Sulfur Content and Isotopic Composition of Lichen Species Bullion Mine; Basin, MT

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Background

- Lichens are useful indicators of environmental impact.

- Variables Of Interest
  - ❑ Stable isotopic composition of carbon and sulfur
  - ❑ Species richness and distribution
  - ❑ Heavy metal concentrations

- Established methods for assessing the sources and effects of air pollution.

Lichen specimens divided by species during identification procedure at Montana State University, July 2011.

Abstract

Photograph of lichen species *Hypogymnia imshaugii*. Scale in inches.

Detailed photograph of lichen species *Pelliqua caninia.*

- Sulfur concentration and isotopic signature in lichen species
- Abandoned precious metal mine in central Montana
- Specimens analyzed for heavy metal concentrations:
  - Lead (Pb)
  - Chromium (Cr)
  - Copper (Cu)
  - Cadmium (Cd)
  - Zinc (Zn)
- Evaluate the potential of lichens to assess human disturbance in remote mountainous areas.

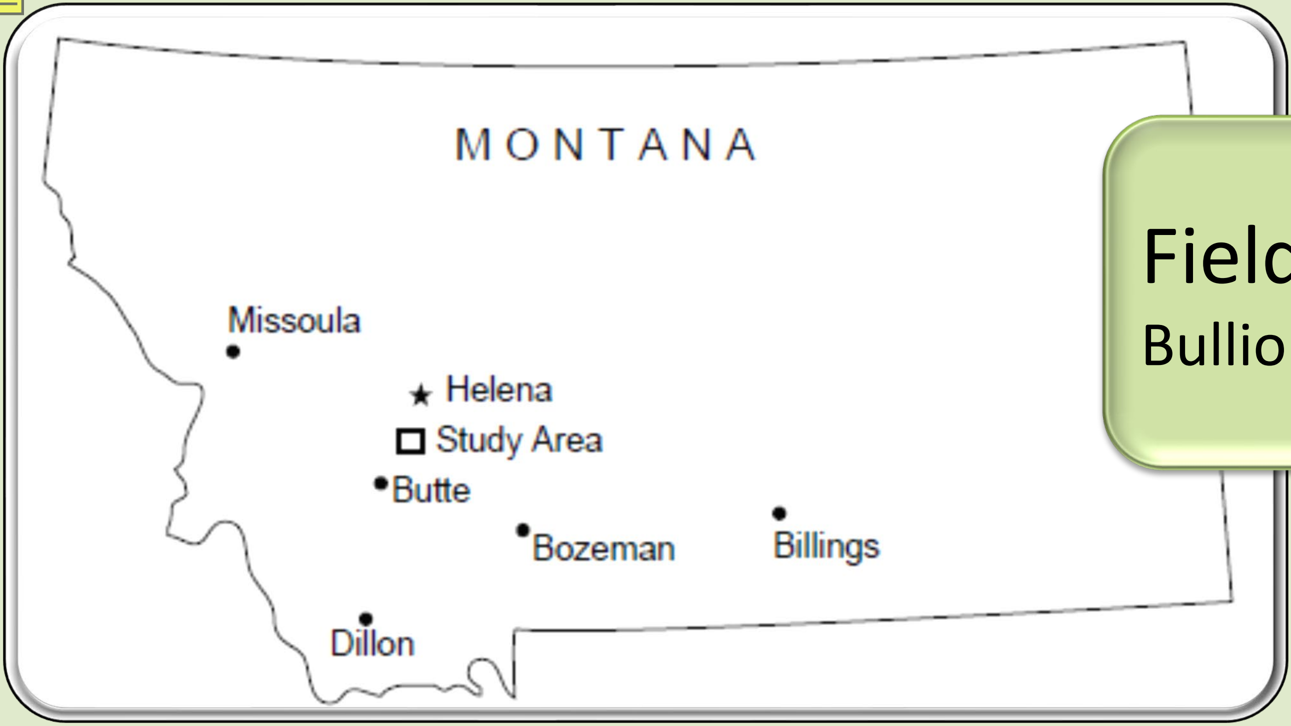
Research Questions

- Can lichens indicate impacts of remote mining operations?
- Are heavy metals present in detectable quantities?
- How can we best isolate sulfur from lichens?
- Do concentrations of sulfur and metals vary spatially or among species/genera?
- Does distance from mine correlate with concentrations?

What is a lichen?

A lichen is . . .

