

Using Chemical Contaminant Profiles to Determine Sediment Depositional History at Little Paint Branch Creek

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Abstract

At Little Paint Branch Creek, a downstream-facing wedge of sediment aggradation has formed due to upstream erosion. It was theorized that a depth v. concentration plot of a trace metal contaminant of the upstream site would reflect a single source of contamination. The downstream site was hypothesized to have a depth v. concentration plot with a broad peak, resulting from a single source of contamination followed by remobilization of upstream sediment. Sediment samples were collected from an upstream and a downstream site, and the <300µm grain size fraction was compressed into pellets. LA-ICP-MS was performed on the pellets to determine trace metal concentrations. The results did not support the hypothesis that the upstream and downstream sites have different trace metal contamination profiles. Rather, both the upstream and the downstream site seem to follow the same trend. It is likely that the downstream site was too far upstream to represent the downstream reach of the stream. However, it was shown that LA-ICP-MS is a viable method for determining trace element concentrations of the coarse-grain sediment found in stream banks.

Introduction

Urbanization & Little Paint Branch Creek

Pre-urbanization: small stream with a low, flat floodplain in a marshy setting

Post-urbanization: the increase in impervious surfaces leads to an increase in the frequency and severity of flooding

Downstream-facing wedge of sediment accretion (Fig. 1): developed as a result of urbanization

- *Upstream banks* are dominated by erosion
 - Stream bank sediment is eroded
 - The channel becomes incised
- *Downstream banks* are dominated by deposition of sediment from:
 - Floods
 - Re-mobilized sediment from upstream banks

