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Assessment of the Mobility of Heavy Metals in the Unsaturated Zone at Small Arms Firing Ranges

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Overview

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  - Lysimeters
  - Synthetic Precipitation Leaching Procedure
  - Sequential Extractions
- Results
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  - Groundwater
- Summary
- Conclusions

Background

- Projectiles : 5.56-mm and 7.62-mm
  - Core:
    - Pb-Sb 98/2 (5.56 mm) or 90/10 (7.62 mmm)
    - 95% of the bullet mass
  - Jacket: Cu-Zn 90/10 (5%)
- Pb, Cu, Sb and Zn in the soils of stop berms above CCME industrial criteria
- May migrate vertically in the vadose zone, and eventually in the water table

Objective

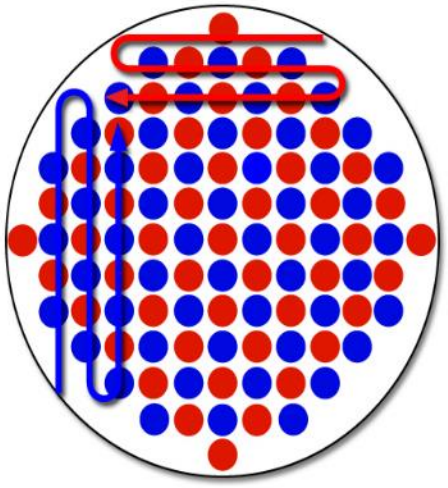
- Soil of stop berms would have to be remediated frequently (every month or so) according to CCME industrial soil criteria
- To perform appropriate risk assessment, information is needed on the mobility of the contaminants in the vadose zone and in groundwater in order for the restoration not to be performed :
  - Too often when strictly relying on industrial criteria
  - Too late when contamination has reached groundwater

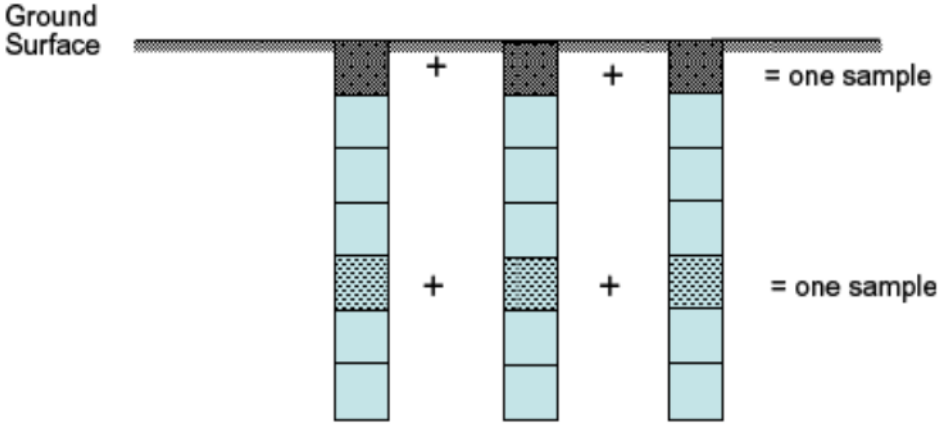
Methods

- Metal (Pb, Cu, Sb, and Zn) concentrations in stop berms surface and sub-surface soils
- Leaching potential of the sub-surface soil contaminants
  - Synthetic Precipitation Leaching Procedure
  - Sequential Extraction
- Metal concentrations *in situ* in the vadose zone
  - Gravimetric lysimeters (GL)
  - Suction cup lysimeters (SL)
- Metal concentrations in groundwater
  - Monitoring wells
- □

Soil Sampling

- Concentrations of heavy metals in the soils on the stop berm of 2 Small Arms Firing Range (SAFR)
  - Systematic multi-increment sampling strategy (SMISS) of the surface soils
  - Depth profiling
  - Total extraction procedure (e.g., USEPA method 3052)
  - Analysis by ICP-MS (e.g., USEPA method 6020A)





Synthetic Precipitation Leaching Procedures (SPLP)

- SPLP tests (EPA method 1312)
  - Collection of 0-15 and 0-30 cm depth samples using SMISS
  - SPLP extractant
    - H_2SO_4/HNO_3 60/40
    - pH 4.20
  - Soil/extractant 1/20
  - 18 hours
  - Rotary mixer
  - Resulting solution were filtered and analyzed for Cu, Pb, Sb, and Zn by ICP-MS
  - Results are compared with Health Canada Drinking Water Criteria (HCDWC)