- Not a plant
- Categorized as a *cryptogam*
- Symbiotic partnership between a photobiont and a fungus
- Diverse in size, growth form, and color
- An evolutionary success: over 14,000 species



Field Site:

Bullion Mine; Basin, MT

- Basin Mining District; Jefferson County, Montana.
- Mined for gold and silver between 1897 and 1955.
- Superfund National Priorities List site in 1999.
- Ore body contains metallic sulfides:
  - Pyrite (FeS_2)
  - Galena (PbS)
  - Sphalerite ($(Zn,Fe)S$)
  - Tetrahedrite $(Cu,Fe)_{12}Sb_4S_{13}$
  - Arsenopyrite ($FeAsS$)
- Initial cleanup completed in 2002; still actively monitored by the EPA.

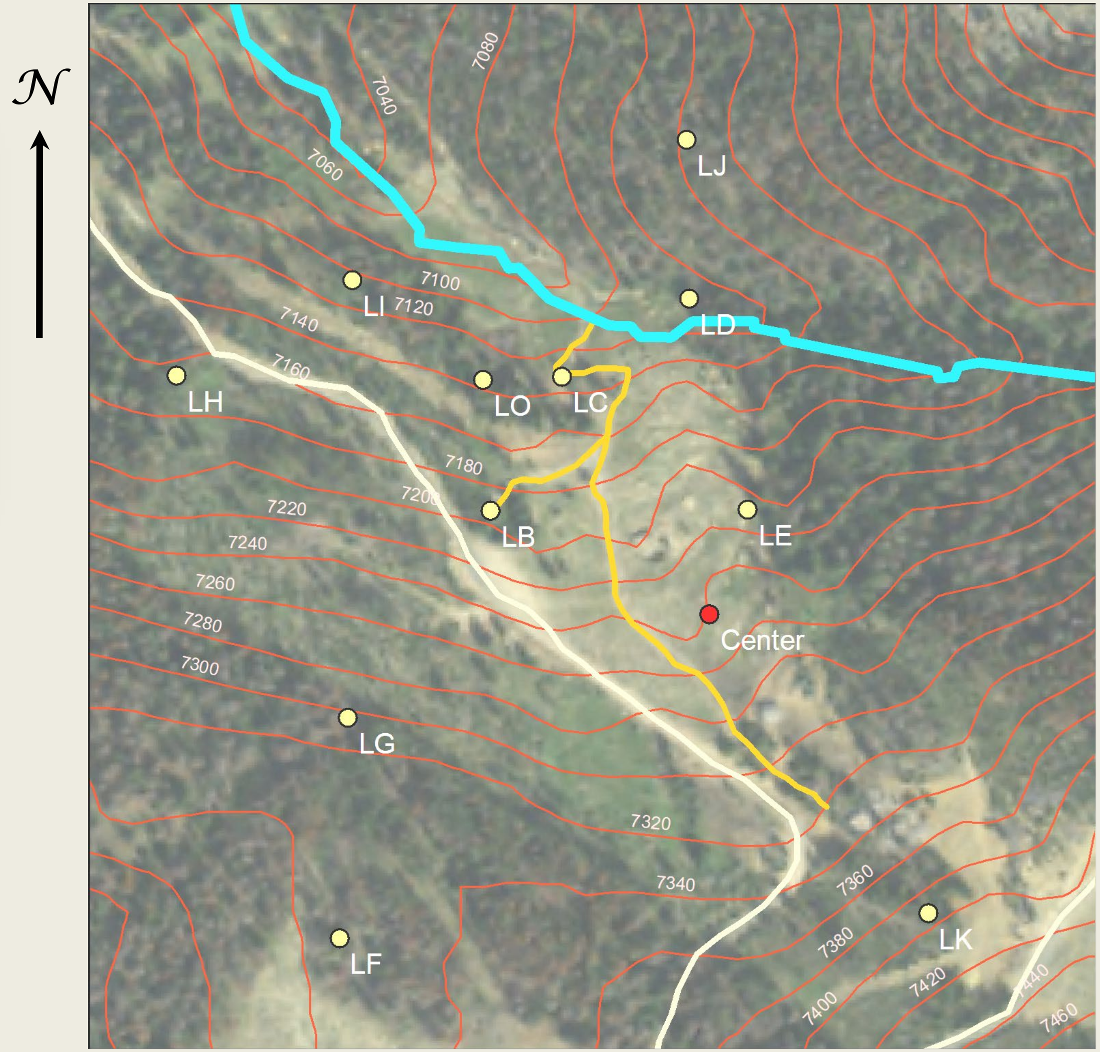
Field Methods

- Twenty-six samples consisting of six lichen species.
- Eleven locations at distances of 40-250 m. from the center of Bullion
- Sampling conducted in a roughly radial pattern, as allowed by disturbance and abundance.
- Samples stored in paper envelopes in a cool, dry, dark place.
- Water samples of acid mine drainage, preserved with cadmium chloride, collected with basic field chemistry

