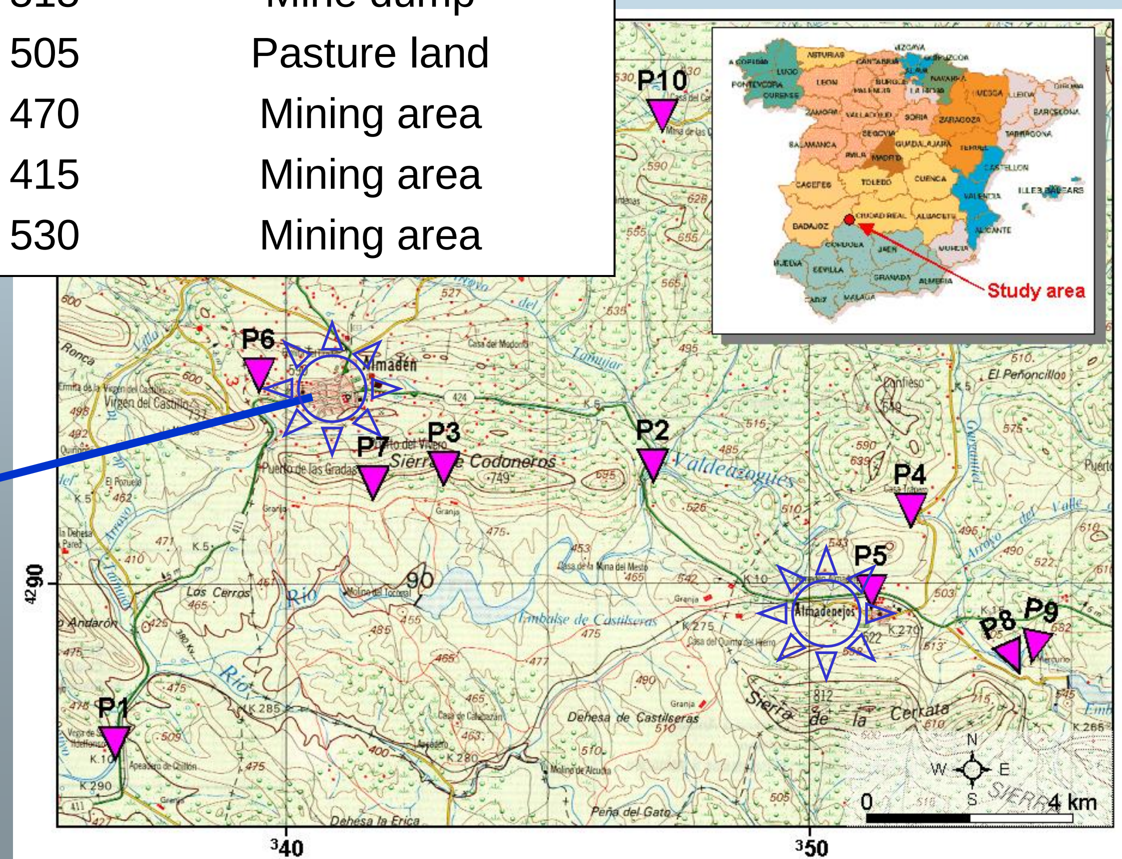


- ✓ Slope correction
- ✓ Drainage systems and pond (leacheates storage and treatment)
- ✓ Soil amendments for mine tailing recovery
- ✓ Plant species selection for phytostabilization and landscape integration
- ✓ Monitoring points

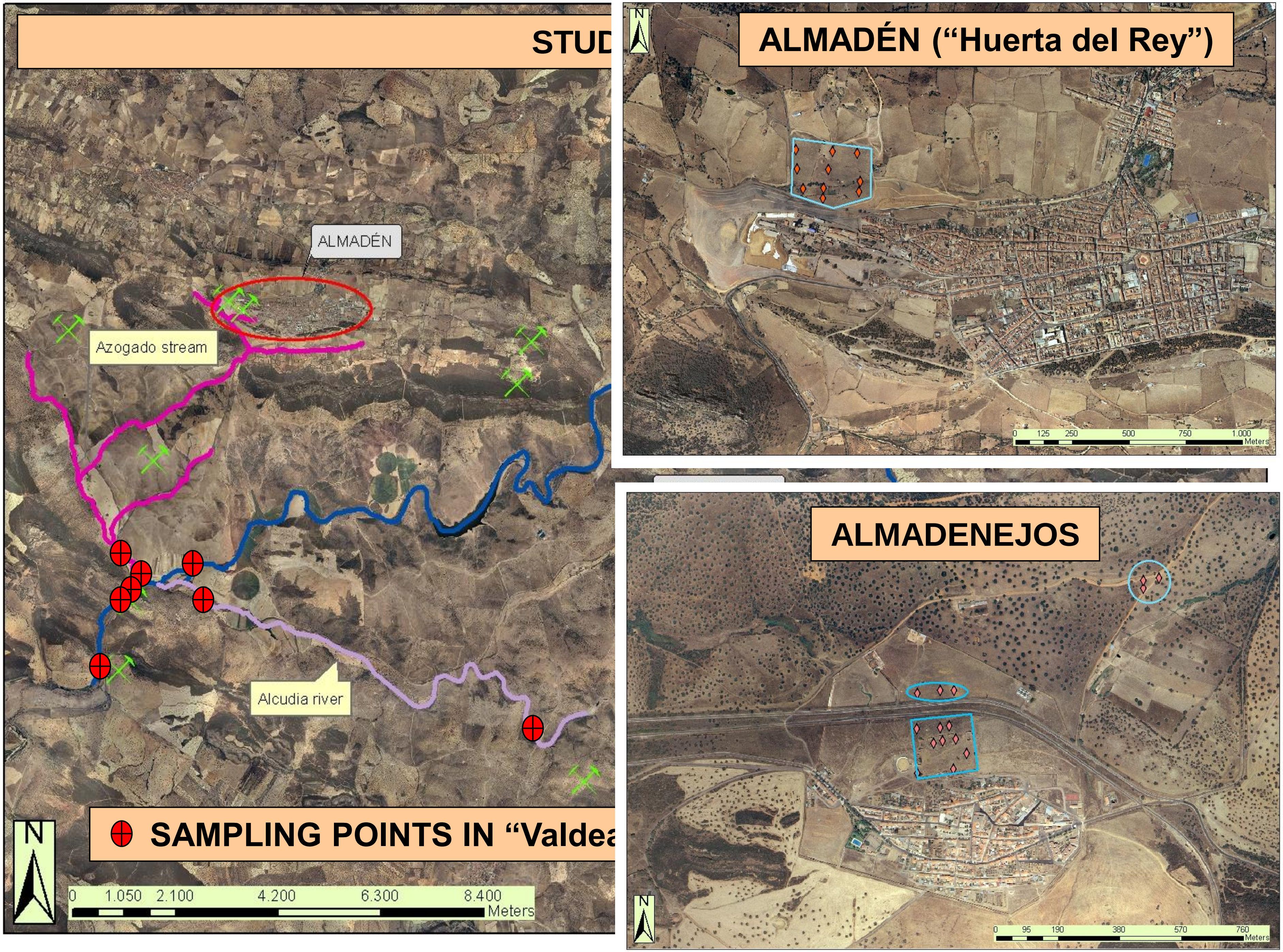
- Reduction > 90% Hg in air and particles
- Landscape integration
- Visual impact reduction
- Social acceptation