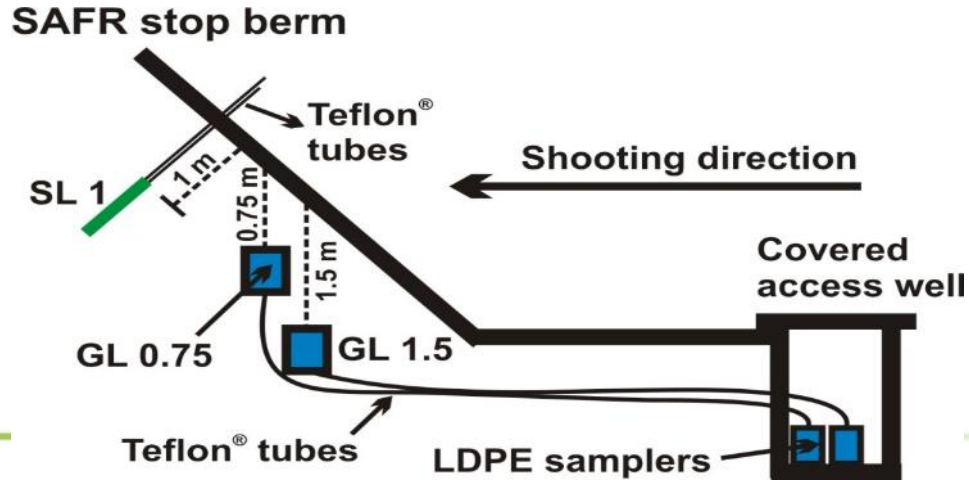
Sequential Extractions (Tessier protocol)

- Fraction of metals:
  - Exchangeable
  - Linked to carbonates
  - Linked to iron and manganese oxides
  - Linked to organic matter
  - Totally insoluble

- Used in the mining industry to perform environmental risk assessment
- Risk is considered high if fractions (1) and (2) are large
- Ongoing

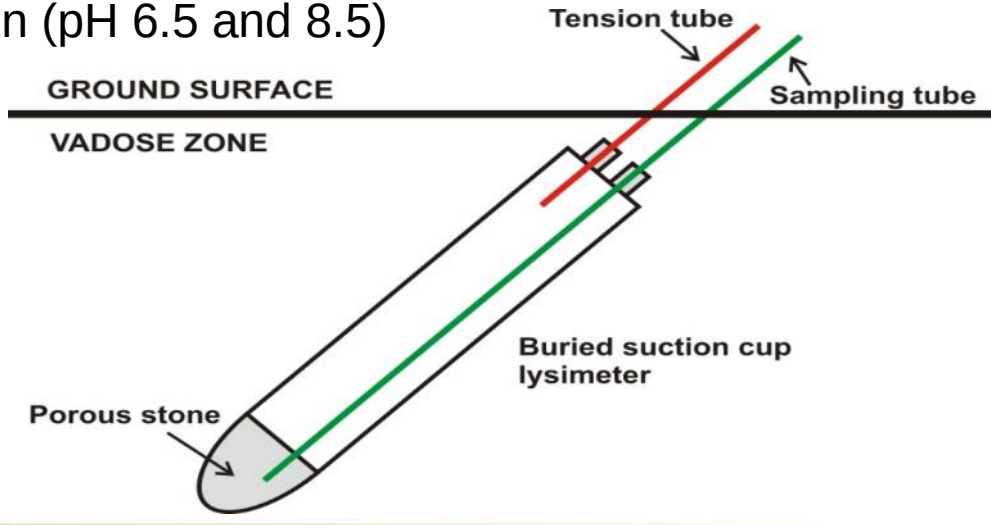
Gravimetric Lysimeters (GL)

- Disturb considerably the surrounding area
- Can be installed easily during range construction
- Max depth ~ 2 m
- Measure the total amount of metals leaching
- Adequate for all metals



Succion Cup Lysimeters (SL)

- Nylon, PVC or PTFE
- Easy to install on operating stop butts
- Minimal disturbance of soil
- Any depth (PTFE or PVC)
- 2 m bgs (nylon)
- Measure the dissolved metal concentration
- Not adequate for Sb and Cu
- Only nylon SL for Pb (any pH) and Zn (pH 6.5 and 8.5)

