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INTERRUPTED CASE STUDY: REMNANTS OF A LEAD PAST

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Part I: Mystery in Divina Eco Park

The Divina Eco Park is a Conservation Unit that houses a vast portion of the Atlantic Forest. Several attractions are on site, such as trails, zip lines, cave exploration and buoy cross in the Beans River, which cuts through the Park. This one has about 35 thousand ha of extension, with more than 1200 ha of forest.

On a Sunday afternoon in the early 2000s, Victoria and Igor decided to go to the Park, where they met. They could not wait to spend a romantic moment together and see a friend of the couple, Mr. Paulo, who works there as a janitor. However, that afternoon, the meeting was not possible. When they arrived, they were told that their friend was sick and away from work.

- What a pity. Do you think that after walking around the Park for a while, we could visit him? – asked Igor.

- Sure we can. He lives a little further down the route from Beans River, in the Beans Village, doesn't he? - Victoria asked the caretaker who was replacing his friend.

- That's right, still inside the Park. There's a small village down there, just ask for Mr. Paulo, everyone knows where he lives.

After the tour, the two headed towards the village. It did not take long, and they found the house where Mr. Paulo was resting. He was very surprised to see the couple.

- Wow, what are you doing here? - Mr. Paulo asked.

- Hello, Mr. Paul. We went to the Park today, found out you are sick and decided to pay you a visit. Are you better? What happened? - asked Igor.

- I've been feeling pain in my stomach and head, nausea, paleness and imbalance. So I went to the local doctor and had some blood tests done. I was poisoned with lead. But now I'm much better, thank God. - said, Mr. Paulo.

- Lead poisoning? - Victoria asks indignantly. - How did this happen?

- The doctor believes that the water that supplies the Vila is contaminated. My wife and some other friends here in the area also got sick.

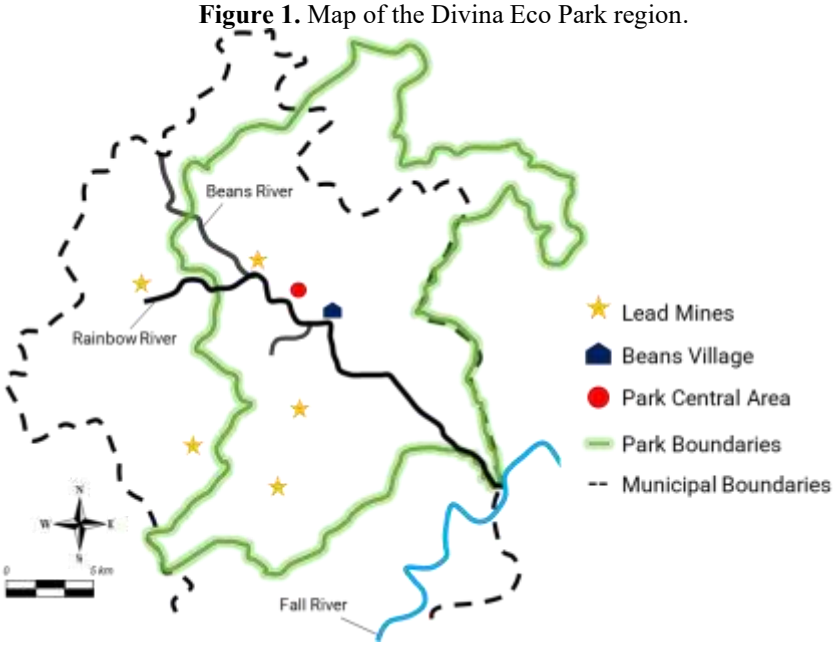
Victoria and Igor, who are graduate students in the chemistry department at the university in the region, had an idea.

- Mr. Paulo, let's do some research and find out what happened, all right?

- All right, my dears.

Very concerned about Mr. Paulo, the two researched the Divina Eco Park region when they got home and found the following map.

Figure 1. Map of the Divina Eco Park region.



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 the Beans Village inhabitants and justify the relevance of these hypotheses.

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

Part II – Looking at the Past to Understand the Present

Continuing their research, Victoria and Igor found some information about the Garden Mining Company that used to exist in the region, whose mines are identified with yellow stars on the map they had studied.

