

Analysis of the Use of Sorghum in Phytoremediation Processes Involving Gold Mining Waste in the Municipality of Marmato

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ABSTRACT

A study was conducted focusing on the capacity of sorghum to accumulate cyanide molecules in contaminated soils—cyanide being a compound that enables gold dissolution in water and is highly toxic if ingested. Cyanide is found in large quantities in watercourses such as the La Cascabel Stream in the municipality of Marmato, and in smaller amounts in adjacent soils due to the molecule's natural degradation; even in small quantities, however, it causes soil phytotoxicity for most plants. In situ tests were carried out, taking into account that the cyanide molecule is more stable in an aqueous medium; mining residues—such as cyanide-contaminated sands—are discharged into watercourses, transported, and deposited on floodplains through fluvial processes, contributing to a significant increase in heavy metals and toxic components and resulting in soil degradation. The study quantified the use of phytoremediation for soil decontamination and assessed the plants' capacity to absorb organic and inorganic contaminants, presenting comparative data between plants grown in non-cyanide-contaminated soil and those grown in soil containing mining residues and subjected to cyanide-laden irrigation.

Keywords: Contamination, Degradation, Phytotoxicity, Phytoremediation, Mining, Toxic Substances.

INTRODUCTION

Human dependence on non-renewable resources has existed since the very beginning. Over time, exponential population growth has intensified inter-community relations and trade based on territorial wealth, fostering an inherent reliance on mineral extraction. Due to the precarious conditions of the populations inhabiting these regions—particularly those in remote regions living in extreme poverty—illicit trading practices and improper engineering methods have emerged, often stemming from a lack of understanding regarding the associated processes and environmental impacts. Consequently, this paper aims to evaluate the use of sorghum for the phytoremediation of soils contaminated by gold mining waste in the municipality of Marmato, Colombia.

Cyanide is a leaching agent—composed of nitrogen and carbon—that occurs naturally in small quantities in bacteria, fungi, algae, vegetables, and fruits, as well as in plants such as sorghum, beans, soybeans, bamboo shoots, alfalfa, and cassava (cases of livestock poisoning from the latter have been documented). However, cyanide is manufactured in large quantities for various industrial applications, including the production of acrylic plastics, nitrile, steel hardening agents, photographic materials, pharmaceuticals, synthetic rubbers, binding additives, and surgical bandages. It plays a particularly significant role in the mining industry, where sodium cyanide is used in gold processing to separate the metal from its host ore via hydrometallurgical methods—a necessary approach because physical or gravimetric separation is unfeasible due to the low concentration of the

target mineral relative to the surrounding rock. Given this context, the objective of this manuscript was to analyze the use of sorghum in phytoremediation processes involving gold mining waste in the municipality of Marmato.

THEORETICAL FRAMEWORK

2.1 Gold Mining and Soil Contamination

Gold mining activities cause significant physical and chemical transformations in terrestrial ecosystems. In particular, artisanal, small-scale, and medium-scale mining operations generate substantial volumes of waste known as overburden (stripped material with no commercial value) and tailings, which result from ore processing.

2.2 Nature of Mining Waste

Mining tailings are typically characterized by:

Unfavorable physical properties: Poor structure, high compaction or extreme permeability, low water-holding capacity, and a lack of organic matter.

Toxicity from heavy metals and metalloids: High concentrations of elements such as mercury (Hg), arsenic (As), lead (Pb), cadmium (Cd), and iron (Fe), resulting from the petrological composition of sulfide deposits.

Presence of chemical reagents: Residues of reagents used in the processing stage—primarily cyanide (CN^-) in the form of metal complexes or free cyanide, and elemental mercury from amalgamation processes.

Acid Mine Drainage (AMD): Exposure of sulfide minerals (such as pyrite, FeS_2) to air and water triggers oxidation reactions that generate acidity (H_2SO_4), increasing the solubility and mobility of heavy metals in the soil and adjacent water bodies.

2.3 Socio-Environmental Context of Marmato, Caldas

The municipality of Marmato, located in the department of Caldas (Colombia), has a mining history spanning over 450 years, centered on the extraction of gold and silver from both veins and alluvial deposits. The coexistence of traditional or ancestral mining with large-scale operations has created a complex socio-environmental situation:

Topographical and territorial pressure: The rugged terrain of El Burro Hill dictates the disposal of waste rock and tailings, which are frequently dumped directly onto hillsides and into watersheds (such as the Cascabel Creek or the Cauca River).