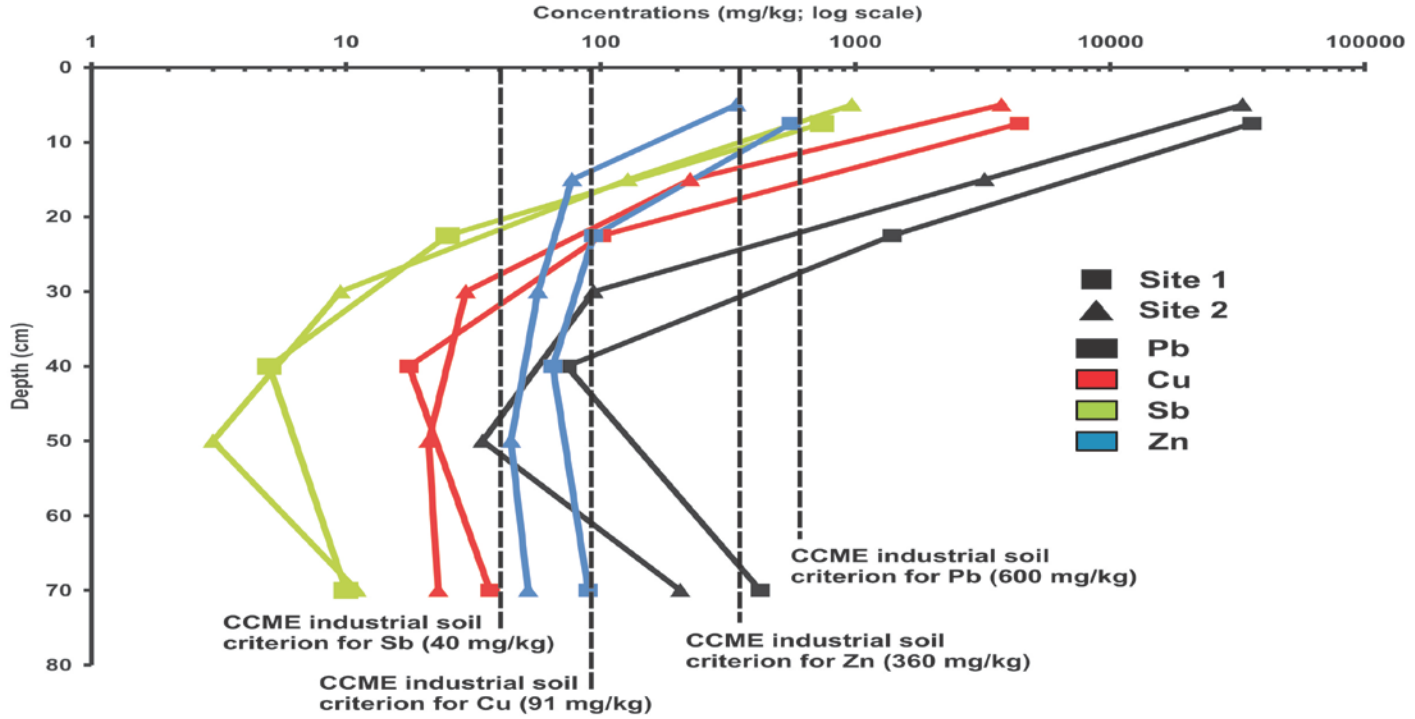


Pore Water and Groundwater Sampling

- Pore water sampling at various depths
  - GL – Sites 1 and 2
    - PTFE cylinders (pierced at the bottom; 27-cm diameter, 32-cm high) connected to a LDPE 10-L sampling bottle via a PTFE tube
      - Site 1: 0.75 m and 1.5 m bgs
      - Site 2: 0.3 m, 0.55 m, 0.75 m, 1.5 m bgs
    - Sampling bottles were located in an access well
  - SL – Site 1
    - PTFE, 30-cm length, horizontal inclination 67°
    - 1, 1.5, 2, 3, 4.5, and 6 m bgs
  - GL and SL were sampled ~once a month on an over 5-y, and 3-y period, respectively (only years 2010 and 2011 are reported here)
- Groundwater sampling
  - Observation wells were located in the immediate vicinity of the stop berms

