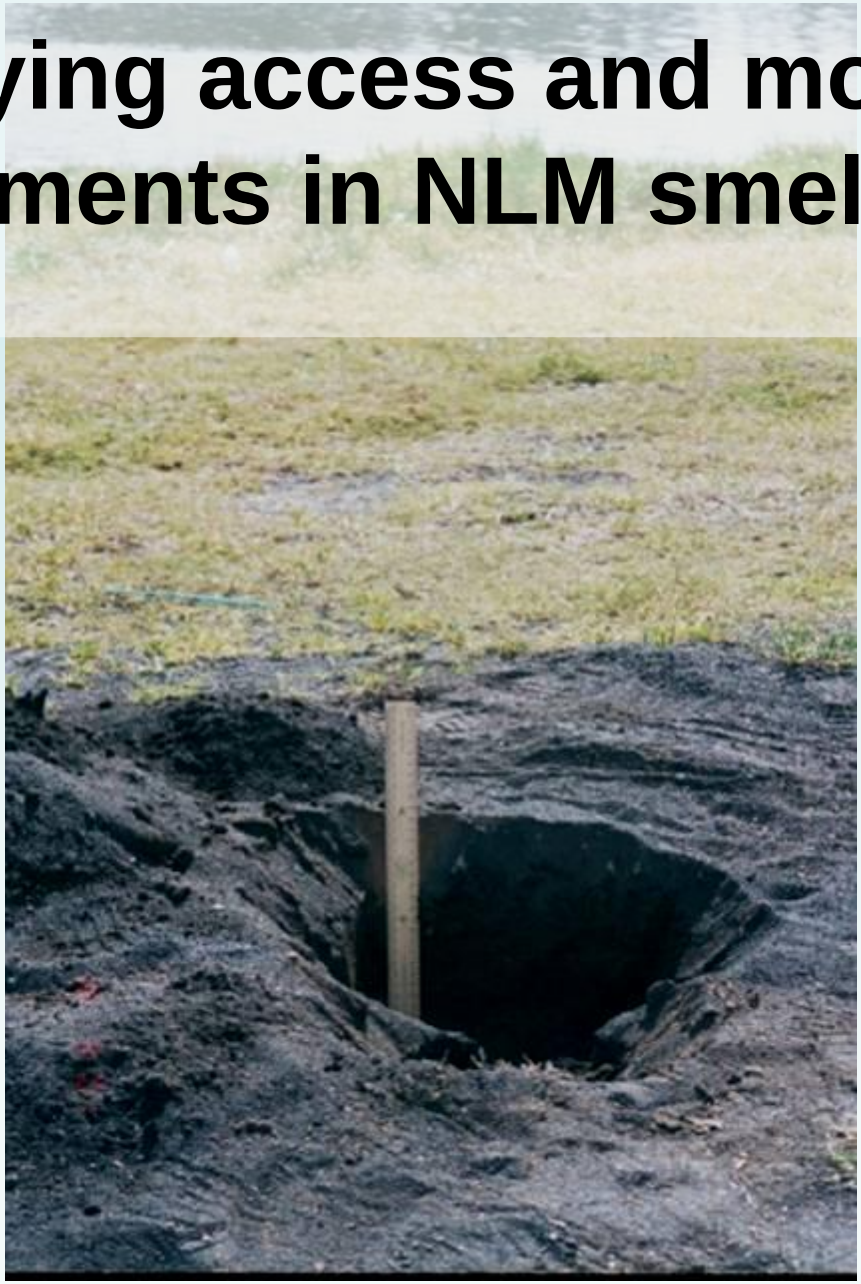
Quantifying access and mobility of toxic elements in NLM smelter slags



A.L. Morrison
July 2015

MACQUARIE
University

Scale of the slag issue

- Approximately 2.1 M tonnes (~650,000 m^3) of slag exported to the community;
- Pb in exported slag (~1-2%) represents >1000 years of declared* smelter stack emissions;
- A covering of the residential area of Boolaroo to a depth of 300mm;
- Waste costs externalised around $400M in todays $’s (@$200/tonne).

*National Pollution Inventory (NPI) 1999-2003 maximum 20 tonnes/yr (2001)

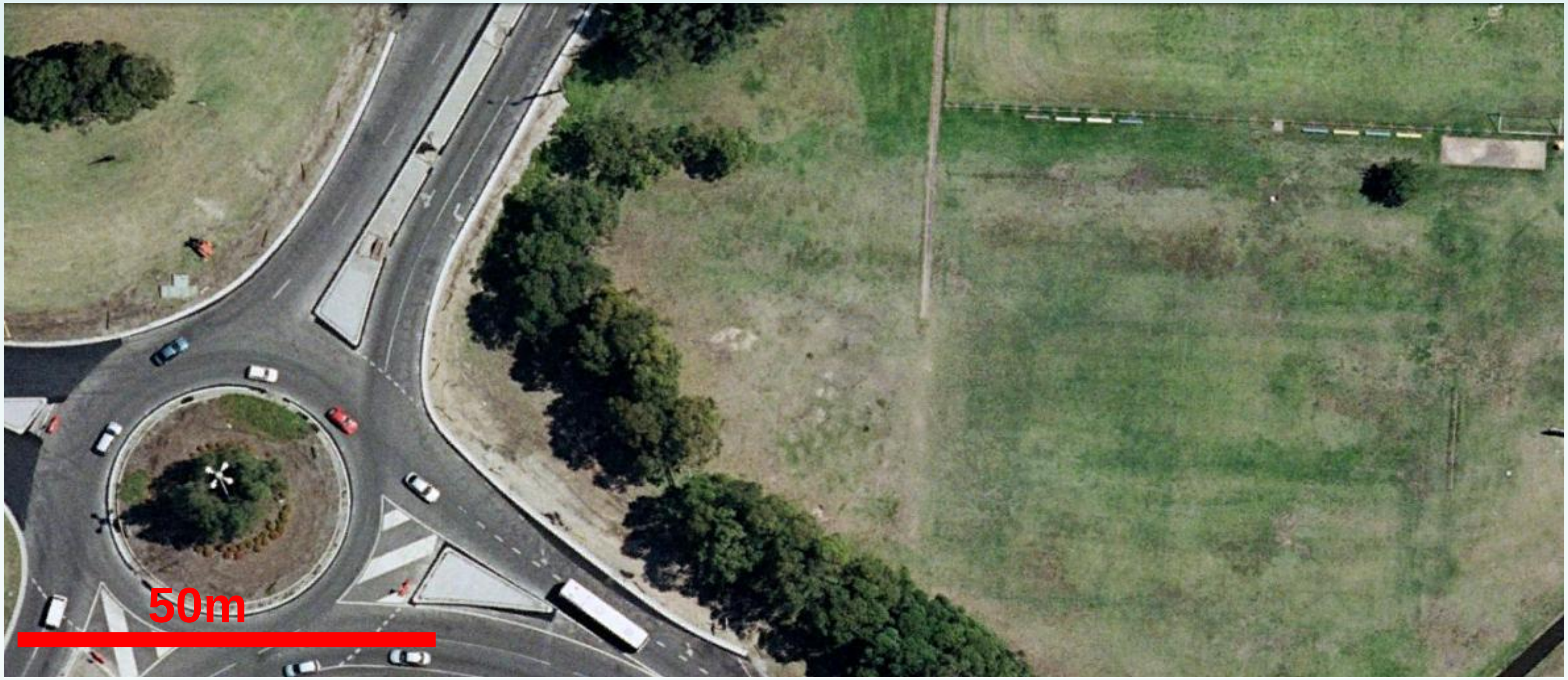
North Lake Macquarie, NSW

Creek Reserve Road, Boolaroo (CR)

Slag infill during creek bank restoration

Tredennick Oval, Boolaroo (TN)

Slag layer over old landfill



Lion’s Park, Eleebana (ELB)

Slag used in stabilisation berm during landslip remediation

The Myth

“Slag produced by Pasminco Metals-Sulphide has a lead content of about 0.7%. **The lead is bound up in a glass like structure and does not readily leach out.** Lead in crystal drinking glass for example is about 22% and is chemically bound up in the glass in a similar way.”

Pasminco Community Newsletter cited in LMCC Planning and Environment Minutes, July 1992.

The Withheld Truth

“most of the heavy metals present in the slag are in readily bioavailable forms. **It is likely that ingested slag, reaching the gut would readily release lead, zinc, cadmium and copper, and this could have toxic consequences**”

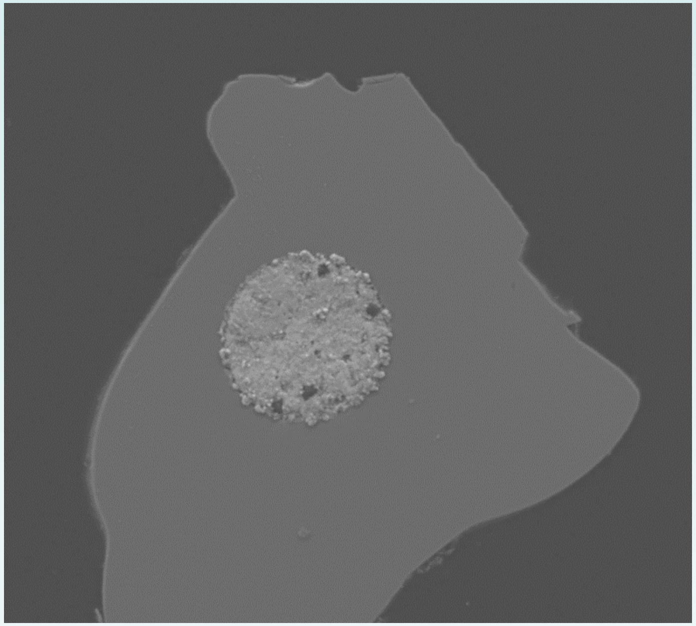
G.E Batley, CSIRO Investigation Report CET/LHIR077, June 1992.

These earlier results were confirmed in the study of bioaccessibility (Morrison and Gulson) published in 2007 and subsequently by others (Kim et al., 2009).

Hypothesis

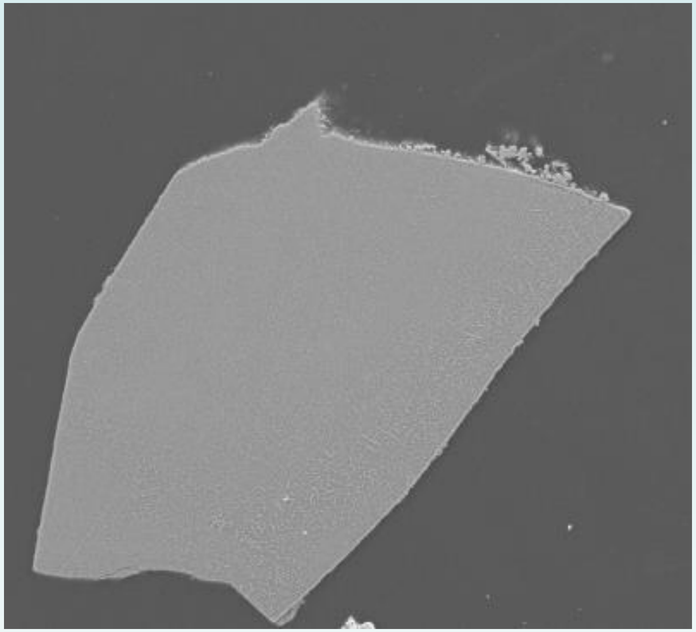
- Slag is benign in the environment
- Metals contained in the slag remain insitu when exposed to infiltrating fluids e.g. rainwater, seawater, acidic leachates

Morphology needed for hypothesis to be correct



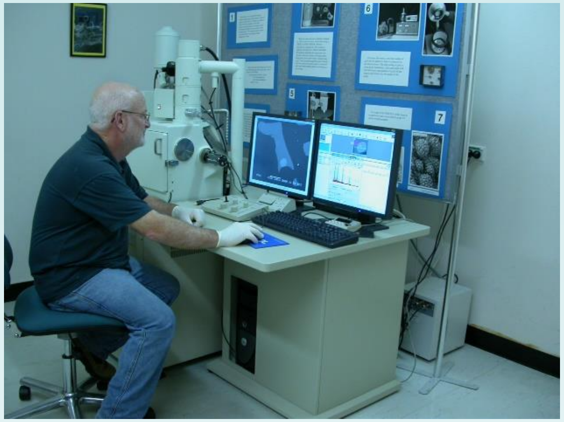
Toxic metal inclusions are all surrounded by an impervious silicate slag matrix

and/or



Toxic metals form part of the structure of the impervious silicate slag matrix

SEM

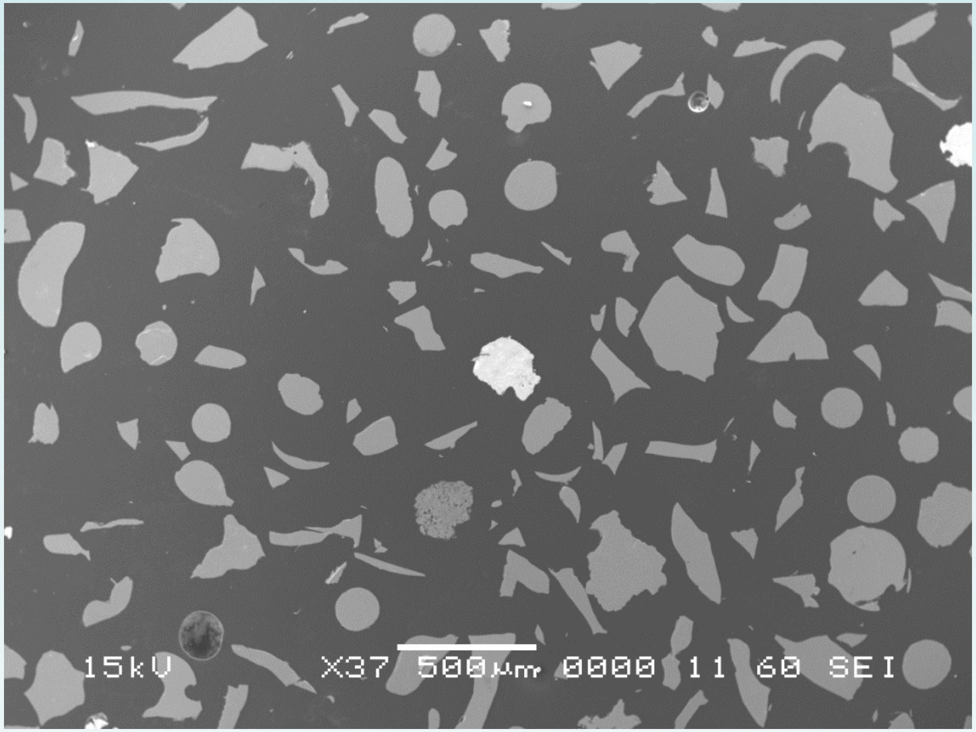


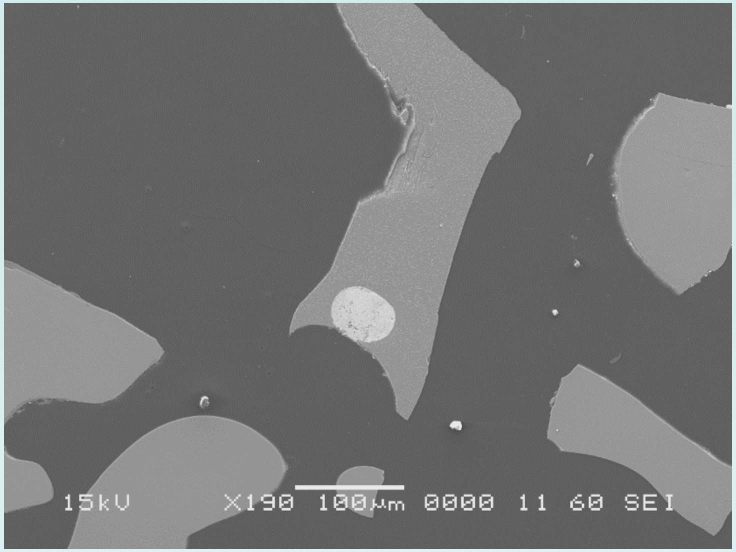
Allows detailed examination of individual particles and the attached EDS system can determine semi-quantitative chemistry over a wide range of elements.

