Determining the Levels and Sources of Mercury in Strawberry Creek

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Abstract Strawberry Creek begins in the Berkeley Hills, flows through the UC Berkeley campus, and discharges into the San Francisco Bay. Historically, some labs on campus impacted Strawberry Creek with mercury discharges. Total mercury concentrations from sediments were determined at several sites along the creek. The questions investigated in this study are: 1) What are the levels of mercury in Strawberry Creek? And, if mercury is detected, 2) What are the possible sources? Concentrations were calculated at 11 sites using surface sediment samples, which is where mercury tends to accumulate. Sediment samples will be obtained because one of the primary controls of mercury concentration in sediment is grain size. There is a strong correlation between an increase in mercury concentration and an increase in the amount of fine material. The following equation calculates the sediment concentration normalized to percent fines (ug/g): $[Hg]_{norm} = [Hg]_{sed} / F_{63}$. $[Hg]_{norm}$ is the sediment concentration normalized to percent fines (ug/g). $[Hg]_{sed}$ is the bulk sediment concentration (ug/g). F_{63} is the percent fines (<63um), expressed as a fraction ($0< F_{63}<1$). When mercury enters a creek, it settles on the sediment. Mercury prefers fine material, in contrast to coarse material. The results are expected to show that a significant increase in mercury may identify possible sources. The California Regional Water Quality Control Board sediment target is 0.4 ug/g. Any results greater than 0.4 ug/g will be investigated as a possible source.

Introduction

Mercury can lead to severe poisonings which can be fatal when eating contaminated fish from waters with very low mercury levels (Friberg & Vostal, 1997). Fish bioaccumulate mercury in the water. Furthermore, mercury is a neurotoxin that affects developing fetuses and young children (CRWQCB, 2000). Newborn babies of mothers exposed to methyl mercury during pregnancy by consumption of contaminated fish have higher mercury levels than their mothers (Skerfving, 1971). Prenatal poisoning occurs because methyl mercury passes the placental barrier (Engleson and Herner, 1952).

The San Francisco Bay Regional Water Quality Control Board has listed all segments of San Francisco Bay as impaired due to mercury pollution. Since it is an unacceptable health risk to humans and animals, the removal of mercury is a high priority (San Francisco Bay Regional Water Quality Control Board, 1998). This is based on the exceedance of the numeric objective for mercury in water and the bioaccumulation of mercury in fish. The numeric objective in water is 0.05 ug/L and basically the same value as the criterion for consumption of organisms (i.e. fish) is 0.051 ug/L (EPA, 2000). Because of the high levels of mercury in fish, the Regional Water Quality Control Board (RWQCB) announced that fish from San Francisco Bay should not be eaten.

Strawberry Creek begins in the Berkeley Hills and drains into San Francisco Bay. It is an urban creek that may be contaminated from stormwater runoff and direct discharge (Charbonneau, 1987). Mercury in stormwater runoff may be from anthropogenic air pollution that is deposited on the ground and washed into a creek during a storm event. Mercury in direct discharge may be from labs or old machines that used mercury.

This study of mercury will help determine the levels of mercury in Strawberry Creek. In addition, any sources of mercury may be identified. For example, mercury in San Francisco Bay is mostly from the Gold Mines, where hundreds of thousands of pounds of mercury were abandoned (Hunerlach, et al) after the Gold Rush. Mercury helped separate gold from the sediment. After the Gold Rush, the miners abandoned the mercury in sluices of the gold mines. Presently, in the South Bay, most of mercury is coming from the New Almaden Mines in the Santa Cruz Mountains via the Guadalupe River (CRWQCB, 2000). Mercury was also abandoned in those mines and studies showed that mercury contaminated the Guadalupe River and the South Bay.

Previous research of mercury in Strawberry Creek only determined the concentrations of mercury; however, the sources of mercury were not addressed. For example, The Alameda Countywide Clean Water Program conducted sampling and analysis of embedded sediments from creeks (i.e. Strawberry Creek) and stormdrains throughout Alameda County during summer and fall of 2000 (Alameda Countywide Clean Water Program, Sept. 2000). The objectives of their survey were: to produce a synoptic survey of the distribution of mercury in creek and stormdrain sediments and to support coarse-scale loads (Alameda Countywide Clean Water Program, July 2000). The Regional Water Quality Control Board has recently requested that stormwater programs evaluate mercury in their watersheds. The project is called "Joint Stormwater Agency Project to Study Urban Sources of Mercury."