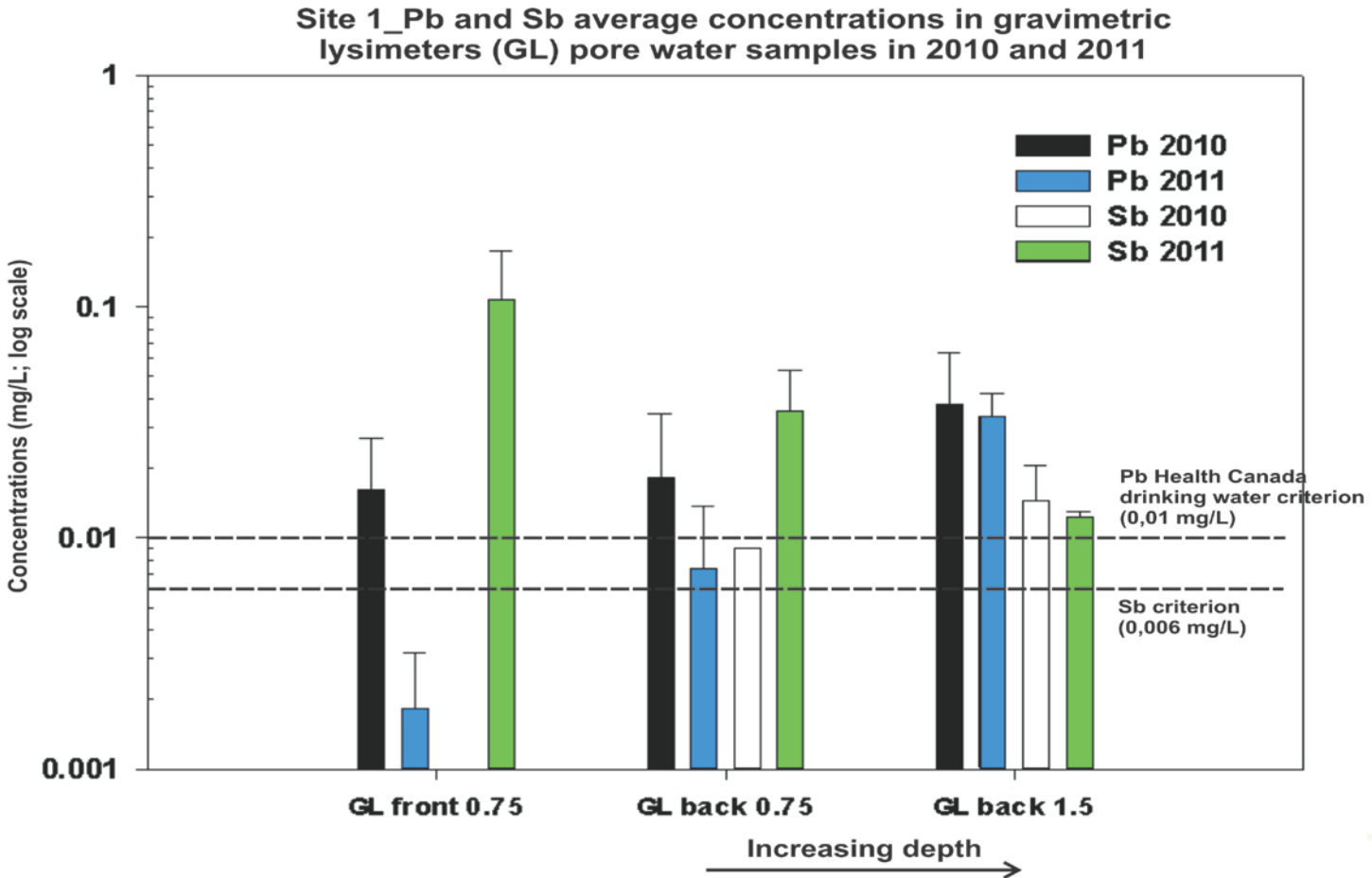
Results – Soil Concentrations

- Surface soil concentrations of Pb, Cu, Sb and Zn above industrial CCME criteria
- Soil concentrations of heavy metals fall below industrial criteria at depth > 30 cm