Pollution load: Various studies in the area have recorded critical concentrations of mercury, cyanide, and heavy metals in the soil and sediment. This poses a risk to public health and local flora and fauna, while also limiting land use for agricultural and livestock activities.

2.4 Phytoremediation as Environmental Biotechnology

Phytoremediation is an eco-technology based on the use of photosynthetic plants and their root-associated microbiota to contain, degrade, remove, or immobilize organic and inorganic contaminants present in soil, water, and sediments.

2.5 Sorghum (*Sorghum bicolor* L. Moench) in Phytoremediation

Sorghum (**Sorghum bicolor**) is a C4 photosynthetic grass native to tropical and subtropical regions. Its main biological advantages include:

High biomass production: It grows rapidly, producing abundant foliage and stem mass within short growing seasons (3 to 4 months).

Deep, dense root system: It develops a fibrous root network capable of exploring large volumes of soil and mechanically stabilizing the substrate.

Tolerance to abiotic stress: High resistance to drought, salinity, extreme pH levels, and low-fertility marginal soils.

2.6 Metal Uptake, Tolerance, and Translocation in Sorghum

Sorghum has been widely documented as a hyper-tolerant plant (or high-biomass accumulator) regarding various trace elements:

Exclusion and chelation mechanisms: It synthesizes phytochelatins and metallothioneins (cysteine-rich proteins) that complex heavy metals in the cytoplasm and sequester them within cell vacuoles to prevent metabolic damage.

Behavior regarding key metals (Cd, Pb, Hg, Zn): Although it does not always meet the strict definition of a "hyperaccumulator" (based on dry tissue concentrations), it compensates for moderate uptake levels through its large total biomass volume, resulting in massive net removal per hectare.

2.7 Degradation of and Tolerance to Cyanide Compounds

Sorghum naturally produces cyanogenic glycosides (primarily dhurrin) as a defense mechanism against herbivory. This provides it with specialized metabolic machinery to process and inactivate cyanogenesis:

Enzymes such as β -cyanoalanine synthase allow it to metabolically incorporate free cyanide (CN^-) and transform it into amino acids (such as asparagine) without suffering phytotoxic effects at moderate concentrations.

This property makes sorghum a candidate species for the co-remediation of soils simultaneously impacted by heavy metals and cyanidation residues.

2.8 Legal and Regulatory Framework for Mining and Phytoremediation in Colombia

The evaluation of biotechnological strategies in mining areas is grounded in Colombia's environmental and mining regulatory framework:

1991 Political Constitution of Colombia: Articles 79 and 80 (right to a healthy environment; the State's duty to prevent and control factors contributing to environmental degradation and to restore degraded ecosystems).

Law 99 of 1993: Created the Ministry of the Environment and the National Environmental System (SINA), establishing principles for environmental prevention and restoration.

Law 685 of 2001 (Mining Code): Regulates mining activity in Colombia, requiring the development of Environmental Management Plans (PMA) and the rehabilitation of areas affected by mining operations.

Law 1658 of 2013: Establishes provisions to eliminate the use of mercury in mining nationwide, promoting clean technologies and remediation programs for contaminated sites.

Mining-Environmental Guidelines (Ministry of Mines and Energy & Ministry of the Environment): Technical reference tools that promote the rehabilitation of areas degraded by extractive activities through revegetation and slope stabilization techniques.

Most of the cyanide found in surface water, groundwater, and soil originates from industrial processes—specifically discharges from mineral mining—which can enter water bodies via runoff and subsequently contaminate groundwater. When cyanide is released into the environment through industrial spills, it may exist as hydrogen cyanide, a substance with an atmospheric half-life of 1 to 3 years (ATSDR, 2006). Potassium cyanide and sodium cyanide are transported in water, where microorganisms and tiny organisms transform them into less harmful chemical substances; however, other portions leach into groundwater from landfills and

industrial waste disposal sites. In these locations, microbial transformation is often inhibited by high cyanide concentrations, allowing the substance to migrate through the soil and into the groundwater, resulting in levels that exceed permissible limits in Colombia, as shown in Table 1.