The questions I will answer are: What are the levels of mercury in Strawberry Creek? Is the level safe for the public? Where is the mercury coming from? Is the College of Chemistry a possible source?

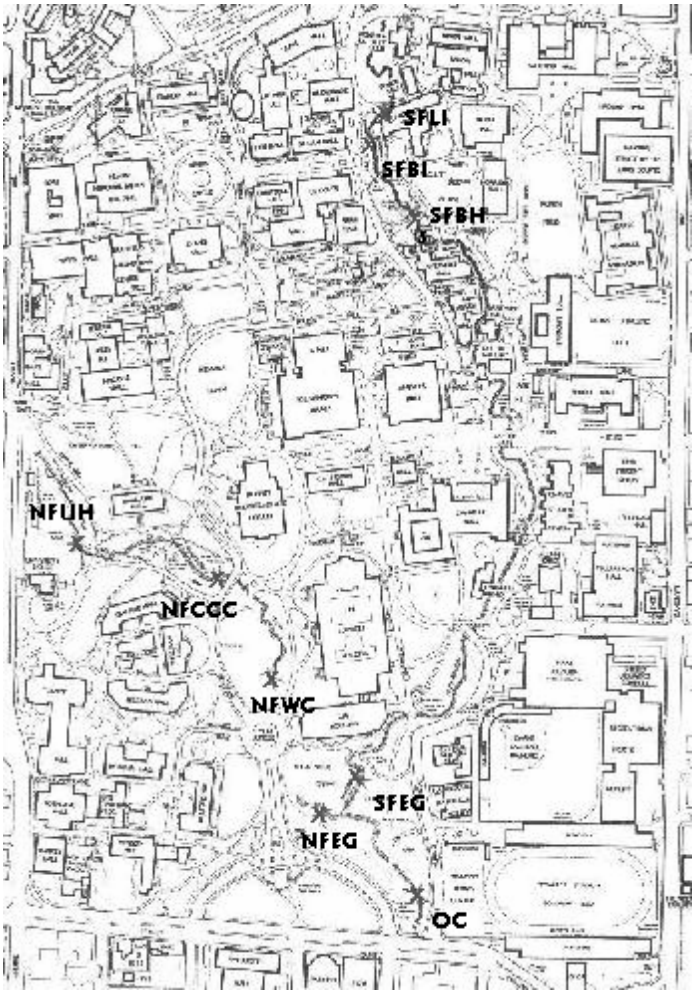
The study will address these questions in two ways. First, by taking water samples, during a first flush event, the amount of mercury from stormwater runoff is determined. Second, by taking sediment samples in Strawberry Creek, possible sources of mercury will be discovered. Different levels of mercury will determine possible sources. For example, if the headwaters of the creek have low levels of mercury and the samples taken below the College of Chemistry have significantly higher levels, then this realization concludes that the College of Chemistry is a source of mercury.

Methods

Water samples were taken in the North Fork Cross Campus Culvert and the South Fork Eucalyptus Grove. Sediment samples were taken in the Strawberry Creek North Fork background, Strawberry Creek South Fork background, North Fork Eucalyptus Grove, South Fork Eucalyptus Grove, West Circle, Cross Campus Culvert, University House, Birge Hall, Big Inch, Little Inch, and Oxford Culvert. The following table identifies the abbreviated locations and the map illustrates the campus sites:

Name	**Abbreviation**
Oxford Culvert	OC

North Fork Eucalyptus Grove	NF EG
West Circle	NF WC
Cross Campus Culvert	NF CCC
University House	NF UH
North Fork Background	NF B
South Fork Eucalyptus Grove	SF EG
Birge Hall	SF BH
Big Inch	SF BI
Little Inch	SF LI
South Fork Background	SF B



