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D'où vient le plomb ? :

L'utilisation de *l'environmental forensics* pour la fixation des objectifs de dépollution du site d'une ancienne unité de traitement des métaux précieux à Vienne dans l'Isère

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VIENNE

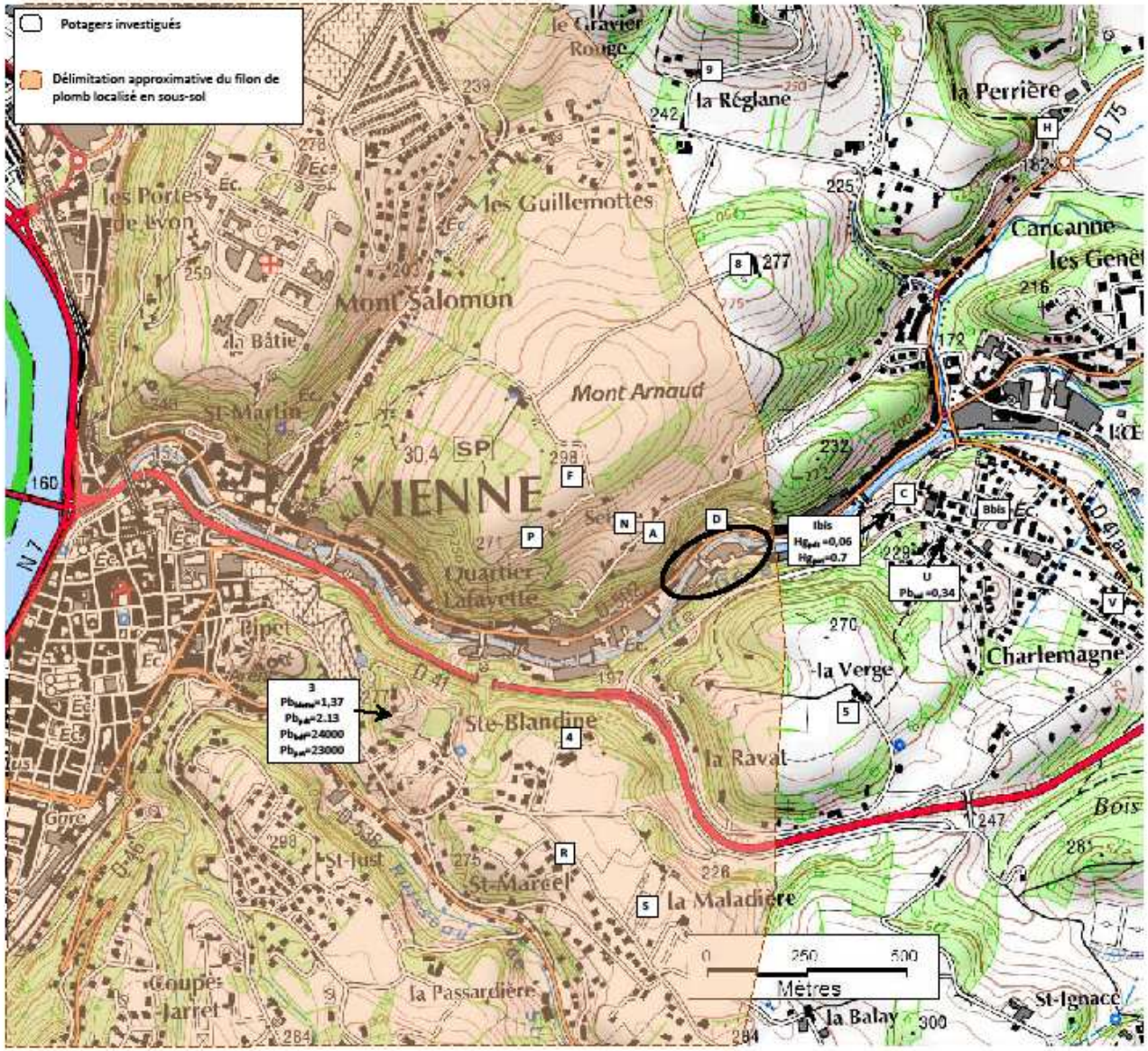
La vallée de la Gère est connue depuis l'antiquité romaine pour être riche en filons de plomb

Arrêté préfectoral de remise en état du 13 janvier 2009 :

Plomb :110 mg/kg.

Anamyse du "bruit de fond" 1100 mg/kg.

Le recours aux prestataires de "environmental forensics" permet de fixer des objectifs de remise en état raisonnables.



Sal=salade ; pdt=pomme de terre ; Hg=mercure ; Pb=plomb ; pot= sol potager ;bdf=sol bruit de fond

Figure 4 : Cartographie des anomalies détectées dans les potagers investiguées en mg/kg poids frais

Echantillons

Case Study

Environmental Forensics Helps Establishing Clean Up Criteria in a Mining Area (for Lead)