Experimental field plots

Plot	Location	Altitude (m a.s.l.)	Land use
P1	Valdeazogues river	368	River banks not used
P2	Source of Jardinillo	435	Not used open Mediterranean forest
P3	Sierra de Cordoneros	520	Pasture land with shrubs
P4	NE of Almadenejos	435	Crop cultivation
P5	Almadenejos smeltering site	508	Pig farming
P6	Almadén mercury mine	515	Mine dump
P7	Sierra de Cordoneros	505	Pasture land
P8	El Entredicho mine	470	Mining area
P9	El Entredicho mine	415	Mining area
P10	Las Cuevas mine	530	Mining area




ALMADÉN
Mercury mine tailing
Almadén
Av de la Libertad
N-502
CR-424
Av de Esp
N-502
N-502
Mediterranean Oak Forest
"Dehesa"


STUD
ALMADÉN
Azogado stream
Alcudia river
SAMPLING POINTS IN “Valdea
N
0 1.050 2.100 4.200 6.300 8.400
Meters
ALMADÉN (“Huerta del Rey”)
N
0 125 250 500 750 1.000
Meters
ALMADENEJOS
N
0 95 190 380 570 760
Meters

METHODOLOGICAL PROCEDURE FOR SOIL SAMPLES

Soil sampling

Soil profiles to a depth of > 100 cm
Samples obtained with a metal cylinder (depth < 25 cm)
Samples obtained with a hoe (depth < 15 cm)

↓

Storage & transport

Samples stored in plastic bags, labelled and transported to laboratory (part of them at 4ºC)

↓

Pre-analyses treatment

Samples are air-dried and sieved to separate fine earth fraction (<2 mm)

↓

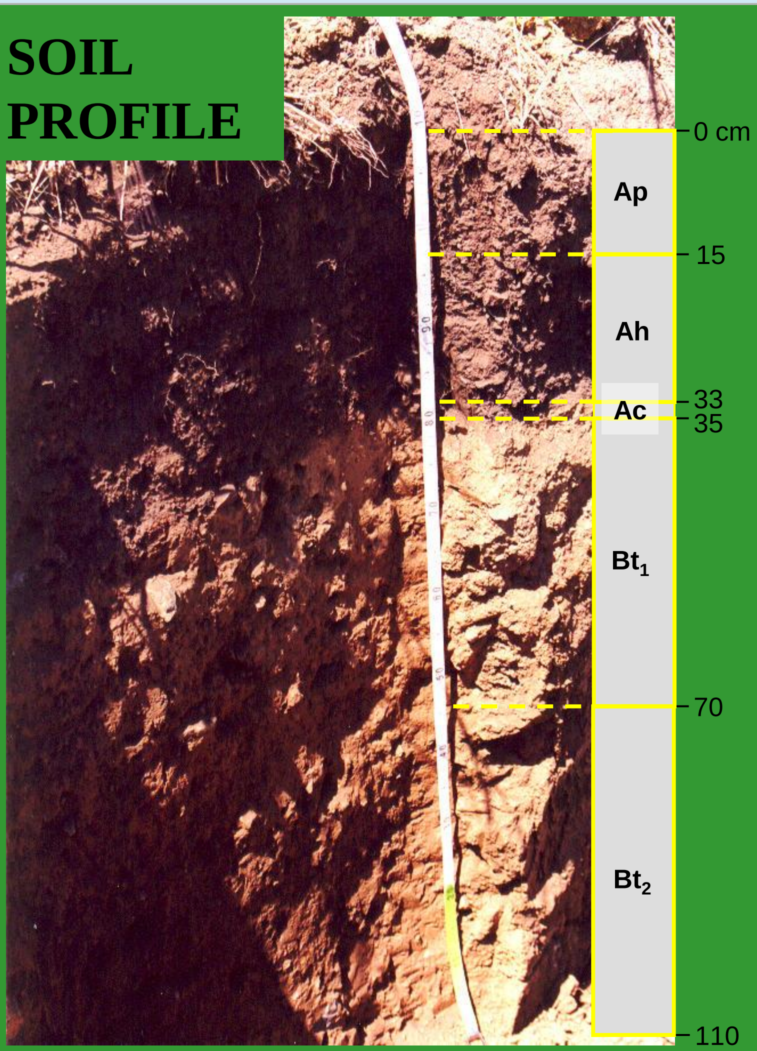
Physical & chemical soil analyses

- Colour: Munsell Colour Table
- Texture (Bouyoucos)
- pH and EC (1:2.5 H_2O and satured paste)
- Organic matter (Walkley and Black)
- Carbonate content (Bernard calcimeter)
- Cation Exchange Capacity (EPA Method 9081)
- Soluble and exchangeable cations ……

SOIL SAMPLES

SOIL PROFILES (Soil samples form each one of the formal diagnostic horizon) / SOIL (Top layer) / SOIL BULK / RHIZOSPHERE SOIL

SOIL PROFILE



Location: Camino de Los Santos in the Dehesa of Castilseras

Situation: Amadenedejos-Gargantiel Road (CR-4192)

UTM Coordinates: 352 180 Eastings, 428 9592 Northings

Altitude: 480 m a.s.l.

