



Evaluation on the Concentration of Heavy Metals in Surface Waters in the Municipality of Pratápolis-MG

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Abstract

Mining causes numerous environmental impacts; among them we have to mention the water contamination due to the residues inherent to the activity. “Morro do Níquel”, a mining site, located in southwest Minas Gerais, Brazil, has promoted an increase in the mining activity in the region. There has also been an increase in the amount of residues and substrates produced with the intensification of the mining activity. Being a purification derivative and the extracted minerals processing, the heavy metals have been accumulating in the ecosystem, being able to interfere with the population’s quality of life and health in the municipality of Pratápolis. Heavy metals are a class of highly reactive and some toxic substances. Such toxicity is caused by the inability of the organism to metabolize them, leading to bioaccumulation. Therefore, the present research aims to determine the presence of heavy metals in the surface water, supplying water and irrigation water in the city of Pratápolis-MG, in addition to evaluating the water quality through physical and chemical analyzes.

Subject Areas

Analytical Chemistry, Environmental Chemistry

Keywords

Surface Water, Heavy Metals, Environmental Health

1. Introduction

With the discovery of precious metals in the late seventeenth century, mining

became one of the most important economic activities in Brazil. Extraction of precious metals, rock formations, petroleum and mineral coal expanded and the consequences to the environment and human life arose along with this practice [1] [2]. The contamination of soil, surface and groundwater, deforestation, river sedimentation and pollution, and instability of the ecosystem due to the evasion of animals from their habitat and death of aquatic life are some of the environmental impacts felt in areas of intense mineral exploration [3].

Morro do Niquel, located in the southwest of Minas Gerais state, has brought about an increase in the mining activity in the region and, to detriment of that, several companies have settled in the region in order to exploit their riches and resources, causing severe environmental impacts [4].

Located in this region, the municipality of Pratápolis has 8807 inhabitants according to the latest survey carried out by the Brazilian Institute of Geography and Statistics (IBGE). Its main source of employment is the mining activity, which is responsible for the production of thermo phosphates, nickel iron, magnesium silicate and crushed stone [5].

As a derivative of the extraction of these resources, the heavy metals, present a high degree of contamination for water and soil, being one of the many environmental impacts felt by the region as a result of this extraction as well as significant impacts to the population's health [6]. Among the derivatives generated by the mines, we can highlight the slag, a substance obtained from the casting of several metals which serves as a carrier substance for the purification of the extracted metals. It is composed basically of oxides and metallic atoms in their rudimentary form. It still has properties to control the melting points, besides minimizing the re-oxidation process of the final products. The disposal of the produced slag is carried out after solidification [7].

Heavy metals or trace elements are a class of highly reactive and some extremely toxic substances. Such toxicity is caused by the inability of the organism to metabolize them, leading to the bioaccumulation of these substances. It is mentioned as major heavy metals: aluminum (Al), titanium (Ti), tin (Sn), tungsten (W), chromium (Cr), cobalt (Co) and manganese (Mn), sodium (Na), potassium (K), barium (Ba), calcium (Ca), iron (Fe), zinc (Zn), copper (Cu), nickel (Ni), magnesium (Mg), arsenic (As), lead (Pb), cadmium (Cd), mercury (Hg) [8]. To be classified as trace element, a substance has to meet a series of criteria such as high atomic number, high atomic mass and high specific mass.

However, Hawkes highlights that in addition to the above criteria, such substances must form insoluble hydroxides and sulfides, salts that produce colorful solutions and complexes. Having met all of such criteria, the metal may be considered heavy metal or trace element, being the principal way of removing effluent is with pH alteration and consequently precipitate formation [9] [10] [11].

Heavy metals are classified by health care agencies as highly toxic and teratogenic substances because they are able to cross the placental barrier and interfere with the fetus development and even cause miscarriage. In addition, they present serious harm to human reproduction, causing sterility in more severe cases of

intoxication [12].