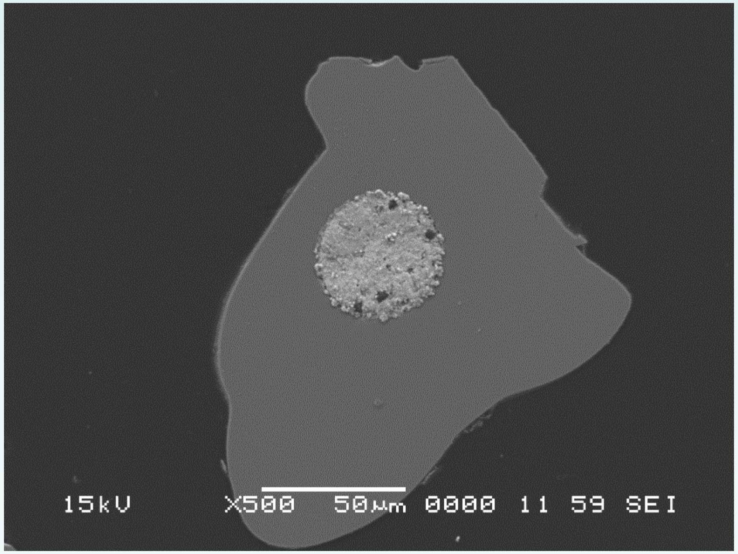
QEMSCAN

Automated analyses using EDS of ~1-2μm “spots”, software then maps individual particles over a sample. Automation allows large numbers of particles to be chemically mapped but at a lower degree of precision.

SEM Analyses







Sample sized -250+180 µm

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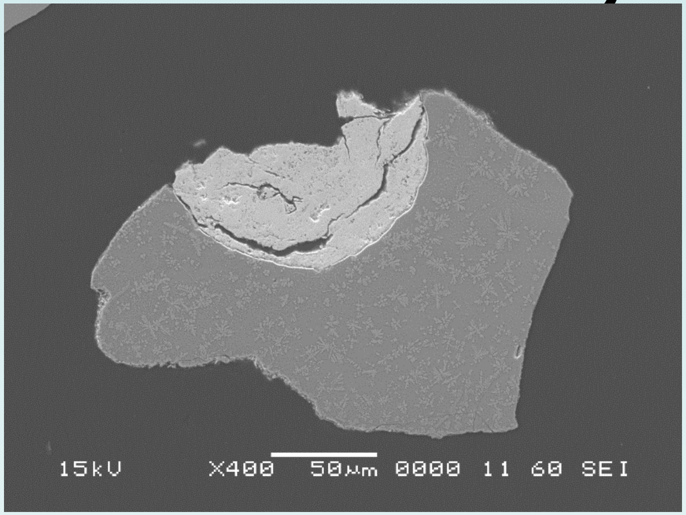
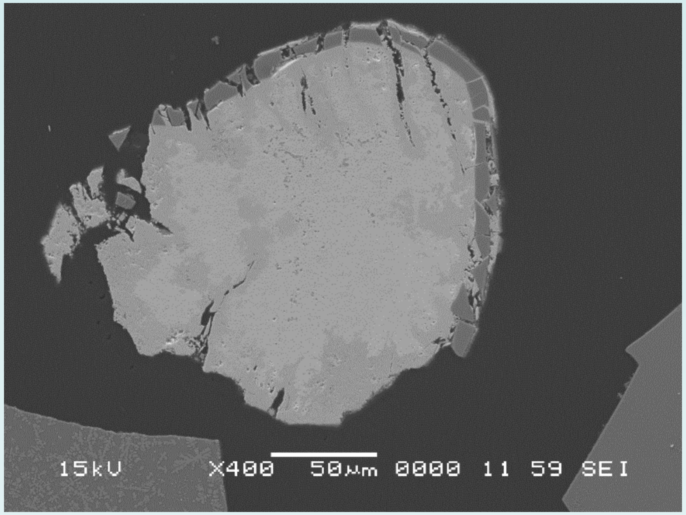
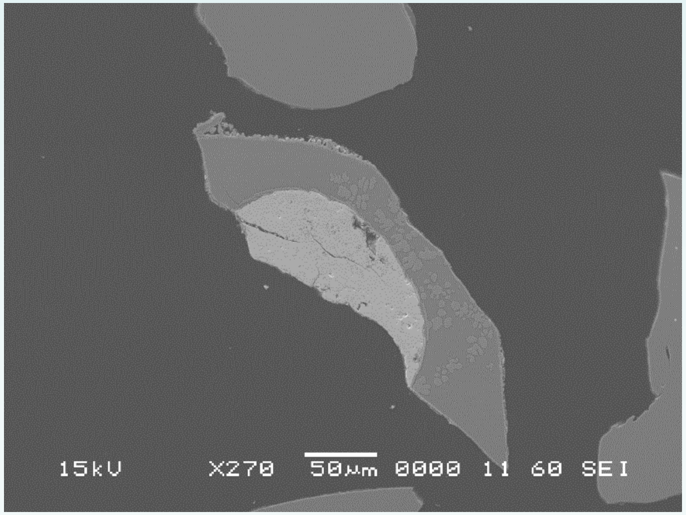
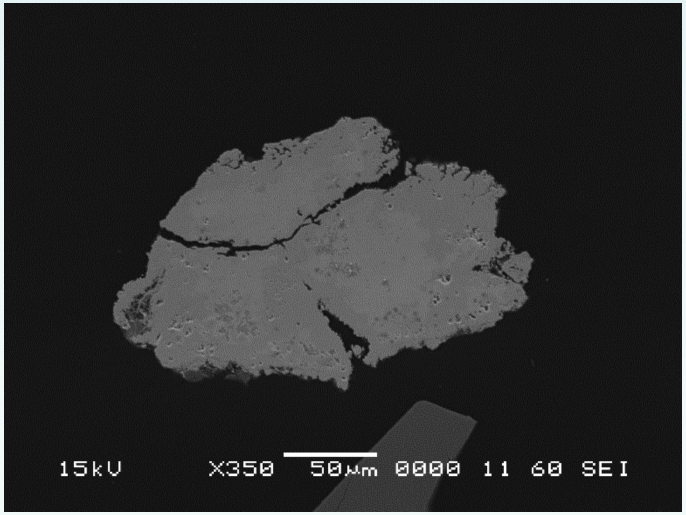
SEM Analyses

Sample sized -250+180 µm



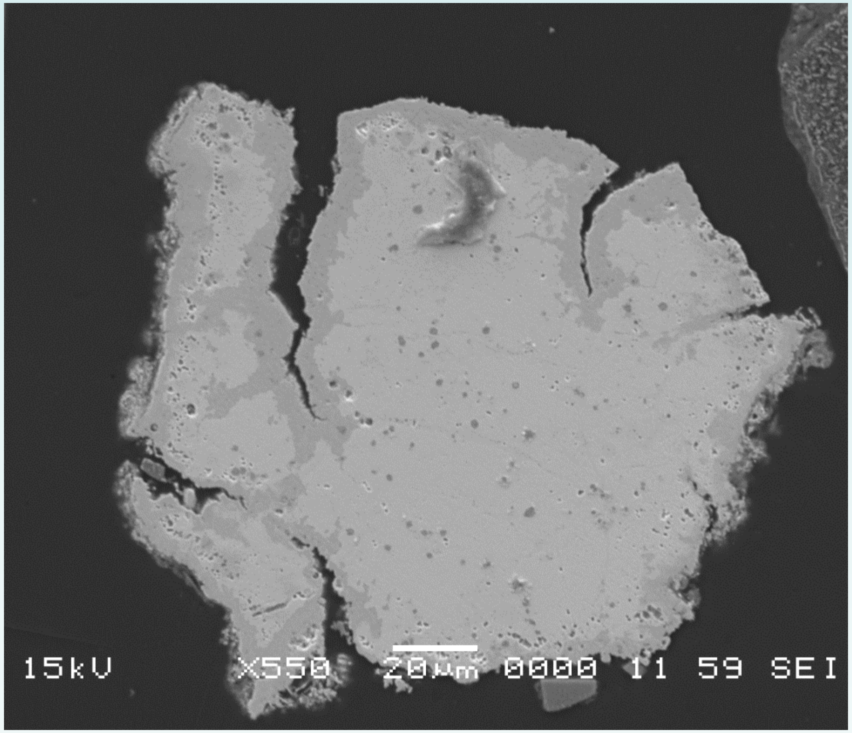


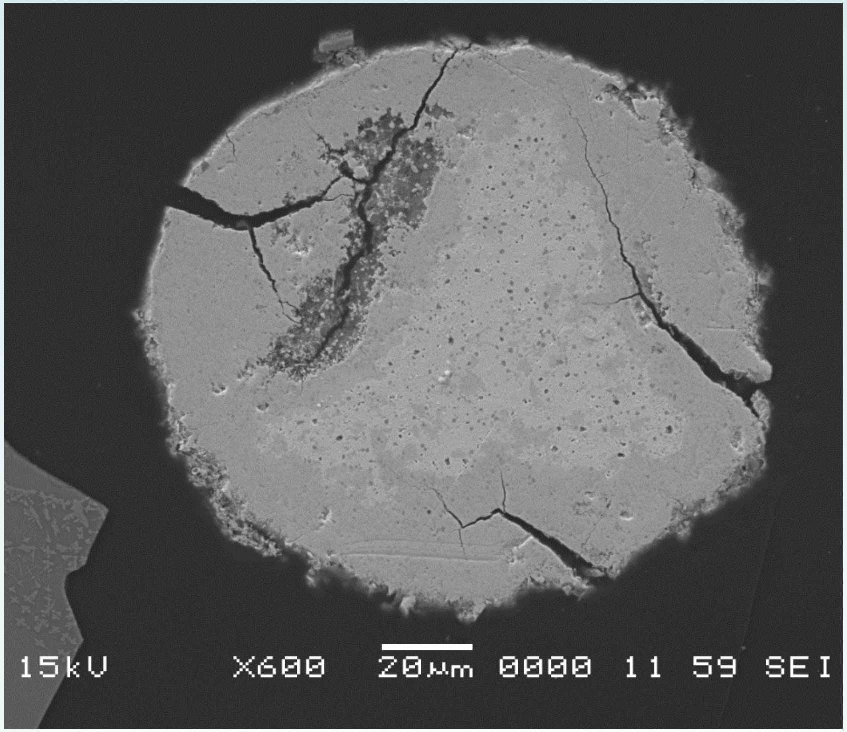




SEM Analyses

Sample sized -250+180 µm





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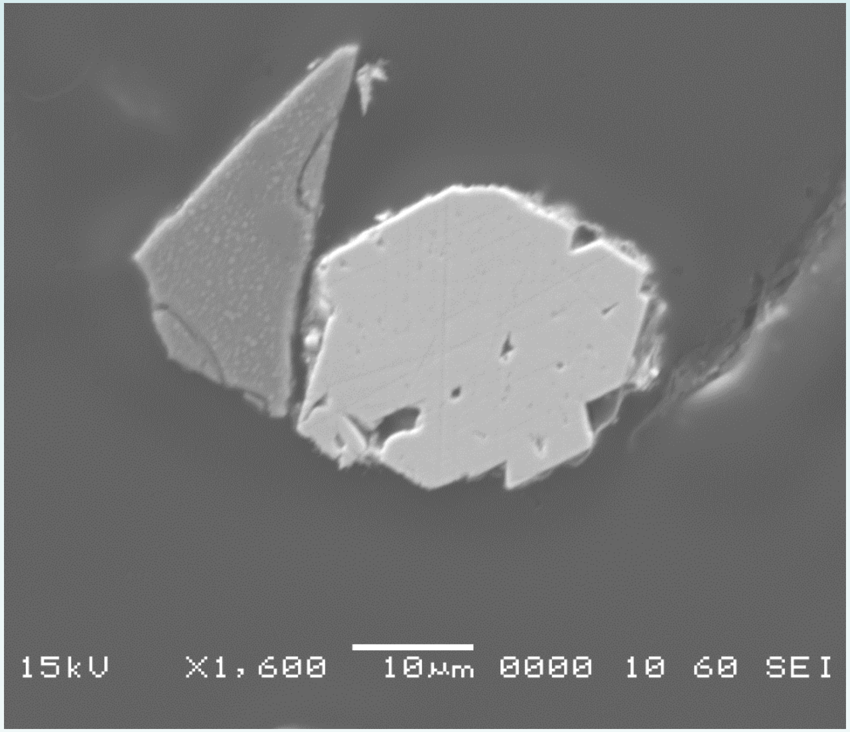
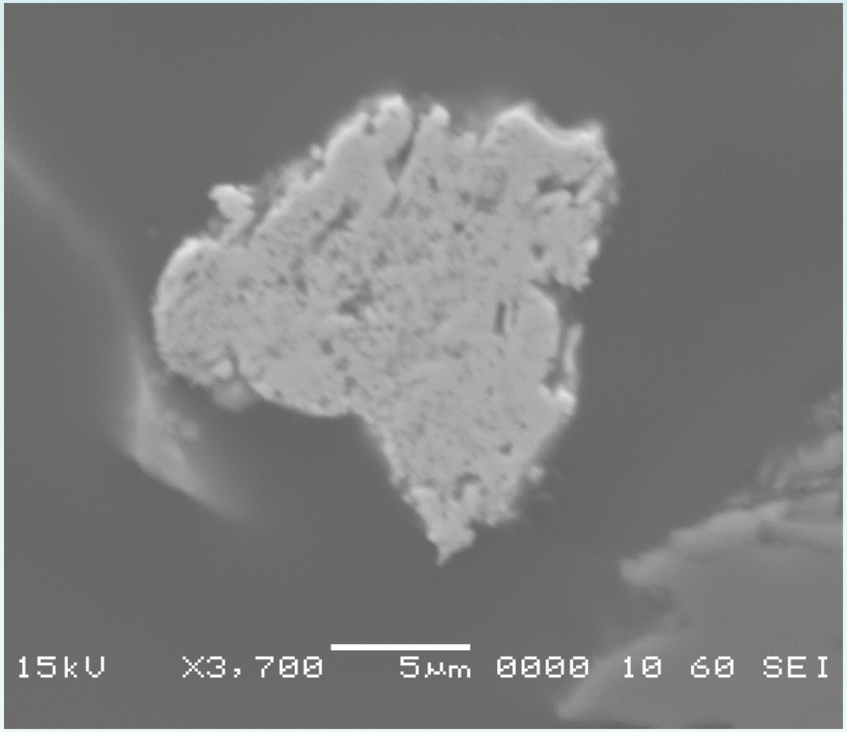
SEM Analyses