Table 1. Maximum permissible value of NACN.

Provision	Water for domestic use	Flora and Fauna	Drinking wáter
Maximum Permissible Values – Colombia (ppm)	0,2	0,05	0,1

Source: Decree 475 of 1998, Ministry of Public Health

In the municipality of Marmato, Caldas department, the environmental impacts of gold mining are evident. These stem from poor regulatory enforcement and inadequate procedures within the cyanidation process, resulting in uncontrolled discharges into local watercourses—specifically the Cascabel and Pantano streams. Studies assessing contamination levels from gold processing by-products have revealed the presence of toxic substances (such as cyanide), as well as inert solids, domestic and industrial wastewater, and solid waste. Cyanide entering the water supply via spills and leaks from cyanidation circuits is transported downstream, subsequently contaminating adjacent soils within the micro-watershed.

Phytoremediation

Phytoremediation involves the decontamination of soil and wastewater or the cleansing of air using plants; these enable the removal of organic and inorganic soil contaminants, as well as the removal, transfer, stabilization, or concentration of substances toxic to the soil and other living organisms. Successful implementation requires knowledge of the plant's growth habitat and its adaptability to soil and climatic conditions (Singh et al., 2003). Furthermore, the selection process necessitates an understanding of the plant's growth rate and its capacity to tolerate and accumulate contaminants, allowing for the estimation of uptake speed and the time required to achieve target remediation levels (Schnoor, 1997). Although phytoremediation is a promising technique that significantly mitigates environmental impacts—particularly those caused by heavy metals—it is important to recognize that achieving desired conditions may require multiple planting cycles, depending on the degree of soil contamination; while the method offers numerous advantages for soil recovery, it also presents several limitations that must be considered.

METHODOLOGY

Sampling

The La Cascabel stream micro-watershed covers a total area of 39,000 square meters within the floodplain, extending from the settlement known as the Llano to the stream's confluence with the Cauca River. This area allows for the collection of water from the headwaters to assess cyanide levels—identified as the primary pollutant resulting from gold processing activities in the surrounding area.

Three samples were taken from the the Cascabel stream and three from the Pantano stream; these were collected in plastic containers at intervals of at least 20 meters along the watercourse. The samples were gathered at varying distances from the stream to evaluate its impact on soil contamination levels, and they will be grouped according to this variability.

Determination of cyanide content

Two methods were used to determine the cyanide content in each of the samples. The first was a spectrophotometric method, which allows for the identification of cyanide concentration in aqueous media by detecting it in the form of simple salts and complex radicals. The second was a volumetric method, in which cyanide (CN) is titrated with silver nitrate (AgNO₃) using potassium iodide (KI) as an indicator; the indicator

detects a slight excess of titrant by causing a color change in the solution. The resulting data, shown in Table 2, were analyzed at the CIMEX Minerals Institute.

Table 2. Results of cyanide concentration determination for a pulp sample with 50% solids content and pH 11.