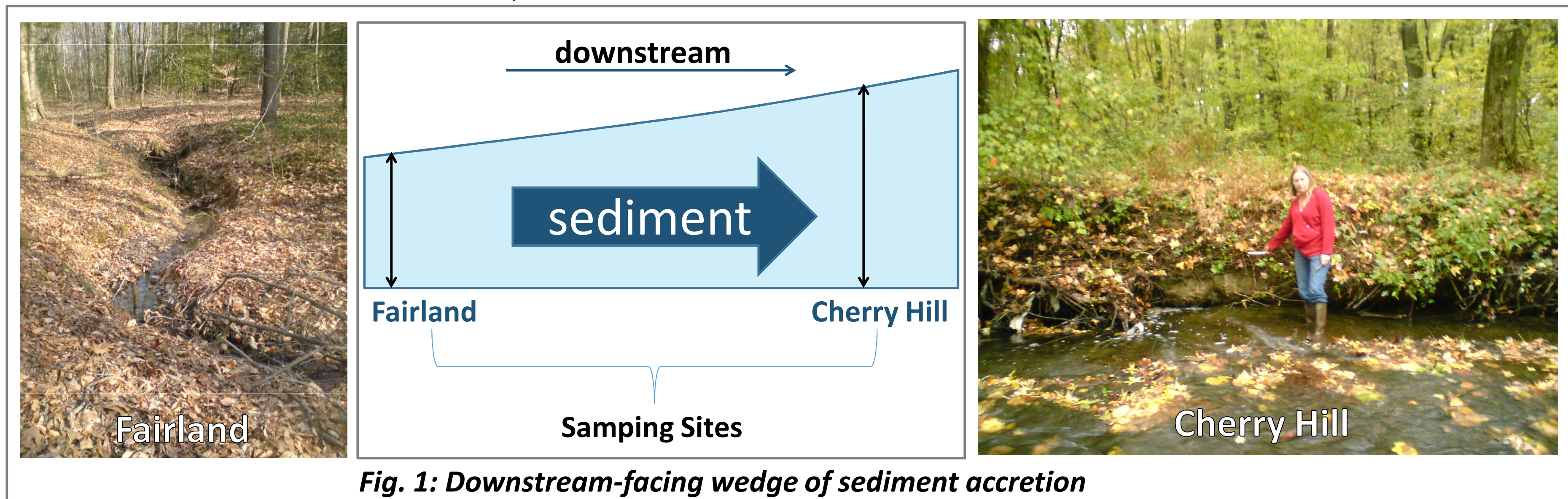


Fig. 1: Downstream-facing wedge of sediment accretion

Contaminant Behavior

- Anthropogenic trace metal contaminants present in this watershed
- Concentration of trace metal contaminants sorbed onto sediment varies with depositional environment (Fig. 2):
 - **Lake core:** the contaminant was introduced to the lake from a single source
 - the oldest stratigraphic layers are relatively free of contamination
 - then a spike in contaminant concentration when the contaminant is introduced
 - concentration tapers off, and eventually disappears as the source disappears
 - **Bay core:** much broader peak
 - indicates the presence of more than one source over time
- ✳ **Where is the sediment coming from?**

