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CASE STUDY: RIVER OF ORES

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Part I: City Notices

Upperland is a small town, with around 6700 inhabitants, situated on the banks of the Fall River, which supplies water to the municipality. In the river's valley, one can find Atlantic Forest conservation areas and numerous limestone caves. On a spring afternoon in 2007, the Upperland population received the following notice in the mail.

Figure 1. Notice sent to Upperland's residents.

Upperland City Hall
Municipal Health Department

Dear citizen,

The Health Department of Upperland has been notified of lead poisoning cases in the population. Symptoms include joint pain, headache, abdominal pain, nausea, pallor, dizziness and loss of appetite.

Soon, we will carry out a clinical evaluation of the population through blood tests. Investigations will also be made to provide information about the origin of the contamination.

In case emergency, go to the nearest hospital. Attn.,

Angelina R.
Angelina Ramona
Health Officer

Very worried about the situation, the Health Officer of Upperland, Angelina Ramona, calls her cousin, Joana, who is a chemistry graduate student.

- Hi, there! How's it going? – Asks Angelina.

- Oh, you know, it's going. Mom sent me a picture of the city notice. It looks like a serious problem.

- Yeah. I wanna talk to you about that. I need your help to find out what's causing the contamination of the river.

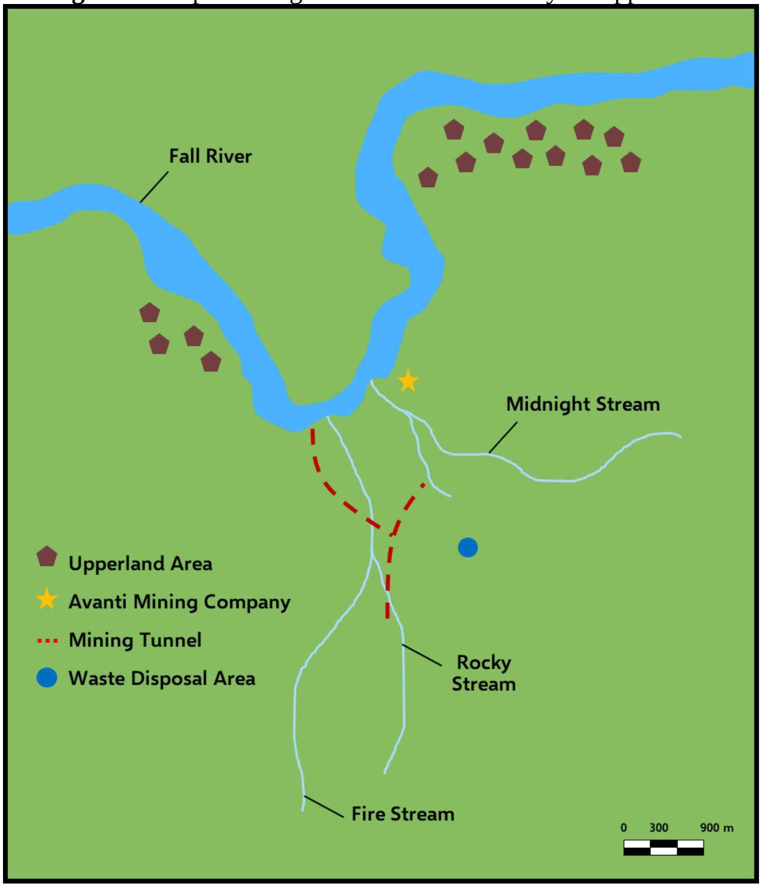
- Of course. Happy to help. I'll do some research and share anything I find.

- I appreciate the help.

- How's aunt Carol? – They keep chatting on the phone.

They hang up. Joana goes online in search of information about Upperland and finds the following map.

Figure 2. Map showing the area around the city of Upperland.



Activities – Part I

1. What do you already know about the case study situation? Have you read about similar situations? What experiences related to the subject addressed in this case have you had previously?

2. Based on the case narrative, **formulate hypotheses** about the origin of the lead contamination of Upperland inhabitants and justify the relevance of these hypotheses.

3. Based on the case narrative, **propose a question** for your group to investigate.

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Part II – The Avanti Mining Company

Continuing her research, Joana finds more information about the Avanti Mining Company, formerly active in the region, whose mining tunnels, waste disposal area and processing plant are indicated on the map she located previously.