Metal Concentration in the Vadose Zone

Pb and Sb > DW criteria detected in GL at depth of 1.5 m



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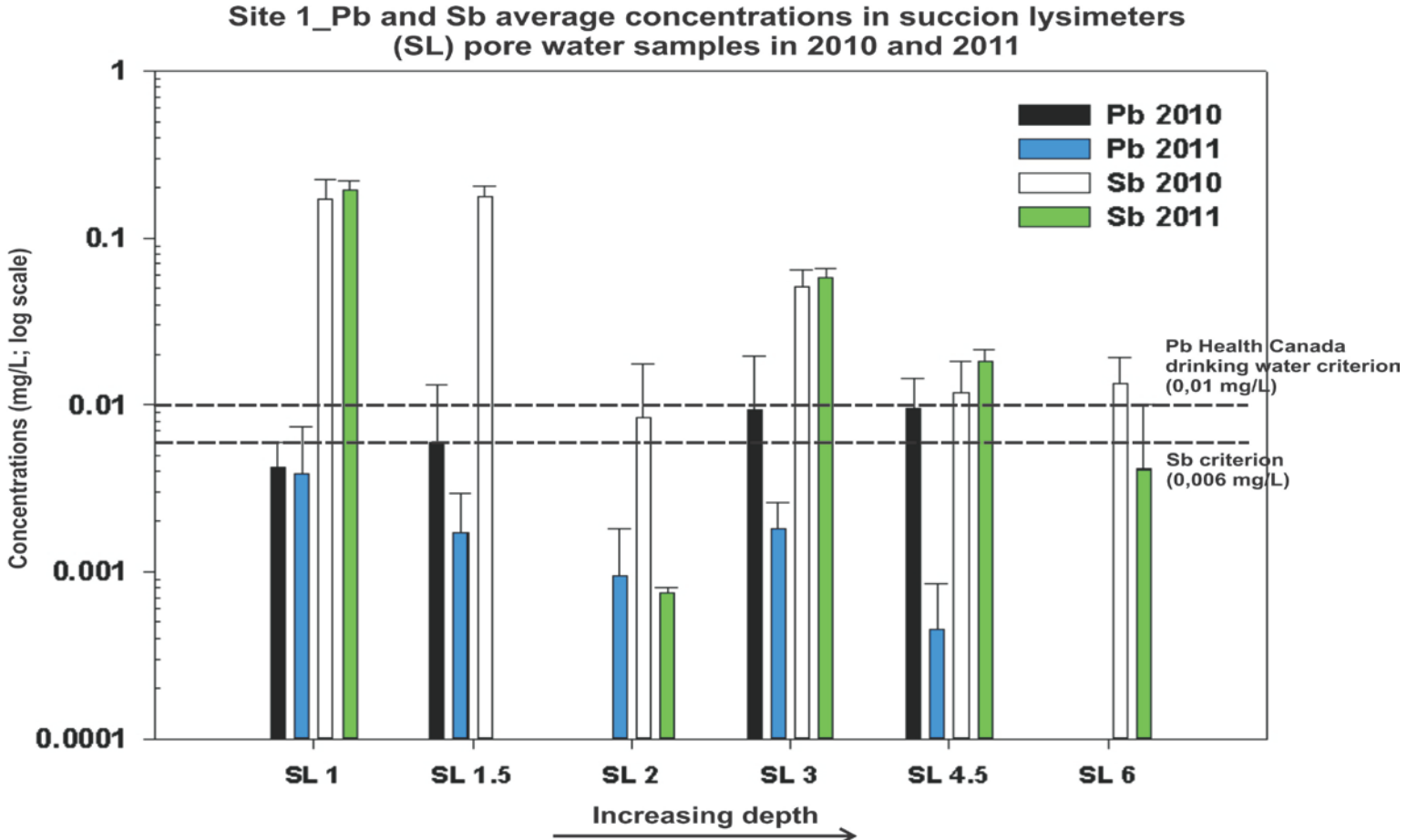
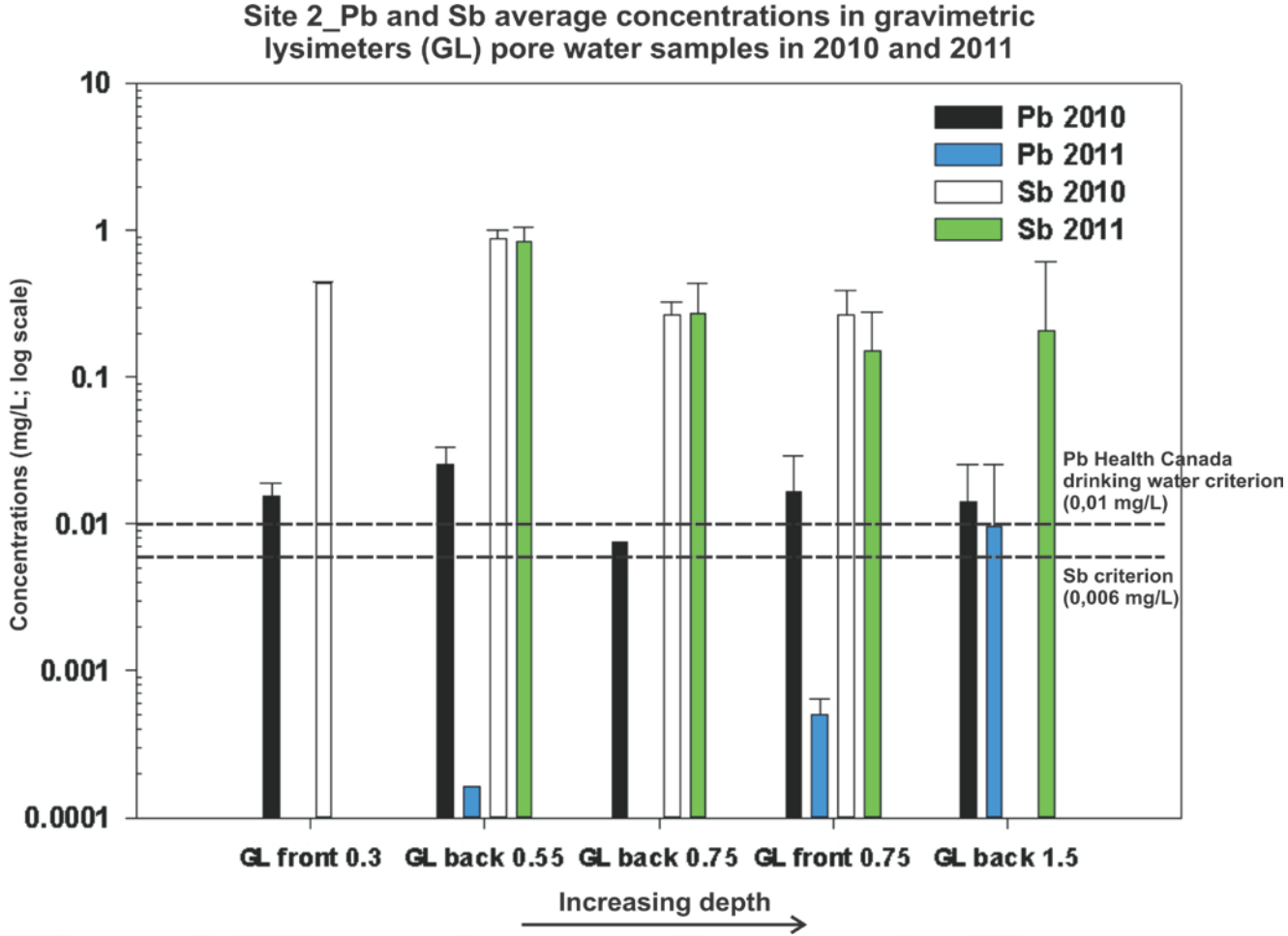
Vadose Zone