Bullion Mine, Jefferson County. Basin, Montana

Lichen Sample Sites
Bullion Mine; Basin, MT
July 2011

Sample Site	Dist. from Cntr (m)
LB	92.05
LC	111.25
LD	125.27
LE	42.37
LF	193.12
LG	146.91
LH	241.40
LI	193.12
LJ	193.12
LK	146.91
LO	137.90



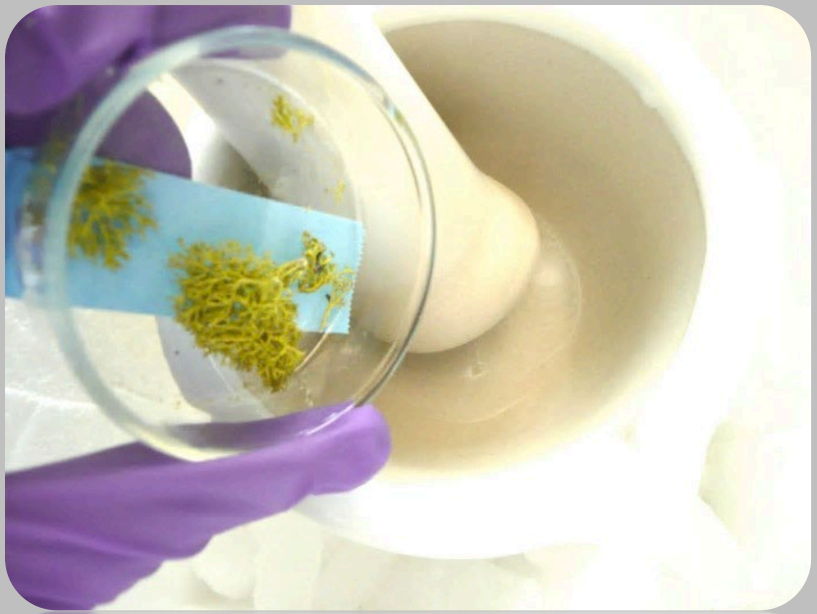
Lab Methods

1. Lichen identification
   - chemical tests
   - investigate spore structure under a dissecting microscope
   - examine structure of fruiting bodies.

2. Unpulverized specimens analyzed for preliminary C/S ratios

Eltra CS-2000 Carbon-Sulfur Determinator

3. Lichens pulverized by freezing with liquid nitrogen and grinding into a fine powder.



Whole lichen prepared for pulverization

Lab Methods: continued

Begin with chemically-untreated lichen powder

1

Aliquots (15 mg) of lichen powder taken randomly, when-ever necessary

Continuous flow-isotope ratio mass spectrom-etry (CF-lichen)

2

30 (1 g) aliquots of lichen powder

$BaSO_4$ precipitated by Parr Bomb™ oxidation

Continuous flow- isotope ratio mass spectrometry (CF-$BaSO_4$)

3

4 (4 g) aliquots of lichen powder

$BaSO_4$ precipitated by Parr Bomb™ oxidation

Mixed $BaSO_4$

SO_2 prepared from 5 aliquots of $BaSO_4$, by SO_2 extraction line techniques

Dual-inlet isotope ratio mass spectrometry (DI-IRMS)

4

3 (1g) aliquots of lichen powder

Rinse sample with 400 ml Milli-Q water to separate H_2O-soluble SO_4

Isolate elemental S fraction (soxhlet extraction, 24 hrs with CH_2Cl)

Concentrate extracted CH_2Cl, Parr Bomb™ for volatile organo-sulfur

Acid volatile S extraction (2 hrs in 6 N HCl with N_2 headspace)

Isolate chrome reducible sulfur (0.2 M $CrCl_2$, 2 hrs in 12 N HCl with N_2 headspace)

Parr Bomb™ residue for acid resis-tant organic sulfur compounds

All fractions precipitated as $BaSO_4$, and analyzed by continuous flow-isotope mass spectrometry

Four methods for extracting S from the lichen thallus. Methods 1-3 are described in Yun (2004). Method 4 is modified from Lefticariu (2006). Methods 1, 2, and 4 are used in this study. Figure adapted from Yun 2004.