"For more than half a century, nearby activities along the Beans River have affected the region, putting it at constant ecological risk. Among the activities carried out, including agriculture, sewage discharge and population expansion, mining has always been in focus, as the region contains large reserves of copper, lead and zinc. The former Garden Mining Company, located inside the Park, ended its activities in 1992 due to technological difficulties in processing the ore, which was essentially composed of galena, with up to 75% lead and 2.6 to 3.4 kg of silver per ton. The main mine was located on the banks of the Rainbow River, a tributary of the Beans River, which in turn is a tributary of the Fall River, a region where a lot of rainfall occurs. During the entire exploration period, the waste material was piled up along its banks".

- It has been a long time since the mining company was deactivated. Is it even possible that the water is contaminated, as suspected by Mr. Paul? - Victoria asks.

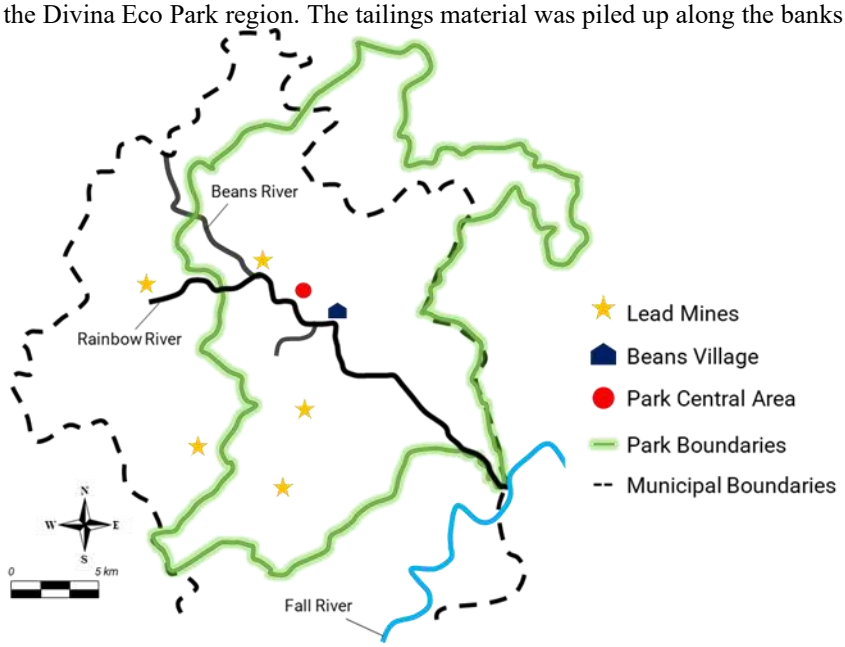
- Heavy metals, such as lead, are not degradable and end up remaining for long periods in aquatic environments, accumulating mainly in the sediment. And, if I'm not mistaken, the water used in the Beans Village comes from the Beans River. Therefore, the doctor's hypothesis is entirely plausible. – Explains Igor.

- Understood. How about we analyze the Beans River sediments to understand the situation better and help the Village community? - Victoria asks.

- I was going to suggest that myself.

Victoria and Igor analyze the map of the region, seeking to choose sampling points for sediment in Beans River that offer support for the investigation they intend to carry out. Furthermore, the couple begins to speculate on how to analyze the sediment.

Figure 1. Map of the Divina Eco Park region. The tailings material was piled up along the banks of rivers in the region.



Activities – Part II

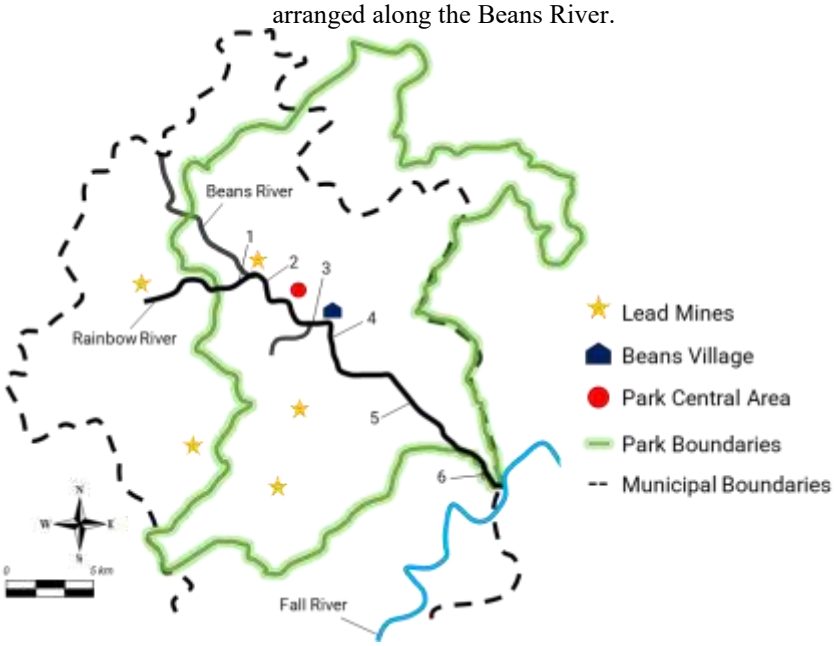
1. Considering the problem proposed by your group in Part I, demarcate points for the collection of sediment samples to help Victoria and Igor in their investigation. Justify your choice of sampling points.