"The municipality of Upperland was the site of lead extraction and refining activities for over 50 years. The main mining company in the region was Avanti, which between 1954 and 1995 carried out the extraction of galena. Its activities ceased due to the depletion of the mineral deposits. However, even after a decade of the company's closure, mining waste remains in the region. Some of the other actions that put the region at constant environmental risk are the depositing and stacking of waste in areas close to the former company buildings and along the banks of the Fall River; the release of large amounts of particulate lead into the atmosphere, which were deposited in nearby areas of the processing plant; and the release of effluents directly into Fall River. Part of the tailings was also used by the Upperland residents to pave the city's streets".

The next day, Joana gets early to the lab at the university to tell Stephany, her friend, about the situation in Upperland and the information she has found so far.

- It's been so long since the company closed. Do you think it is possible that the water is still contaminated by lead? – Joana asks.

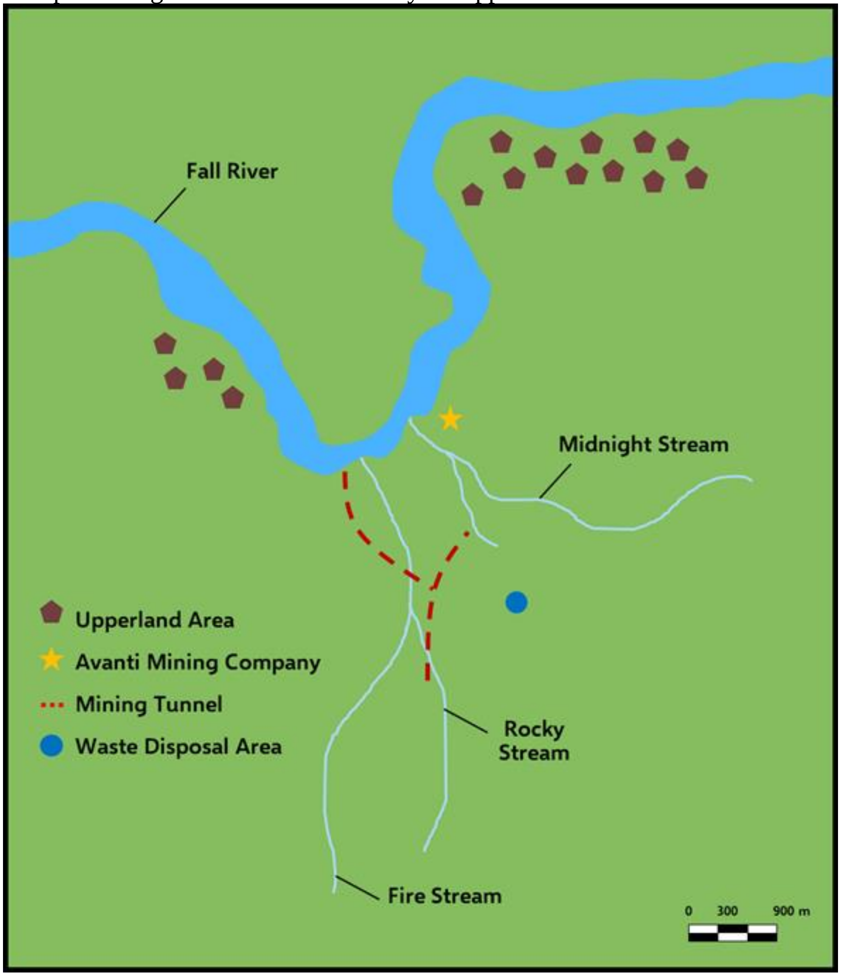
- It is not impossible. Metals are not biodegradable and can accumulate for years in river sediments. With physical-chemical changes, the metals can end up solubilizing.

- I was planning to visit my parents out there this weekend. Do you wanna come with me? We could collect some sediment samples around the river and streams and analyse them later.

- Of course! It would be fun to visit your city.

The girls get back to the map (Figure 3) and start thinking about points along the Fall River and its streams where they could collect sediment samples. They also start to figure out how to analyse the samples.

Figure 3. Map showing the area around the city of Upperland. Fall River runs from left to right.



Activities – Part II

1. Considering the problem proposed by your group in Part I and the document available on Tidia-Ae© presenting the map of the River Fall and its tributaries, demarcate points for the collection of sediment samples to help Joana and Stephany in their investigation. Justify your choice of sampling points.

2. Helping Joana and Stephany analyse the sediments is also a mission of your group. Search for two instrumental analytical techniques that can determine the concentration of heavy metals (lead and zinc) in **sediment samples and argue in favour of the one considered the most appropriate by your group**. The argument can be based on the following aspects: cost of equipment and analysis, complexity of manipulation, sample throughput, detection limits, sample size, and other factors the group find interesting.