Lab Methods: continued

- ❑ Ground specimens were freeze dried before extraction.

Freeze-drying station

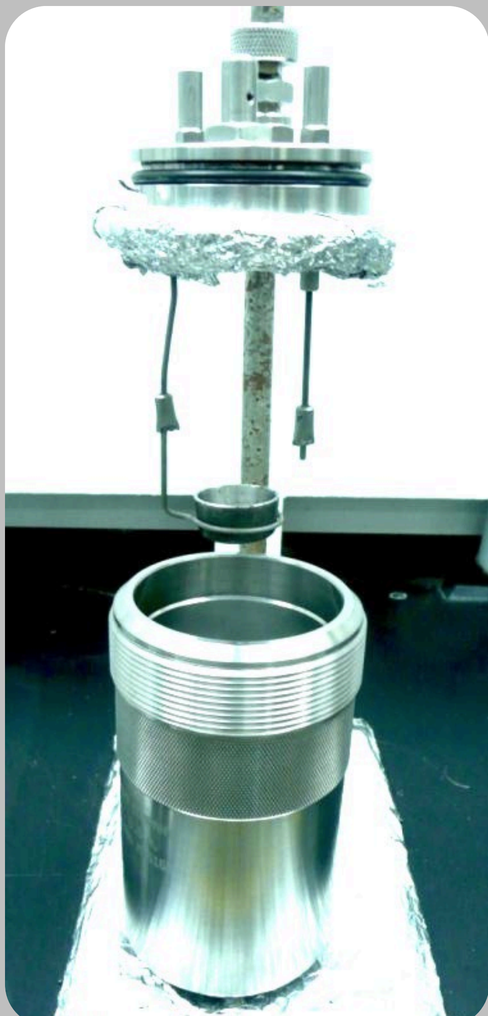
- Water-soluble sulfur
- Elemental sulfur
- Acid-volatile sulfur
- Acid-soluble sulfate
- Chrome-reducible sulfides
- Solvent-soluble organosulfur

- ❑ Three samples selected for sequential extraction.

Soxhlet extraction setup for elemental S

Extraction line for acid volatile S

Lab Methods: continued



Parr ® Oxygen Bomb

- Sulfur collected as silver sulfide or barium sulfate
- Twenty-three samples oxidatively combusted to liberate sulfur within the thallus.
- Analyzed for stable-isotopic composition using a Finnegan MAT 252 isotope ratio mass spectrometer

