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

Sylvie Brochu¹, Mathieu Laporte-Saumure¹, Louis-Julien Roy¹ and Richard Martel²
¹: DRDC ²: INRS

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NOTICE
(U) This document has been reviewed and DOES NOT CONTAIN controlled goods technical data.
Overview

- Background
- Objective
- Instrumentation/Methods for the Vadose Zone
  - Lysimeters
  - Synthetic Precipitation Leaching Procedure
  - Sequential Extractions
- Results
  - Soils
  - Vadose zone
  - 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 mm)
    - 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
    - $\text{H}_2\text{SO}_4/\text{HNO}_3$ 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
Vadose Zone

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

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<tr>
<th>Observation wells</th>
<th>Cu ug/L</th>
<th>Pb ug/L</th>
<th>Sb ug/L</th>
<th>Zn ug/L</th>
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<td>&lt; 0,9</td>
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</tbody>
</table>
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