They are also classified as substances with high carcinogenic power, as they alter the cellular structure, organelles functioning, plasma membrane structure, and deregulate biochemical functions, which in the process of mitotic cell division can cause failures, resulting in carcinogenesis [13]. Some of these metals are used by the human body to make it work well such as zinc, molybdenum and iron, but the concentrations of these metals must be within the reference values, because when in excess they cause severe intoxication. Other metals such as mercury, cadmium, and lead have unknown biological function, or not even have one and are dispensable to the body, and when in high concentrations in the body also cause toxicity [14].

The major contaminant heavy metals are arsenic, cadmium, lead, chromium, manganese and mercury, because when in high concentrations and accumulated in the organism they affect several organs and systems, causing a great collapse to the person's homeostasis [13].

Symptoms resulting from heavy metal poisoning, be it essential or non-essential to the body, are commonly similar, mentioning anuria (absence of urine), partial or total blindness, hemorrhagic diarrhea, drowsiness, mental confusion and hypertension as the principal and the mostcommon [14].

The main routes for absorption of these metals are the oral and respiratory route, and may occur through the cutaneous route in rarer cases [15].

In order to control the concentration of heavy metals within acceptable parameters, the National Council of the Environment (CONAMA) published in the Brazilian Federal Register the resolution n. 397 of April 3, 2008, where it standardizes the inorganic and organic parameters for effluent discharge (National Council of the Environment—CONAMA, 2008) [16].

As shown in **Table 1**, acceptable inorganic parameters that avoid problems to the environment and human health are observed.

With the intensification of the mining activities and increase in the amount of residues and substrates produced in the process by companies besieged in this region, the heavy metals from the purification and processing of extracted minerals have been accumulating in the ecosystem, which can interfere in the population's quality of life and health.

The decrease in the release of these metals into the environment is of vital importance for both the ecosystem and the population's health, since they cause serious problems when accumulated in high concentrations in the organism and can lead to death.

Therefore, the evaluation on the concentrations of nickel, manganese, lead, chromium and cadmium in this area enables actions to control the release of these metals by industries in the region as well as actions to remove and correct concentrations of heavy metals in the waters of the region.

This research consists of analyzing the physico-chemical parameters of water and determining the concentrations of heavy metals as a precautionary measure,

Table 1. Inorganic parameters in maximum concentrations to be discharged in effluents, according to the resolution n° 397 of April 3, 2008.

Inorganic parameter in maximum concentrations (mg/L)	
Total Arsenic (As)	0.5
Total Barium (Ba)	5.0
Total Cadmium (Cd)	0.2
Total Lead (Pb)	0.5
Dissolved Copper (Cu)	1.0
Total Chromium (Cr)	1.0
Total Tin (Sn)	4.0
Dissolved Iron (Fe)	15.0
Dissolved Manganese (Mn)	1.0
Total Mercury (Hg)	0.01
Total Nickel (Ni)	2.0
Total Zinc (Zn)	5.0

Source: CONAMA, 2008. Adapted by the author.

in addition to ascertaining compliance with the parameters established by CONAMA resolution n. 397 of April 3, 2008.

2. Materials and Methods

The present research was carried out in the municipality of Pratápolis, located in southwest Minas Gerais state, 378 km from the state capital, Belo Horizonte. It has 8807 inhabitants according to the last survey conducted by IBGE in 2010. It occupies an area of 215.5 km² with a population density of 40.86 inhabitants per km². The municipality is rich in minerals and belongs to the basin of Rio Grande, presenting tropical rainy climate, with dry winter and average annual temperature over 18°C and precipitation of 1709 mm.

The samplings were carried out in different urban and rural areas in the municipality of Pratápolis, in the southwest region of Minas Gerais state. The collection points were defined in order to meet the objectives of the research, so the sampling areas include the water catchment areas for urban supply, the rural areas close to the city where the agricultural activity is predominant, food establishments that have the water in the production processes of its products and public schools with a large flow of students, **Table 2**.