AAnylist 800 AAS

- Eight samples analyzed for heavy metals by atomic absorption spectroscopy

Results

Table 1

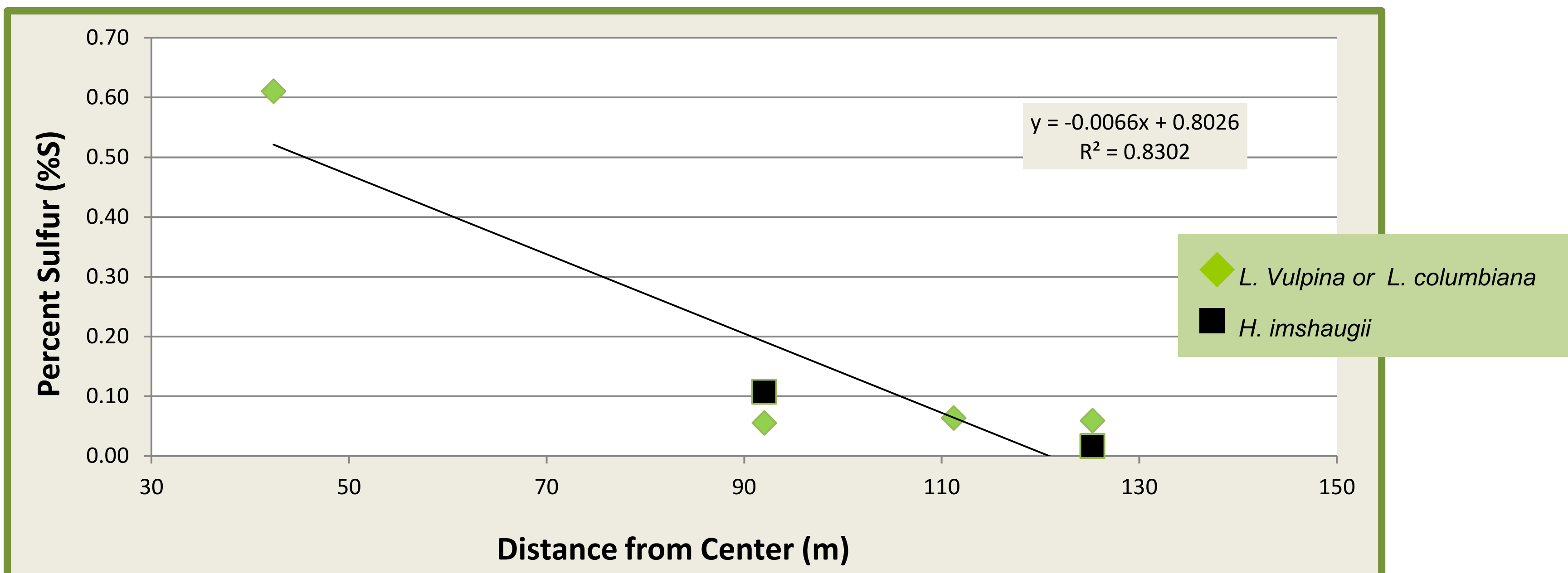
Percent Sulfur by C/S Determinator

Lichen	%S
Hypogymnia sp.	0.130
Letharia sp.	0.204
Letharia sp.	0.251
Letharia sp.	0.215
Letharia sp.	0.158
Letharia columbiana	0.138

Table 2

Percent Sulfur by Gravimetric Methods

Lichen	Dist. (m)	%S
Hypogymnia imshaugii	92.05	0.107
Hypogymnia imshaugii	125.27	0.017
Letharia vulpina	111.25	0.055
Letharia vulpina	125.27	0.063
Letharia vulpina	42.37	0.610
Letharia columbiana	92.05	0.059