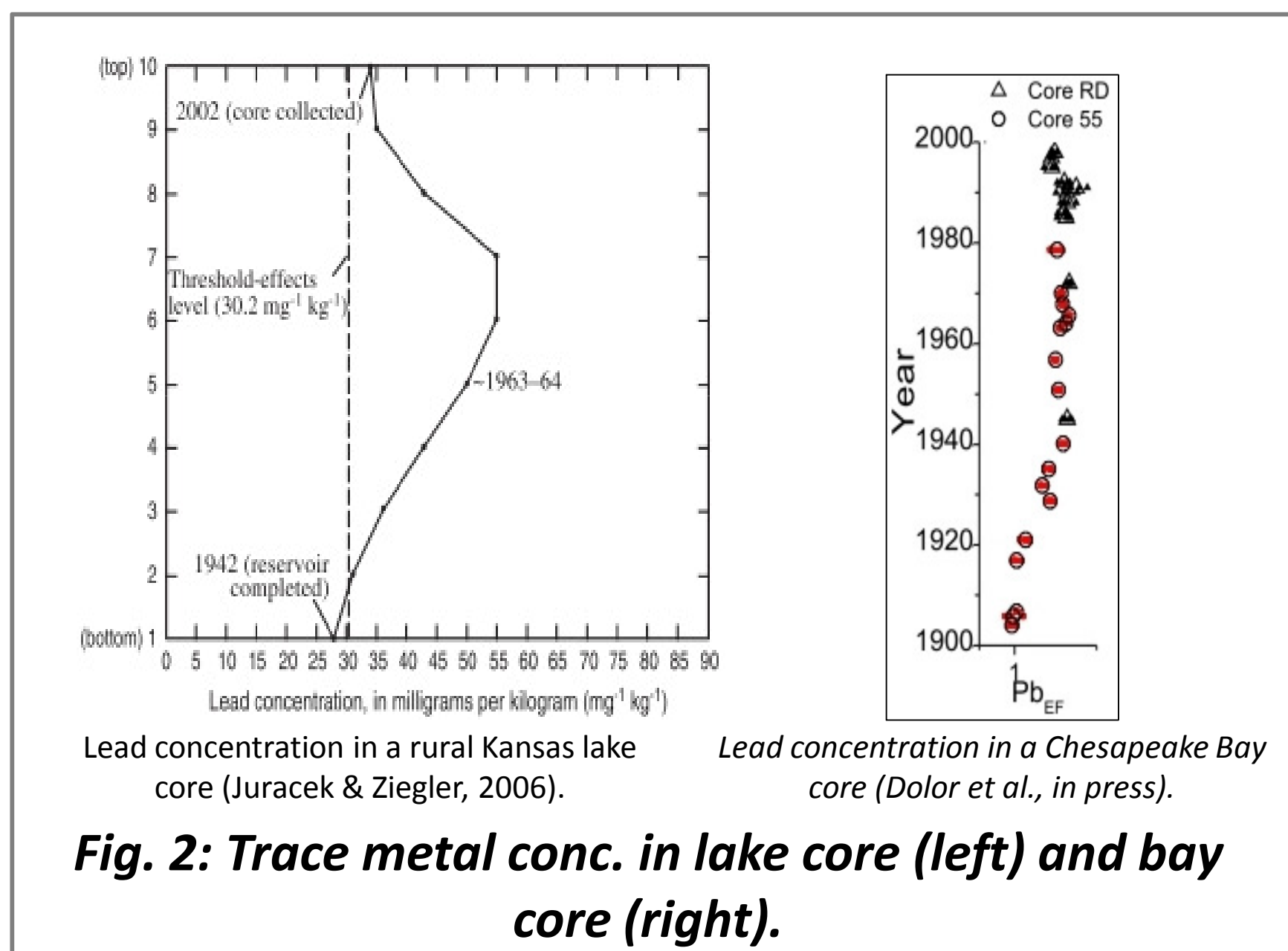


Fig. 2: Trace metal conc. in lake core (left) and bay core (right).

LA-ICP-MS

- ICP-MS has been used in many studies to determine contaminant concentrations in sediment cores or bank samples .
 - These studies used *acid digestion* to put the sediment into solution.
- Dolor et al., however, have successfully used laser ablation ICP-MS to derive trace element concentrations in sediment.
- LA-ICP-MS has several advantages over other forms of analysis:
 - Samples require little preparation
 - Can analyze the concentrations of any amount of elements simultaneously
 - Sensitive, with detection limits as low as ng/g to pg/g.
 - Safer than acid digestion.
- Most of analyses, however, have been done either on individual mineral grains or on fine sediments.
- ✳ **One of the challenges in this study is to determine whether high quality LA-ICP-MS analyses can be obtained from coarser-grained sediments found in stream banks.**

Hypothesis

1. Laser ablation mass spectrometry (LA-ICP-MS) of compacted sediment samples can be used to determine contaminant profiles in stream bank sediment because they contain significant amounts of fine grained material.
2. Contaminant profiles of stream bank sediment profiles should fall on a spectrum between the behavior exhibited by headwater small ponds and downstream depositional sites, such as the Chesapeake Bay.
 - a. At headwater sites, the contaminant concentration is the result of a single source of contamination; therefore, the sediment profile should show a sharp peak in concentration, followed by a gradual decline, corresponding to a decline in contaminant source (like Fig. 3: Case 1).
 - b. At the furthest downstream site, the sediment profile will reflect a single source of contamination followed by erosion of upstream banks re-releasing contaminants into the watershed (like Fig. 3: Case 2).