The samples obtained on the North and South Fork background allow me to evaluate whether mercury is originating on campus. The North Fork background is located near the end of Le Conte Ave. The South Fork background is located near the Botanical Gardens, next to the Fire Trail. The samples collected at the North Fork Eucalyptus Grove will determine if the mercury is coming from labs on the Northwest part of campus. For example, two of these labs are Koshland Hall and Genetics and Plant Biology Building. Samples taken on the South Fork Eucalyptus Grove will determine the amount of mercury coming from Valley Life Sciences Building and the Life Sciences Addition. The Cross Campus Culvert sample will indicate the mercury coming from Lawrence Berkeley National Laboratory. The University House sample will show the concentration of mercury entering campus. Since the College of Chemistry has previous fines from discharges of mercury, both the Big Inch and the Little Inch permit me to evaluate the College of Chemistry as a possible mercury source. Birge Hall and Le Conte Hall

were using machines with mercury. Their drainages combine before reaching the creek and samples were collected at that drainage on the creek. The Oxford Culvert allows me to check individual North and South Fork loads. Labs in Barker Hall also drain into the creek before the Oxford Culvert.

The majority of all forms of mercury eventually accumulate in the bottom sediment (Friberg and Vostal, 1972). Surface sediment samples are necessary to collect mercury (Gill, 1999). This is why eleven sediment samples are being taken. For example, two sediment samples will be collected at the Big Inch and the Little Inch to determine if the College of Chemistry is a possible source. Since mercury prefers to settle on fine particles, rather than coarse particles, sediment size was also investigated. For example, the percent of fine material < 63um were also calculated. The next formula enables me to calculate the sediment concentration normalized to percent fines (ug/g):

$$[Hg]_{norm} = [Hg]_{sed} / F_{63}$$

$[Hg]_{norm}$ = Sediment concentration normalized to percent fines (ug/g)

$[Hg]_{sed}$ = Bulk Sediment concentration

F_{63} = Percent Fines (<63um), expressed as a fraction ($0 \leq F_{63} \leq 1$)

Water samples were taken in the North and South Forks of Strawberry Creek. According to Method 1669 (Environmental Protection Agency, January 1996), “clean” hands and “dirty” hands must be followed. “Clean” hands passed the bottle to the “dirty” hands person, who collected the water sample. This was a grab sample, which was only taken once. This was taken during a wet weather event because it was collected within one hour of precipitation greater than 0.3” (Smoley, 1993).

Sediment samples were also obtained according to the “Soil Sampling Quality Assurance User’s Guide” (Environmental Protection Agency, 1989) protocol of “clean” hands and “dirty” hands. The “dirty” hands person collected several sediment samples from the same site with soil sampling equipment. Up to 6” of sediment was obtained. Then, we mixed the sediment in a bucket to create a composite sample. The “clean” hands person passed the bottle and the “dirty” hands person placed the composite sediment into that bottle (Mason and Lawrence, 1999). Non-talc gloves were also used. The soil sampling equipment and the bucket were disinfected and cleaned for the next site. New gloves were also used for each site. Composite sediment samples were taken at each site. .