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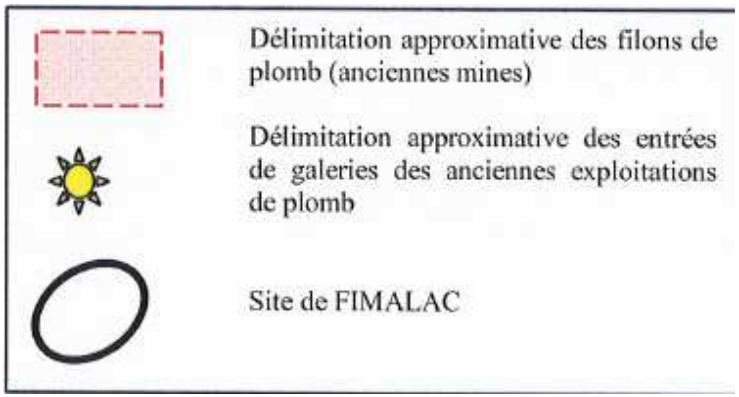
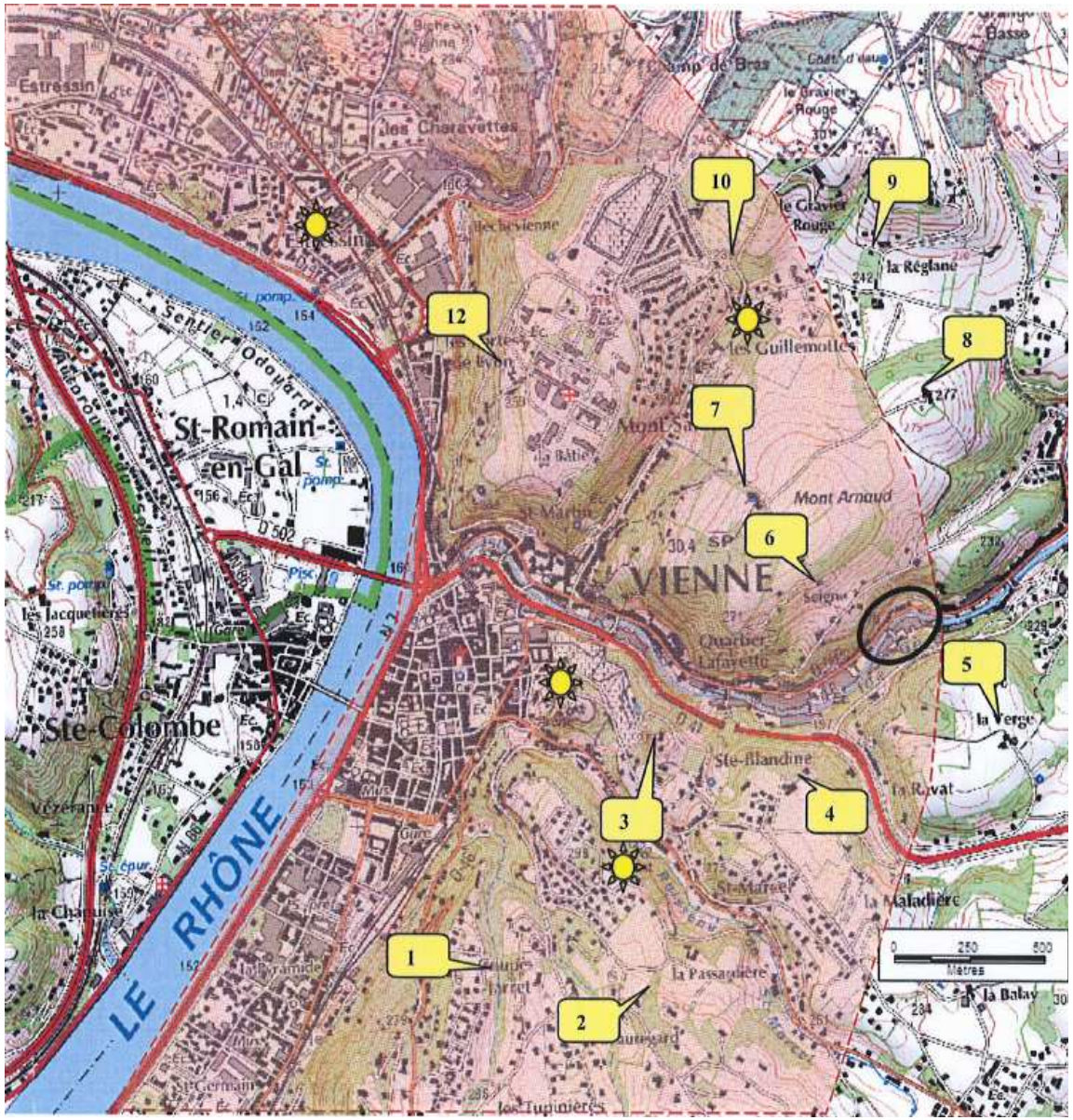
CASE STUDY – Historical Foundry in Vienne, FR

Historical foundry **(still in operation) located in the Valley of Gere area – an area with suspected high metal background values in soil due to the presence of many metal sources, including:**

- ***Ancient Pb mines***
- ***Other foundry sites***
- ***Agricultural parcels***
- ***Industrial sites*** *(e.g., along the valley and in various cities)*





Environmental Investigations / Goals

PHASE I – Establish on-site metal background values – to be used as on-site cleanup limits if above regulatory established limits

- ✓ Foundry soil needed remediation
- ✓ Site-specific cleanup limits had to be established
- ✓ Some of the cleanup limits of metals in soil (established by the regulatory agency, namely: Pb-110 ppm; Hg – 0.6 ppm, Cd – 0.9 ppm, As – 25 ppm, Cr – 52 ppm, Ni – 39 ppm, Co- 10 ppm) seem too low (based on literature review and considering the particularities of the study area)

PHASE II – Investigate the sources of elevated metals in soil and vegetation in the area (off-site locations)

- ✓ Pb, As, Cd, Cr, Co, and Hg exceeded regulatory limits in various off-site areas
- ✓ Pb and Cd exceeded regulatory limits in vegetation from several agricultural parcels in the area

Forensic Approach – PHASE I

We have used **environmental forensic techniques** to investigate the natural background values of Pb, As, Cd and other metals in on-site soils; the techniques used included:

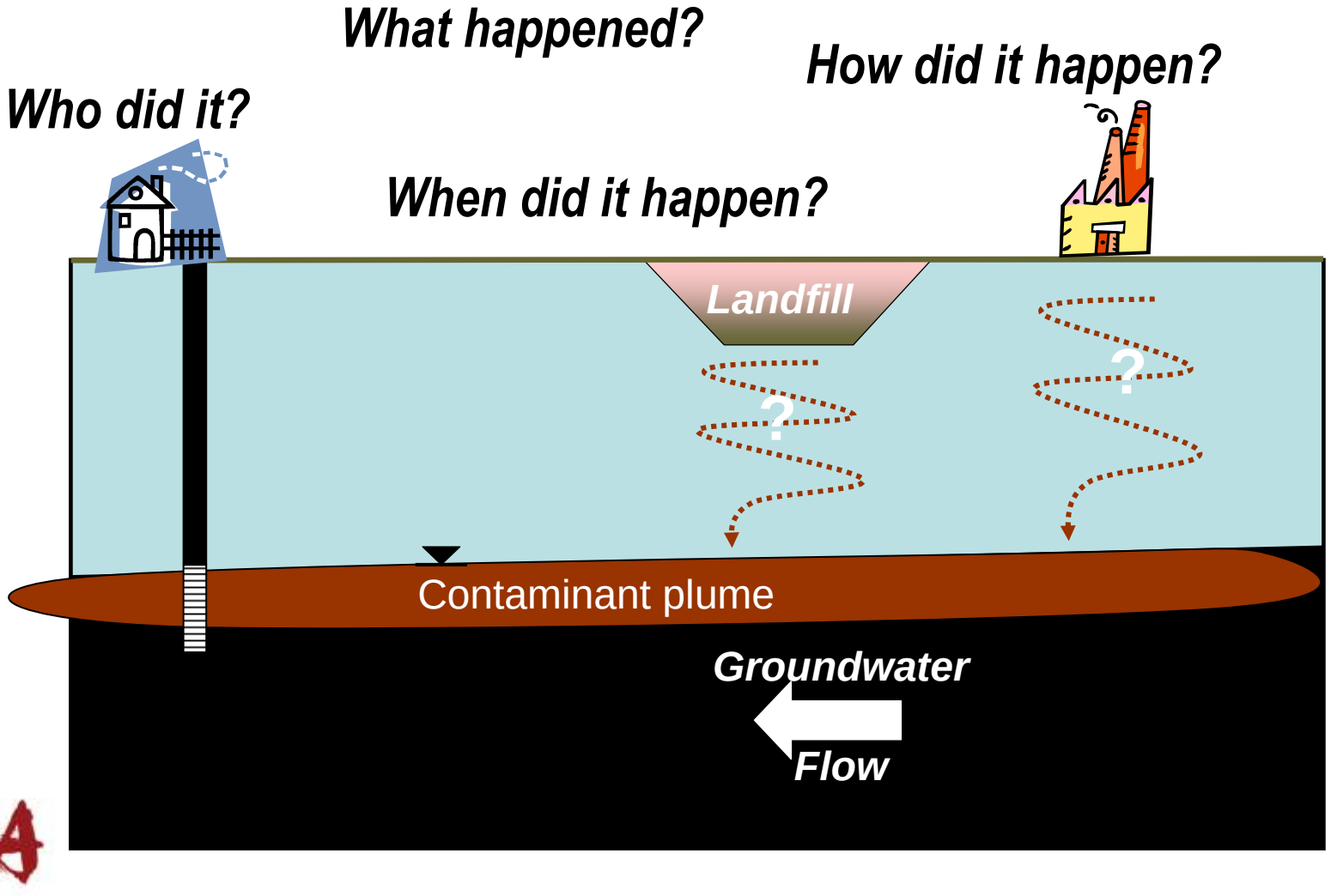
- Historical document and environmental data review
- Chemical fingerprinting
- Mineralogical fingerprinting

Forensic Science

Reconstruction of past events based on the evidence that remains

…often just **a trace**

What can you do with Environmental Forensics?



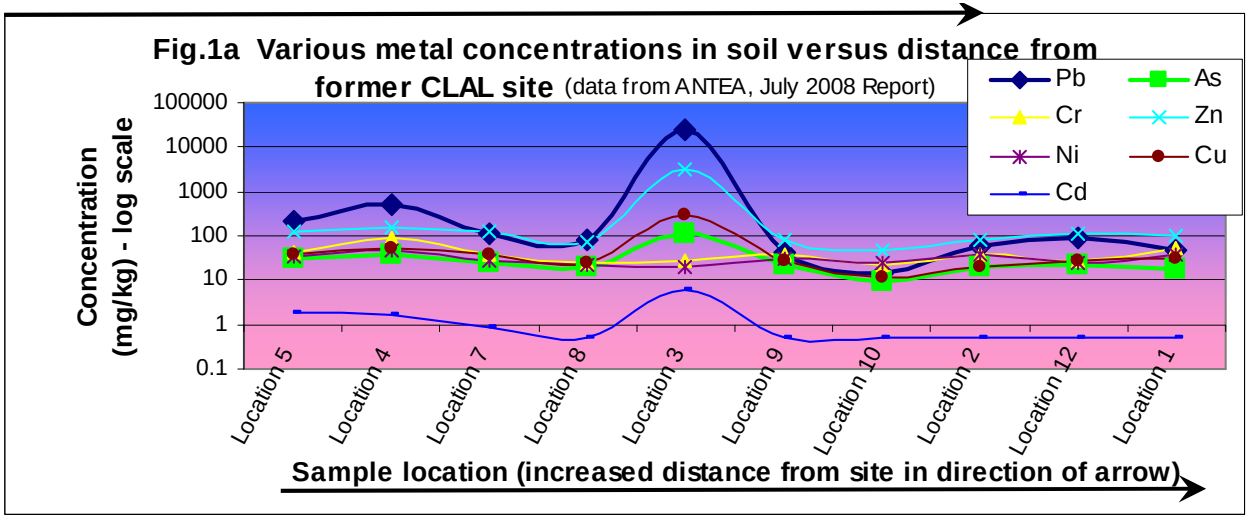
Historical Document and Environmental Data Review – Relevant Findings