Pb and Sb e DW criteria detected in SL at depth of 4.5 m

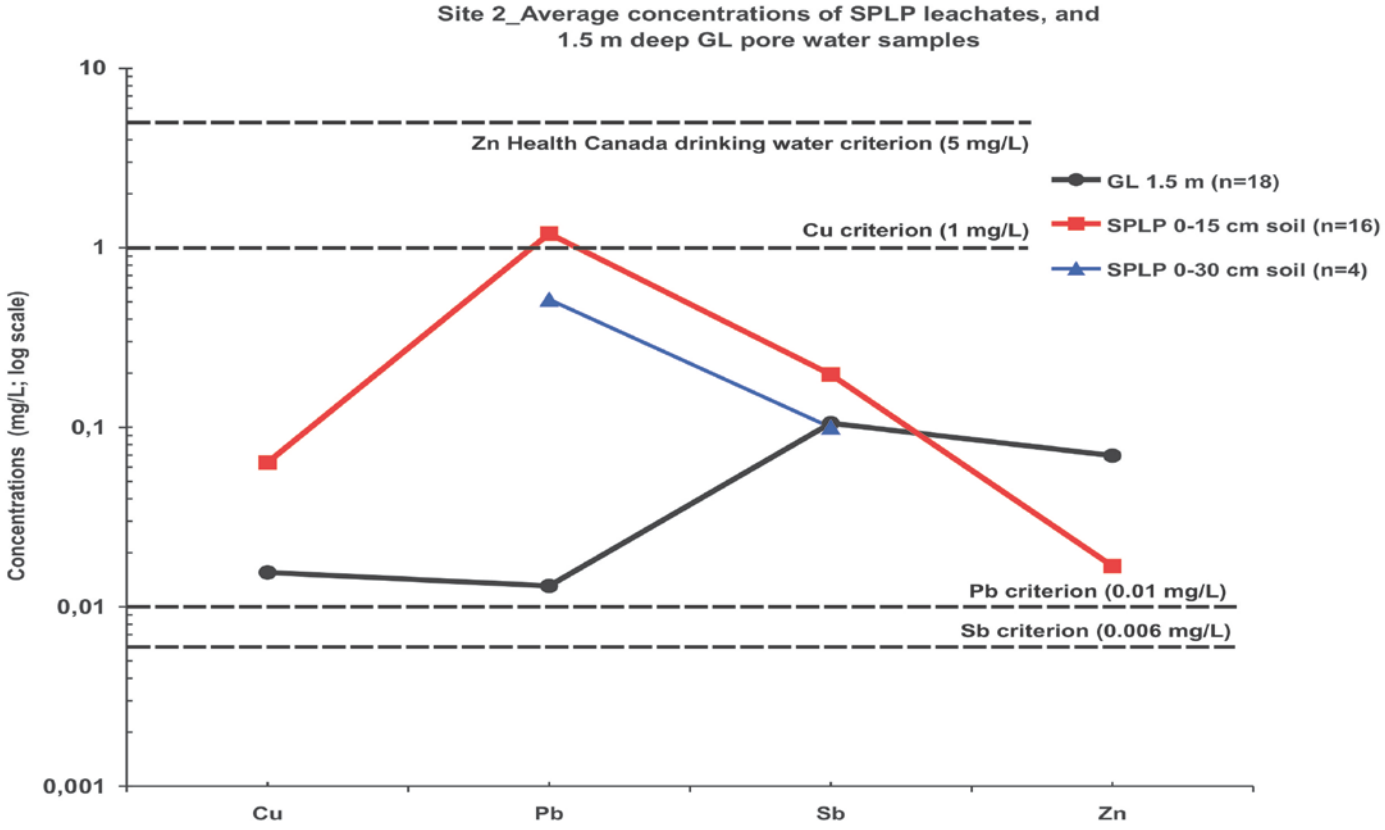


Vadose Zone


Site 2_Pb and Sb average concentrations in gravimetric lysimeters (GL) pore water samples in 2010 and 2011
Concentrations (mg/L; log scale)
10
1
0.1
0.01
0.001
0.0001
Pb 2010
Pb 2011
Sb 2010
Sb 2011
Pb Health Canada drinking water criterion (0,01 mg/L)
Sb criterion (0,006 mg/L)
GL front 0.3
GL back 0.55
GL back 0.75
GL front 0.75
GL back 1.5
Increasing depth