Sample sized -20 µm





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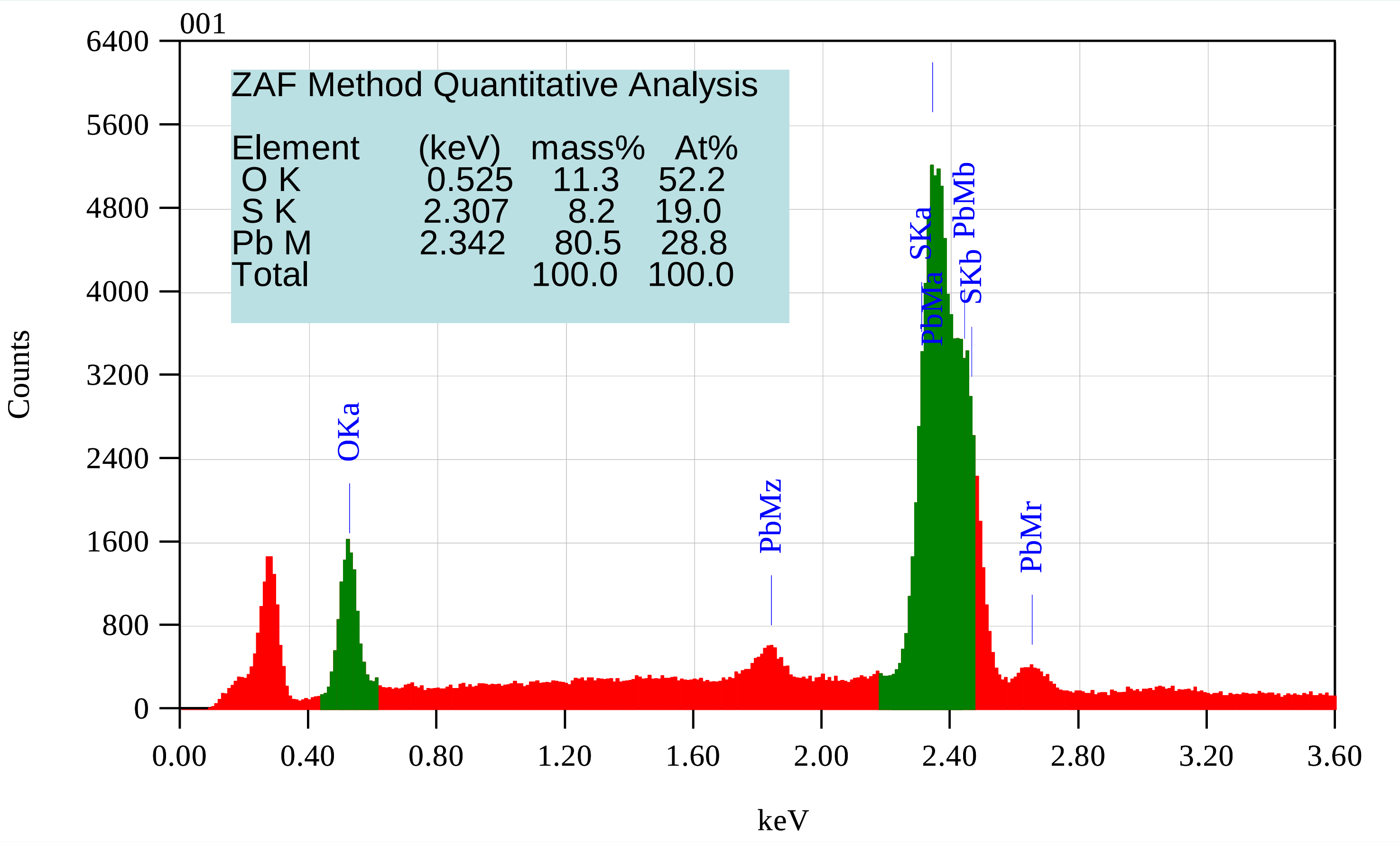
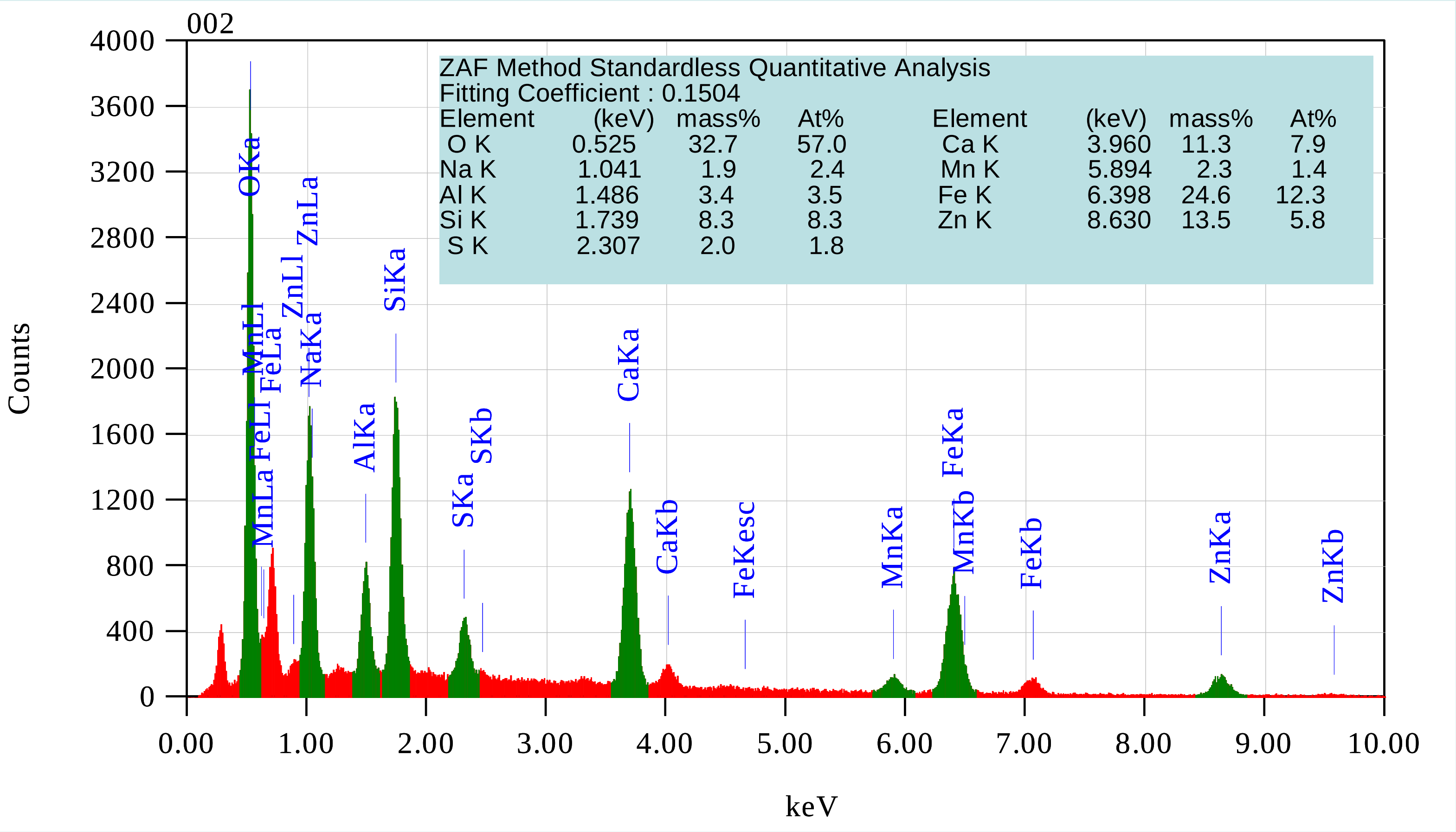
Spectral analysis of nodules

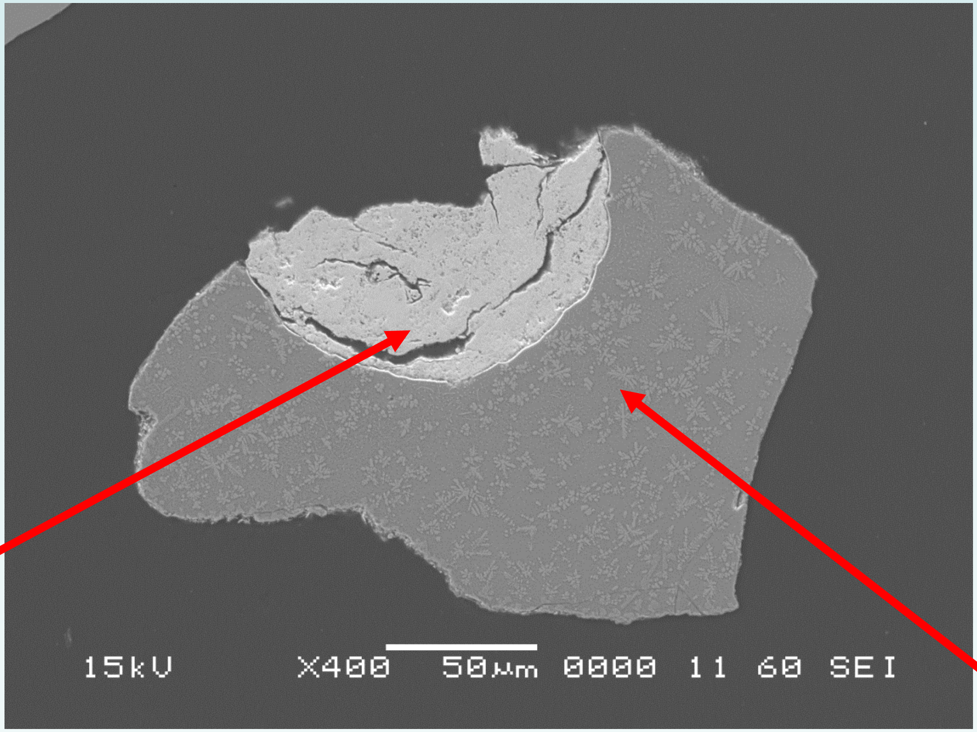


These results suggest that the compound formed is likely to be metallic lead and its oxidation products possibly PbO.$PbSO_4$ (monobasic lead sulfate, larnachite) which would have elemental ratios of 2:1:5 (Pb:S:O). Larnachite had been previously also identified as a component of the slag by XRD

Spectral analysis of glassy phase



Location for significant trace elements

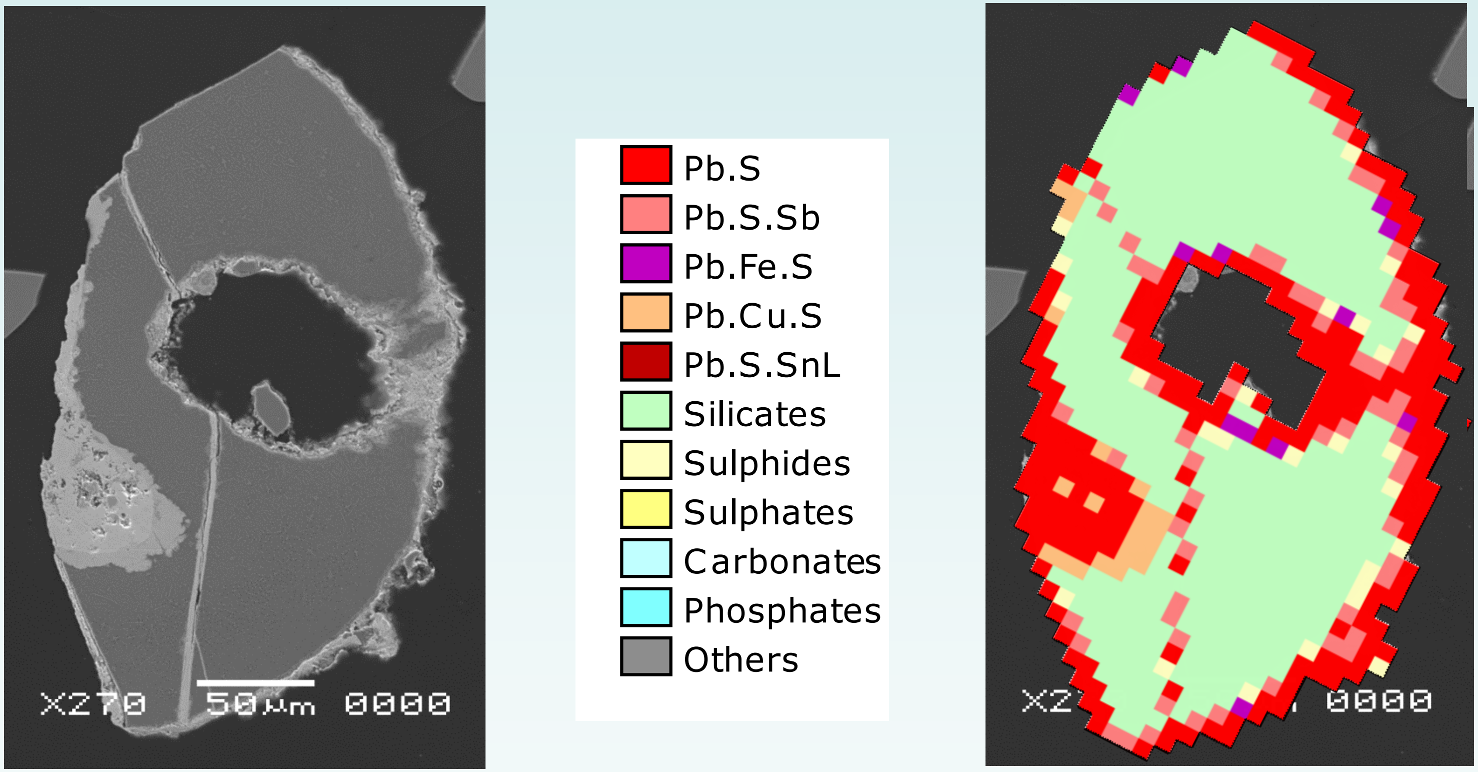


Pb, Sb, As, Cd, Ag

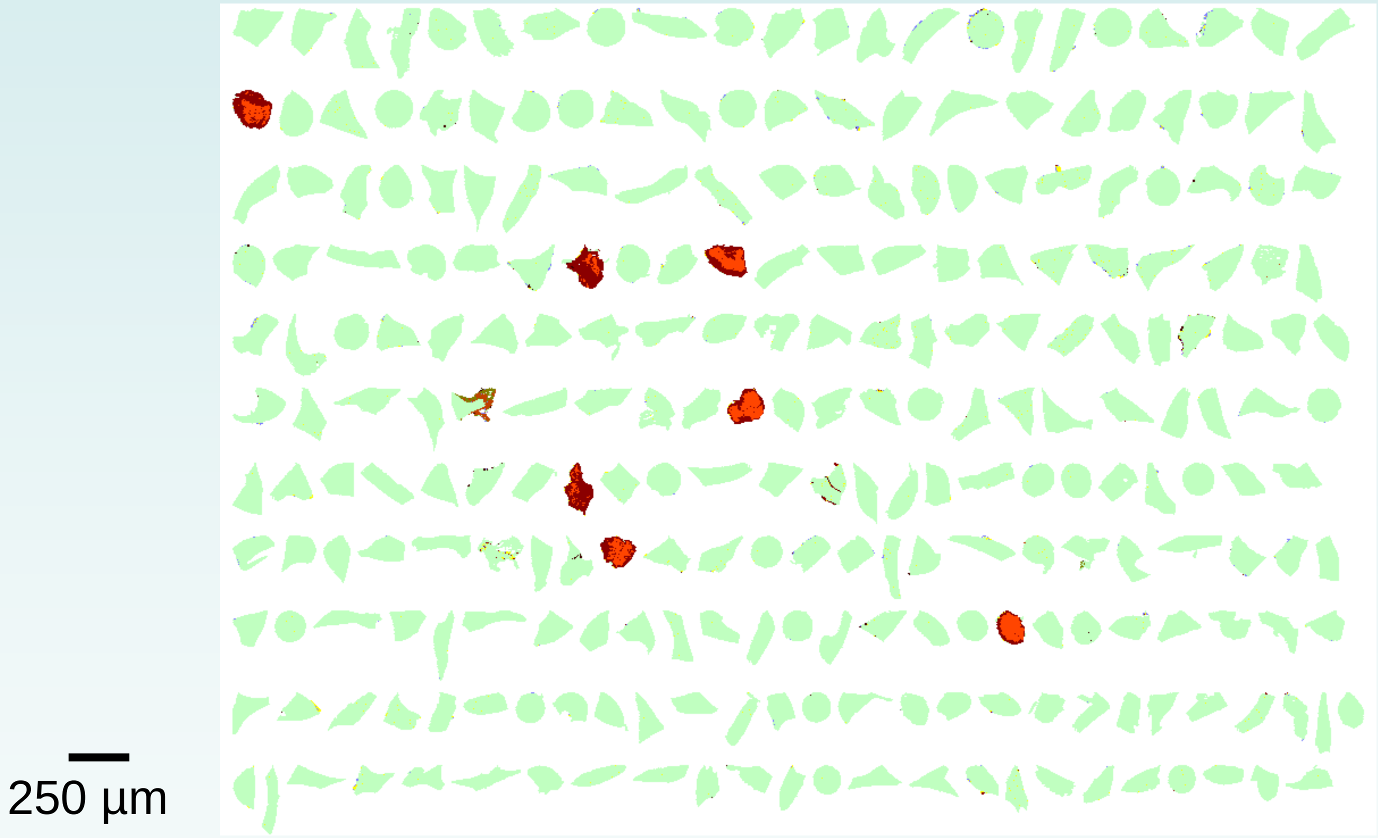
Zn

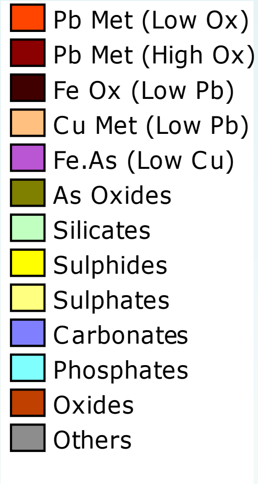
Availability of toxic species to infiltrating fluids