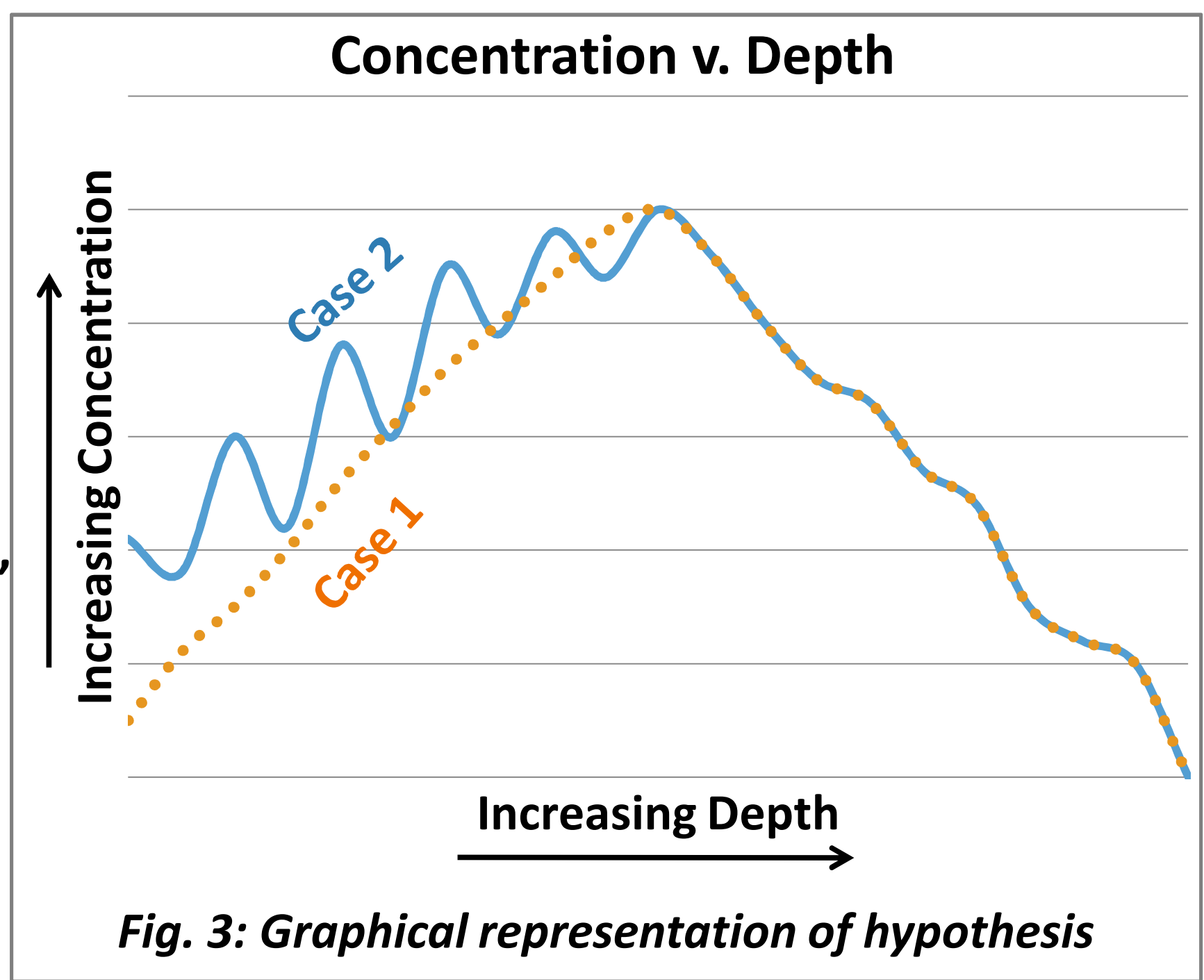


Fig. 3: Graphical representation of hypothesis

Methods

Two Sites: Fairland (upstream) and Cherry Hill (downstream) (Fig. 4)

Sampling Procedures

1. A stainless steel tool was used to first scrape off the first few centimeters of sediment, and then collect the sample.
2. Samples were collected in increments from the top to the bottom of the stream bank

Sieve procedures

Grain size was restricted to <300µm to get a sample that is representative of sediment that:

- has approximately equal potential for trace metal sorption
- is small enough to be transported through the watershed by fluvial processes
- best represents the fine grain fraction throughout this watershed

Sample preparation for LA-ICP-MS

Samples were compressed into pellets to decrease the effects of local heterogeneity, and make a coherent sample.