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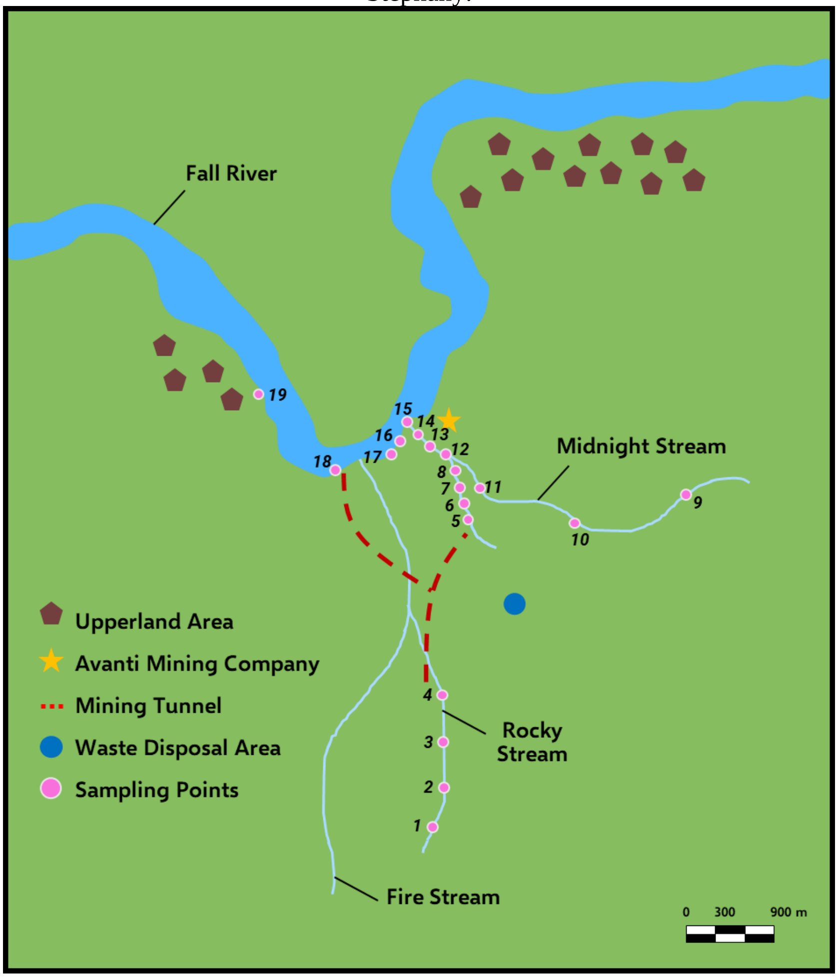
Part III – Diving into the River

Based on the map presented before, Joana and Stephany chose 19 sediment sampling points on the Fall River and its streams. Figure 4 below, presents the points they have chosen.

Figure 4. Map of the municipality of Upperland, showing the 19 sediment sampling points chosen by Joana and Stephany.



For a longitudinal study, Joana and Stephany decide to collect sediment samples throughout the year, in the months of May, September, November and January. After collected, the samples were oven-dried (at 40 ºC) and sieved (with a 2 mm mesh). Pb and Zn contents were determined in two fractions: pseudototal and exchangeable. For the pseudototal fraction, samples were digested in microwave digestion system, with HNO_3 and HCl (3:1), according to the SW 846-3051A method. After cooled, the suspension was filtered through filter paper. The exchangeable fraction was extracted with $BaCl_2$ 0.1 mol L-1, in circular agitation for 2 hours and collected by centrifugation. The determination of Pb and Zn was performed using a Thermo Scientific iCAP 6500 for Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES).

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Activities – Part III

1. a) What connections can be established among the sampling criteria adopted by Joana and Stephany and those your group chose? b) What criteria were used by the characters that were not used by your group and vice versa? c) Do you think it is relevant to change the sampling points proposed by your group? **Justify your answers.**

2. Do you think the equipment proposed by your group should be changed in accordance with what was suggested by the characters? **Justify your answer.**

3. The metal concentration in sediments is commonly determined by **pseudototal**, **bioavailable** and **exchangeable fractions**. Define and exemplify the use of such concepts.

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Part IV – Solving the Problem

Joana searched a little more and found out the following information about zinc and lead in sediments, which she shared with Stephany.