2. Helping the couple analyse the sediments is also a mission of your group. Search for two instrumental analytical techniques that can determine the concentration of heavy metals (Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn) 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.

Part III – Submerging in Beans River

Like their group, Victoria and Igor thought of sediment collection points along the Beans River. Figure 3 shows the location map of Divina Eco Park and the six sampling points they chose.

Figure 3. Study area location map. Victoria and Igor demarcated the six sampling points identified on the map, arranged along the Beans River.



After collecting the sediment samples, using a Vanveen dredge, at the points described, Victoria and Igor processed the samples to determine the metal concentrations according to the following experimental procedures:

Preparation of sediment samples for determining the concentration of bioavailable metals: from 1.00 g of sieved and dried sample, add 25.00 mL of 0.10 mol L^{-1} HCl, subject the mixture to stirring at 200 rpm for two hours and subsequent filtration of the suspension. Store the filtrate at 4 °C.

Preparation of sediment samples to determine pseudo-total metals: from 0.50 g of sieved and dried sample, digest with 15.00 mL of concentrated HNO_3 p.a., leave at rest for 12 hours, and heat up to 160 ºC for four hours. Then, add 8.00 mL of 30% H_2O_2 (v/v), heating at 160º C for another 30 minutes. Transfer the samples to a 100.00 mL volumetric flask, completing the volume and removing the undigested portion by filtration.

The Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn concentrations in the samples were measured by Atomic Absorption Spectrometry (AAS) using a Hitachi (Model Z-8100) spectrometer.

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Activities – Part III

1. a) What connections can be established among the sampling criteria adopted by Victoria and Igor 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.

Part IV – Going Deeper in the Beans River

Doing some more research, Victoria finds the following information, which she decides to share with Igor.

"*Lead is a bioaccumulative metal with no known biological function for plants and humans. Upon entering a body of water, most of the lead is retained in the sediments, and very little is transported in surface or groundwater. Zinc is a metal associated with lead in the form of galena and, in the aquatic environment, predominantly attaches to suspended material before accumulating in the sediment. It must be made clear that changes in environmental conditions can affect the bioavailability of these metals so that they become available again to the water column, thanks to oxidation-reduction reactions or resuspension processes of physical (current), biological origin (activity of organisms living in sediments) and human (navigation).*"

- That is, even ten years after the mining company ceased its activities, these may still influence the lead concentration at the site. - Comments Igor.

- Exactly! With the analyses we carry out, in addition to determining the bioavailability of metals in the environment, we can predict the risks of these metals for the region's population and the environment. - Answers Victoria.

Below are the results found by Victoria and Igor from the experiments carried out according to the procedures indicated in Part III of the case study.

Table 1. Concentration of pseudo-total metals in sediments from Beans River at different sampling points.

Sampling Points	Concentration (mg kg^{-1})								
	Zn	Cu	Cr	Mn	Fe	Ni	Cd	Pb	Al
1	**5497,36**	**103,95**	63,97	2785,36	53841,28	41,31	10,00	**7569,78**	7989,67
2	**1412,29**	**133,23**	37,30	1205,80	48231,18	31,98	2,00	1823,94	14089,86
3	416,5	26,66	29,32	449,16	23590,93	< LoD	ND	205,25	13787,8
4	**1032,65**	**95,27**	42,64	421,05	33777,58	27,32	ND	117,25	25723,07
5	329,96	**109,32**	30,00	1159,86	54725,42	28,00	ND	115,98	25223,30
6	**639,83**	47,99	34,66	731,15	32324,97	24,66	ND	635,82	18261,73

LoD = Limit of detection. ND = Not detected. Values in **bold** represent those that exceed the maximum permissible concentration. Shaded values represent those that exceed the negligible maximum concentration.

Table 2. Concentration of bioavailable metals in sediments from Beans River at different sampling points.