For the physico-chemical tests, bottles with a maximum capacity of 2 liters washed with water, soap and deionized water were used, where at the collection points, the bottles were also washed for the third time with the sample to set the collection flask. With the aid of a thermal box to maintain the parameters to be analyzed, the samples were kept under refrigeration until stored in the laboratory refrigerator. Samples were identified in Arabic numbers according to the order in which they were collected and arranged according to the classification of the sampling area.

Table 2. Characterization of sampling areas.

Identification	Identification Type of sampling area
1	Secondary Supply Zone—Santana River
2	Industry/Food trading
3	Industry/Food trading
4	Industry/Food trading
5	Rural area—Irrigation water and livestock
6	School
7	Rural area—Irrigation water and livestock
8	Industry/Food trading
9	School
10	Primary supply area—Palmeiras River

In order to determine the metals the water was collected using borosilicate glass vials containing 5 mL of 40% HNO₃ for the total capacity of the vessel, which was 1000 mL. The contact with the vial mouth both with hands or any metallic object was avoided in order to stop problems from contamination, homogenizing for better action of the preservative. The interval between digestion and analysis for metal determination did not exceed 72 hours.

All metal and physico-chemical analyzes followed strictly the guidelines recommended by the Brazilian Standards (NBR) approved by the Brazilian Association of Technical Standards (ABNT).

The concentration of the metals Nickel (Ni), Cadmium (Cd), Chromium (Cr), Lead (Pb) and Manganese (Mn) was determined with acid digestion of the samples and the solutions obtained were analyzed by Flame Atomic Absorption Spectrometry (FAAS) as analytical technique.

3. Results and Discussion

3.1. Physico-Chemicals Tests: Turbidity, Color and Odor

The chemical physical parameters were analyzed aiming to classify the water quality of the target region of the intense ore exploration. All norms for collection and storage of samples determined by the current methodology of the partner laboratory were followed.

All the results obtained from the tests carried out on the 10 samples were evaluated following the recommendations of CONAMA resolution 357/2005 [17].

For turbidity evaluation, the reference value is up to 50 NTU (Nephelometric Turbidity Units). Samples 1 and 10 presented turbidity superior to the reference values whereas the other samples showed normal values. While sample 1 presented turbidity between 100 and 150 NTU, sample 2 presented turbidity between 50 and 100 NTU. The increased turbidity of the water can be explained by the large amount of suspended solids, vegetal substances and silica in the two samples that presented changes. The presence of sand and clay interferes with

turbidity values.

The resolution also emphasizes that the water must be colorless and odorless, *i.e.* free of any pigmentation and any odor. It was observed the inadequacy of the two samples collected in supply areas. This can be explained by the presence of dissolved solids and other substances, since both samples were collected in water catchment areas. As in turbidity, the presence of sand and clay must also be taken into account.

Sample 1 showed a characteristic odor of ammonia that can be a result of pollution from domestic sewage and livestock activity in the region, with the production of animal waste that leads to the increase of microorganisms besides those already existing in the aquatic environment.

3.2. Physico-Chemicals Tests: Solids

Resolution 357/2005 does not recommend reference values for total solids; however, it provides 500 mg/L as the limit value for total dissolved solid concentration, so sample 1 is inadequate under regulation whereas sample 10 presents in the limit value. It should be noted that those are the samples without any previous treatment and collected directly from the watercourse. In contrast, sample 5 did not present significant values for an inadequacy and the other samples were classified as adequate.

Of the 10 samples, only samples 1, 5, 7 and 10 contained suspended solids. It was verified that the same 4 samples presented sediment after 24 hours at rest, whereas samples 1 and 10 presented more residues on the bottom of the collection flask, being possible to point out similarities between the types of place from which the samples originated. Tests to determine non-sedimentary solids were not carried out, **Figure 1**.