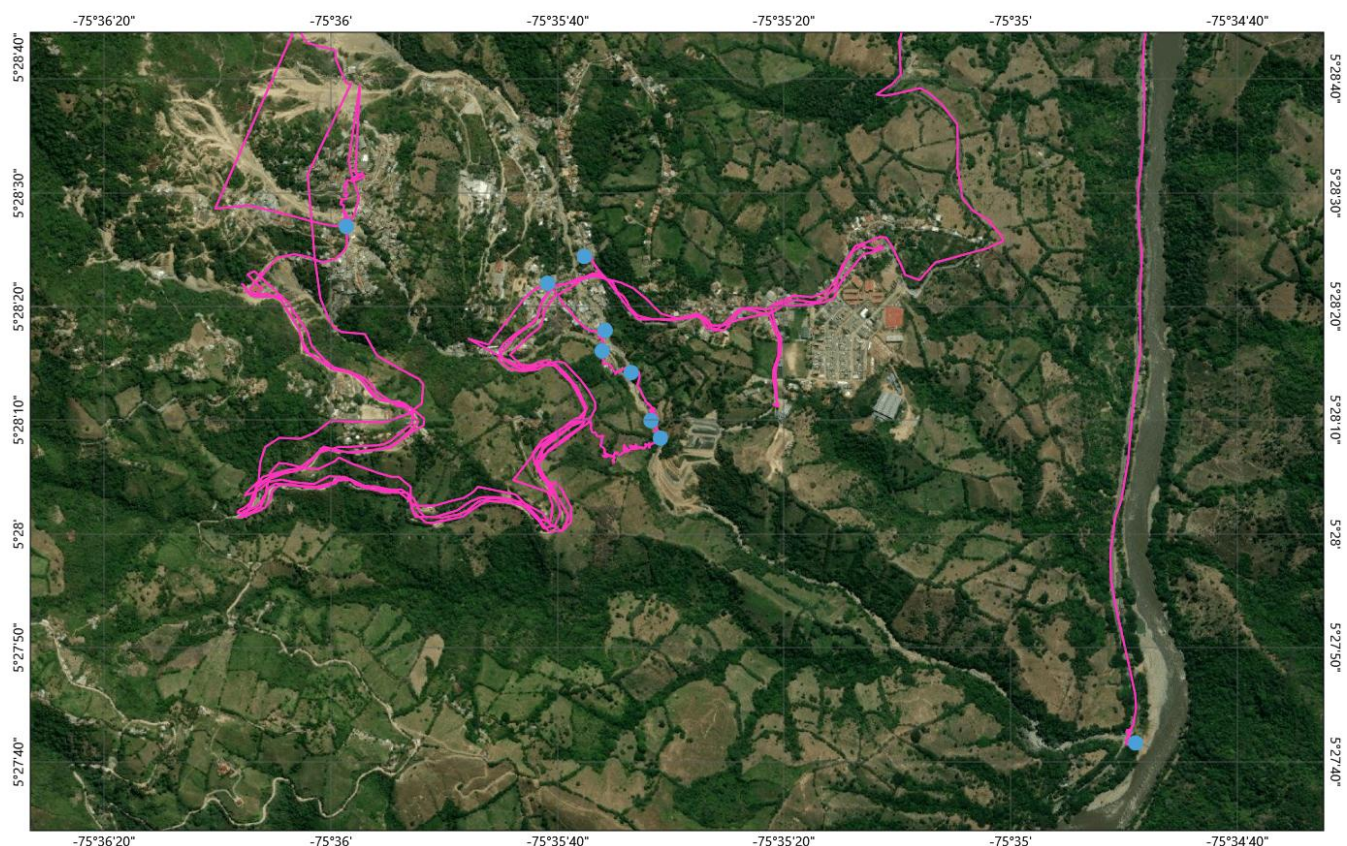
Code	Name (Sampling point)	CN concentration (mg CN ⁻ /g mineral)	CN Concentration (ppm)
E911-1	Reservoir 1	0.0086	8.6
E911-2	Reservoir 2	0.0047	4.7
E911-3	Reservoir 3	0.0066	6.6
E911-7	Bell 1	0.0357	35.7
E911-8	Bell 2	0.0184	18.4
E911-9	Bell 3	0.0189	18.9
E911-10	Cracking 1	0.0145	14.5
E911-11	Cracking 2	0.0150	15.0

Source: CIMEX Laboratory Results Report

As evidenced by the results obtained from the samples, and despite the values being lower than the quantities used in processing operations, the laboratory analyses reveal cyanide levels exceeding permissible limits for animal and human consumption.

The sampling points within the Cascabel stream watershed are shown below; this allows for sample quartering and the determination of average cyanide levels for the experimental analysis.

Figure 1. Georeferenced sampling points in the La Cascabel watershed, Municipality of Marmato.



Source: Prepared by the author

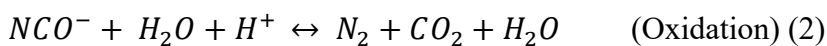
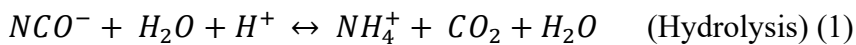
To ensure the samples are representative, quartering is performed to obtain homogeneous material for experimentation; this accounts for the fact that cyanide decomposes upon contact with the atmosphere—thereby affecting result analysis—so a sample will be selected and tested under defined concentration limits.

Definition of parameters

The removal of cyanide via photochemistry is a natural process in soils exposed to the atmosphere—provided they are not in constant contact with cyanide-contaminated water sources. Therefore, the chemical reactions resulting from the oxidation of cyanide compounds under atmospheric conditions are described below to determine their influence on the experiment.