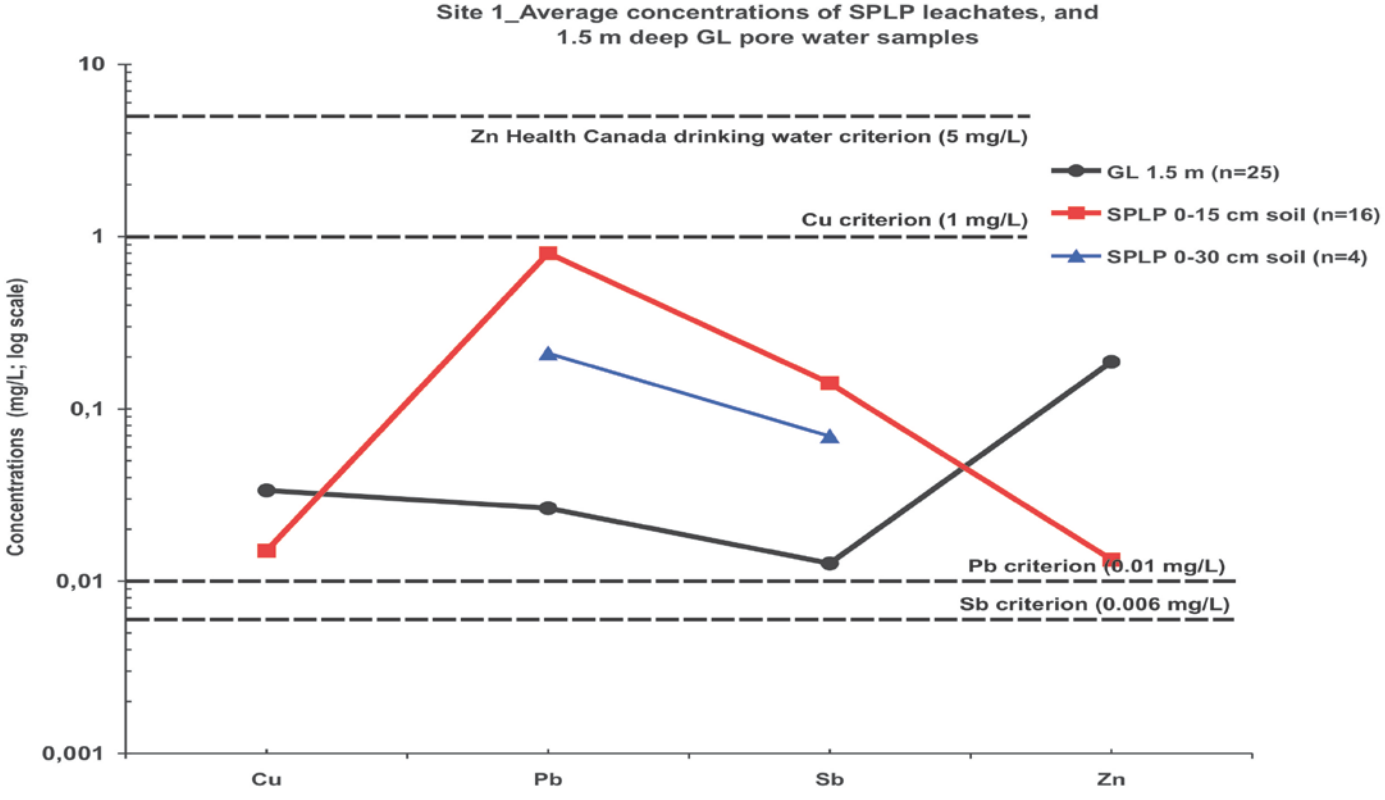
Synthetic Precipitation Leaching Procedures (SPLP)

Leaching of contaminants from soils exposed to rain at pH 4.2 (EPA 1312)



SPLP vs GL

- Sb and Pb are the most mobile in the vadose zone
- [Sb] and [Pb] in SPLP overestimates those of GL



Groundwater

Observation wells	Cu ug/L	Pb ug/L	Sb ug/L	Zn ug/L
PO-242-8m 16/4/9	1,1	2,5	2	1,3
PO-243-7m 16/4/9	2	5,3	1,5	1
PO-249-9m 16/4/9	1,4	2	1,5	1
PO-242-8m 5/9/9	1,1	1,9	1	1
PO-243-7m 5/9/9	2	12,4	2,1	2,5
PO-249-9m 5/9/9	2,6	9,6	2,1	2,3
PO-242-7m 9/7/11	< 0,9	< 3	< 8	1,5
PO-243-7m 17/7/11	0,8	3,5	0,1	1,2
PO-249-9m 9/7/11	< 0,9	< 3	< 8	2,4

Summary

- Soils:
  - Pb, Cu, Sb and Zn exceed CCME industrial criteria
  - Mainly concentrated 30 cm bgs
- Vadose zone (GL)
  - [Zn] and [Cu] < HCDWC
  - [Sb] and [Pb] > HCDWC at 1.5 m bgs
  - [Sb] and [Pb] in SPLP overestimates those of GL at 1.5 m
  - [Sb] > HCDWC at 4.5 m bgs (SL)
  - Sb still detected at 6-m bgs (SL)
  - Pb still detected at 4.5 m bgs (SL)
- Groundwater: seldom detected at 7 to 9 m bgs

Conclusions

- Migration of Pb, Sb, Cu and Zn bgs
  - Cu and Zn not of concern
  - Sb and Pb are the most mobile
  - Important dilution factor when the contaminants reach the groundwater
- Surface soil concentrations of Pb, Cu, Sb and Zn:
  - Not an appropriate assessment of the environmental risk
  - CCME prescribes a specific site assessment
    - Costly and time consuming
- SPLP: Early warning of a potential contamination of the water table that has to be carefully interpreted
- A monitoring of the vadose zone should be done in order to avoid any metal pollution of water table, particularly for shallow groundwater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