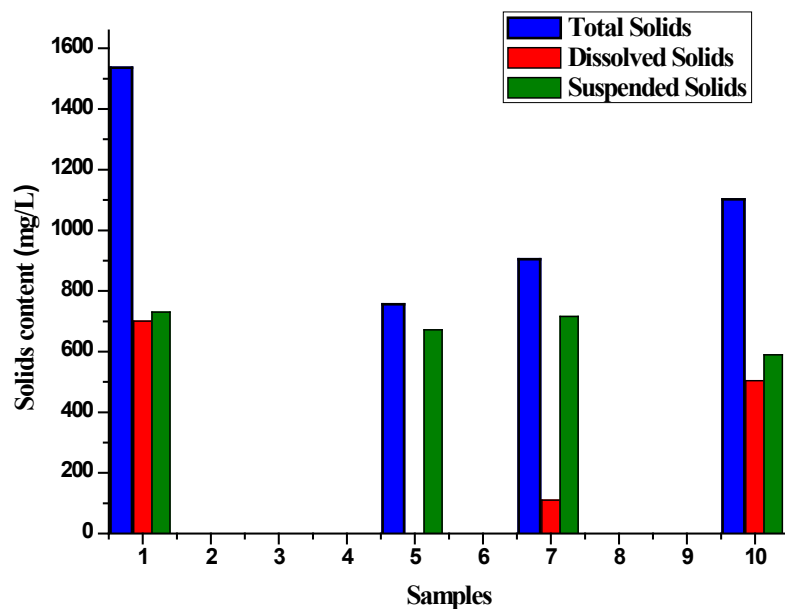


Figure 1. Graph of solids present in samples 1, 5, 7 and 10.

3.3. Physico-Chemicals Tests: pH and Conductivity

Below 150 $\mu\text{S}/\text{cm}$ values are considered adequate in the analysis of the electrical conductivity of the water whereas the ideal pH values for water supply and irrigation can vary between 6 and 7.3, according to resolution 357/2005.

All samples presented adequacy having an average pH of 6.62 ± 0.16 . The highest pH was of sample 3 with a value of 6.81 and the lowest pH was that of sample 8 with a value of 6.22, **Table 3**.

For conductivity, no sample presented values that were discrepant or out of the reference values established by resolution 357/2008.

Sample 9 presented higher electrical conductivity with 64.8 $\mu\text{S}/\text{cm}$ and sample 3 showed lower conductivity being 56.5 $\mu\text{S}/\text{cm}$. The mean conductivity of the samples was $61.42 \pm 2.78 \mu\text{S}/\text{cm}$, **Table 3**.

3.4. Physico-Chemicals Tests: Organic Matter, Alkalinity, Total Chlorides and Hardness

According to CONAMA Resolution n. 357, the amount of organic matter (OM) estimated in the samples should be 2.60 mg/L to 4.00 mg/L, while the maximum value of total chlorides present in water is 250 mg/L, **Table 4**.

In relation to hardness, to be classified as hard water, the water must contain an alkaline salt concentration higher than 150 mg/L. Between 0 and 50 mg/L is considered soft water, between 50 mg/L and 100 mg/L is moderate and values above 200 mg/L are considered to be very hard.

The resolution also regulates that water with alkalinity higher than 400 ppm are unsuitable for use and need to undergo alkalinity-removing treatments.

In the organic matter analysis, the average content was $2.75 \pm 0.51 \text{ mg/L O}_2$ consumed. No sample had a high content of organic matter, which would favor the eutrophication of the aquatic environment. However, samples 4, 5, 8 and 9 present low values. In samples 4, 8 and 9 it can be justified that the samples have come from the urban supply, which contributes to diminished values, since the water treatment by the responsible company eliminates part of the organic matter.

Table 3. pH and electrical conductivity values.

Samples	pH	Conductivity
1	6.56	59.7
2	6.61	60.8
3	6.81	56.5
4	6.71	58.6
5	6.64	63.0
6	6.67	64.1
7	6.66	62.5
8	6.22	64.2
9	6.61	64.8
10	6.73	60.0

Table 4. Values of organic matter, alkalinity, total chlorides and hardness of the samples.