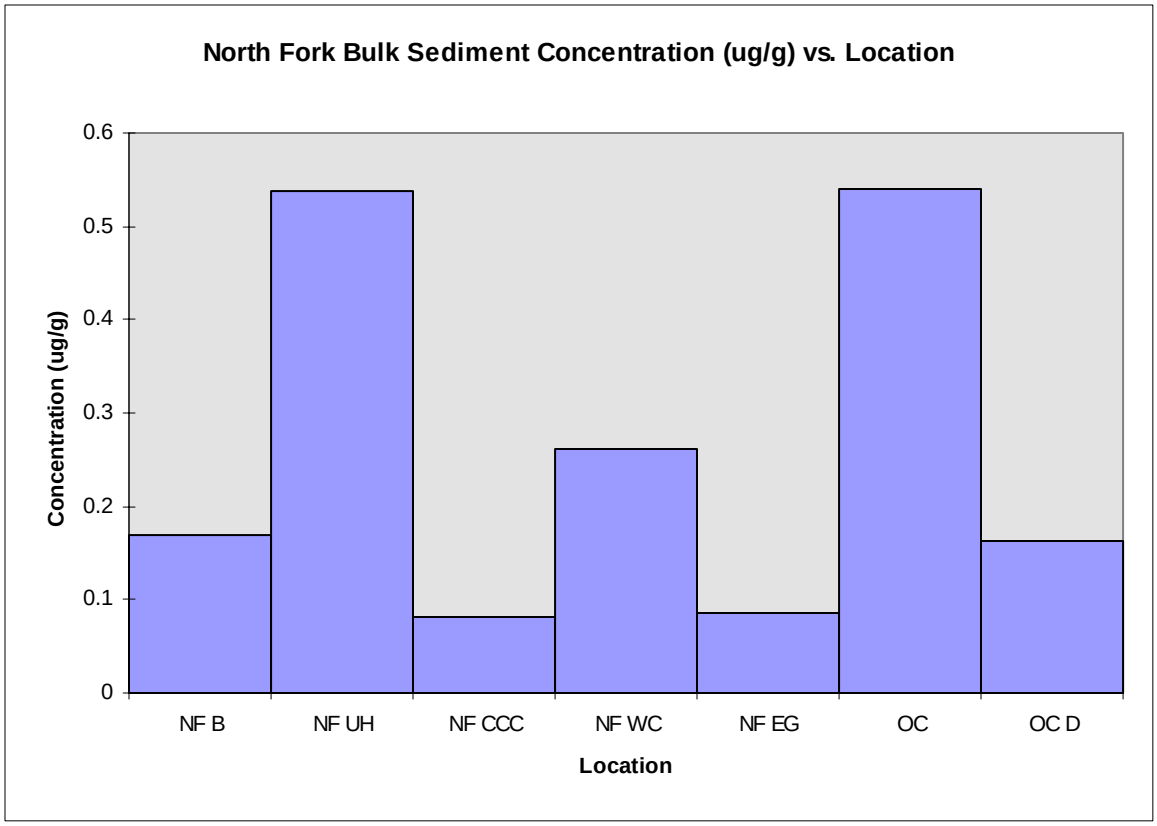
The water samples allow me to answer the question: What is the mercury concentration of Strawberry Creek during a first flush event? The sediment samples enable me to answer the following questions: What are the levels of mercury in Strawberry Creek? Where is the mercury coming from? Is the College of Chemistry a possible source? Might other labs on campus responsible? Both sampling procedures allow me to answer the question: Are these levels safe or hazardous to the environment and the public?