QEMSCAN particle mapping

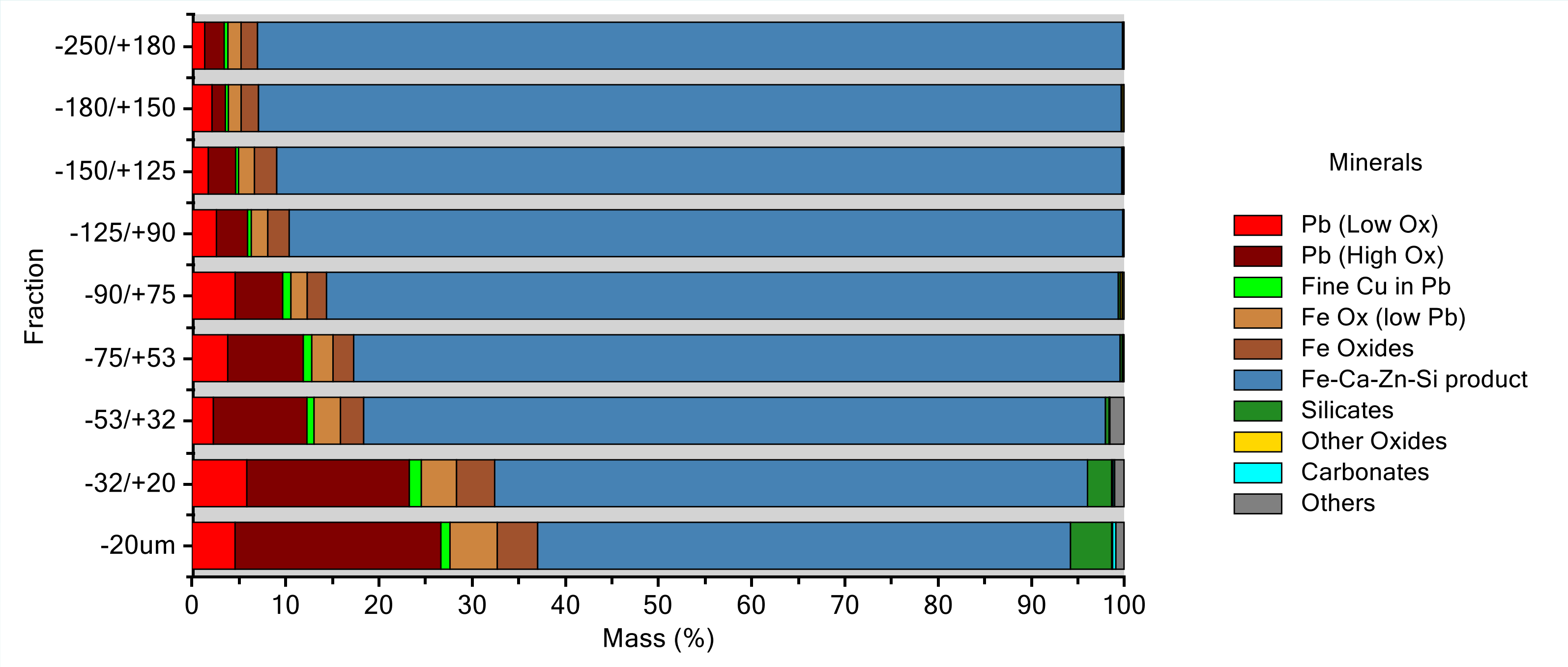


QEMSCAN particle mapping





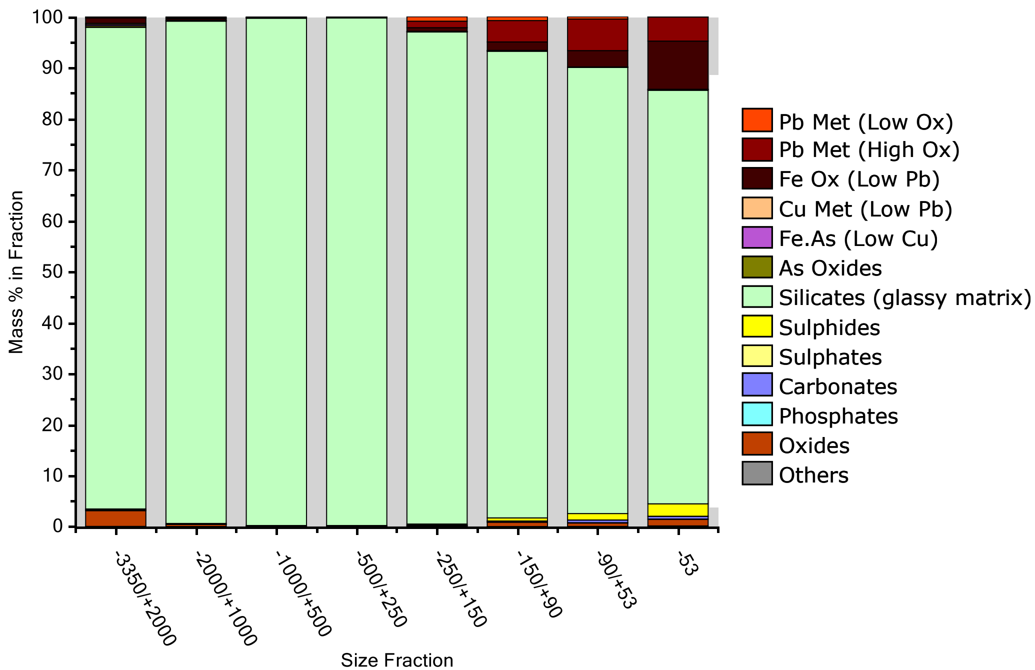
Modal Mineralogy



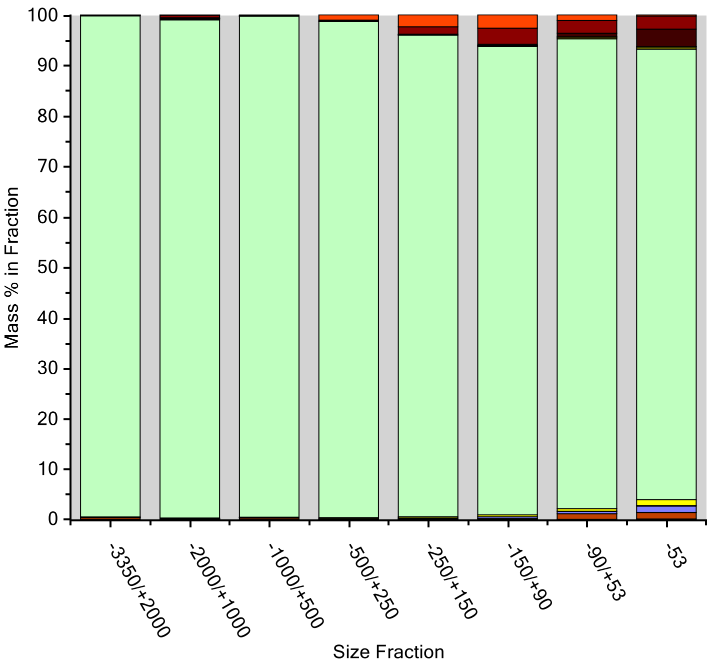
Outcomes: Mineral Mapping

- Slag contain ~1% Pb phases and 97% vitreous silicate glass

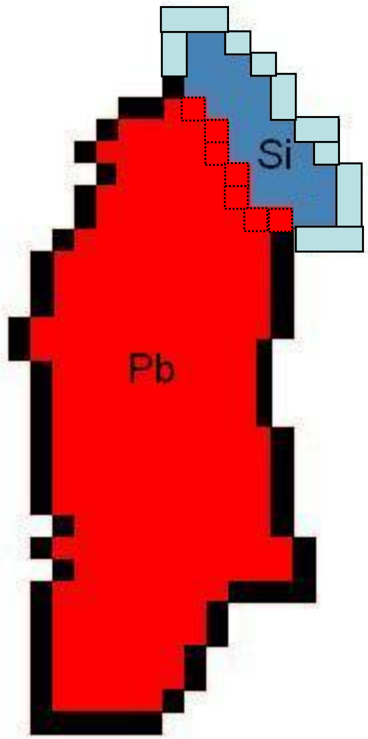
Creek Reserve (CR1)



Tredennick Oval (TN2)

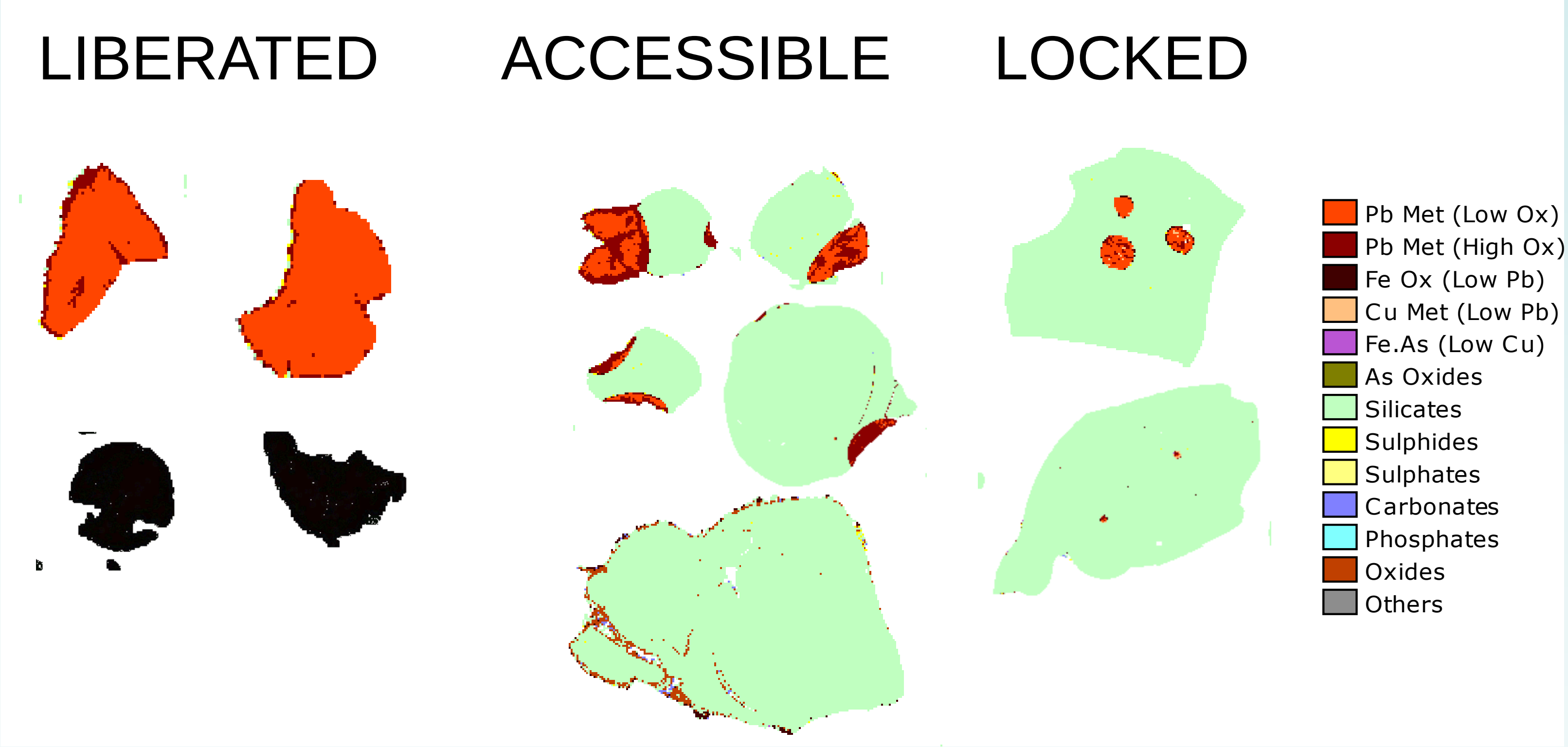


Phase Association Schematic



- Pb in contact with epoxy/background
- Pb in contact with Pb only
- Pb in contact with Si (or anything else other than Pb) but not epoxy
- Si in contact with Si (or anything else other than Pb)
- Si (or anything other than Pb) boundary with epoxy/background