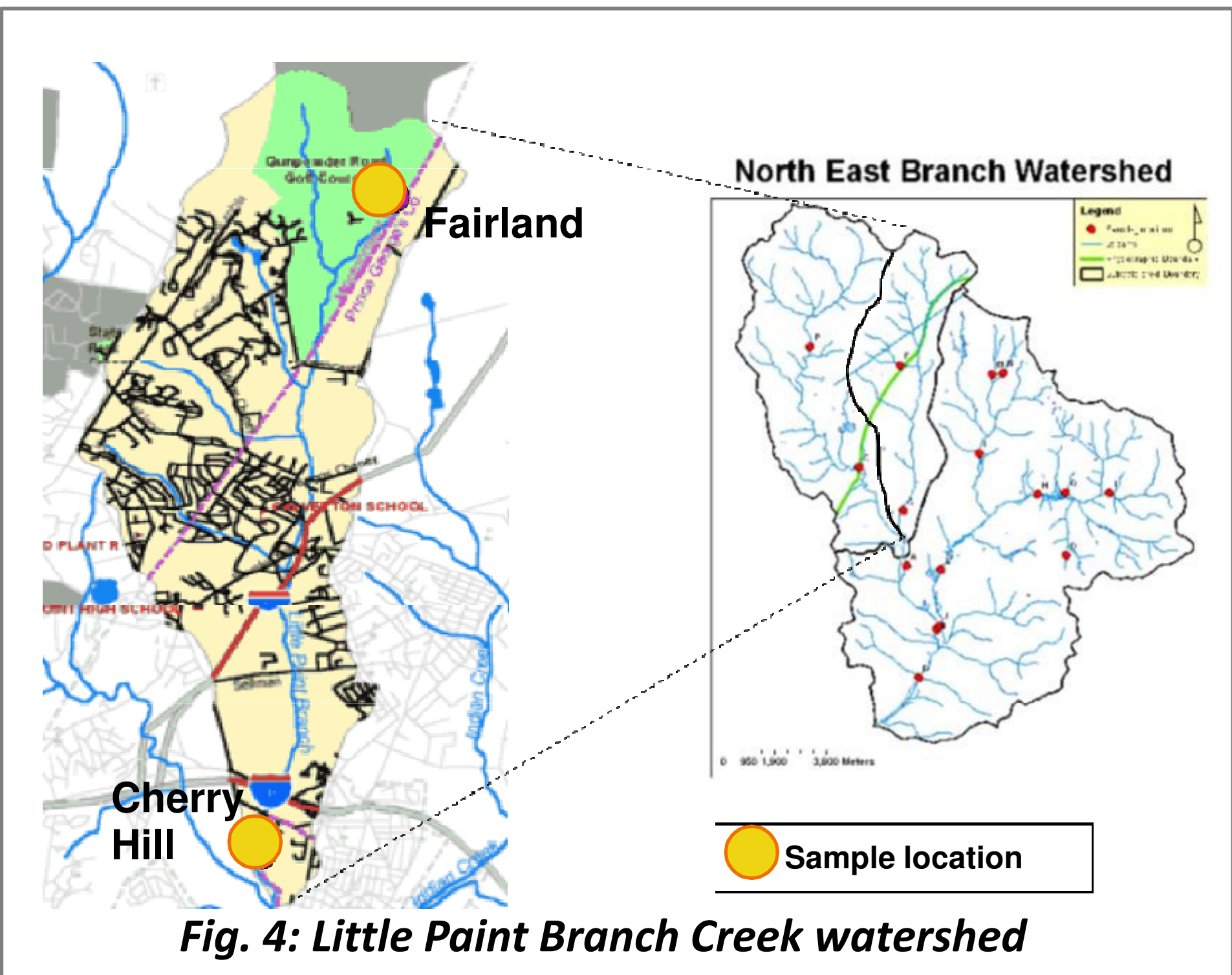


Fig. 4: Little Paint Branch Creek watershed

LA-ICP-MS analyses were conducted in the Plasma Mass Spectrometry Laboratory at the University of Maryland

Equipment used:

- New-wave UP-213-nanometer laser ablation unit
- Finnigan Element2 single collector ICP-MS.

Results

Enrichment Factor Calculation

$$EF = \frac{(X/Fe)_{sample}}{(X/Fe)_{ref}}$$

$(X/Fe)_{sample}$ the ratio of conc. of the analyte to the conc. of iron in the sample

$(X/Fe)_{ref}$ the ratio of the conc. of the analyte over the iron in the standard reference material