"*Lead is a bioaccumulative metal with no biological function for both plants and humans. Upon falling into a body of water, most of the lead is retained in the sediments and very little is transported in surface or ground water. Zinc is associated with lead in the form of galena, and, in an aquatic environment, it predominantly attaches to suspended material before accumulating in the sediment. Changes in the environmental conditions can affect the bioavailability of these metals, so that they can become available into the water column, due to oxidation-reduction reactions, or to resuspension processes of physical (flow), biological (activity of organisms living in sediments) and human (navigation) activity*"

- In other words, even though the mining company has been closed for more than ten years, it still can affect the region. – Joana comments.

- This is all due to the waste that was left in the open air, without any protection.

- A report that I've found indicated a total of 180 Gg of residues was disposed in the region. I'm sad for my relatives still living there.

- It's a very unfortunate situation, Joana. However, our research may help in finding a solution, as we can determine the bioavailability of the metals and be able to predict the real risks of these substances to the Upperland population and the environment.

- Thanks for the help, Stephany!

From the experimental procedures presented in Part III of the case study, Joana and Stephany arrived at the results in Tables 1 and 2.

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Table 1. Pseudototal and exchangeable lead content (mg/kg) in sediment samples at different sampling points.

POINT	MAY		SEPTEMBER		NOVEMBER		JANUARY	
	PTOT	EXCH	PTOT	EXCH	PTOT	EXCH	PTOT	EXCH
1	95,8	< 0,1	90,8	< 0,1	22,9	< 0,1	127	< 0,1
2	3,9	< 0,1	14,9	< 0,1	19,2	< 0,1	21,4	< 0,1
3	6,8	< 0,1	78,0	< 0,1	15,9	< 0,1	55,4	< 0,1
4	162	< 0,1	118	< 0,1	111	< 0,1	99,4	< 0,1
5	10653	7,1	6268	8,4	9224	11,5	19113	6,3
6	2073	1,7	3867	2,4	1396	3,2	6886	2,3
7	17741	5,1	4348	1,7	3620	2,2	16750	6,0
8	5021	< 0,1	2211	< 0,1	4961	0,7	6307	6,2
9	38,1	< 0,1	42,9	< 0,1	50,7	< 0,1	43,4	< 0,1
10	29,1	< 0,1	40,4	< 0,1	33,4	< 0,1	31,4	< 0,1
11	221	0,7	121	< 0,1	179	< 0,1	78,2	< 0,1
12	273	< 0,1	635	< 0,1	235	< 0,1	475	1,6
13	394	0,2	337	0,2	622	0,2	203	< 0,1
14	904	2,4	261	< 0,1	8549	47,9	1146	0,8
15	2029	2,6	3689	2,4	3950	25,0	6135	3,1
16	21631	471	19638	246	12530	199	24300	241
17	26,4	< 0,1	17,5	< 0,1	18,9	3,3	23,9	< 0,1
18	690	3,4	16,2	< 0,1	740	3,5	686	1,2
19	21,3	< 0,1	16,5	< 0,1	5,6	< 0,1	15,0	< 0,1

PTOT = Pseudototal Fraction; EXCH= Exchangeable Fraction.

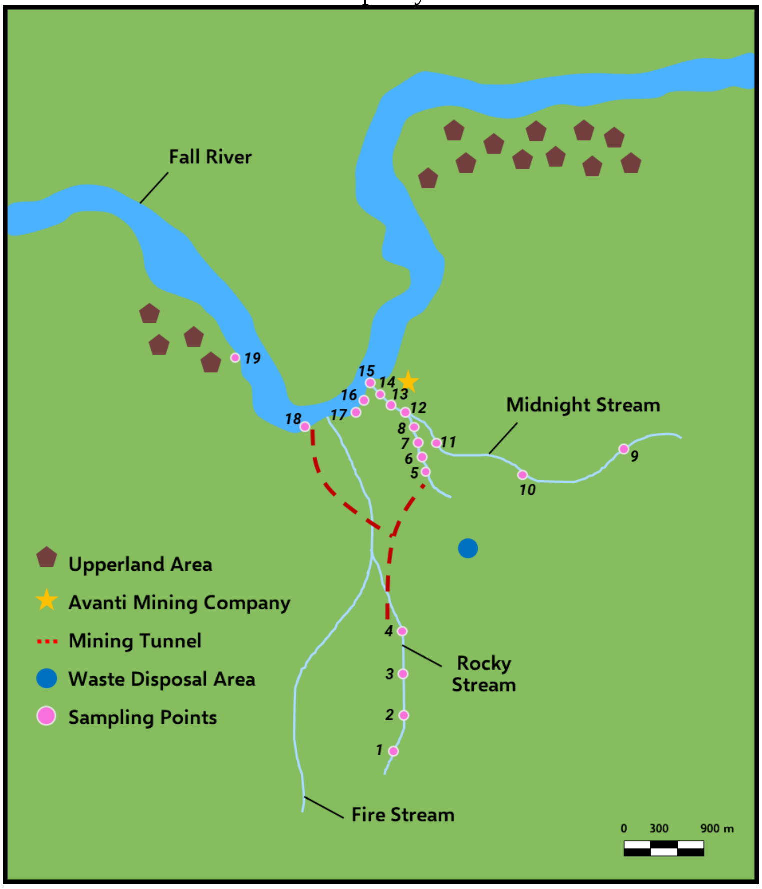
Table 2. Pseudototal and exchangeable zinc content (mg/kg) in sediment samples at different sampling points.