ACCESSIBILITY MODEL



>90% reaction surface exposed

>9% reaction surface exposed

Reaction surface exposed limited to <9%

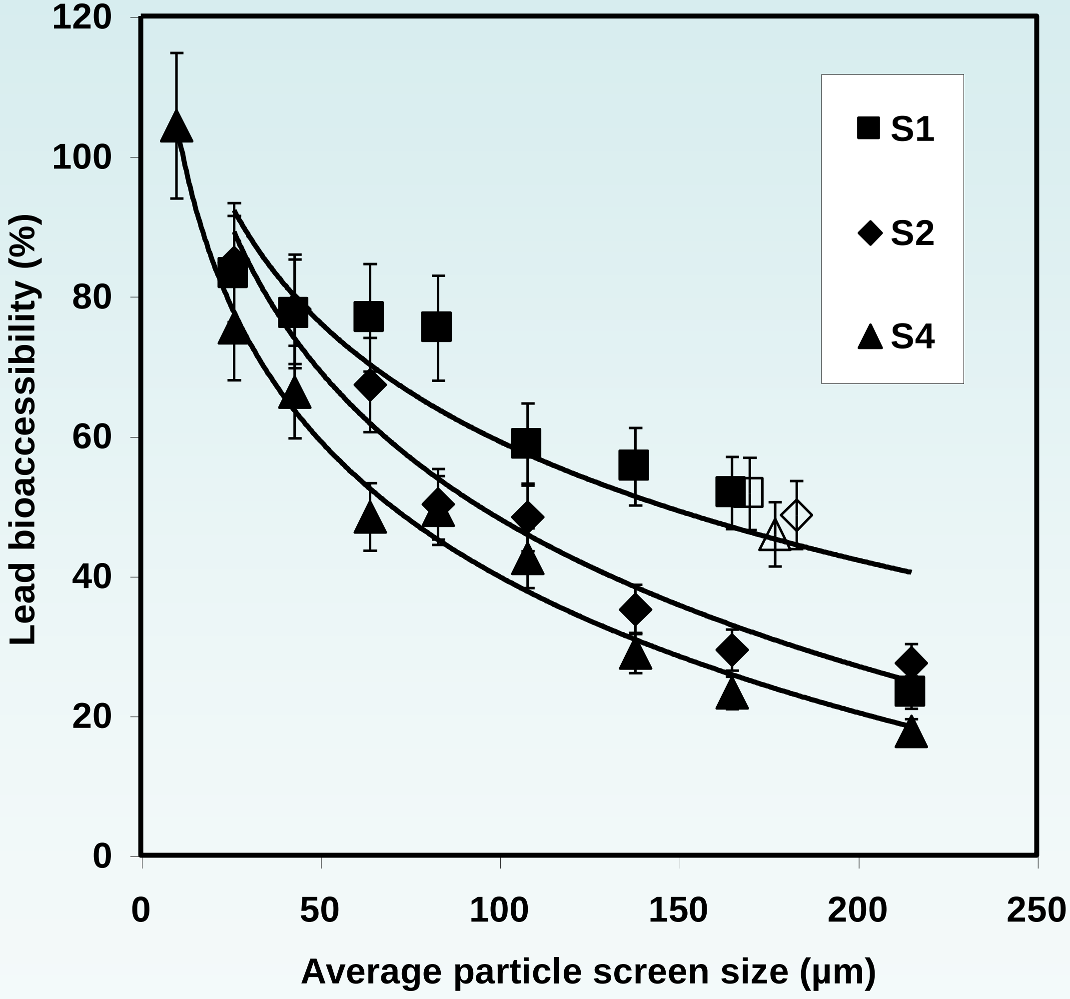
Size dependence of accessibility of Pb species in sample TN1 (%)

SIZE (µm)	LIBERATED	ACCESSIBLE	LOCKED	TOTAL
-3350/2000	6.83	72.39	20.77	100
-2000/1000	0.52	85.27	14.21	100
-1000/500	0.56	58.79	40.65	100
-500/250	86.04	11.50	2.47	100
-250/150	87.92	11.16	0.92	100
-150/90	78.72	20.25	1.03	100
-90/53	73.37	24.36	2.27	100
-53	37.66	59.02	3.32	100

Overall accessibility of Pb species in samples (-250 µm) (%)

SAMPLE	LIBERATED	ACCESSIBLE	LOCKED	TOTAL
CR1-2	76.7	21.8	1.5	100
CR1-3	56.4	41.0	2.6	100
CR2-2	69.6	25.6	4.8	100
CR2 (comb)	42.3	51.2	6.5	100
TN1-2	59.1	39.8	1.2	100
TN1 (comb)	65.3	30.7	4.1	100
TN2-2	79.7	19.0	1.4	100
TN2-3	56.0	43.0	1.1	100

Bioaccessibility of Pb species in slag samples (-250 µm) (%)



Overall accessibility of Pb species in samples (S1) (-250 µm) (%)

Screen Size (µm)	Pb LOW OX av.dia (µm)	Pb HIGH OX av.dia (µm)	Bio-accessibility %	**LIBERATED** (%)	ACCESSIBLE (%)	LOCKED (%)
-250+180	12	9	23.2	35.6	50.3	14.1
-180+150	16	12	51.8	40.4	42.2	17.4
-150+125	22	10	55.6	34.3	51.7	14.0
-125+90	17	12	58.7	39.7	50.0	10.4
-90+75	10	7	75.4	61.3	31.4	7.4
-75+53	11	8	76.8	55.9	38.5	5.6
-53+32	9	9	77.4	51.0	44.1	4.9
-32+20	5	7	83.1	62.3	34.9	2.9
-20	6	6	100.0	56.4	41.4	2.2

Conclusions on Accessibility

- Pb phases in the slags are mostly separate from the glassy slag matrix
- The Pb phases are generally unprotected from infiltrating fluids
- A consequence is that the Pb contained in the slags will be vulnerable to leaching over time

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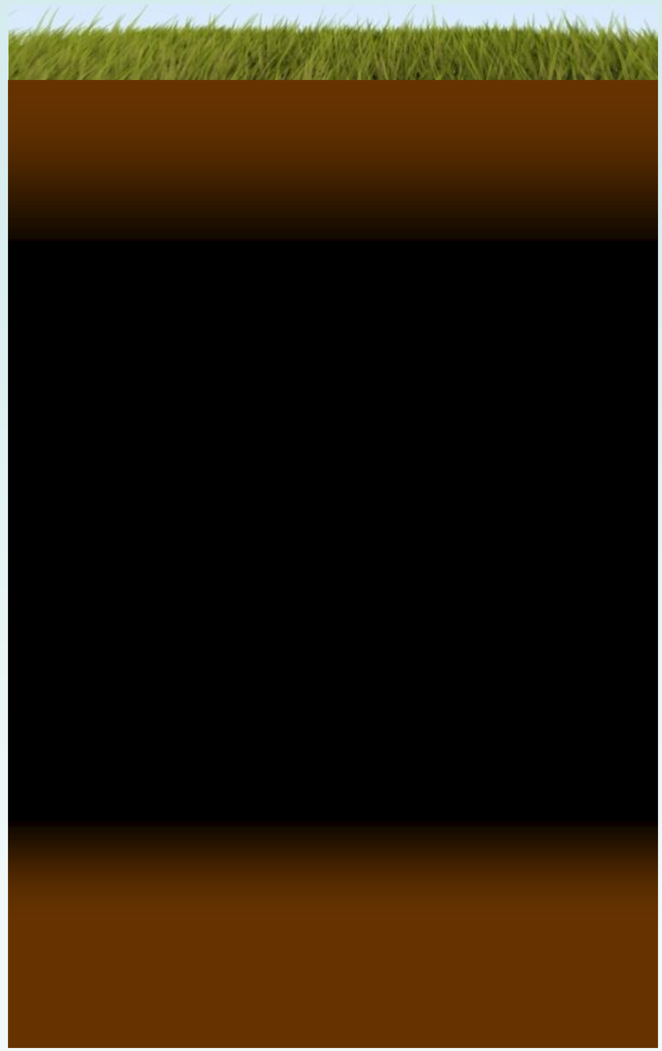
Sampling Program Extension

- Develop chemical soil profiles at three locations
- Sample at known slag emplacements
- Incrementally sample to subsoil below slag layer
- Chemically and morphologically analyse sample increments

Sampling and Analysis Methods

- Auger Sampling (100 mm Φ /100mm increments)
- Duplicate holes for each site approximately 1m apart
- Subsampling and sizing of increments
- Comprises 35 replicated samples
- Chemistry using X-Ray Fluorescence (XRF)
- Chemistry using ICP-AES (for Pb, Zn, Cu) and ICP-MS (for Ag, As, Cd, Sb,Se)
- Elemental mapping using electron dispersive spectrometry (EDS)

Generic soil/slag infill profile



Grass (sometimes) and topsoil (sometimes) of varying thickness

Mixed soil/slag at interface

Slag only layer of varying thickness (400 – 600mm)