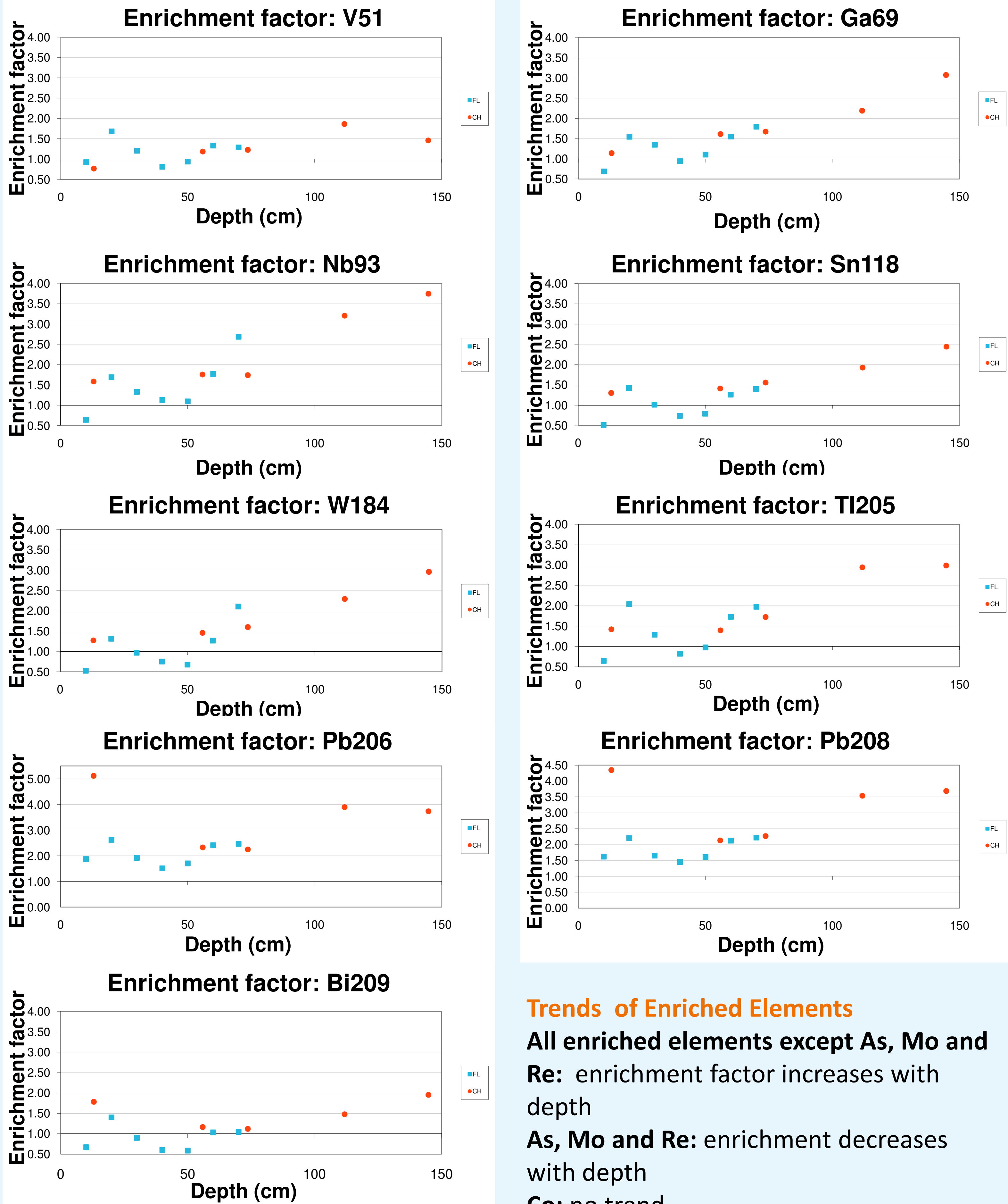
Consistently Enriched Elements:

V W
Ga Re
As Ti
Nb Pb
Mo Bi
Sn

(compared to MAG-1 and avg. crustal values)