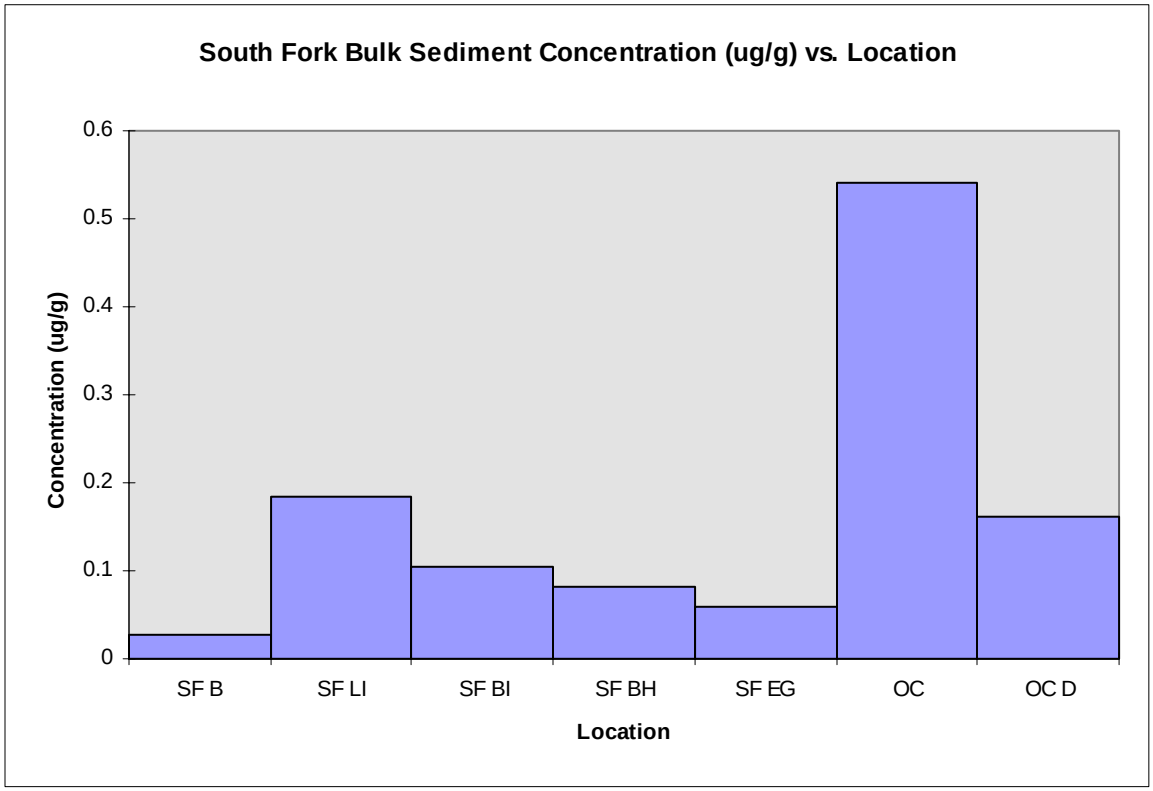
Water samples were collected on September 1, 2000 at the Cross Campus Culvert for the North Fork and the Eucalyptus Grove on the South Fork before convergence with the North Fork. On April 3, 2001, sediment samples were obtained at eleven sites. These sites are the Oxford Culvert, the Eucalyptus Grove (North & South Forks), West Circle, Cross Campus Culvert, University House, Birge Hall, Big Inch, Little Inch, and the headwaters (background) on both the North and South Forks of Strawberry Creek.

Results

The water samples showed that the North Fork had 0.77 ug/L and South Fork had 2.50 ug/L. Recall that the EPA standard is 0.05 ug/L. Note that these samples were taken during a wet season event and it was also the first significant storm in that season.

The following Chart I and Chart II illustrate the sediment sample results:


North Fork Bulk Sediment Concentration (ug/g) vs. Location
Concentration (ug/g)
0.6
0.5
0.4
0.3
0.2
0.1
0
NF B
NF UH
NF CCC
NF WC
NF EG
OC
OC D
Location