Landuse: Rain fed cultivation

Slope: Flat or near to flat (0 – 2%)

Soil classification (USDA): Alfisol, Xeralf, Haploxeralf, Mollic Haploxeralf

0–15 cm; Colour: 5YR3/2 (dry), 5YR2.5/1 (wet); sandy loam texture; superficially ploughed horizon with no structure; high biological activity; abundant fine roots; high porosity; diffuse and wavy lower boundary.

15–33 cm; Colour: 5YR3/4 (dry), 5YR2.5/2 (wet); sandy loam texture, crumb structure, few rock fragments angular 5-10 mm; angular rock fragments (5–10 mm); high biological activity, abundant fine roots; medium to high porosity; occasional pieces of charcoal; medium faint reddish brown mottles at the lower limit; smooth lower boundary.

33–35 cm; Colour: 5YR4/2 (dry), 5YR3/2 (wet); sandy loam texture, moderately calcareous soil reaction; concretionary accumulation of calcium carbonate due to anthropogenic influence; clear and wavy lower boundary.

35–70 cm; Colour: 7.5YR5/4 (dry), 7.5YR4/4 (wet); loam texture, moderate blocky angular structure, angular rock fragments (> 3 cm); low biological activity, few medium roots, low porosity; slightly sticky and plastic; diffuse lower boundary.

70–110 cm; Colour: 7.5YR4/4 (dry), 7.5YR3/4 (wet); loam texture, blocky angular structure, few angular rock fragments (> 3 cm); very low biological activity, very few medium roots; very low porosity; sticky and plastic; lower boundary not reached.

DETERMINATION and DISTRIBUTION of MERCURY

Mercury content determination:
Two Atomic absorption spectrophotometers
(AMA – 254 Leco Instruments)

Periodical comparison between ICP-MS (Ciemat, UAM); Use of BCR / NIST reference materials; Intercalibration exercises

SEQUENTIAL EXTRACTION PROCEDURE IN SOILS SAMPLES (Sánchez *et al.*, 2005)

Fraction	Extracting agent
Water soluble	H_2O
Exchangeable	1 mol·L^{-1} NH_4Cl (pH = 7)
Carbonates	1 mol·L^{-1} CH_3COONH_4 (pH = 4.5 HNO_3)
Easily reducible	Tamm´s solution (oxalic acid/ammonium oxalate, pH = 2.8)
Soluble in 6 M HCl	6 M HCl
Oxidizable	8.8 mol·L^{-1} H_2O_2 (pH = 2, HNO_3) 1 mol·L^{-1} CH_3COONH_4 (pH = 2 HNO_3)
Final residue	Aqua regia / HF

SEP procedures tested: BCR (EUR 14763 EN); Giulio & Ryan (1987)

METHODOLOGICAL PROCEDURE for VEGETATION SAMPLES

Vegetation source
- Natural conditions: Field
- Naturalized conditions: Lysimeter
- Controlled conditions: Greenhouse and culture chamber

↓

Vegetation sampling
- Herbaceous plants: Roots + Aerial part
- Woody plants: Branches with leaves and fruits

↓

Transport & storage
- Samples are stored in paper bags, labelled and transported to laboratory
- Roots and rhizosphere soils are stored in plastic bags in fridge

↓

Pre-analysis treatment
- Samples are air-dried and divided into different fractions (root, leaf, branch, fruit…)
- Samples are washed into ultrasonic bath

↓

Mercury content determination
- Total mercury is determined in each plant fraction using an Advanced Mercury Analyser (AMA-254)

Hg content in soil and plant species and their corresponding transfer factors

Plot (soil)	Hg Total ($mg\ kg^{-1}$)	Hg Soluble ($mg\ kg^{-1}$)	Hg Exchangeable ($mg\ kg^{-1}$)	Hg easily-available ($mg\ kg^{-1}$)
P4	21.3 ± 1.1	0.09 ± 0.01	0.28 ± 0.02	0.37 ± 0.02
P5	550 ± 58	1.04 ± 0.03	4.4 ± 2.3	5.4 ± 2.3

Plot	Plant specie	Hg – Plant (aerial part) ($mg\ kg^{-1}$)	TFt[1]	TFa[2]
P4	*Eruca vesicaria*	2.12 ± 0.2	0.099 ± 0.011	5.8 ± 0.7
P5	*Marrubium vulgare*	38.5 ± 3.2	0.070 ± 0.009	7.1 ± 3.1
	Cynoglossum cheirifolium	43.48 ± 0.2	0.079 ± 0.008	8.1 ± 3.4

1 TFt (Hg total) = [Hg] Plant / [Hg]total Soil

2 Tfa (Hg- easily available) = [Hg] Plant / [Hg] easily available Soil

Note: TF in this study is the equivalent to BAF

Soil parameters (Bulk soil *vs* Rhizozphere) in different Almadén plots (plant / crop species)

Comparison of different extractant agents to evaluate Hg availability in soils (AB-DTPA (pH 7.6); BCR; Ciemat SEP; $CaCl_2$; $NaNO_3$; $(NH4)_2SO_4$; Acetic Acid (0.11 M)...

Soil wash-off?

Influence of fertilization on soil availability and plant uptake? (doses, application form…), Effects of +N / -N ; +P / -P; pH changes; …..