This occurs under two scenarios:

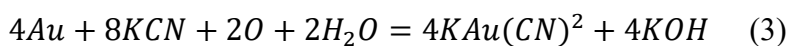
Hydroxyl radicals—even in the absence of radiation, provided conditions are favorable—cause the oxidation of free cyanide; this applies to the radical generated during the photolysis of the compound, which reacts almost immediately with the cyanide due to excitation triggered by sunlight.



Studies on cyanide compounds indicate that in soils shallower than 30 centimeters, ultraviolet rays can accelerate cyanide chemical reactions, converting the substance into cyanates; therefore, the experiment is conducted under controlled conditions to prevent cyanide loss through direct contact with the atmosphere and to avoid leaks that could directly influence the results.

Calculation of concentrations

In the industry, the chemical reaction of gold in dilute cyanide solutions is described by the Elsner equation.



Typically, approximately 500 grams of potassium cyanide (KCN) are used per tonne of solution (water)—that is, about 0.5 grams of cyanide per liter of solution—quantities that result in high concentrations in most cyanidation circuits. Potassium cyanide (KCN), hydrogen cyanide (HCN), and sodium cyanide (NaCN) are available on the market; the latter is the most widely used commercially and was the one selected for this experiment.

To determine a viable cyanide concentration based on the quantities used by the gold industry in its cyanidation processes, an experiment involving the sowing of sorghum seeds was conducted using three (3) cyanide concentration variables: 0 grams; 0.5 grams (equivalent to 499.8 ppm, or approximately 500 ppm, based on the NaCN molecular weight of 27.03 g/mol); and 1.5 grams (equivalent to 1499.9 ppm, or approximately 1500 ppm). These solutions were administered at a rate of 5 milliliters daily, adjusted for the weight of the seedling (soil and plant), with 10 seedlings planted for each concentration level, as shown in Table 3:

Table 3. Cyanide dosage at known concentrations

Parameters	CN (1)	CN (2)
Vol. (L/m ³)	1.0	1.0
Ppm	499.8	1499.9
M (mol/L)	0.01849	0.05549

Source: Prepared by the author.

Sample pH

To ensure the chemical reaction of the cyanide molecule and subsequently measure free nitrogen in both the soil and the plant, NaOH with a concentration of 0.01M was added to the solution to simulate the Elsner equation and achieve a more accurate simulation in terms of pH conditions, obtaining a value by colorimetry using a 9 litmus paper strip.

Soil management

The contaminated soil samples from the Cascabel stream watershed underwent quartering; the samples showed an average initial cyanide concentration of 14.75 ppm—levels lower than those typically used in processing operations, likely due to losses occurring during atmospheric exposure and the sampling process itself.

To simulate the constant soil degradation conditions caused by industrial wastewater discharges into tributaries such as the Cascabel and the Pantano streams, the samples were quartered and planted. This process yielded sufficient material for soil sampling and analysis, as well as bromatological analysis of the plants to track the consumption of cyanide compound molecules. Three planting scenarios using sorghum seeds were established to define two experimental variables: planting in non-cyanide-contaminated soil (control), and planting in soil spiked with specific cyanide concentrations—specifically 500 ppm (using 10 samples) and 1500 ppm (using 10 seedlings/plants). These setups provided the necessary material to determine the required quantities for total nitrogen bromatological analysis.

Planting of seedlings

The contaminated soil samples from the Cascabel stream watershed were quartered; the samples showed an average initial cyanide concentration of 14.75 ppm—levels lower than those typically used in processing operations, likely due to losses occurring during atmospheric exposure and sample collection. Consequently, a solution with two known concentrations was prepared to measure the uptake of nitrogen molecules—an element naturally absorbed by hyper-accumulating vegetation. Ten samples (or plantings) were prepared for each estimated concentration—totaling 20 plantings—using high-quality forage sorghum seeds (98% purity, 80% germination probability, in compliance with ICA Resolution 77287), alongside 10 control samples planted in untreated soil without the addition of the cyanide solution.

The seedlings were allowed to grow for 80 days—the period during which maximum growth is achieved—and an additional sampling was conducted at 30 days to determine nitrogen molecule uptake during the initial growth stage. Growth was monitored for each individual plant and compared against the growth trend of a seedling planted in non-cyanide-contaminated soil; the resulting data are presented in Table 4.