POINT	MAY		SEPTEMBER		NOVEMBER		JANUARY	
	PTOT	EXCH	PTOT	EXCH	PTOT	EXCH	PTOT	EXCH
1	53,9	< 0,1	64,5	< 0,1	55,0	< 0,1	50,4	< 0,1
2	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
3	< 0,1	< 0,1	31,2	< 0,1	< 0,1	< 0,1	2,6	< 0,1
4	12,7	< 0,1	0,8	0,1	4,1	< 0,1	2,7	< 0,1
5	2387	1,2	925	7,6	3621	13,7	3829	4,7
6	163	0,9	486	< 0,1	160	0,8	625	< 0,1
7	1149	0,5	966	< 0,1	505	0,6	1167	1,6
8	153	< 0,1	103	< 0,1	284	0,4	316	2,6
9	< 0,1	< 0,1	< 0,1	< 0,1	1,9	< 0,1	< 0,1	< 0,1
10	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
11	6,5	< 0,1	6,4	< 0,1	9,2	0,3	< 0,1	< 0,1
12	23,6	< 0,1	46,7	< 0,1	28,9	1,9	18,1	< 0,1
13	149	< 0,1	40,8	< 0,1	54,5	4,7	18,2	< 0,1
14	81,7	< 0,1	41,6	< 0,1	350	5,7	47,0	< 0,1
15	341	1,4	379	1,1	548	4,5	293	< 0,1
16	32376	446	41669	261	32960	278	22130	331
17	6,9	4,3	1,4	1,2	2,5	1,7	7,1	< 0,1
18	412	0,5	222	0,4	847	4,4	262	< 0,1
19	2,4	1,2	1,1	< 0,1	0,7	< 0,1	3,8	< 0,1

PTOT = Pseudototal Fraction; EXCH= Exchangeable Fraction.

During the evaluation of the data, Stephany and Joana get back to the sampling points selection (Figure 5). Points 1 and 9, which represent the headwaters of Rocky and Midnight Streams, respectively, were chosen as reference points because they are in a higher altitude and, supposedly, were not impacted by the mining activities. Point 19 is also a reference, as it is immediately above the affected area. Points along the streams and on the Fall River were chosen to verify the direct effects of mining and waste disposal in the area. Point 16 represents the place where the wash water was poured.

Figure 5. Map of the municipality of Upperland, showing the 19 sediment sampling points chosen by Joana and Stephany.



Another important information for the evaluation of the results concerns the climate of the Upperland region, which is characterized in the summer months by hot temperatures and rainfalls (average temperature above 22 °C) and in the winter months by infrequent frosts (average temperature below 18°C).

Since the Brazilian legislation does not have reference values for metals in sediments, Joana and Stephany sought international environmental legislations to assist them in the evaluation of the data. Table 3 presents the values used by them.

Table 3. International reference values (mg/kg) for the maximum permissible concentration of lead and zinc in sediments.

Metal	Spain	Canada	USA	Netherlands
Lead	600	112	218	530
Zinc	3000	-	410	720

Activities – Part IV

1. What connections can be established between the data acquired by Joana and Stephany (Tables 1 and 2) and the sampling points they chose (Figure 5) for the understanding of the “legacy” and the impact of the Avanti Mining Company’s activities in the Upperland region?

2. What conclusions can be drawn on the adverse effects on the environment in the Upperland region from the comparison of the data obtained by Joana and Stephany (Tables 1 and 2) with international reference values for the maximum permissible concentration of lead and zinc in sediments (Table 3)? **Justify your answer.**

3. Did the data interpreted so far confirm the hypotheses formulated by your group in Part I of the case study? **Justify your answer.**