Field experiments and greenhouse studies
(hydroponic cultures and pots filled with Almadén soil)

Rumex induratus **(Almadén new – ecotype??)**

- **Found in mercury open pit and mine tailing.**
- **Arid conditions.**
- **High mercury root uptake and translocation capacity.**
- **Growth reduction less than 23%.**
- **3-8 times less content in aerial part than *Marrubium* but higher biomass.**
- ***Rumex* more Hg tolerant than *Marrubium*.**

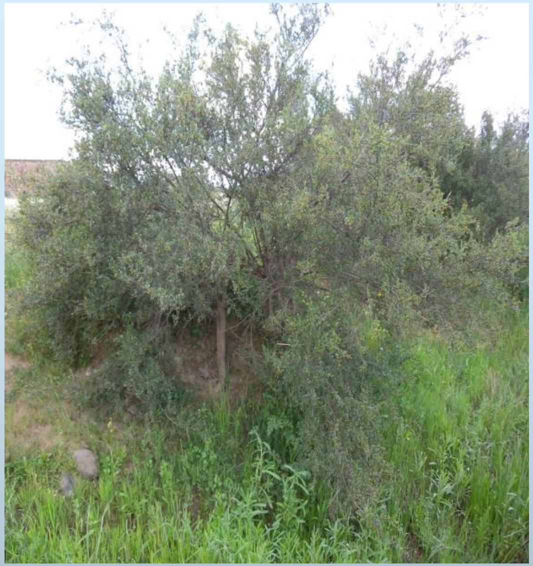
Marrubium vulgare ***(Traditional medical uses!!!)***

- **Found in old metallurgical areas and mine activities zones (Hg soil: 500 mg kg^{-1} dw).**
- **Poor biomass production.**
- **Mercury in plant (aerial part) 20-60 mg kg^{-1} dw.**
- ***Marrubium* higher Hg content in plant than *Rumex*, but less root uptake and translocation capacity.**

- ***Rumex induratus* is capable of extracting more efficiently the available Hg.**
- **The translocation of micronutrients is reduced due to high Hg content.**

Riparian vegetation

Nerium oleander



Flueggea tinctoria

Tamarix canariensis

Typha domingensis

- ✓ Shrub and Macrophytes.
- ✓ Water-sediment-plant interactions.
- ✓ Hg uptake and translocation.
- ✓ Rhizosphere role.
- ✓ Microbiology.

- Erosion control
- Ecosystem protection
- Phytobarriers? Rhizofiltration?

Phragmites australis

DEHESA DE CASTILSERAS… 9000 ha to be managed

……What is a “dehesa”?

Agriculture (dryland and irrigation farming)

Forestry (Wood, cork)

Game (Hunting)

Cattle farming. *Merine* breed of sheep

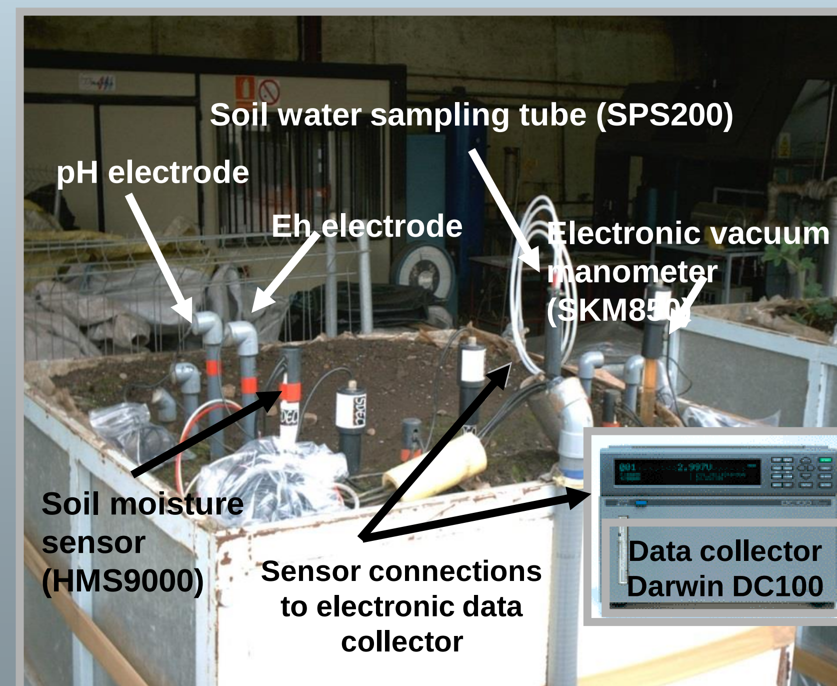
LYSIMETERS from Almadén (located in CIEMAT)

And…. eggplant, wheat, chickpea, lettuce, potato, rape, lavender…..

Close-to-real conditions.
Monitoring soil parameters in the soil profile (soil horizons)

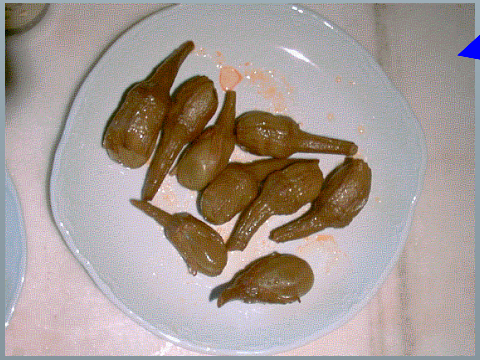
- ✓ Food and feed crops (including local cultivars).
- ✓ Industrial crops.
- ✓ Traditional medicinal plants.
- ✓ Nutrients vs contaminants (Hg).
- ✓ Fertilization effect on Hg uptake.

•Best agronomical practices.
•Impact on local diet….



According to WHO-IPCS Food Additives Series: 52. Safety evaluation of certain food additives and contaminants. World Health Organization (Geneva, 2004), 42.6 μg/day of total Hg could be consumed, so:

Eggplant	**[Hg] (μg kg^{-1})**	**Maximum portion (g fruit day^{-1})**
Fruit with stalk and calyx	**190.2**	**224.0**
Fruit without stalk and calyx	**65.4**	**651.7**



Common vetch *(Vicia sativa L.)*

Lysimeter, greenhouse and field conditions

According to DIRECTIVE 2002/32/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 7 May 2002 on undesirable substances in animal feed:

Common vetch	**[Hg] (mg kg^{-1})**	**Hg limit for animal nutrition (mg kg^{-1})**	**Consumption recommended**
Seeds	**< 0.1 (0.02-0.006)**	**0.1**	**YES**
Fodder	**0.07 up to 0.48**	**0.1**	**NO**

Lupine *(Lupinus albus)*

Lysimeter, greenhouse and field conditions

Animal feed (Directive 2002/32/EC Commission directive 2003/100/EC)