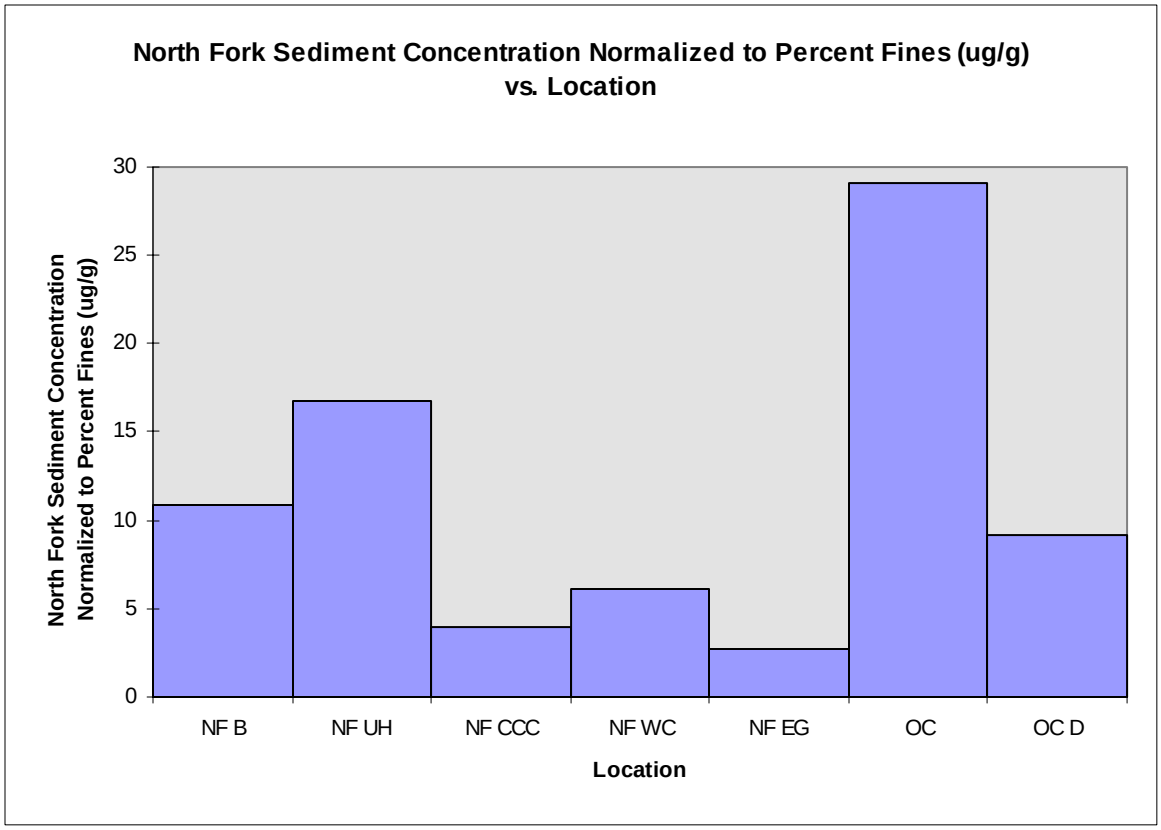

South Fork Bulk Sediment Concentration (ug/g) vs. Location
Concentration (ug/g)
0.6
0.5
0.4
0.3
0.2
0.1
0
SF B
SF LI
SF BI
SF BH
SF EG
OC
OC D
Location