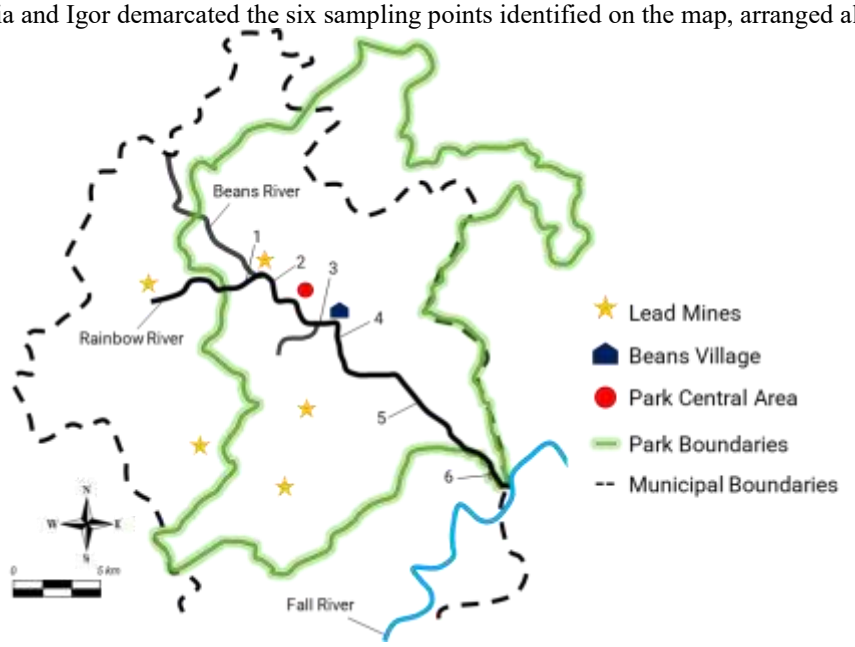
Sampling Points	Concentration (mg kg^{-1})								
	Zn	Cu	Cr	Mn	Fe	Ni	Cd	Pb	Al
1	**5247,27**	9,49	ND	355,64	478,91	ND	4,50	**5280,57**	926,99
2	**802,47**	7,07	ND	205,41	863,92	1,83	1,25	556,31	641,12
3	179,55	5,24	ND	286,02	537,89	ND	ND	100,92	501,26
4	69,05	17,47	ND	301,12	520,59	3,08	ND	42,59	1033,94
5	14,91	3,50	ND	178,28	559,01	ND	ND	21,66	726,46
6	515,75	14,72	ND	623,88	826,01	4,41	ND	370,98	752,05

ND = Not detected. Values in **bold** represent those that exceed the maximum permissible concentration. Shaded values represent those that exceed the negligible maximum concentration.

To evaluate the results, Victoria and Igor resume the choice of sampling points (Figure 4). The justifications offered by them for that choice were: points 1 and 2 are closest to the lead mines

and can provide data from the most affected region; points 3 and 4 can provide data on the human contribution (visitation activities to the Park and the occupation of Beans Village) for contamination; and points 5 and 6 may provide data that allow investigation of material transport along the Beans River.

Figure 4. Victoria and Igor demarcated the six sampling points identified on the map, arranged along the Beans River.



Below are the reference values used by Victoria and Igor to assess the concentration of metals analyzed in the sediments. Values below the negligible maximum concentration indicate that adverse environmental effects can be considered insignificant. Values above the maximum permissible concentration represent the probable occurrence of adverse effects on the environment.

Table 3. Maximum permissible concentrations and maximum negligible concentrations (mg kg^{-1}) for metals analyzed by Victoria and Igor in the sediments collected in the Beans River.

Maximum Concentration	Zn	Cu	Cr	Mn	Fe	Ni	Cd	Pb	Al
Negligible	145	36	116	-	-	35	1,1	132	-
Permissible	620	73	1720	-	-	44	30	4800	-

Source: Crommentuijn et al. (2000).[1]

Activities – Part IV

1. What connections can be established between the data acquired by Igor and Victoria (Tables 1 and 2) and the sampling points they chose (Figure 4) for the understanding of the "legacy" and the impact of the Garden Mining Company's activities in the Divina Eco Park region?

[1]CROMMENTUIJN, T. et al. Maximum permissible and negligible concentrations for metals and metalloids in the Netherlands, taking into account background concentrations. **Journal of Environmental Management**, v. 60, n. 2, p. 121-143, 2000.

2. What conclusions can be drawn on the adverse effects on the environment in the Divina Eco Park region from the comparison of the data obtained by Victoria and Igor (Tables 1 and 2) with reference values for metals 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.**