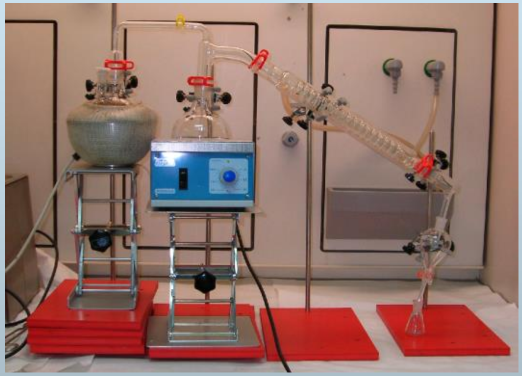
Lupine	[Hg] (mg kg^{-1})	Hg limit for animal nutrition (mg kg^{-1})	Consumption recommended
Seeds	0.01 - 0.03	0.1	YES
Fodder	0.06 - 0.14	0.1	NO

Human consumption (WHO – IPCS, 2004)

Lupine	[Hg] (mg kg^{-1})	Maximum portion (kg fruit day^{-1})
Seeds	0.01 - 0.03	3.97 – 1.38

Lavender *(Lavandula stoechas L.)*

PRODUCTS



ESSENTIAL OIL

LAVENDER TEA

$[Hg]_{\text{lavender tea}}$ $[Hg]_{\text{lavender essential oil}}$
$< 0.5\ \mu g\ kg^{-1}$

SUITABLE

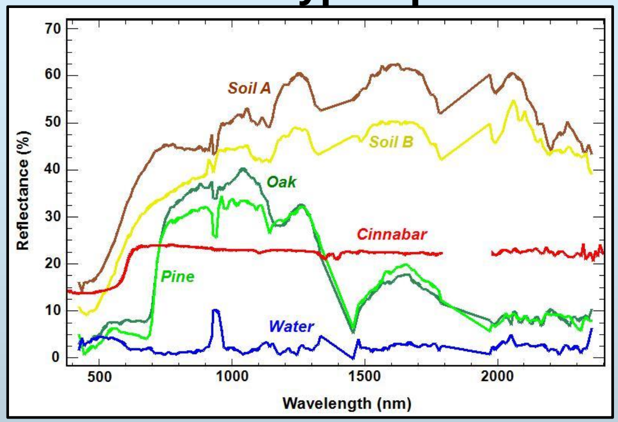
According to WHO-IPCS Food Additives Series: 52. Safety evaluation of certain food additives and contaminants. World Health Organization (Geneva, 2004), 42.6 µg day^{-1} of total Hg could be consumed, so:

Crops	[Hg] µg kg^{-1}	Maximum portion (kg grain day^{-1})	IN PRACTICE
LENTIL CHICKPEA	6 – 36	1.2 – 6.6	26 – 144 Dishes/day
BARLEY	5 – 24	1.7 – 8.9	12 – 59 L beer/day

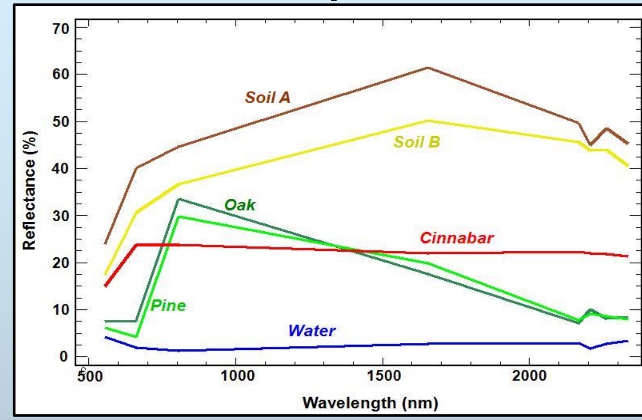
Monitoring using GIS and remote sensing

Field spectroradiometer

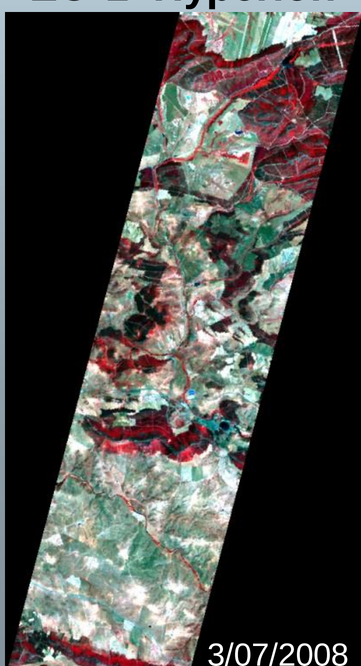
Field and hyperspectral



Multispectral



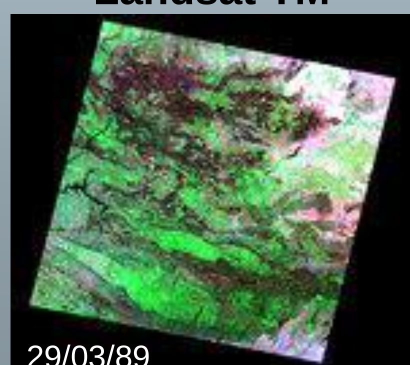
EO-1 Hyperion



Available sensor data

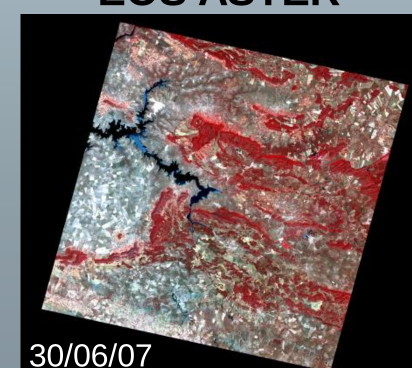
(Hyperspectral and multispectral)