Samples	Organic matter (mgO ₂ /L)	Hardness (mg/L)	Total Chlorides (mg/L)	Alkalinity (ppm)
1	3.20	40.0	12.41	34.0
2	2.88	61.0	5.68	31.0
3	3.52	34.0	5.32	30.0
4	2.24	64.0	3.54	35.0
5	2.00	51.0	3.89	36.0
6	2.96	40.0	6.74	33.0
7	3.28	55.0	2.84	32.0
8	2.40	58.0	4.61	35.0
9	2.24	49.0	3.20	36.0
10	2.80	35.0	12.76	35.0

Sample 5, which has come from the rural area, presented lower OM content, and also below the reference value. It is not possible to explain the reason for the decrease in OM content, since the sample comes from artesian wells, and it is not cleared by the official if there is any type of treatment. It should also be noted that sample 1 is the one with the highest OM content; this can be due to the dumping of domestic sewage and animal waste in the vicinity of the collection zone, **Table 4**.

Regarding hardness, no sample presented to be hard or very hard, having a mean hardness of 48.7 ± 10.89 mg/L. Samples 1, 3, 6, 9 and 10 were classified as soft water, while samples 2, 4, 5, 7 and 8 were classified as moderate water, with sample 4 being the highest hardness among the samples with 64.0 mg/L and sample 10 was classified as the least hard at 35.0 mg/L.

For the total chlorides, the mean value of the samples was 6.10 ± 3.62 mg/L. Samples 1 and 10 have shown normal values for chloride content, however, these values are higher than the other samples and this is due to the fact that samples are taken “in natura” from catchment areas where domestic and industrial waste is dispensed, besides the various agricultural and livestock activity areas.

With average alkalinity of 33.7 ± 2.12 ppm, all samples had very satisfactory values for alkalinity. Sample 4 of higher alkalinity with 36.0 ppm and sample 3 with the lowest alkalinity with 30.0 ppm (**Table 4**).

3.5. Determination of Heavy Metal Concentration

Using Flame Atomic Absorption Spectrometry (FAAS) the present study evaluated the presence of nickel (Ni), cadmium (Cd), chromium (Cr), lead (Pb) and manganese (Mn), which are derivatives present in the resulting slag of nickel purification.

Of the five heavy metals analyzed, concentrations of chromium and manganese were detected in the ten samples. Highlighting that in certain samples, the

parameters recommended by CONAMA resolution n. 397/2008 were altered [16].

As shown in **Table 5**, sample 10 had the highest chromium concentration with 0.35 mg/L whereas samples 3, 7 and 8 had no detectable concentrations (<0.03 mg/L) by the spectrophotometer. The total chromium concentrations found had an average of 0.1 ± 0.11 mg/L.

Samples 6, 8, 9 and 10 presented values above the parameters recommended by CONAMA, which is 0.1 mg/L, being classified as inadequate. Sample 4 presented the limit value of 0.1 mg/L.

Since chromium is an essential trace element, it can be found in various free form oxidation numbers in the environment. The worrying forms are chromium VI and chromium III, these two forms are more bioaccumulative, being that chromium VI has high carcinogenic power [18].

The form differentiation of this metal is not possible by conventional methods, with more improved methods for separation being available. Thus, this research did not have the specific quantification of each form, classifying the reading as total chromium.

The high levels of chromium in the samples can be explained by the presence of the mining activity in the region besides the processes of tanning that are usually predominant in countryside cities surrounded by rural areas. The slag discharge and other tailings from the mining activity associated with the process of tanning on the farms are direct contributors to the increase of the chromium concentration in the water. It is highlighted that sample 10 comes from the secondary catchment area and sewage dispensing zone of the city, which contributes to the increase of concentrations, since all domestic and industrial sewage is released at the collection point of this sample, **Figure 2**.

In the manganese analysis, sample 9 presented the highest concentration with 0.3 mg/L, with the mean sample concentration being 0.046 ± 0.091 mg/L. No traces

Table 5. Values of organic matter, alkalinity, total chlorides and sample hardness.

