

Get the Lead Out!

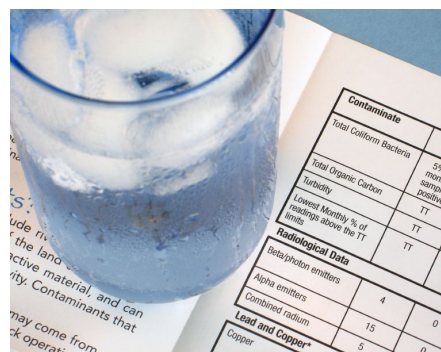
An Interdisciplinary Case Study for Science Students

by

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Part I— Lake County Emergency

At Lake County Community Hospital, Dr. Barbara Elliot raced to the emergency room. There, she found 6-year-old Suzy Smith, whom she had seen just yesterday with what the doctor had thought was a case of flu. Suzy's mother, Jane Smith, sighed with relief when Dr. Elliot stepped into the room.

“Thank goodness you're here! Suzy can't seem to keep any food down. She's so pale and weak ... I'm worried about her.”

“Let's have her spend the night, Jane, so I can keep an eye on her. I suspect there is something going on here besides the flu. I'd like to run a series of tests on her.”

After checking Suzy's vital signs, the doctor got the little girl settled into a hospital room.

Dr. Barbara Elliot was new to Lake County, Colorado. During the year she had been practicing there, she had observed that a large number of her pediatric patients had similar symptoms: sleeplessness, stomachache, vomiting, diarrhea, and anemia. The doctor was becoming convinced that there was an underlying problem—some common cause.

When Dr. Elliot got back Suzy's blood test results, she was alarmed to see that the blood contained elevated lead levels. Her thoughts immediately shifted to the abandoned mining district only a few miles away. Was it possible that this was the source of lead in Suzy's blood? Could contamination from the old mines be responsible for the large number of sick children she had seen over the past year?

Background

The mining district of Lake County, Colorado, is about 120 miles west of Denver and was the site of gold mining as early as 1859. In the 1870s, silver and lead were also mined. During World War II, large amounts of zinc, lead, and copper were extracted at the site.

Mining at the location has since ceased, but there remains a large quantity of resultant waste at what is known as the “California Gulch Site,” a 15-square-mile area that serves as a watershed. Among the waste products from mining operations are mine tailings, slag piles, waste rock piles, and abandoned mine shafts.

Questions

1. (a) Describe a general process of mining lead from ore, including the name and formula for the primary ore that contains lead. (b) Define terms used in the process such as *ore*, *smelt*, *gangue*, *refine*, *slag*, and *mine tailings*.
2. During the smelting process, sulfur dioxide gas is produced. When dissolved into water, what compound is produced? Write the chemical equation(s) for this process.
3. What is a watershed? What might be some possible environmental effects of an area like this being mined for lead in light of your answers to questions 1 and 2? (*Hint*: What is the effect of an acid on an insoluble compound such as lead(II) sulfide?)
4. What are considered safe levels of lead in human blood in parts per million (ppm)?
5. What are some of the effects of overexposure to lead for adults? For children?
6. How are patients with high levels of lead in their blood treated?

Part II—Water Testing in Lake County

Based on the elevated lead levels in children that she and her colleagues had seen, Dr. Eliot believed that lead ores from the nearby mining district may have contaminated both the soil and water in the area. Contained within this 15-square-mile area is the California Gulch watershed. It empties into the nearby Arkansas River and provides the community with agricultural irrigation, recreation, and municipal drinking water.

Dr. Elliot and several other prominent citizens have been able to successfully persuade local officials to contract an environmental study of the area's soil and water. You are a chemist who works with the contracted environmental lab. Your primary area of concern is water testing for the presence of lead in groundwater samples using atomic absorption spectrophotometry (AA). Colleagues will be testing for other metals in the water. Residential soil samples from Lake County will also be tested.

Questions

1. Outline how flame spectrophotometry works by explaining the following:
 - The absorption of light energy at characteristic wavelengths.
 - The proportionality of light absorbed to sample concentration using Beer's Law.
2. Define and diagram the basic parts of an atomic absorption spectrophotometer including the nebulizing chamber (or aspirator), the flame, light source, monochromator, and detector.
3. Why must all equipment in this analysis be acid washed?
4. What concentration (ppm) of lead in drinking water is considered dangerous ("action level") by the U.S. Environmental Protection Agency (EPA)

Part III—Lead Remediation in Lake County

Samples of groundwater in and around Lake County have been shown to have lead levels as high as 8 ppm as a result of your water analysis. These concentrations are well above the EPA action level of 0.015 ppm. Analysis of residential soils has found levels there to be as high as 1000 ppm; therefore, the EPA has begun evaluating the site for remediation.

There are two major categories of remediation for “heavy” metals such as lead. One method requires the physical movement of contaminated soil to a treatment facility and subsequent transfer of “clean” soil to the affected area. The second method involves phytoremediation, the removal of toxic substances by living plants. Because funding is limited, this second method has been chosen.

The following are four types of phytoremediation: phytoaccumulation, phytodegradation, rhizodegradation, and phytovolatilization. Research indicates that phytoaccumulation is ideally suited for the Lake County site.

You are a member of the EPA’s Superfund Response Team. You and your team must now decide on the most effective way to implement phytoaccumulation in the Lake County area. As part of your research, you should access the following resources in order to answer the questions below. (*Note:* The first resource is a lengthy report; you only need to read the first nine pages.)