Landsat TM

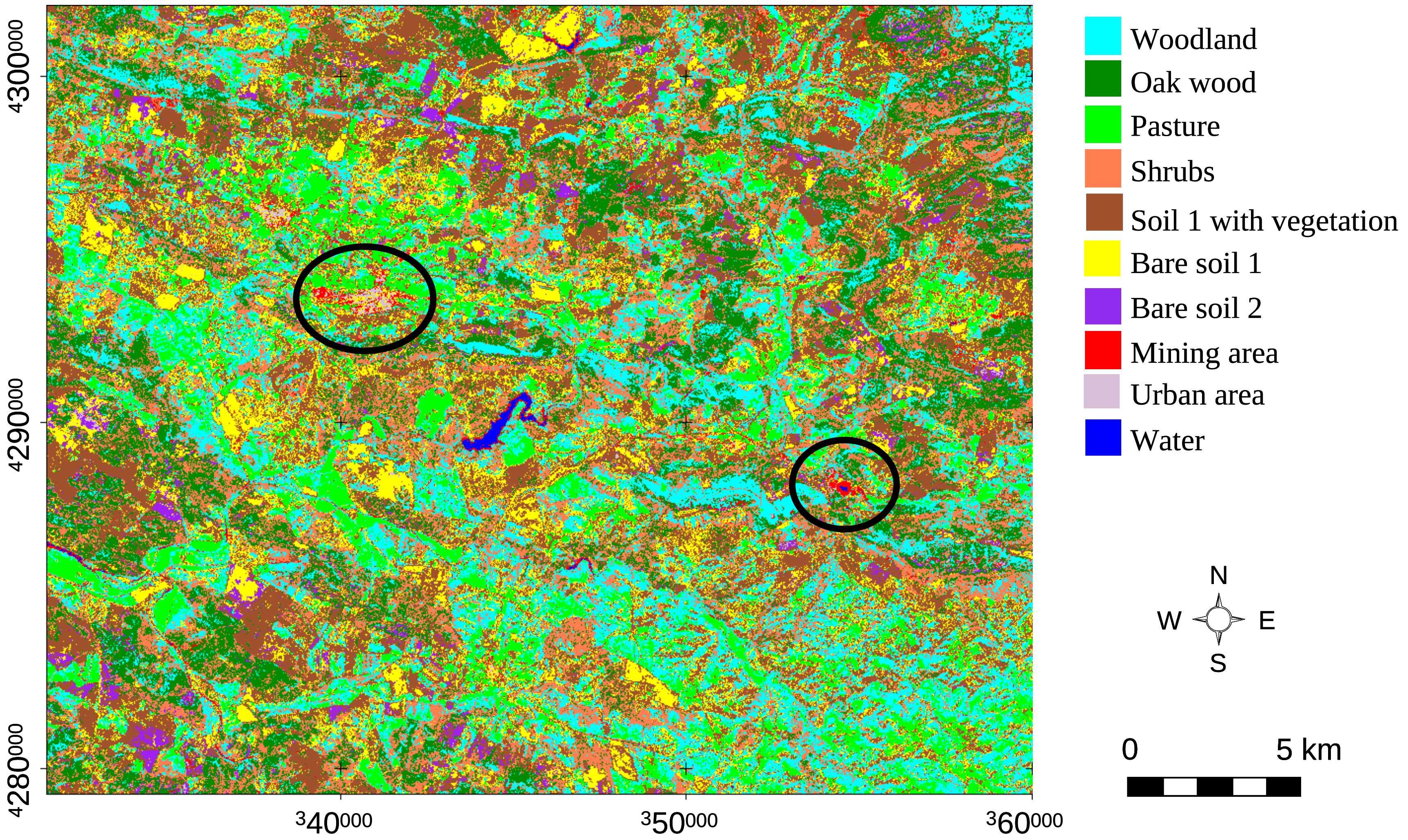


Landsat ETM

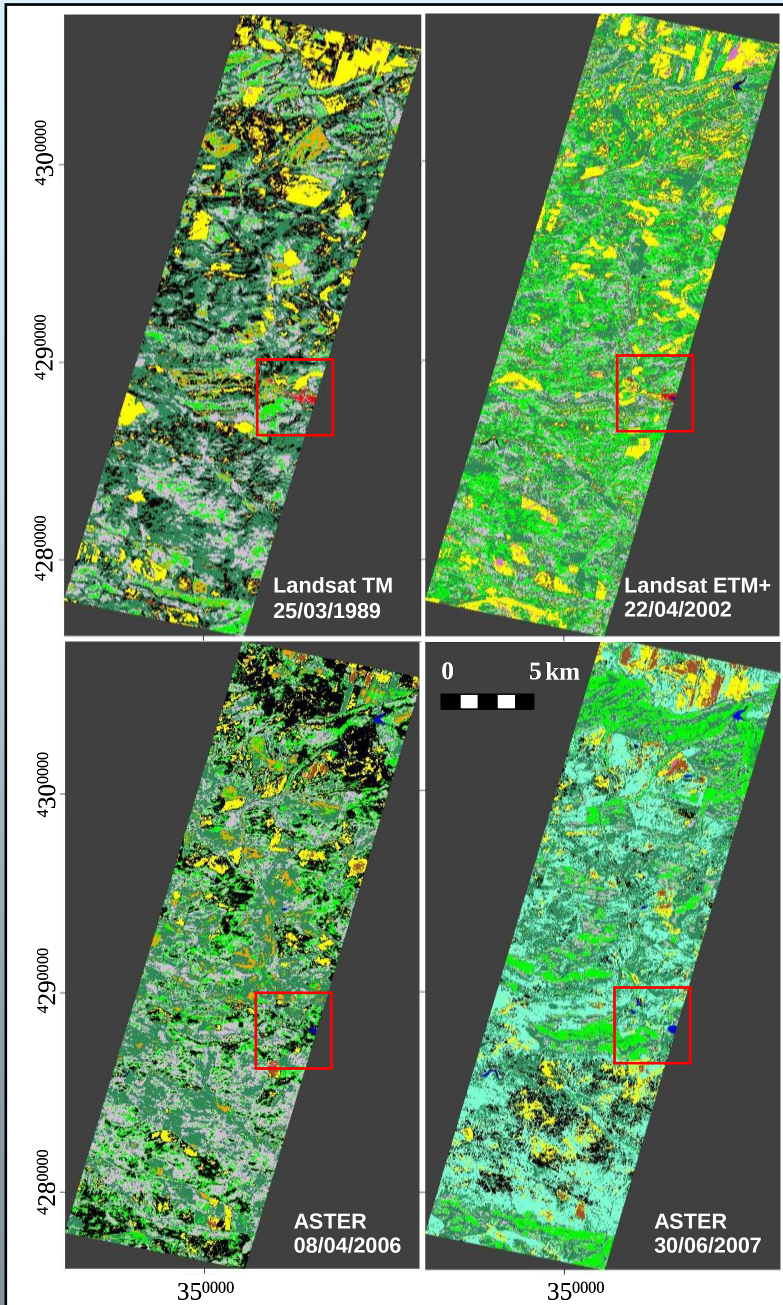