Results: continued

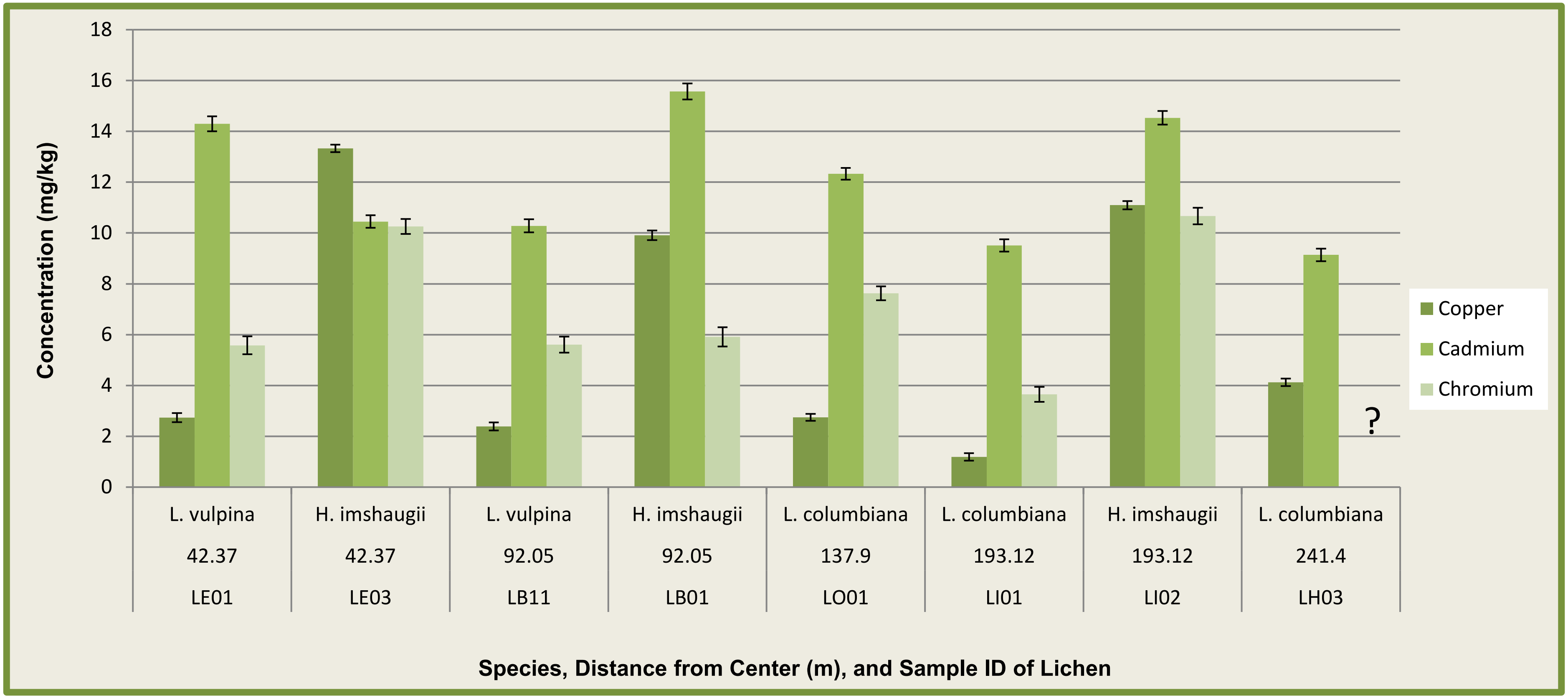


Figure 1: Concentration of copper, cadmium, and chromium (mg/kg or ppm) in eight lichen specimens from five different sample locations.

- No apparent trend between Cu, Cd, or Cr concentrations and radial distance from field site

Results: continued

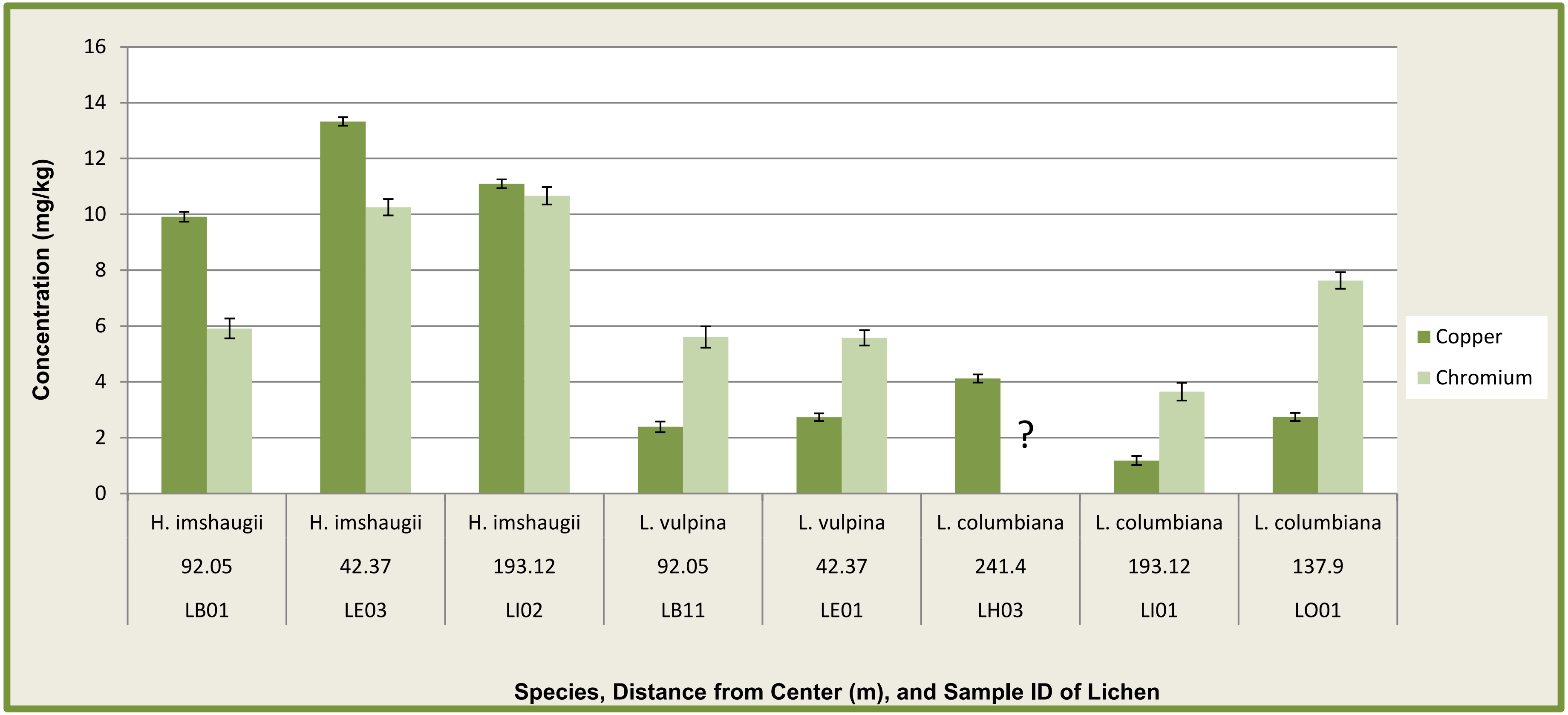


Figure 2: Concentration of copper, and chromium (mg/kg or ppm) in eight lichen specimens from five different sample locations.