Mixed soil/slag at interface

Underlying subsoil or fill

Range of Pb and Zn values measured

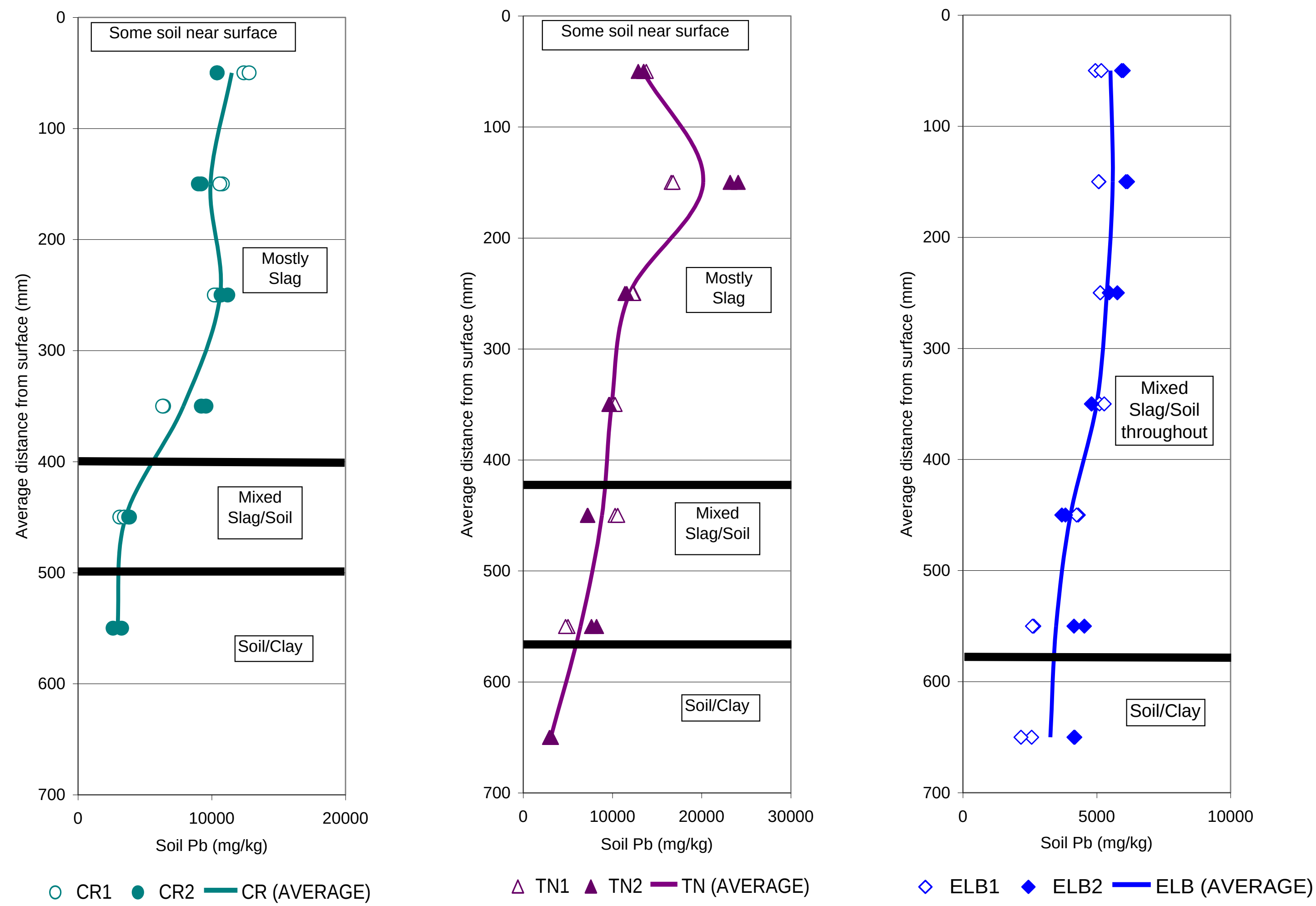
- Pb

  1785 – 17,100 ppm

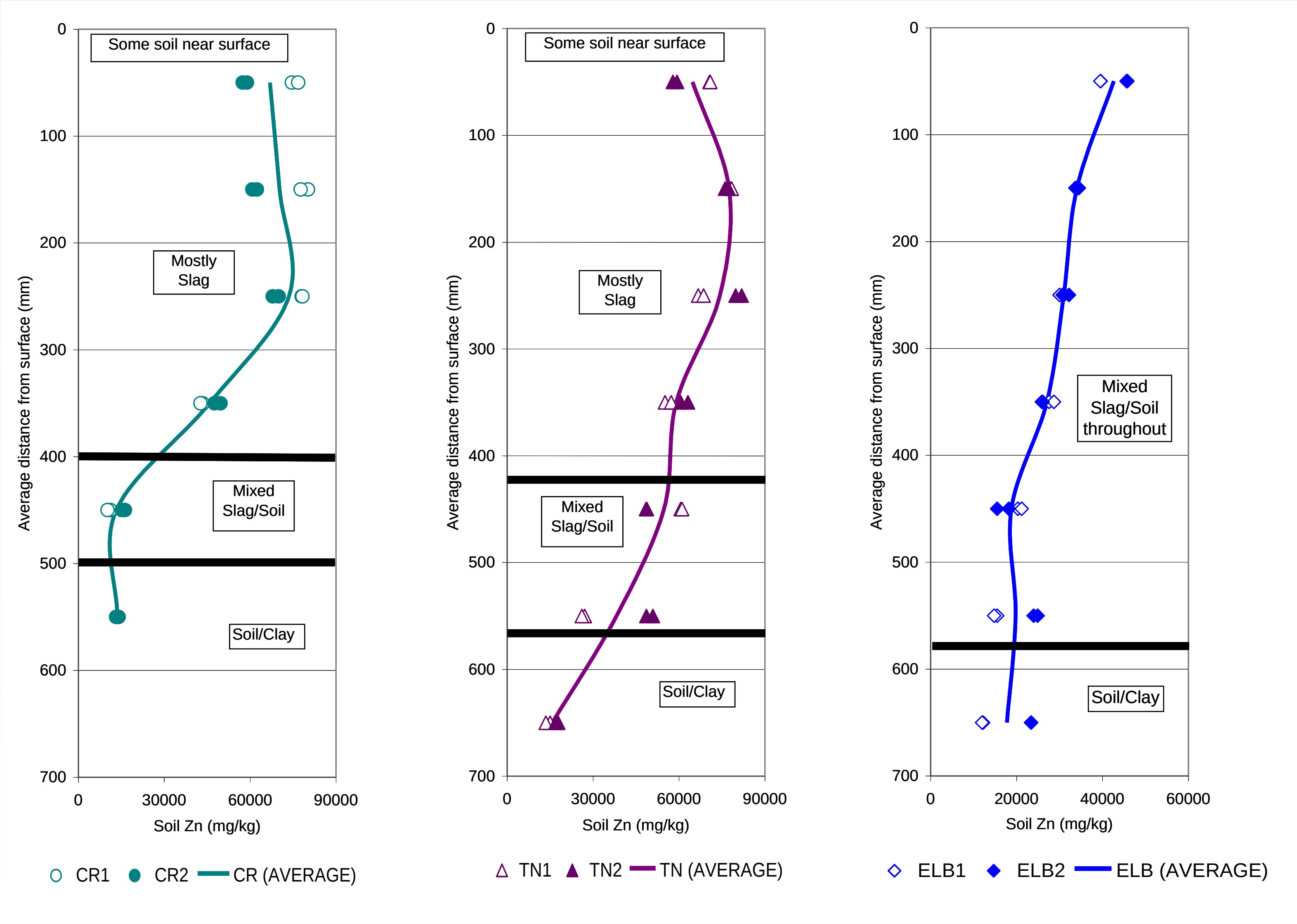
- Zn

  10,700 – 80,850 ppm

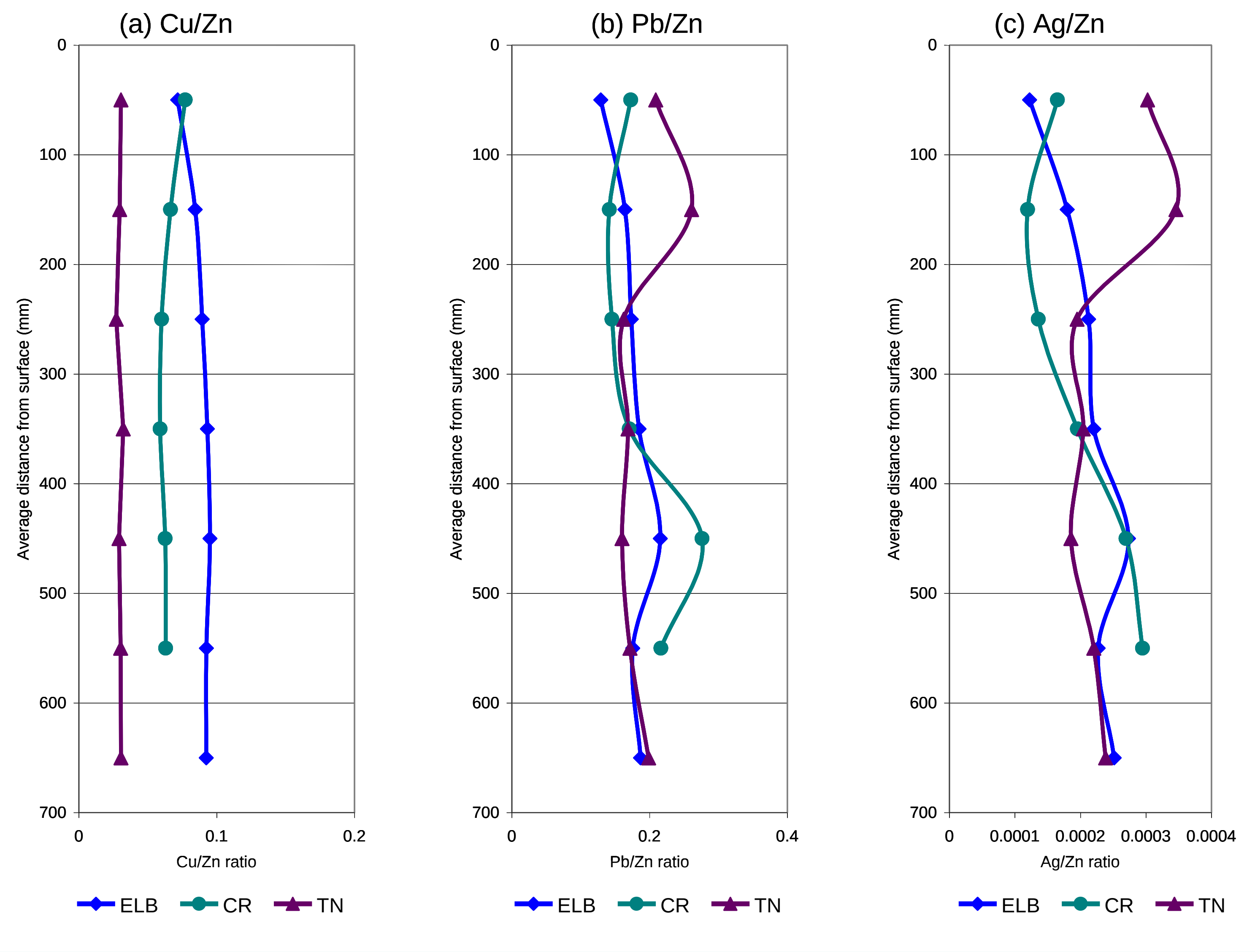
Slag/soil lead (Pb) profiles



Slag/soil zinc (Zn) profiles



Slag/soil elemental ratio profiles



Significance of the soil/slag profile

- Contaminant values are very high when compared to ANZECC soil health investigation levels (HILs)
  - Pb 300 ppm (homes) ; 600 ppm (parks)
  - Zn 7000 ppm (homes) ; 14000 ppm (parks)
- Pb is ~1% of the total material
- Pb (and associated elements) appear to be leaching out of the slag
- Zn (and likely other elements in the glass) appear to be relatively conserved

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Where to from here?

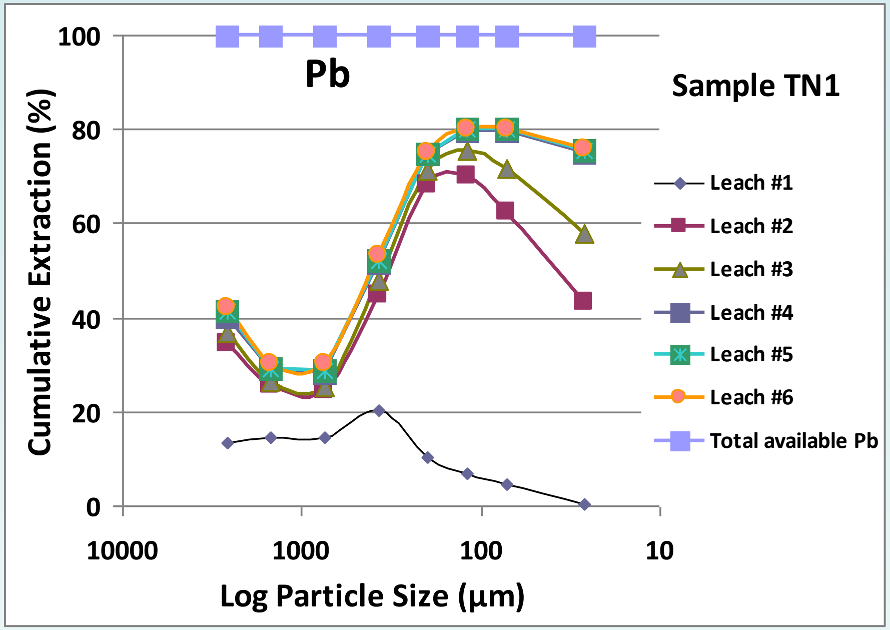
- Leach analysis of these stratigraphically collected slag samples from three selected locations

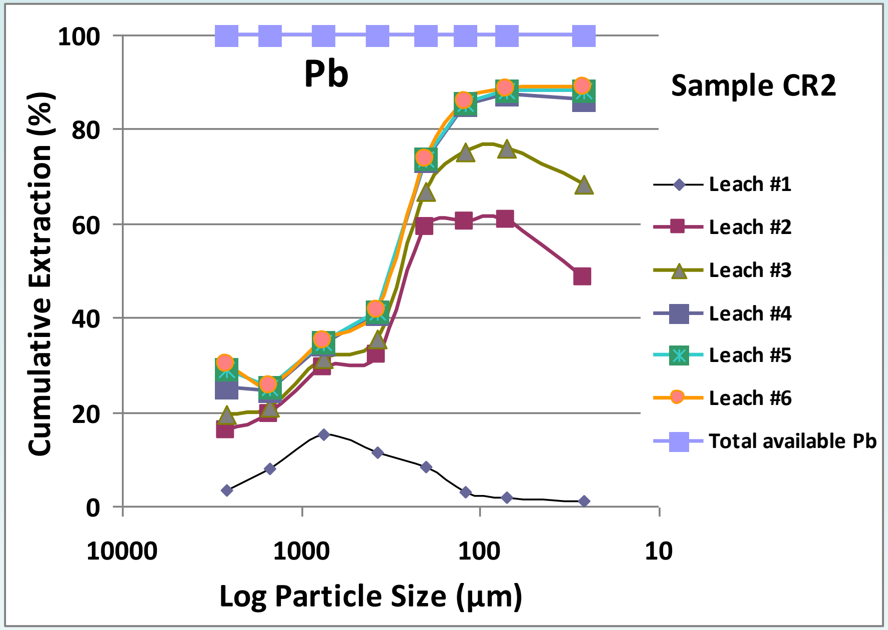
Sequential Leach Extraction for heavy metals :

Fraction	**Leaching Agent**	**pH**
Mobile	1M NH_4NO_3	~6-7
Easily dissolved*	1M NH_4OA_C	6.0
Bound to Mn oxides	0.1M HNO_3-HCl + 1M NH_4OA_C	6.0
Bound to organic matter	0.025M NH_4-EDTA	4.6
Bound to poorly crystalline Fe oxides	0.2M NH_4-Oxalate	3.25
Bound to crystalline Fe oxides	0.1M ascorbic acid+0.2M NH_4-Oxalate	3.25
Residual heavy metals	“near” total digestion conc HCl/HNO3	

***includes exchangeable fraction and occluded carbonates**

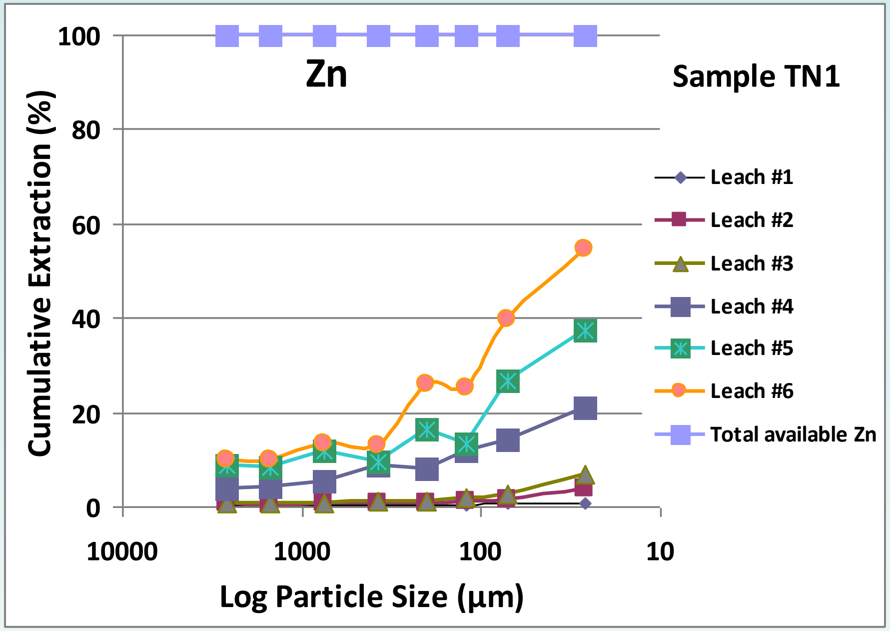
Sequential leach outcomes

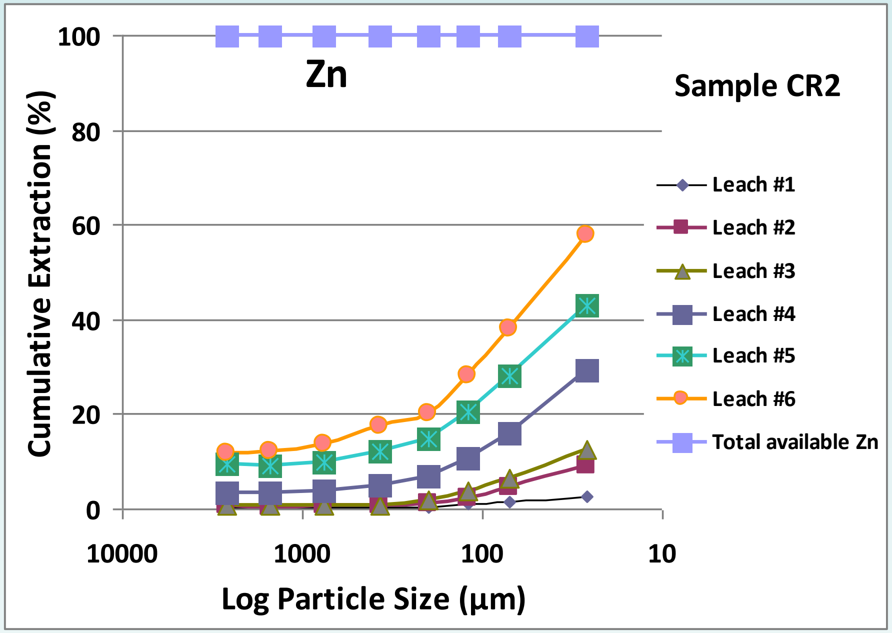




1. **Mobile heavy metals**
2. **Easily dissolved heavy metals**
3. Heavy metals bound to Mn oxide
4. Heavy metals bound to organic compounds
5. Heavy metals bound to poorly crystalline Fe oxides
6. Heavy metals bound to crystalline Fe oxides
7. Residual heavy metals

Sequential leach outcomes





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Leach outcomes for the composite sample (-3.35mm)

(cumulative extraction %)

Composite sample	Leach #1	Leach #2	Leach #3	Leach #4	Leach #5	Leach #6	Leach #7
CR1 (Pb)	**11.8**	**29.3**	**32.0**	**36.2**	**36.7**	**37.2**	**100.0**
TN1 (Pb)	**15.2**	**31.5**	**33.2**	**36.4**	**36.7**	**37.8**	**100.0**
CR1 (Zn)	**0.3**	**0.8**	**1.0**	**4.4**	**11.0**	**15.0**	**100.0**
TN1 (Zn)	**0.2**	**0.6**	**0.8**	**6.0**	**10.9**	**13.4**	**100.0**

- ~30% of the Pb in the composite samples was mobile or easily dissolved, this is compared to only ~0.7% of the Zn.

Leach outcomes for the composite sample

(cumulative extraction %)

Composite sample	Leach #1	Leach #2	Leach #3	Leach #4	Leach #5	Leach #6	Leach #7
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TN1 (Zn)	**0.2**	**0.6**	**0.8**	**6.0**	**10.9**	**13.4**	**100.0**