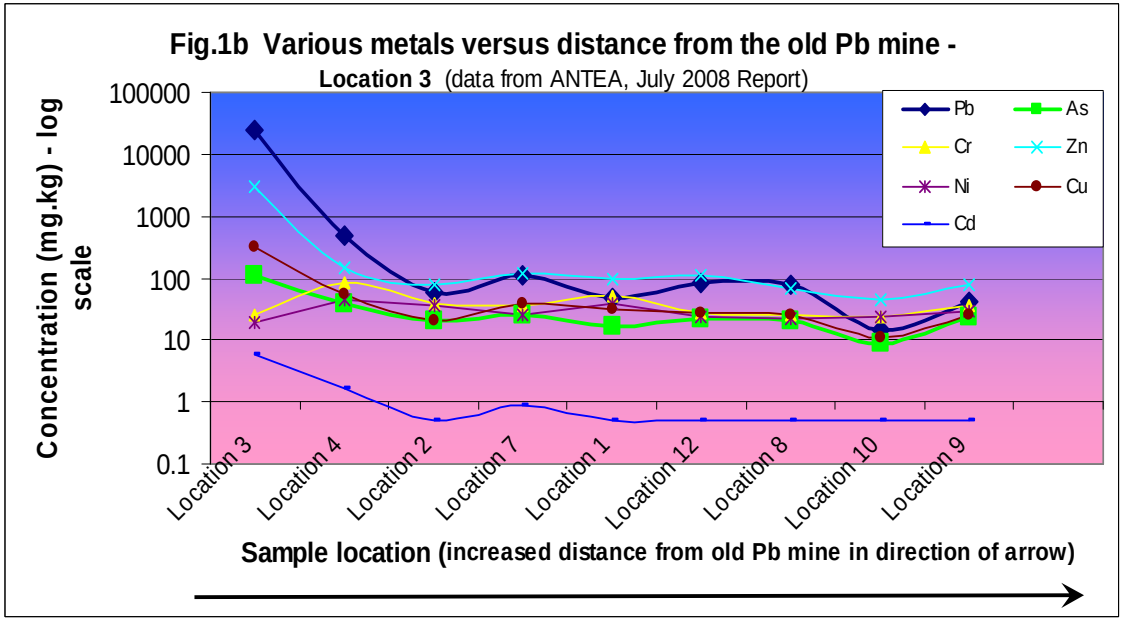
- Historical Information on Foundry Operations
- Available Environmental Reports
- Literature Review of Metal (Pb) Background in Similar Areas

Generally Elevated Metals in the Area and Impact of Old Pb Mines - Confirmed by Background Study

	Fond géochimique local, campagne de 2008 sur échantillons moyens prélevés sur les 30 premiers centimètres du sol									
Désignation d'échantillon	**1**	**2**	**3**	**4**	**5**	**7**	**8**	**9**	**10**	**12**
Chrome total	52	39	26	86	40	36	25	36	23	27
Nickel	39	37	19	45	35	26	22	30	24	24
Cuivre	32	20	310	54	39	39	25	26	11	27
Zinc	100	78	**3 000**	**150**	130	120	70	80	46	110
Arsenic	17	20	110	38	29	25	20	23	9	22
Molybdène	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Cadmium	<0,5	<0,5	5.8	1.7	1.8	0.9	<0,5	<0,5	<0,5	<0,5
Antimoine	<10	<10	64	<10	<10	<10	<10	<10	<10	<10
Baryum	150	110	250	180	150	110	77	90	32	87
Mercure	<0,1	<0,1	0.2	0.4	0.2	0.2	0.1	0.1	<0,1	0.6
Plomb	49	60	**24 000**	**490**	220	110	81	41	15	86

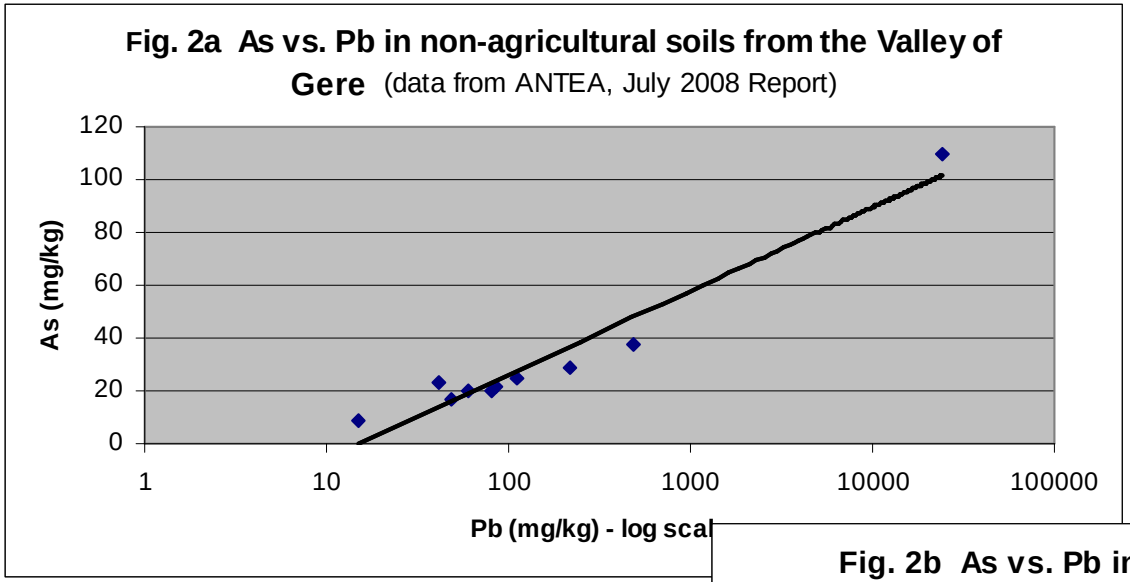
Metal Spatial Distribution Denoted Lack of Site Impact (at 150 meters or more away) **and a Localized Impact from the Sampled Old Pb Mine** (Location 3)