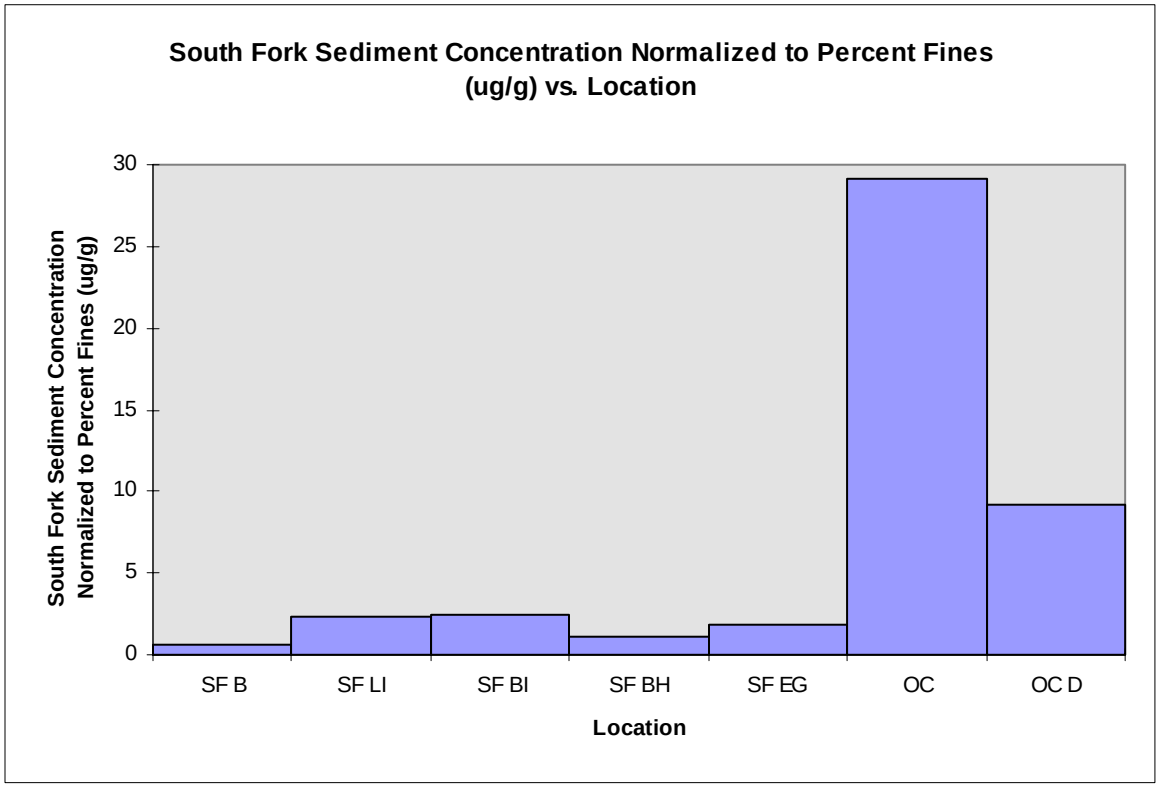
Discussion

This result indicated that mercury was in Strawberry Creek. The concentration of mercury, 0.77 ug/L in the North Fork and 2.50 ug/L in the South Fork exceeded the federally established California Toxics Rule (CTR) criterion for total recoverable mercury (0.051 ug/L). The Cross Campus Culvert was 14 times above the limit. The Eucalyptus Grove was 50 times above the limit. The EPA's safe drinking water standard is 2 ug/L (Environmental Protection Agency Office of Water, 1995). This water was clearly not safe to drink for humans. Furthermore, this mercury flowed into the San Francisco Bay. The impact of mercury is many times worse on the bay, than on the creek. There are more organisms in the bay and some people also eat this fish, even though the Regional Water Board prohibits this.

These concentrations were alarmingly high because they occurred during a first flush event. Since this was the first significant storm event of the season, all of the mercury in the watershed flowed into Strawberry Creek. I believe that most of this mercury was from stormwater runoff, rather than direct discharges from campus labs.

Previous research in the 1987 by Robert Charbonneau, showed that in the dry season event, the concentration of recoverable mercury in water samples averaged 0.2 ug/L. The bulk concentration of mercury in the sediment from Charts I and II averaged 0.19 ug/g. The following Charts III and IV showed the normalized sediment concentration to the percent of fine material <63 um.


North Fork Sediment Concentration Normalized to Percent Fines (ug/g) vs. Location
North Fork Sediment Concentration Normalized to Percent Fines (ug/g)
30
25
20
15
10
5
0
NF B
NF UH
NF CCC
NF WC
NF EG
OC
OC D
Location


South Fork Sediment Concentration Normalized to Percent Fines (ug/g) vs. Location
South Fork Sediment Concentration Normalized to Percent Fines (ug/g)
30
25
20
15
10
5
0
SF B
SF LI
SF BI
SF BH
SF EG
OC
OC D
Location

It was necessary to normalize the concentration of mercury to the percent fines because mercury preferred to settle on fine sediment, rather than coarse sediment. Higher concentrations were observed on samples with more fine sediment. Samples with more rocks and other coarse materials had lower concentrations of mercury. Chart III indicated that there was a higher than average input of mercury near the University House and the Oxford Culvert. The average normalized concentration of mercury was 7.25 ug/g and UH and OC have normalized concentrations of 16.78 ug/g and 29.08 ug/g, respectively. These values were observed very high; however, these values were normalized, and thus, noticeably high. From Chart I, the bulk sediment concentration of UH and OC were 0.537 ug/g and 0.541 ug/g, respectively. These two locations exceeded the numeric target of 0.4 ug/g. Mercury is a naturally occurring element that is present throughout the environment. Human activity may release some of that mercury into the air, water, and soil (Alameda Countywide Clean Water Program, January 2001). I suspect that since the Chancellor's lawn is next to the creek that the erosion of natural deposits of mercury is responsible for the 0.537 ug/g. Because of the construction on Grinnell Path, upstream from the Oxford Culvert, I conjecture that the erosion of natural deposits is also responsible for the 0.541 ug/g.

The Bay Area's pre-anthropogenic average mercury concentration in sediments was estimated between 0.05-0.10 ug/g (California Regional Water Quality Control Board, 2000). The third highest sediment concentration of mercury occurred at West Circle, which was 0.262 ug/g. Even though the concentration was below the numeric target of 0.4 ug/g, note that construction upstream, near Moffitt Library, could be contributing to the higher than average pre-anthropogenic mercury concentration. In general, presently there is more construction in the North Fork watershed than the South Fork watershed, which may explain why the North Fork has higher concentrations of mercury.