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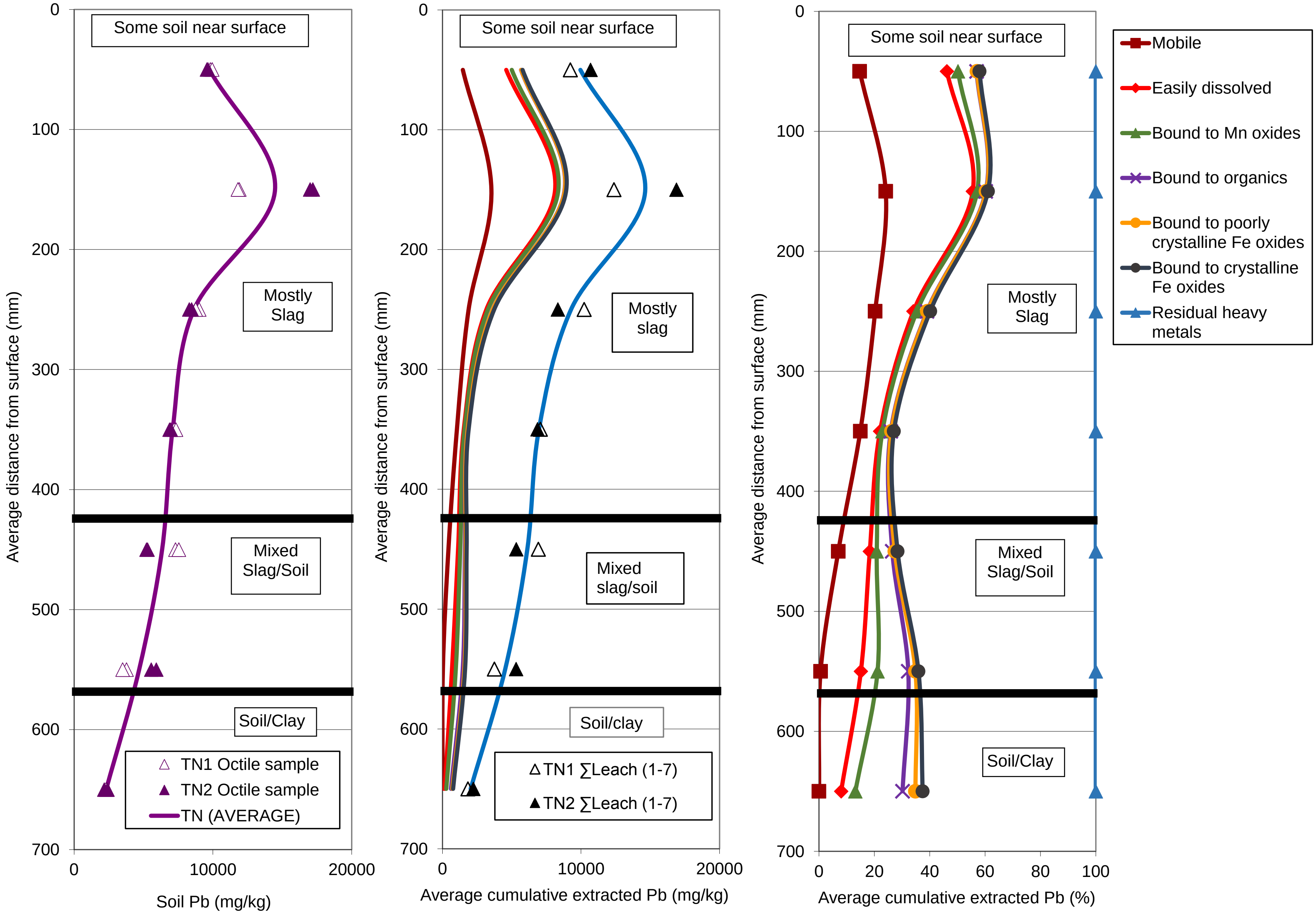
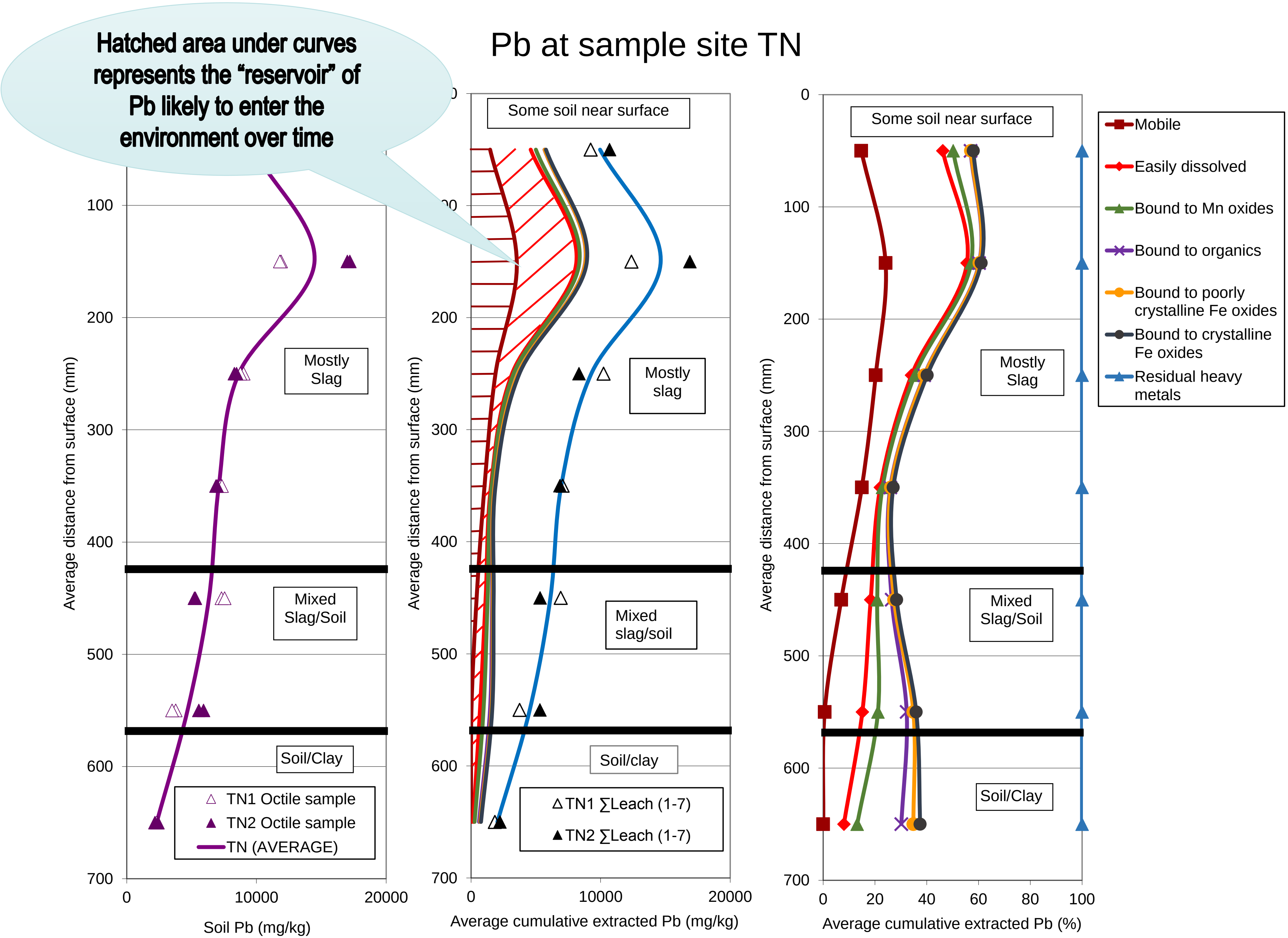
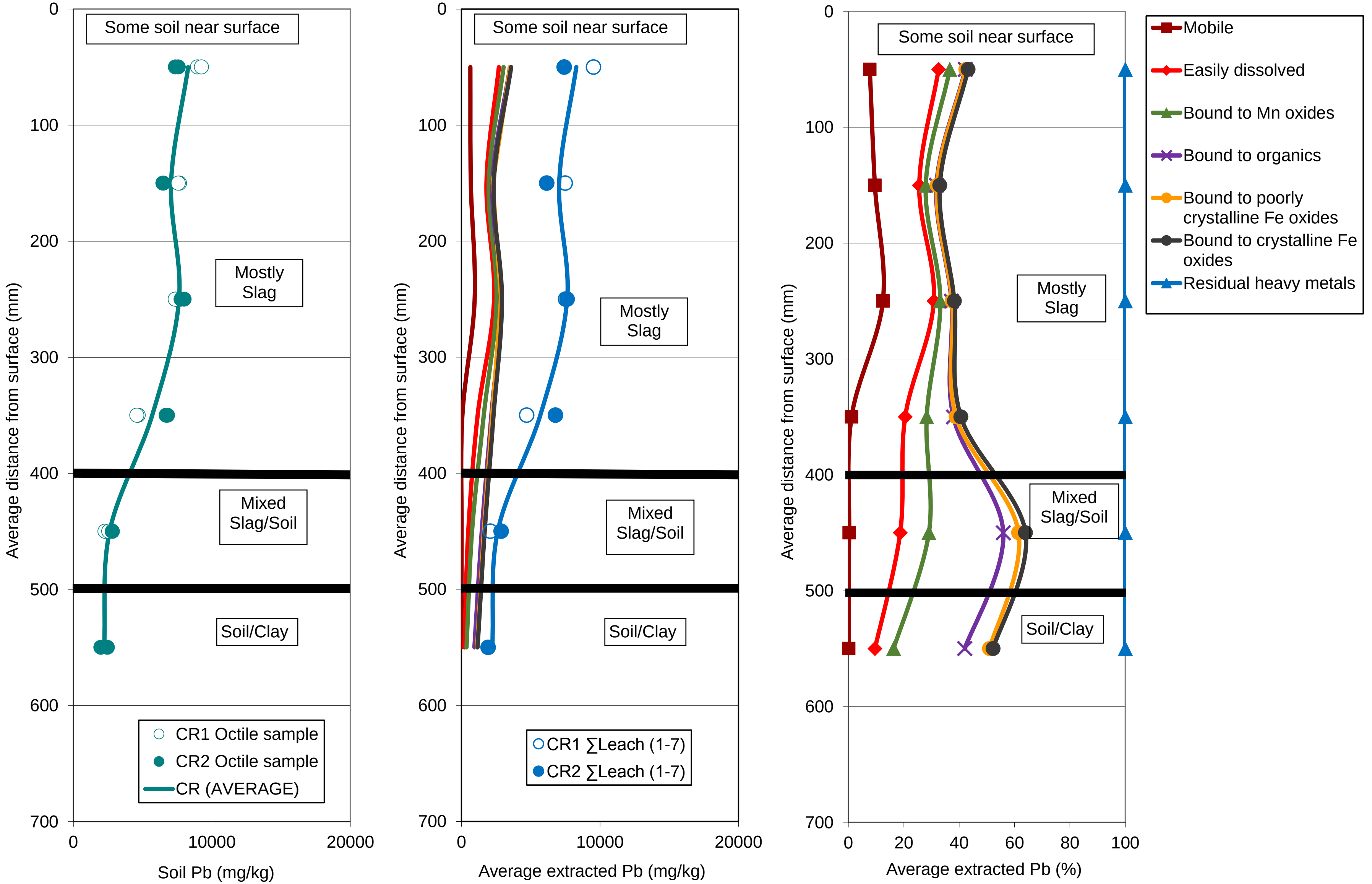
Pb at sample site TN