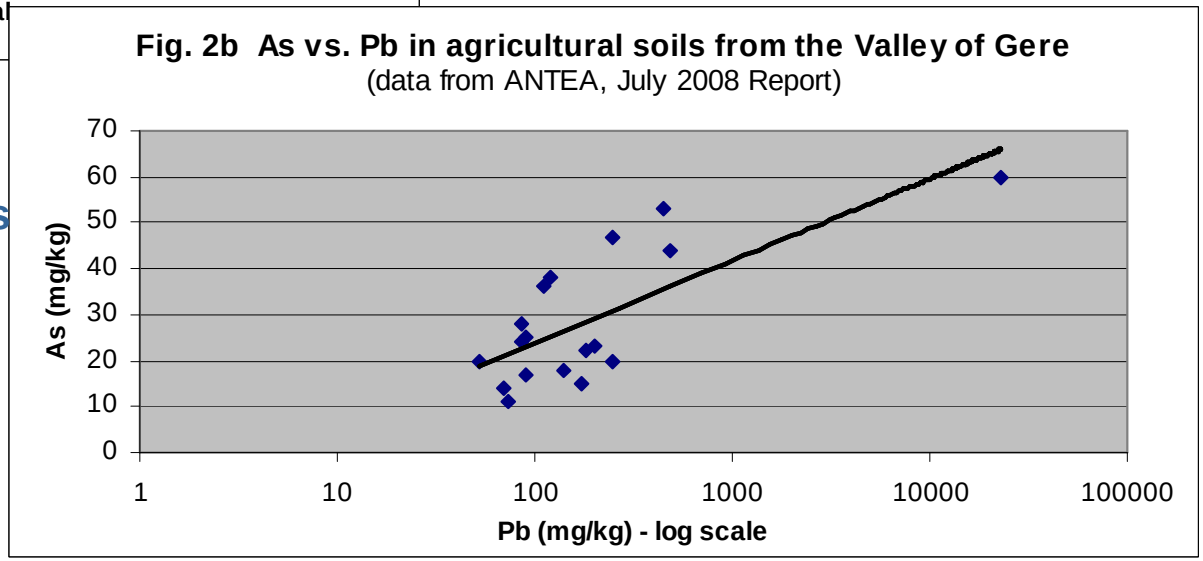
Metal Correlation Plots Confirmed the Suspected Higher Background Values of Metals in Soil in the General Area due to General Mining Impact and Agricultural Localized Impacts

(Below are shown correlation Plots of Lead and Aresenic - as Examples)



The good correlation of Pb and As in general area soils denote mining influences in the whole area

The poor correlation of Pb and As in agricultural soils, with higher As values suggest agricultural impact



Literature Review on Background Values of Metals Confirmed the Suspected Higher Pb Background Values than the Proposed Regulatory Clean Up of 110 ppm

- **Higher values of Pb than proposed site cleanup goal were recorded all around the world in non-contaminated areas:**
  - ✓ Pb values in soil reported up to 150 ppm (in U.K. as reported by Thornton and Culbard, 1986), 160 ppm (in Australia's rural soil according to Brazi et al., 1996), or 225 ppm (in the forest floor of the northeastern United States; Adriano, 2001).
- **Higher values of Pb than proposed site cleanup goal have been recorded in agricultural soils**:
  - ✓ Agricultural soils have reported concentrations of Pb up to 888 ppm Pb (in Ontario, Canada according to Frank et al., 1976) and 1200 ppm of Pb (in England and Wales according to Archer, 1980)
- **Concentration of metals in soil in historical mining areas frequently involve hundreds to thousands of ppm of Pb.**

Chemical Fingerprinting – Results of Metals in Soil Samples

- Using all existing data (on-site and off-site)
- Collecting additional samples from both on-site zones with suspected and unsuspected pollution

SUMMARY of Metal Data

(Newly Proposed CleanUp Limits = Average Values of Metals in Deeper On-Site Soil from Less Impacted Areas)

Metal	Ranges in the background samples collected off-site in 2008	Concentration ranges in top soil from site less impacted areas	Concentration ranges in deeper (0.3-0.6 m) soils from site less impacted areas	Concentration ranges in site soil from highly impacted areas	Previously proposed clean-up limits	Newly proposed clean-up limits - background values for the site soils
Lead (Pb)	15 – 490	540 - 6900	**230 – 2300**	1300 – 110000	110	**1100**
Cadmium (Cd)	<0.5 – 1.8	8.1 – 69	**2 – 17**	580 – 5300	0.9	**9.5**
Nickel (Ni)	19 – 39	18 – 26	**19 – 24**	27 – 8600	39	**same**
Mercury (Hg)	<0.1 – 0.6	0.92 – 31	**0.38 – 9.7**	1.9 – 37	0.6	**5**
Arsenic (As)	9 – 38	25 – 97	**31 – 73**	42 – 360	25	**52**
Cobalt (Co)	4 – 11	7 – 12	**8.1 – 10**	17 – 82	10	same
Chromium (Cr)	23 – 52	**22 - 33**	**23 – 32**		52	same
Tin (Sn)	Not evaluated	10 – 75	**9.6 - 51**	38 – 6200	Not applicable	
Zinc (Zn)	46 – 150	84 – 280	**86 - 220**	2400 – 29000	Not applicable	
Silver (Ag)	Not evaluated	17 – 61	**15 - 36**	93 – 310	Not applicable	
Aluminum (Al)	Not evaluated	9900 – 12000	Not available	3500 - 15000	Not applicable	
Palladium (Pd)	Not evaluated	<10	Not available	<10	Not applicable	
Gold (Au)	Not evaluated	<4	Not available	<4	Not applicable	
Platinum (Pt)	Not evaluated	<10	Not available	<10 - 11	Not applicable	