Chart IV showed that the South Fork was less impacted by mercury. The concentration of mercury in the North Fork background of 0.169 ug/g was much higher than the South Fork background of 0.0265 ug/g. Both concentrations should have been similar; however, the North Fork had six times more mercury. There was no evidence of erosion in the North Fork background, nor any evidence of anthropogenic activity. I believe that the human error was responsible for the high concentration recorded at the North Fork background. Since the experiment started downstream and went upstream, the site previous to the background was the

University House. I suspect that equipment were not disinfected or cleaned thoroughly. Thus, mercury residues remained in the equipment and contaminated the North Fork results. The results showed that direct discharge of mercury from campus labs did not occur.

Some sources of mercury may be from biological methylation of inorganic mercury by microorganisms or other chemical donors of the methyl group in the bottom mud with mercury sediments (Wood, 1968). On the other hand, this type of accumulation does not result in high levels of mercury concentration.

Suggestions on Future Research I recommend water samples be taken in the future to compare with Robert Charbonneau's result and observe the mercury quantity in the creek over time. Because a low detection limit is required to evaluate mercury concentrations in Strawberry Creek and to compare the sample results to the water quality objective, mercury analysis will be performed by EPA Method 1631 "Mercury in Water by Oxidation, Purge and Traps, and Cold Vapor Atomic Fluorescence Spectrometry" (Environmental Protection Agency, July 1996). This analytical method supports water quality monitoring programs authorized under the Clean Water Act. Frontier Geosciences, of Seattle, Washington performs this analysis. This laboratory assisted in the development of Method 1631 (Bodine 2000, pers. comm.). The method detection limit for mercury is 0.2 ng/L (nanograms per liter or parts per trillion).

Grab samples are collected directly into fluoropolymer bottles, and are completely filled to the top (no headspace). The sample temperature will be maintained at 0°C-4° C during shipment to the laboratory. Samples will be composited and preserved at the laboratory to minimize contamination. The samples must be received and preserved by the laboratory within 48 hours of sample collection.

Water samples may not detect mercury in the sediment. For example, total mercury was undetected in polluted rivers in Japan; however, freshwater fish from the river were found to range up to 1 mg/kg (Ueda, et al, 1971). Direct accumulation of methyl mercury had been observed in experimental studies, although the mechanisms by which the fish organism can accumulate methyl mercury have not yet been satisfactorily explained (Hannerz, 1968). However, sediment sampling will help determine the level, if water sampling shows that mercury is undetected. Furthermore, I know that Brooks Rand Ltd and Frontier Geosciences have lower detection limits than the Japanese study from 1971.

The biggest obstacle in future research may be funding. The price for a three-week turn around time is $66 per water sample. The price for a three-week turn around time is $72 per sediment sample and $100 per sample to assess particle size. The price for a future Strawberry Creek study may cost:

$4,070 = (11 water samples)($66 /water sample)(minimum of 3 water sample dates) +
(11 water samples)($72 /sediment sample) +
(11 particle size samples)($100 /particle size sample)

This does not include the price for fluoropolymer bottles, flow measuring device, sampling equipment, shipping within 48 hours, ice, and boots. The cost may exceed $5,000. Also, the exact amount of methyl mercury will not be detected because the analysis will only look for total mercury, not exact values of methyl mercury (Westoo, 1966). However, methyl mercury will be detected in the total mercury.

Conclusion In conclusion, during a first flush event mercury concentration from water samples will be very high. This occurs because the first flush is the first storm event of the season, which cleanses the watershed and discharges mercury into the creek with stormwater runoff. The turbulence of the creek's flow prevents mercury from settling on fine sediment. Mercury concentration in Strawberry Creek are generally safe and in compliance with the numeric objective. The only hot spots in campus are the University House and the Oxford Culvert. The University House mercury concentration is probably from the Chancellor's private lawn, which is near the creek and causes the erosion of natural deposits mercury. The construction on Grinnell Path may be responsible for the concentration of mercury in Oxford Culvert. The construction erodes natural deposits of mercury. I do not believe that the mercury is coming from direct discharge of campus labs. My research only investigated possible sources. More research is needed to prove a source.

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