- Cu and Cr concentrations appear to vary between lichen species
- *H. imshaugii* exhibits higher concentrations of Cu than both species of *Letharia*, regardless of distance from the center of the mine.
- Inversion of Cr and Cu as the dominant metal between genera

Results: continued

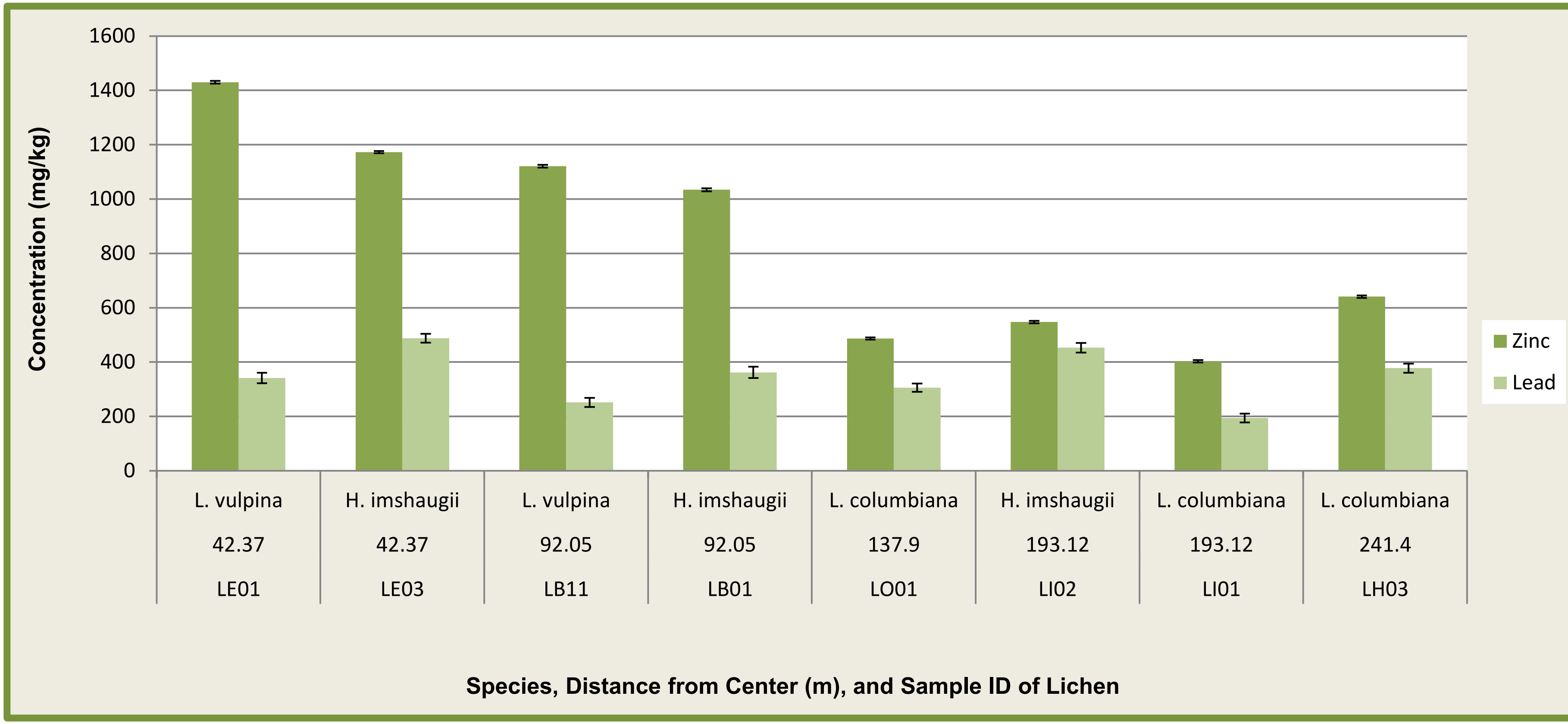


Figure 3: Concentration of zinc and lead (mg/kg or ppm) in eight lichen specimens from five different sample locations.