Note: Association of Zn, Sn, Ag, Pd, Au, and Pt association with Pb suggest site impacts

Mineralogical Fingerprinting

- **Optical and Scanning Electron Microscopy (SEM) of 2 selected on-site soil samples (from a polluted as well as less impacted area)**

Mineralogical Fingerprinting

- **The technique involves particle-by-particle physical and chemical characterization, including:**
  - ✓ Species or minerals associated with targeted metal (i.e., Pb)
  - ✓ External and internal particle morphology (size and shape)
- **It is a precise technique for source determination & allocation, assessment of bioavailability and remediation**
- **We used the technique to evaluate and subtract site contributions (with Pb) from on-site samples (most representative for background evaluation)**

Optical photos of polluted (left) and less impacted (right) On-Site Soil Samples

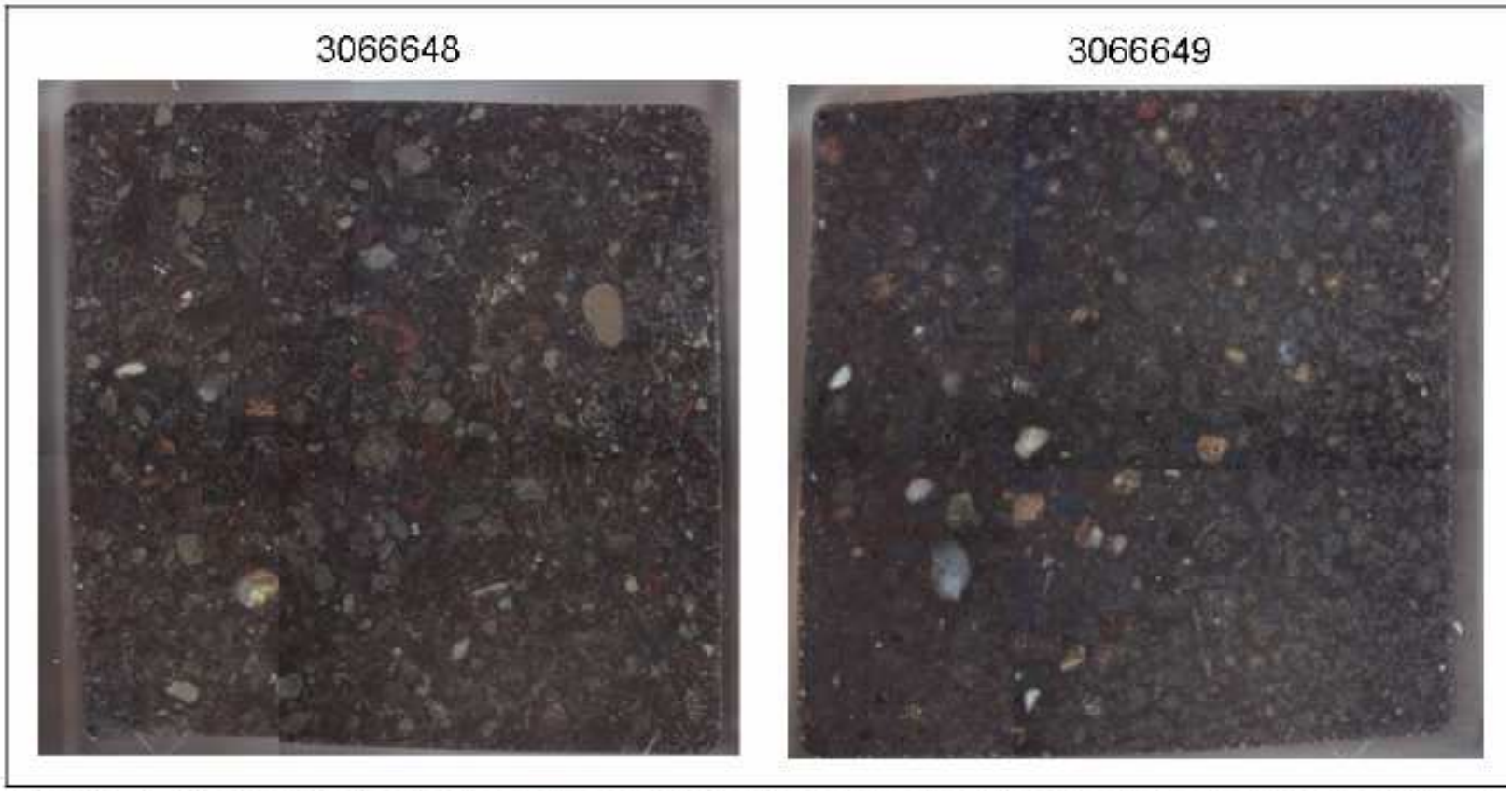


Figure 1. Optical photographs of the epoxy polished 1 inch square mounts of <2 mm sediment samples. Each photograph is a composite of 4 stitched images.