EOS ASTER



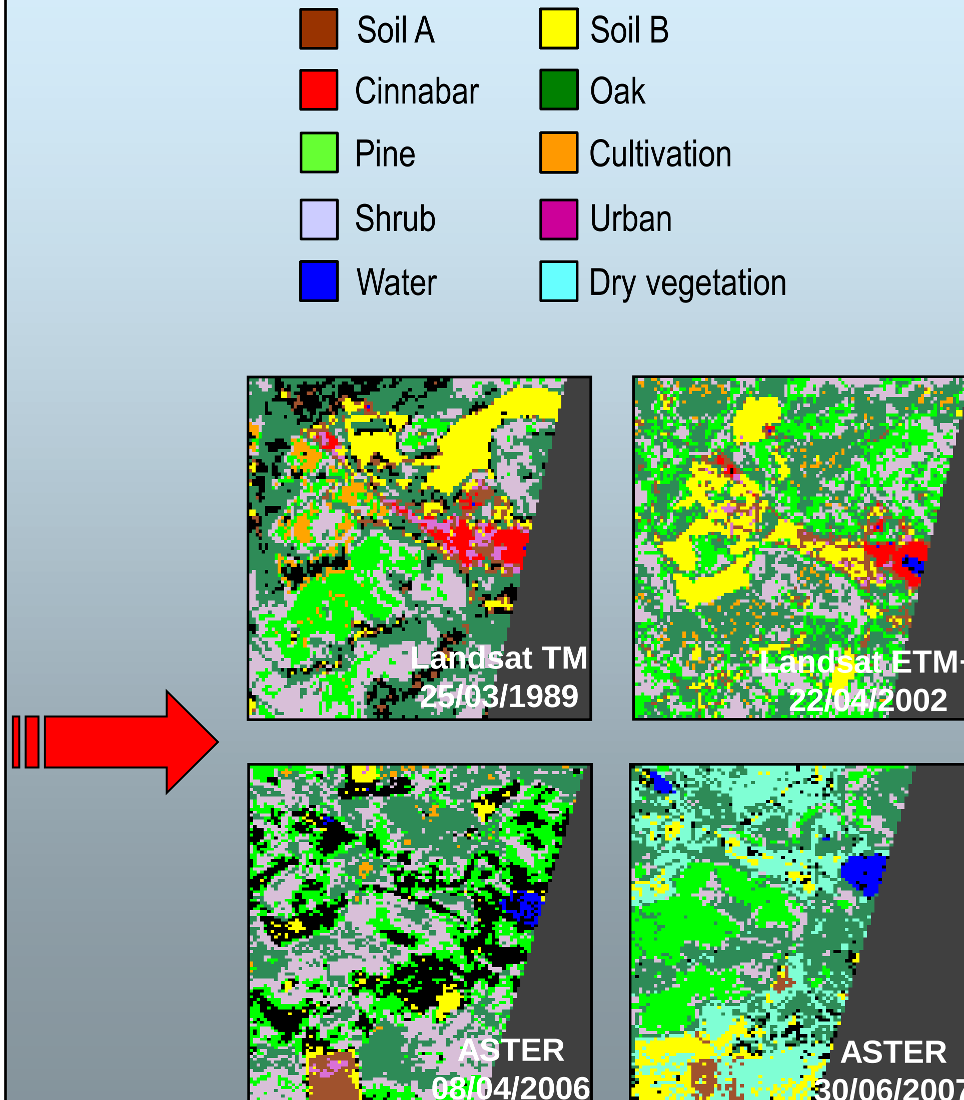
Land use classification of the Almadén area