site name depth (cm)	ENRICHMENT FACTORS													
	Fairlands							Cherry Hill						
10	20	30	40	50	60	70	13	56	74	112	145			
43 CaO	0.08	0.15	0.17	0.10	0.09	0.20	0.16	0.36	0.22	0.54	0.27	0.41		
51 V	0.92	1.68	1.21	0.81	0.94	1.33	1.29	0.77	1.19	1.23	1.86	1.46		
55 Mn	0.59	0.75	0.69	1.13	1.35	2.21	1.72	1.29	0.69	0.73	0.46	0.96		
57 FeO	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00		
59 Co	3.57	2.25	1.45	3.16	1.20	3.14	1.81	1.94	0.94		3.18	3.03		
61 Ni	0.53	1.52	0.99	0.50	0.77	1.03	0.85	1.50	0.78	0.97	1.24	1.80		
63 Cu	0.44	0.72	0.48	0.26	0.29	0.56	0.73	1.23	0.88	0.82	0.55	0.78		
66 Zn	0.25	0.58	0.38	0.20	0.21	0.39	0.39	0.42	0.38	0.46	0.77	0.99		
69 Ga	0.69	1.54	1.35	0.94	1.10	1.55	1.79	1.14	1.61	1.67	2.19	3.07		
72 Ge	0.64	0.00	0.00	0.00	0.00	0.00		3.79	1.44					
73 Ge	0.59	1.65	0.00	1.95	0.00	2.27			1.15			3.79		
75 As	2.74	1.80	1.65	1.59	1.20	1.46	1.21	1.11	1.22	1.27	1.06	1.10		
77 Se	0.98	0.00	0.00	4.32	0.00	0.00	2.47		1.57					
93 Nb	0.64	1.69	1.33	1.13	1.09	1.77	2.68	1.58	1.75	1.74	3.21	3.75		
95 Mo	3.45	3.86	4.18	2.39	2.51	4.20	2.72	3.38	2.80	2.09	4.21	2.31		
97 Mo	3.46	4.64	4.70	2.79	3.56	5.42	3.23	3.73	2.91	2.80	4.46	2.24		
118 Sn	0.51	1.42	1.01	0.73	0.79	1.26	1.40	1.30	1.41	1.56	1.93	2.44		
121 Sb	0.11	0.15	0.12	0.09	0.09	0.12	1.31	0.27	0.20	0.29	0.14	0.19		
123 Sb	0.11	0.18	0.15	0.11	0.13	0.13	1.74	0.26	0.14	0.33	0.14	0.19		
125 Te														
184 W	0.52	1.31	0.97	0.75	0.68	1.26	2.10	1.27	1.46	1.60	2.29	2.96		
185 Re	0.17	3.55	0.32	0.00	0.04	0.00	2.76	3.08	0.76	1.02	2.19	1.18		
202 Hg														
205 Tl	0.65	2.04	1.29	0.82	0.98	1.73	1.98	1.42	1.39	1.73	2.94	2.99		
206 Pb	1.87	2.63	1.92	1.51	1.70	2.41	2.46	5.12	2.33	2.25	3.89	3.73		
208 Pb	1.62	2.20	1.65	1.45	1.60	2.13	2.22	4.34	2.13	2.26	3.54	3.69		
209 Bi	0.67	1.40	0.90	0.60	0.58	1.03	1.04	1.78	1.17	1.12	1.48	1.96		
232 Th	0.53	0.97	1.03	1.07	0.67	1.28	1.35	0.70	0.98	0.92	1.06	1.85		
238 U	0.19	0.31	0.26	0.17	0.16	0.32	0.30	0.27	0.32	0.35	0.44	0.58		

GRAPHS OF ENRICHMENT FACTOR



Trends of Enriched Elements

All enriched elements except As, Mo and Re: enrichment factor increases with depth
As, Mo and Re: enrichment decreases with depth
Co: no trend

Discussion

V, Ga, As, Nb, Mo, Sn, W, Re, Tl, Pb and Bi were all enriched in the stream bank due to anthropogenic pollution. These trace metals are released into the atmosphere during the burning of fossil fuels, production of metals and other industrial goods, and waste disposal. These findings may be a cause for concern

☑ **Laser ablation ICP-MS seems to be an accurate method of measuring trace element concentration from the fairly coarse-grain material (<300µm) that makes up stream banks**

☒ **There is no support for the hypothesis that the contaminant concentration sediment profiles of the headwater site and the downstream depositional site are significantly different.**

- Both profiles behave like headwater sites
 - Most likely: Cherry Hill might be too far upstream to represent the downstream portion of the watershed
 - Bioturbation may also be responsible for this behavior

Acknowledgements

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Dr. Karen Prestegaard

Dr. William McDonough

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