- Trend of decreasing Zn concentration with increasing radial distance from the center of the mine

Conclusions

- Concentrations of sulfur and heavy metals vary
  - Spatially across an area of disturbance
  - Between species occurring in the same location.

- It will be possible to use lichens to assess environmental impact of mining activities in remote mountainous areas, despite the small scale of operation.

- Preliminary data does not confirm the *extent* to which the lichens growing near the Bullion Mine were affected by anthropogenic disturbance.

- Further research:
  - Examine a control specimen
  - Continuing stable-isotope research
  - Conduct a geospatial analysis

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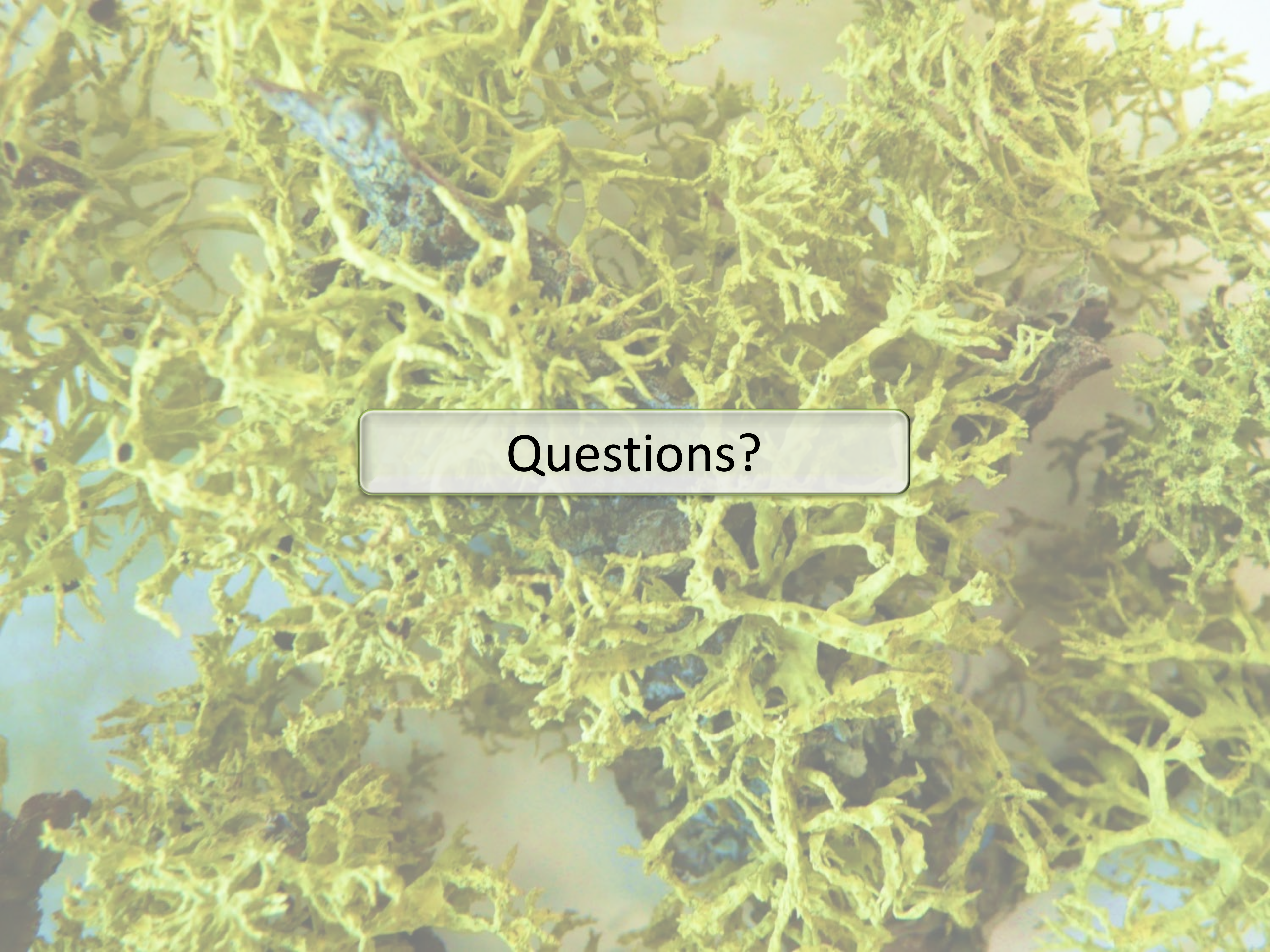

Questions?

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