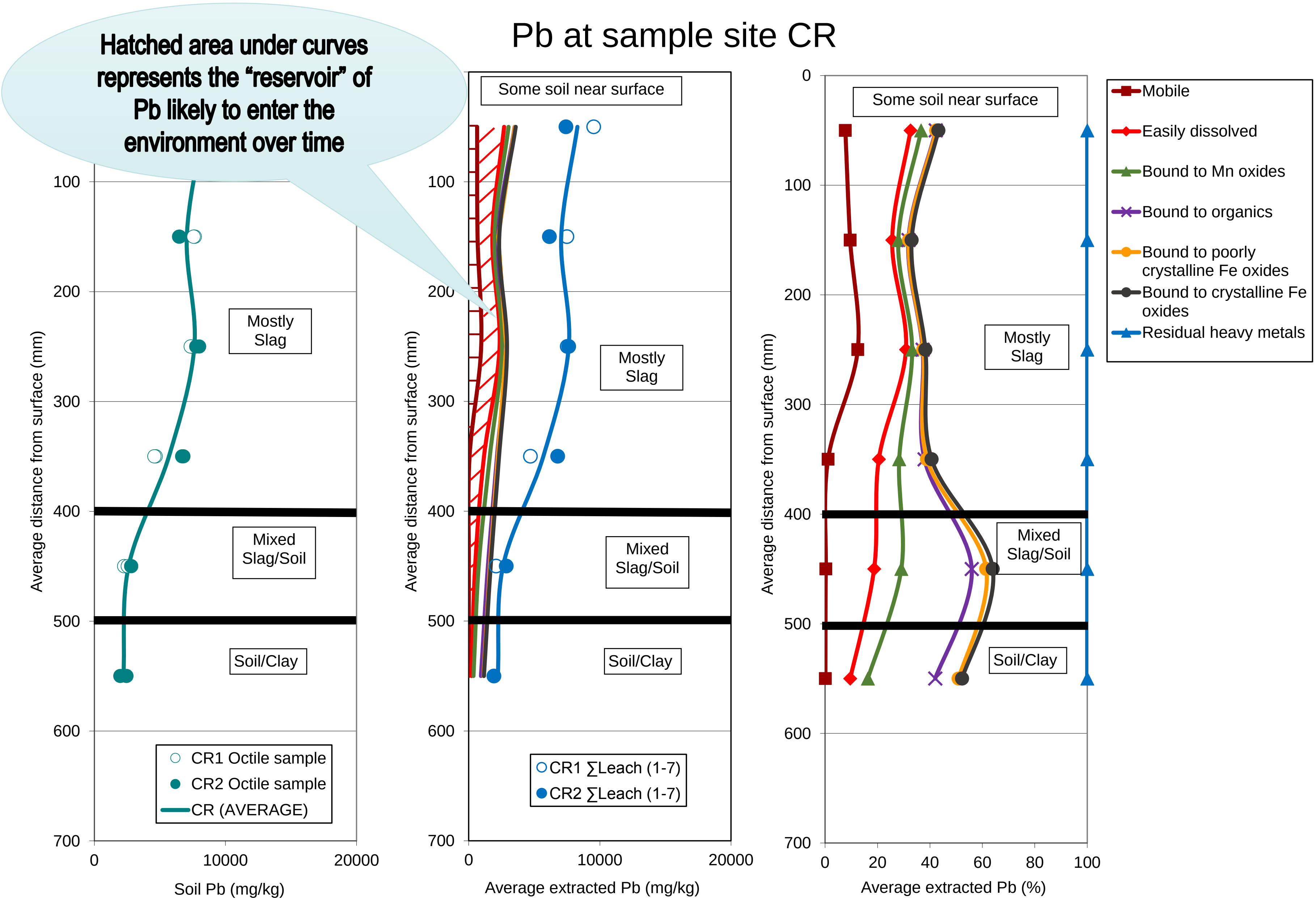
Pb at sample site TN

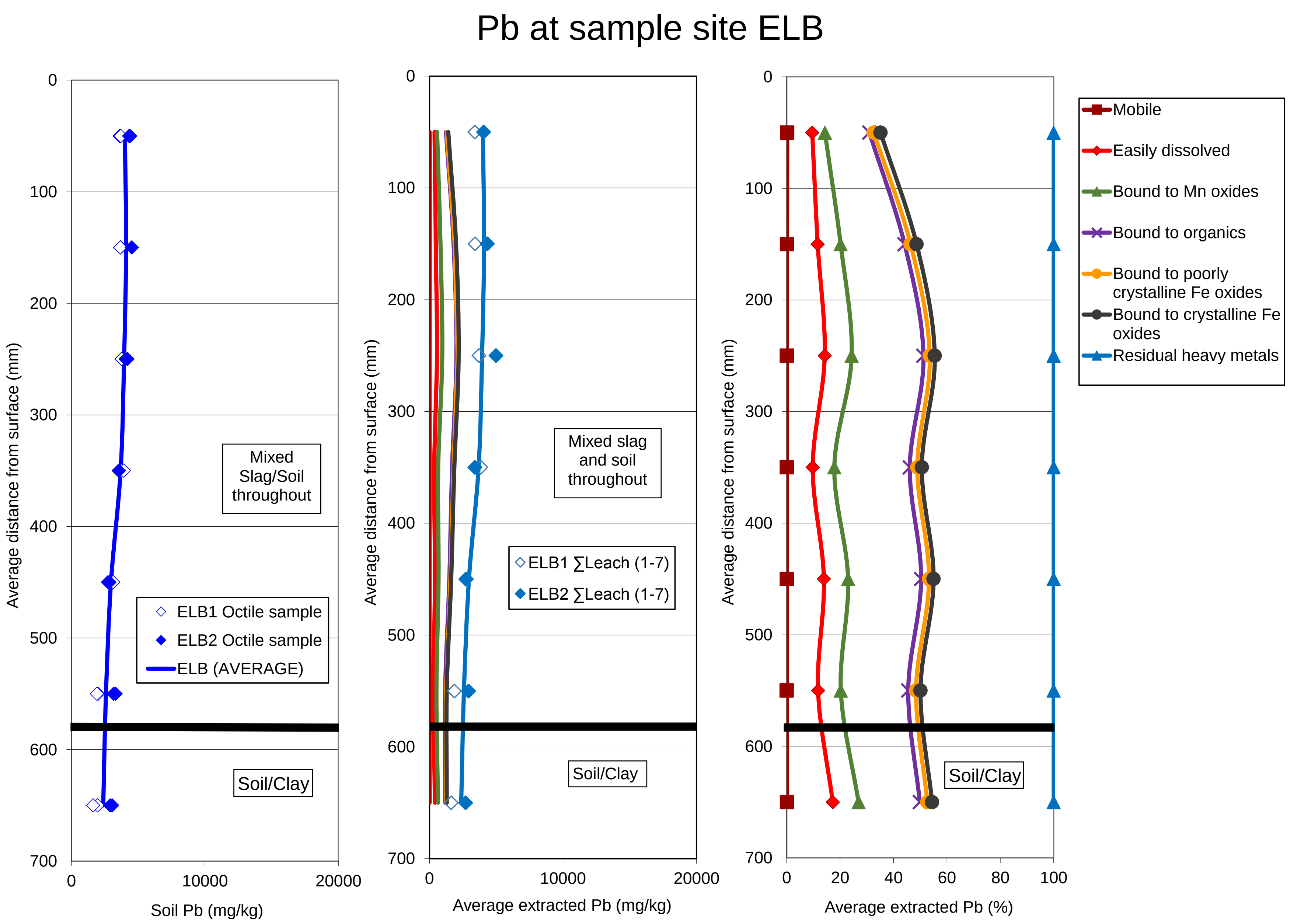


Pb at sample site CR

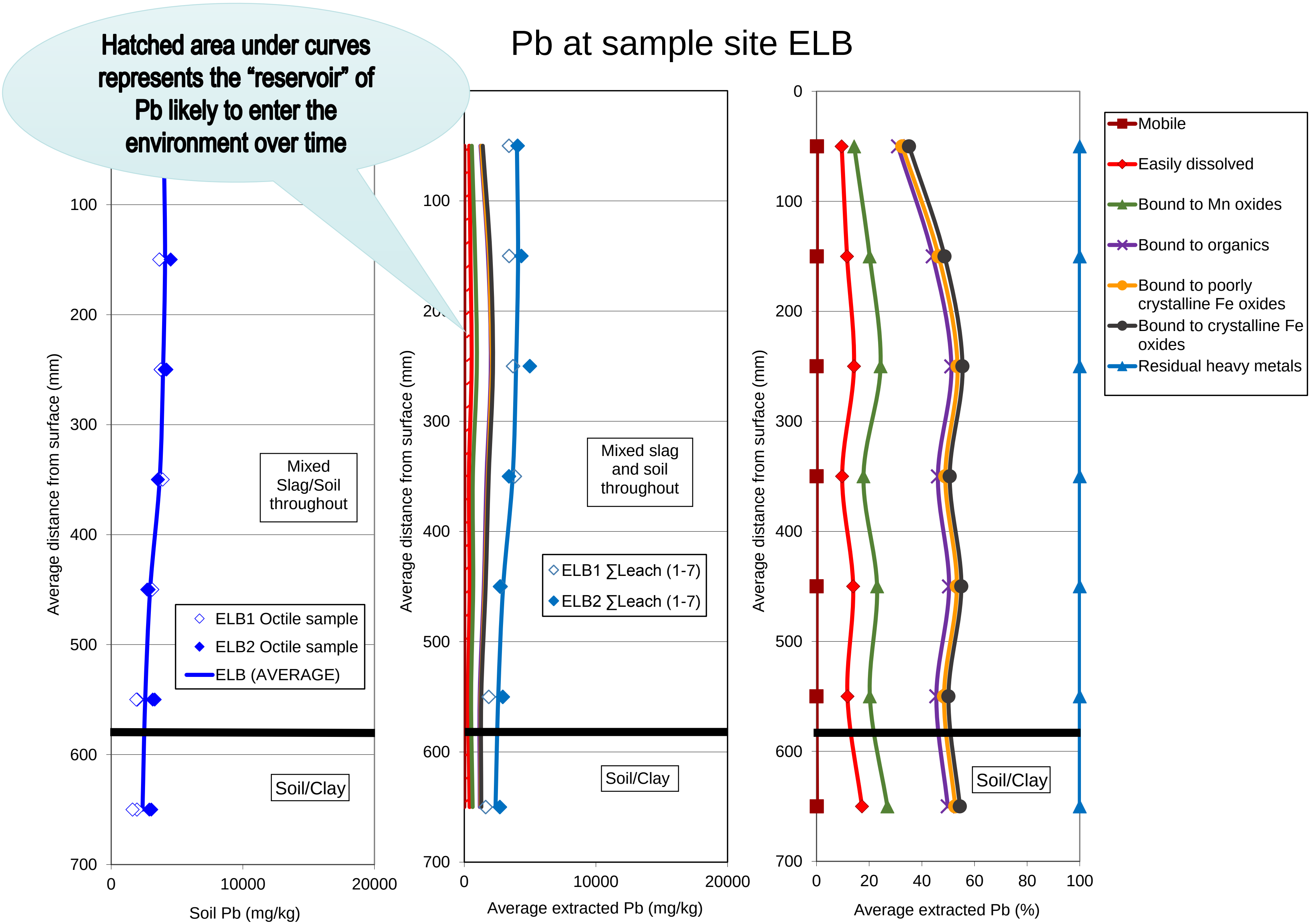


Pb at sample site CR





Pb at sample site ELB
Average distance from surface (mm)
Soil Pb (mg/kg)
Mixed Slag/Soil throughout
ELB1 Octile sample
ELB2 Octile sample
ELB (AVERAGE)
Soil/Clay
Average extracted Pb (mg/kg)
Mixed slag and soil throughout
ELB1 ∑Leach (1-7)
ELB2 ∑Leach (1-7)
Soil/Clay
Average extracted Pb (%)
Soil/Clay
Mobile
Easily dissolved
Bound to Mn oxides
Bound to organics
Bound to poorly crystalline Fe oxides
Bound to crystalline Fe oxides
Residual heavy metals



Pb at sample site ELB
Hatched area under curves represents the "reservoir" of Pb likely to enter the environment over time
Average distance from surface (mm)
Soil Pb (mg/kg)
Mixed Slag/Soil throughout
ELB1 Octile sample
ELB2 Octile sample
ELB (AVERAGE)
Soil/Clay
Average extracted Pb (mg/kg)
Mixed slag and soil throughout
ELB1 ∑Leach (1-7)
ELB2 ∑Leach (1-7)
Average extracted Pb (%)
Mobile
Easily dissolved
Bound to Mn oxides
Bound to organics
Bound to poorly crystalline Fe oxides
Bound to crystalline Fe oxides
Residual heavy metals

Percentage of total Pb remaining in the soil column available to be easily transported into the environment

Sampling Locality	Mobile (%)	Mobile + Easily Dissolved (%)
TN	16.1	36.1
CR	7.8	27.0
ELB	0.1	8.4

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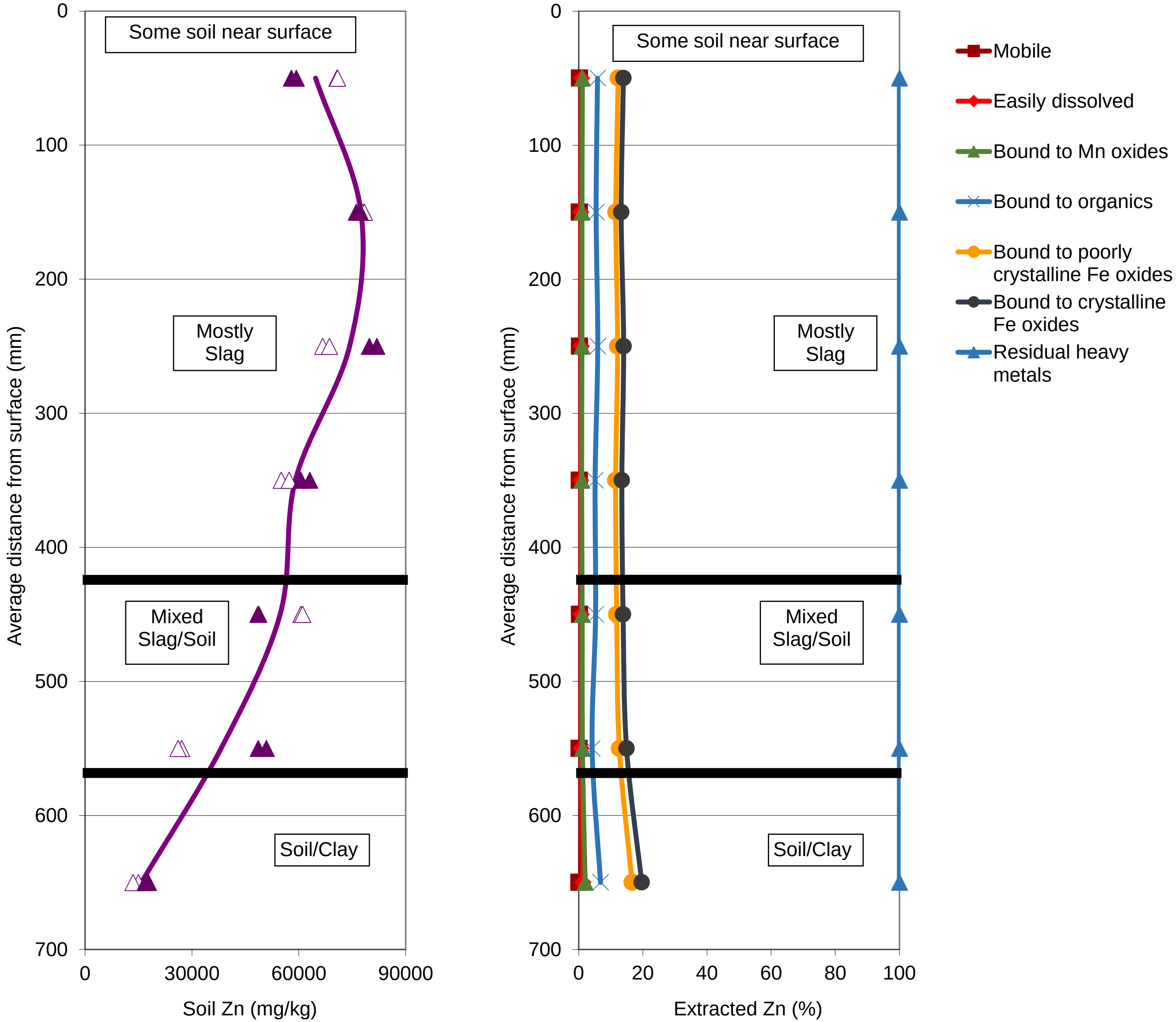
Zn at sample site TN



Outcomes from leach testing

The level of mobile and easily extractable Pb (and associated elements) in the smallest size fractions is high;

- Provides a partial explanation (along with surface area) for the high levels of bioaccessibility in the smallest slag fractions;
- Evidence of redistribution and attachment of Pb to other phases as an indicator of metal migration which has already occurred;
- Saline environment seems to have ensured high levels of Pb mobilisation;
- Overall results suggest that around 30% of the available Pb in the slags may migrate over time;
- Elements like Zn held as part of glassy slag are likely to continue to remain relatively immobile.

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Conclusions

- Given the work to date the hypothesis that the smelter slag is benign appears to be incorrect
- Mineralogical mapping of the slag materials shows clear evidence that most of the Pb in the slag is not contained within the siliceous glassy matrix but is liberated or accessible
- Liberation allows oxidation and leaching to more easily occur
- Evidence is present that migration of some of the Pb has already occurred and contaminants seem to be leaching from the slag into the underlying stratum

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Possible Future Work

- Examine potential leaching rate from existing slag deposits with different infiltrating fluids
- Look at potential for insitu stabilisation of heavy metals using phosphate solutions.
- Determine penetration of Pb (and other contaminants) deep into the subsurface below existing slag layers
- Look at mobility of lead (and other contaminants) in sub-surface layers

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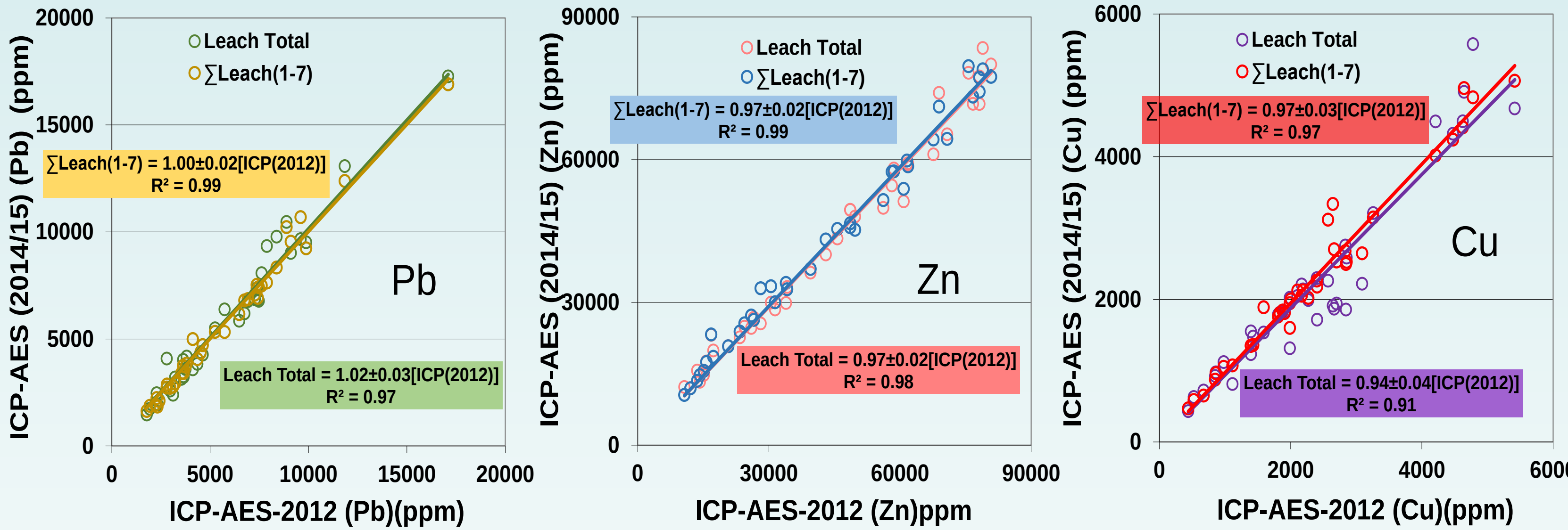
Policy Implications

- Slag contaminants are likely to continue leaching into the surrounding environment

- In-situ maintenance will be complex and ongoing

- Slag deposits occur on private as well as public property

- Determination of who is responsible for clean-up and rehabilitation is likely to be contentious.



Leach Total
∑Leach(1-7)
∑Leach(1-7) = 1.00±0.02[ICP(2012)]
R² = 0.99
Leach Total = 1.02±0.03[ICP(2012)]
R² = 0.97
Pb
ICP-AES (2014/15) (Pb) (ppm)
ICP-AES-2012 (Pb)(ppm)
0
5000
10000
15000
20000
Leach Total
∑Leach(1-7)
∑Leach(1-7) = 0.97±0.02[ICP(2012)]
R² = 0.99
Leach Total = 0.97±0.02[ICP(2012)]
R² = 0.98
Zn
ICP-AES (2014/15) (Zn) (ppm)
ICP-AES-2012 (Zn)ppm
0
30000
60000
90000
Leach Total
∑Leach(1-7)
∑Leach(1-7) = 0.97±0.03[ICP(2012)]
R² = 0.97
Leach Total = 0.94±0.04[ICP(2012)]
R² = 0.91
Cu
ICP-AES (2014/15) (Cu) (ppm)
ICP-AES-2012 (Cu)(ppm)
0
2000
4000
6000