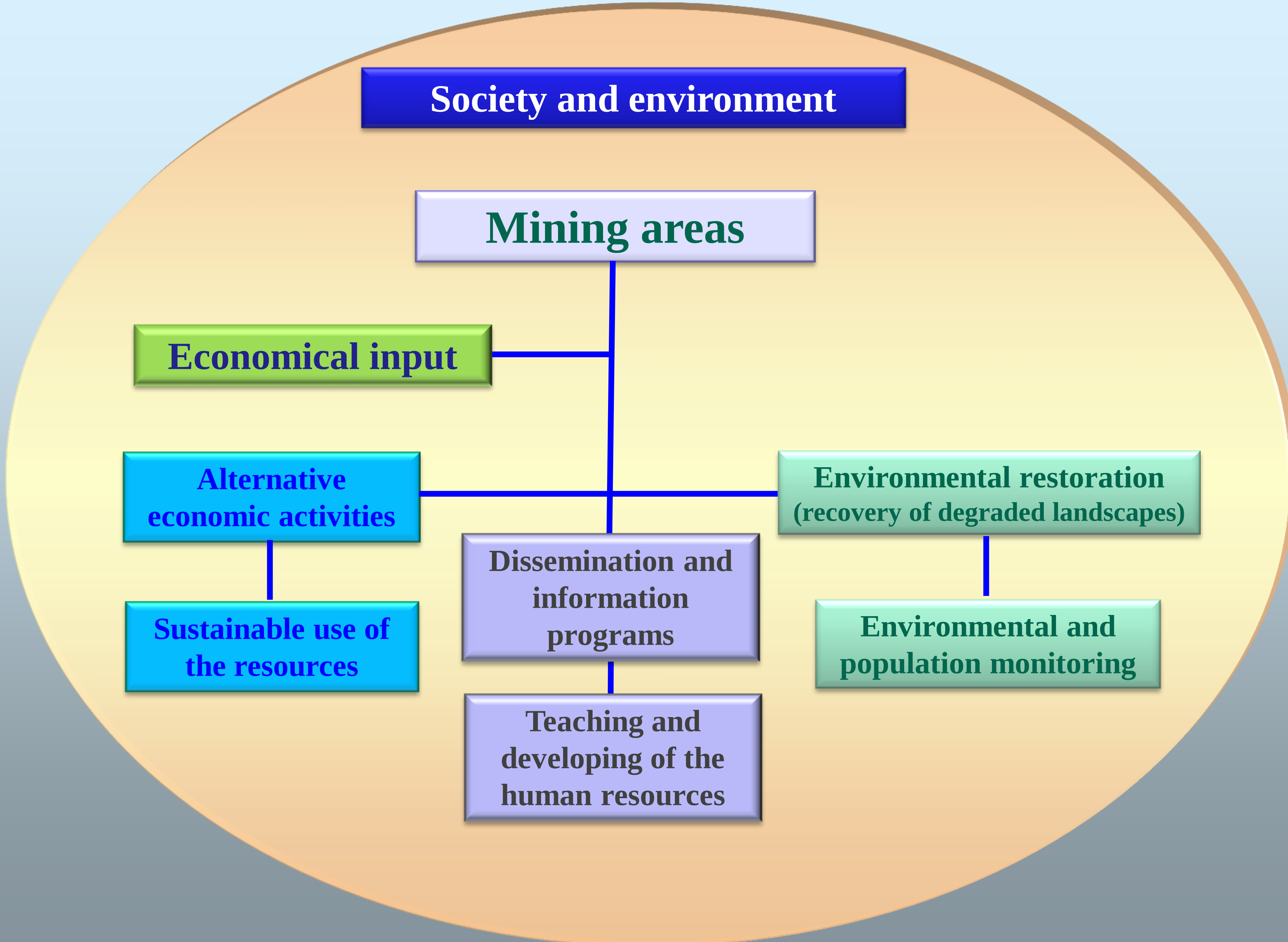
Time series



4300000
4290000
4280000
Landsat TM
25/03/1989
Landsat ETM+
22/04/2002
0
5 km
ASTER
08/04/2006
ASTER
30/06/2007
350000
350000



Soil A
Soil B
Cinnabar
Oak
Pine
Cultivation
Shrub
Urban
Water
Dry vegetation
Landsat TM
25/03/1989
Landsat ETM+
22/04/2002
ASTER
08/04/2006
ASTER
30/06/2007


Society and environment
Mining areas
Economical input
Alternative economic activities
Sustainable use of the resources
Dissemination and information programs
Teaching and developing of the human resources
Environmental restoration (recovery of degraded landscapes)
Environmental and population monitoring

Ongoing research work

- ✓ Improve and standardization of sampling procedures.
- ✓ Standardization and homogenization of procedures to estimate mercury (bio)availability.
- ✓ Improve vegetation sample preparation taking into account leaves type and root system (avoid external contamination).
- ✓ Study of environmental factors on the mercury behaviour under real conditions.
- ✓ Mercury speciation in different soil types (and plants).
- ✓ BAF / TF taking into account specific soil type and plant specie.
- ✓ Riverbank (flooding areas): Interaction soil-plant-water-sediments.
- ✓ Mercury volatilization in semi-arid condition (Almadén).

Ongoing research work and FURTHER KNOWLEDGE NEEDED….

- Mercury decontamination techniques (solar energy; controlled thermal desorption; “green technologies”…..)
- Mercury waste treatment (immobilization) and safe storage.
- Diet survey; toxicological / ecotoxixological and risk models.
- Improvement of spatial surveys and environmental monitoring.
- Knowledge and achieved experience transference.
- Improve the communication/ result dissemination/ stakeholders information and implication / collaboration projects.

Many open questions…… a lot of work to do

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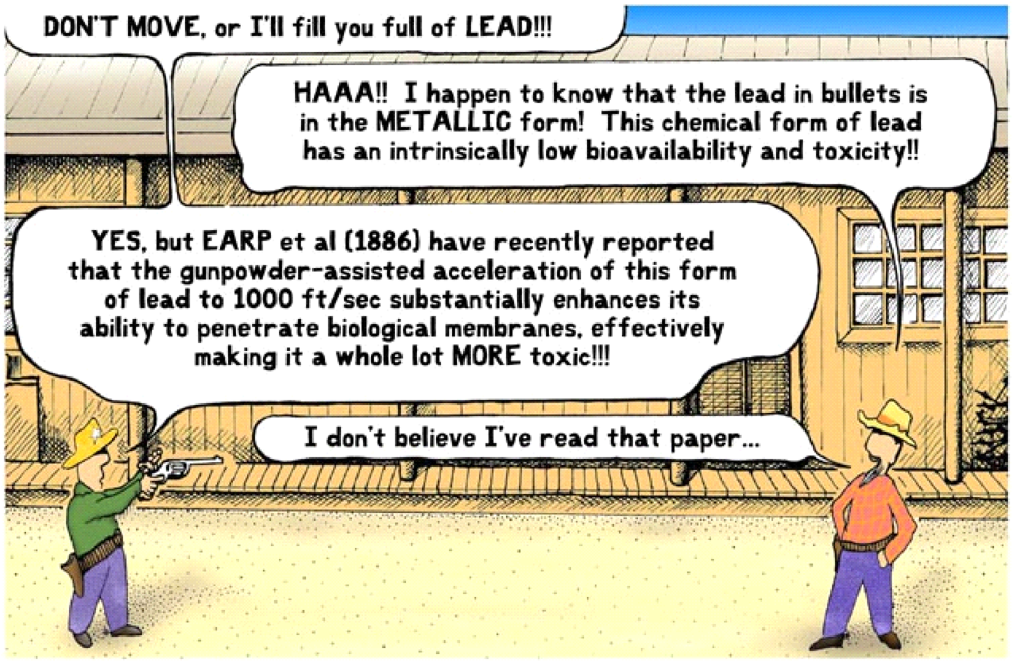

Environmental Scientists in the Wild West

Thank you for your attention

ANALYTICAL CHEMISTS IN THE WILD WEST