SEM Images with EDS Spectra Denoting Chemical/Mineral Composition of Pb Particles

On-Site Polluted Soil (left) and Less Impacted Soil (right)

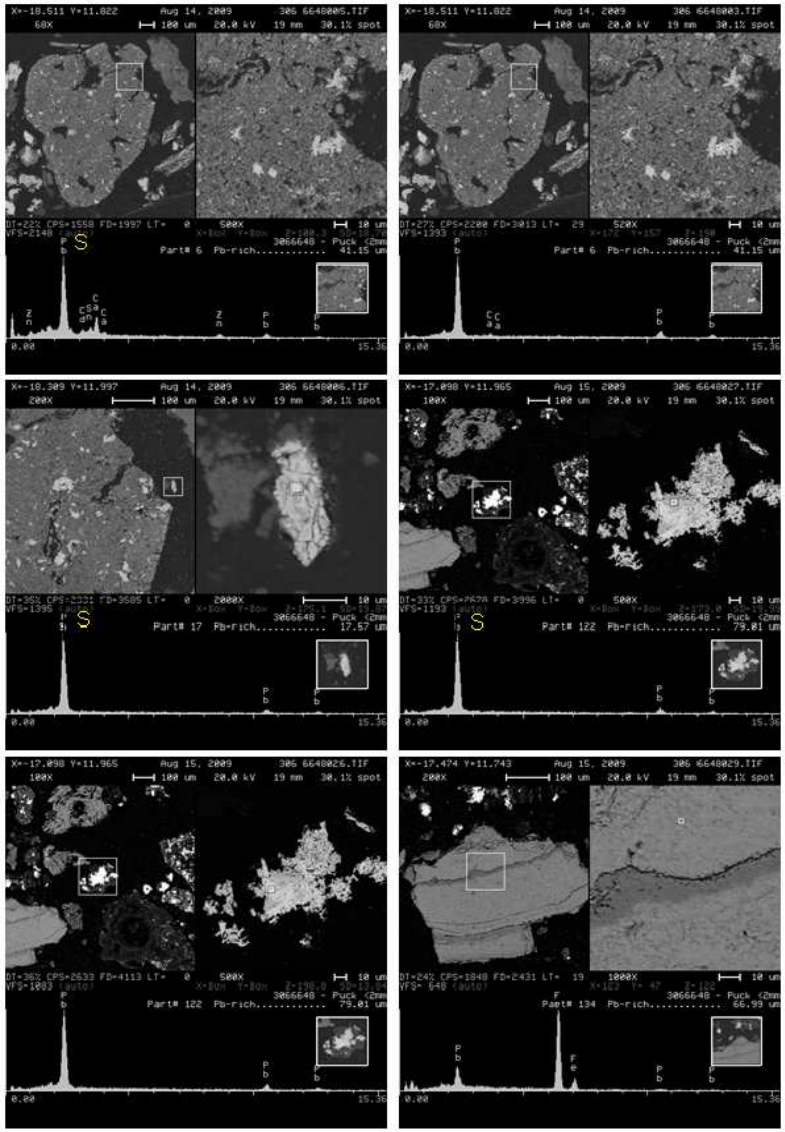


Plate 1. Low and high magnification BE images and EDS spectra of Sols Pollues – Batiment 14 (3066648).

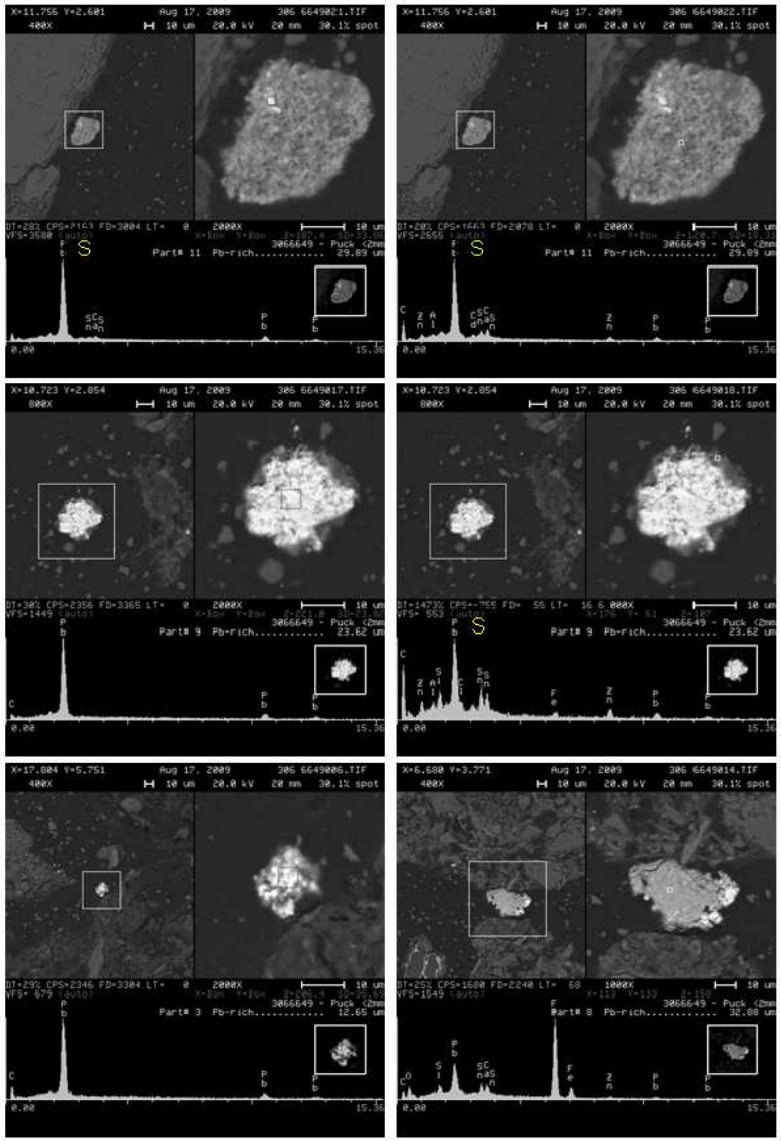


Plate 3. Low and high magnification BE images and EDS spectra of 20090611s102v0-03 (3066649).