- Pivetz, B.E. 2001. Phytoremediation of contaminated soil and ground water at hazardous waste sites. United States Environmental Protection Agency.
<https://www.epa.gov/sites/production/files/2015-06/documents/epa_540_s01_500.pdf>
- Blaustein, R. 2017. Phytoremediation of lead: what works and what doesn’t. *BioScience* 67(9): 868.
<<https://doi.org/10.1093/biosci/bix089>>

Questions

1. According to Pivetz, which type of remediation for lead-contaminated soil would you expect to be more expensive: removal and replacement of contaminated soils or phytoremediation?
2. Why are heavy metals, such as lead, difficult to remove using phytoremediation? (See Blaustein.)
3. Explain how each of the following four phytoremediation processes work: phytoaccumulation, phytodegradation, rhizodegradation, and phytovolatilization. (Use both Pivetz and Blaustein.)
4. Which two of the four processes in Question 3 would be the best choice for the heavy concentration of lead contamination in Lake County? Explain. (Use both Pivetz and Blaustein.)
5. What is a hyperaccumulator? (See Blaustein.)
6. What three or four plants might be good choices for phytoremediation of lead contaminated soils in Lake County? (Use both Pivetz and Blaustein.)



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LAB HANDOUT—LEAD ANALYSIS BY FLAME ATOMIC ABSORPTION SPECTROSCOPY

In this analysis, you will determine the concentration of lead in groundwater samples taken from Lake County.

Using the Atomic Absorption Spectrophotometer (AA), you will be able to measure the concentration of trace amounts of metals in a water sample. We will be measuring lead levels at the parts per million (ppm) level. This requires that the glassware used in the analysis is as uncontaminated as possible. We will therefore use a method called “acid washing” to remove any oxidizable contaminants.

This is a two-day lab. On the first day, glassware will be cleaned. On the second day, the five lead standards will be prepared and these and the groundwater sample will be run on the AA.

The first step in this lab is to wash all glassware used so that it is completely uncontaminated. Acid washing is done to remove any oxidizable contaminants. Six-molar nitric acid is used. *It is crucial that you wear safety glasses or goggles at all times during this lab to protect your eyes!* You will be wearing latex gloves, and it is recommended that you purchase and wear a lab apron (available in the bookstore) to do your acid washing. This will protect your clothing.

Acid Washing (Day One)

Each group will wash the following equipment at one sink:

- DI water bottle (clean this first so that you can use it to rinse all of your other equipment)
- 1-mL graduated pipet
- 1 5-mL graduated pipet
- 1 10-mL volumetric pipet
- 5 200-mL volumetric flasks
- 1 1-L volumetric flask
- 1 150 mL beaker
- 1 25-mL beaker
- 1 Pasteur pipet

Place approximately 50 mL of 6M nitric acid into a 150 mL beaker. Label a 250 mL beaker (does not need to be acid washed) to contain all acid waste.

For each piece of glassware that you wash, add only a small amount of acid. Do not fill to capacity. Rinse glassware with the acid thoroughly by moving the glassware so that the acid completely coats the inside surfaces of each piece. The outside surfaces do not need to be cleaned with the nitric acid.

Use a pipet bulb to draw a small amount of acid into the pipet. Be careful not to draw it into the pump! Acid will damage the pipet bulb.

Rinse well with tap water at least three times (do not re-use the rinse water). Your final rinse is done at least three times with DI water.

Dispose of all acid into the waste container provided under the hood.

Standard and Sample Prep (Day Two)

The solvent for all standards, 1% nitric acid, will be prepared.

Lead standards will also be prepared for a calibration curve on the AA. They will be made up in the following concentrations: 0 ppm, 2.5 ppm, 5 ppm, 7.5 ppm, and 10 ppm. Five 200-mL volumetric flasks will be labeled with each of the concentrations. These “secondary” standards will be prepared from a certified “primary” 1000 ppm standard.

First determine the volume of the 1000 ppm standard required to make a 200-mL secondary standard in the above concentrations. Show your calculations to the instructor and get the instructor’s initials before preparing the standards.

Next, prepare 1 liter of 1% nitric acid solvent. This can be made by pipetting 10 mL of concentrated nitric acid into a labeled 1-L volumetric flask already filled with about 600 mL of deionized water. Swirl to mix, and only then should you dilute the solution to the mark with deionized water. Stopper and invert to mix the solution about 25 times to mix well. *Remember the rule for making up acid solutions: Always add acid to water—never the reverse.*

Obtain approximately 10 mL of the primary standard (1000 ppm). It should be placed in a 25 mL beaker and covered with parafilm when not in use.

Label each of the five 200 mL volumetric flasks with one of the following labels: 0 ppm, 2.5 ppm, 5 ppm, 7.5 ppm, and 10 ppm.

The solvent for each of these standards will be 1% nitric acid.

Your 0 ppm standard will be only 1% nitric acid. Using a pipet, add the correct amount of primary standard (1000 ppm) to each of the remaining four volumetric flasks. Dilute to the line with the solvent finishing up with a Pasteur pipet. This is a disposable pipet and can be thrown away when you have prepared all the standards. Stopper and invert each of the flasks 30 times to ensure complete mixing.

You will be provided with a groundwater sample to test. Pour it into your acid-washed 150 mL beaker and cover with parafilm until you are ready to analyze it.

Running the Standards and Sample on the AA

The AA will be set up, turned on, and allowed to warm up for at least 15 minutes.

Aspirate your 0 ppm sample when the instrument prompts you and zero the instrument. Each standard run will be analyzed three times and the average value will be reported on your screen along with the relative standard deviation (RSD) of the three absorbance readings.

When prompted, wipe off the aspirator with a kimwipe and aspirate your 2.5 ppm standard. Follow this procedure with each of the remaining 3 standards. A calibration line will be displayed when you have finished running your standards.

Next you will be prompted to aspirate your groundwater sample. After it has been analyzed, you will print up a report that will display all of your group’s pertinent information.

Dispose of all standards and groundwater samples into the waste container provided under the hood.