Samples	Manganese (mg/L)	Chromium (mg/L)	Cadmium (mg/L)	Nickel (mg/L)	lead (mg/L)
1	0.04	<0.03			
2	0.028	<0.03			
3	<0.03	<0.03			
4	0.012	0.1			
5	0.035	<0.03			
6	0.007	0.15	<0.1	<0.05	<0.08
7	<0.03	0.05			
8	<0.03	0.15			
9	0.3	0.2			
10	0.04	0.35			

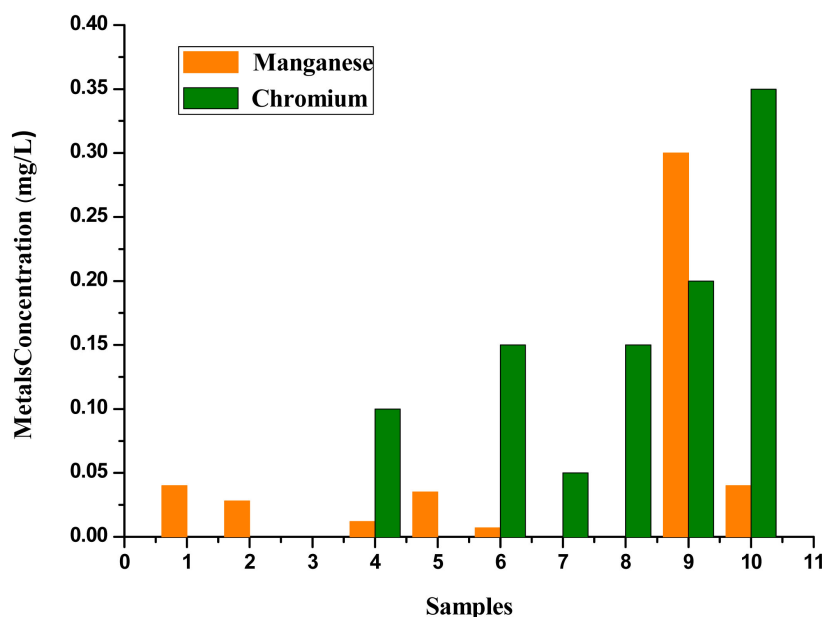


Figure 2. Chromium and manganese quantification in surface waters of Pratápolis-MG.

of manganese were detected in samples 3, 7 and 8. Among the values detectable by the assay, sample 6 showed lower concentration with 0.007 mg/L.

Manganese is found in abundance in the environment and has an excellence in oxidation contributing to the use of its ionic forms in the processes of the metal purification and processing carried out by slag. As a result, metal concentrations have gradually increased over the years, with increasing advances in metal exploration and inappropriate introduction of the derivatives.

All samples were adequate for the expressed concentrations, since the CONAMA parameter is 1.0 mg/L, but this is not a scope for not remaining at the concentrations detected. Monitoring of these concentrations is necessary because they can easily increase with the intensification of economic activities in the region.

4. Conclusions

Due to socioeconomic growth and public policies to protect the environment, sustainable development ensures a balance between exploratory economic activity with increasing production of goods for the sectors of the economy and exploited sources of natural and mineral resources.

It is concluded analyzing the physico-chemical parameters that the water of the municipality of Pratápolis and region is of good quality, since the majority of the parameters were presented within the normality with the exception of some that were shown discretely altered like increased turbidity, ammonia odor, presence of color, organic matter in deficit and excessive presence of solids.

It is also concluded the absence of nickel concentrations in the samples. It is speculated that the absence quantifiable by the analytical method shows the effectiveness in the process of separation and purification of the metal, being practically extracted in its entirety.

It is noteworthy that the high concentrations of chromium have changed due to the economic activities inherent to the region, whereas the concentrations of manganese, even within the regularity, require strict following for preventive monitoring and correction, avoiding the bioaccumulation of this metal in the water. It is essential to develop techniques and processes capable of assisting in the primary need to protect the environment and human health.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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