Summary of Mineralogical Fingerprinting Results

On-Site Soil Sample	Pb-Bearing Particles (Pb occurrences)	Prevalence (approximation based on SEM counts)
Polluted soil	**Pb associated with tin, cadmium and/or zinc** matrix – Linked to foundry operations	90%
	Large particles of anglesite or susannite	< 10%
	Pb in an iron-rich phase and lead phosphate	< 10%
Less impacted top soil	**Pb associated with tin, cadmium and/or zinc** matrix – Linked to foundry operations	70%
	Lead phosphate	One third (approx.)
	Lead in an iron-rich phase	< 1%

→ 30% of Pb from the less impacted sample could be attributed to Background values
→Since Pb concentration in that sample was 3,300 mg/kg (ppm),
→Pb background is approx. 30% x 3,300 = 1,000 mg/kg (ppm) result
Consistent with metal fingerprinting result

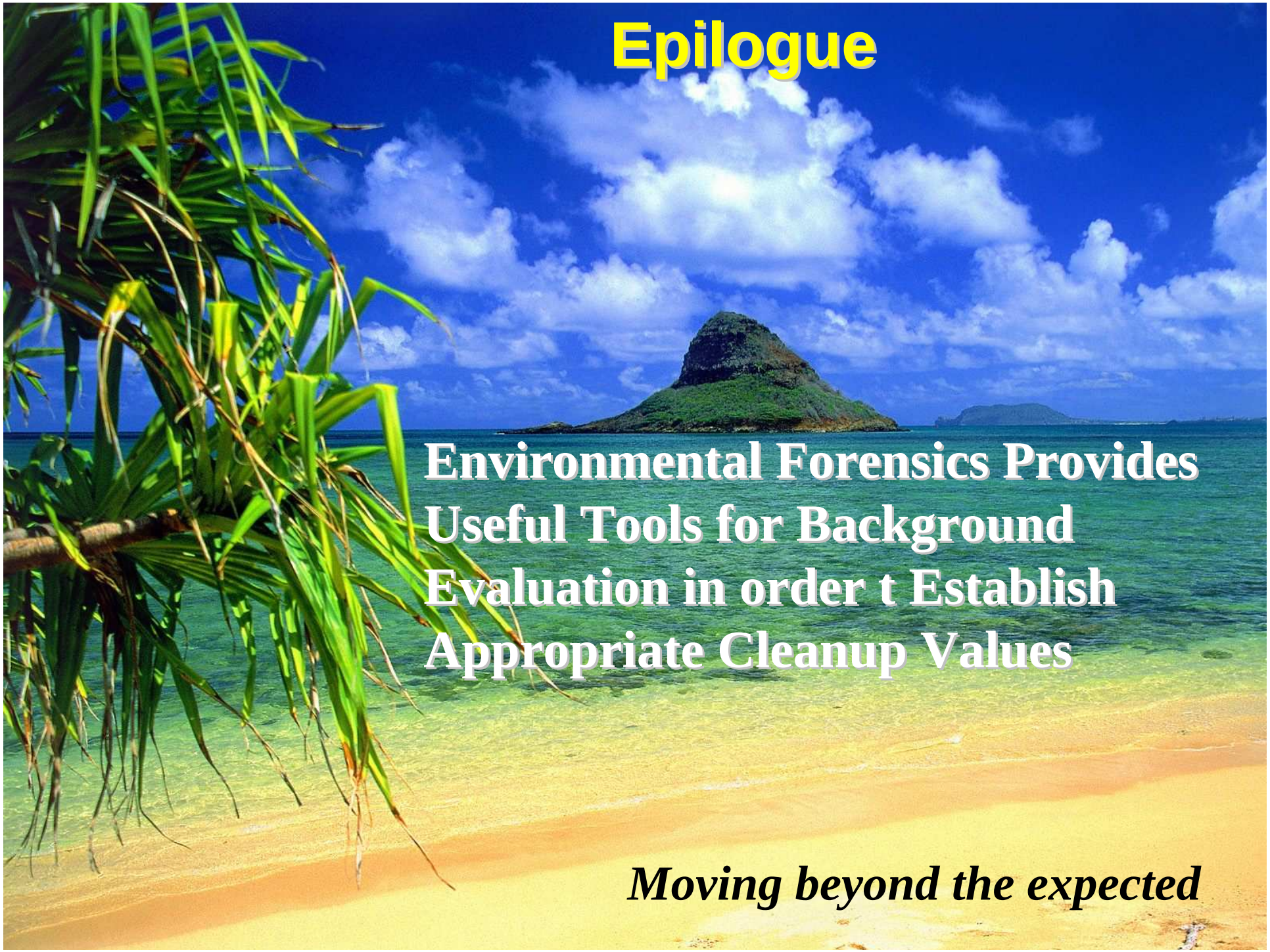
CONCLUSIONS

- A general review revealed many sources of Pb and other metals in the area and thus probable high background values **(especially on-site due to the presence of a suspected ancient Pb exploitation)**

- **An environmental forensic investigation was initiated in order to evaluate background of Pb and other metals in on-site soils**

- The forensic techniques used **included:**
  - ✓ document review and previously collected data evaluation
  - ✓ metal and mineralogical fingerprinting of newly collected samples

- **The results revealed the presence on natural Pb minerals in on-site soils as well as the presence of metals above regulatory established cleanup in little impacted deeper site soils**


Epilogue
Environmental Forensics Provides Useful Tools for Background Evaluation in order t Establish Appropriate Cleanup Values
Moving beyond the expected

Merci de votre attention

Contact

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