Table 4. Seedling growth according to dosage

ID Concentration (ppm)	Growth time (Average cm.)						
	8 days	15 days	30 days	45 days	60 days	70 days	80 days
Cyanide-free	4	9	13	18	27	33	42
E911-10 – 500	3	12	18	23	26	29	31
E911-10 – 1500	7	17	23	25	26	27	28
E911-11 – 500	5	9	14	19	25	28	33
E911-11 - 1500	6	11	17	21	23	25	26
E911-10+11 – 500	4	10	16	19	22	25	29
E911-10+11 – 1500	6	10	15	19	22	24	26

Source: Prepared by the author

RESULTS AND DISCUSSION

After monitoring the growth of the sorghum seedlings and adding a cyanide solution at known concentrations, the samples were sent for soil analysis to determine total nitrogen concentrations, as well as changes in density, moisture, and pH (which yielded values between 9 and 11). The total nitrogen content in the seedlings was also analyzed to determine the sorghum's absorption capacity and the impacts of planting in cyanide-contaminated soil.

Table 5 presents the nitrogen concentration results obtained for plants grown under conditions of no cyanide exposure versus exposure to known cyanide concentrations, as well as for the soils subjected to cyanide treatment.

Table 5. Nitrogen Concentration Results

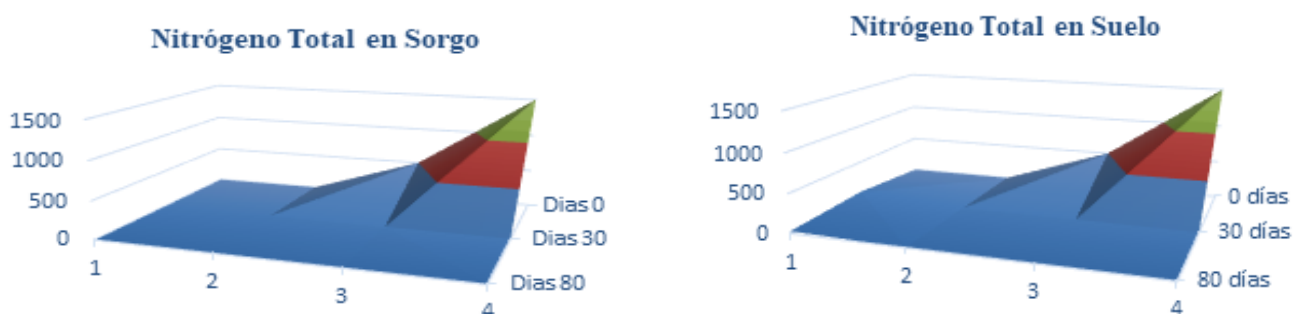
Cyanide concentration (ppm) and planting period	Total N in sorghum	Total N in soil	Soil Density	Soil Moisture
0 – 80 days	1.2g/100g	0.84%	2.27 g/cm ³	7.36%
500 – 80 days	0.7g/100g	0.08%	2.93 g/cm ³	0.70%
1500 – 80 days	1.0g/100g	0.17%	2.97 g/cm ³	1.31%
1500 – 30 days	2.9g/100g	0.17%	2.97 g/cm ³	1.31%

Source: Results report from the Chemical and Bromatological Analysis Laboratory, National University of Colombia, Medellín Campus.

Sowing was carried out at concentrations of 0, 500, and 1,500 ppm over an 80-day period—a cycle covering the various growth stages of the sorghum plant. An additional sowing at a concentration of 1,500 ppm was conducted for a 30-day period to measure the plant's absorption capacity, following the observation of accelerated growth—an atypical behavior regarding nitrogen (N) uptake periods—in the previous trial.

Figure 2 shows the nitrogen concentration in both the sorghum and the soil.

Figure 2. Nitrogen concentration in sorghum and soil.



Source: Prepared by the author

A similar trend in Total Nitrogen measurements is observed in both the sorghum plants and the soil, characterized by a significant decrease at the 80-day mark. This pattern reflects the chemical reactivity and the residual uptake by the sorghum plants—a process proportional to the soil's recovery capacity under the experimental parameters. The study utilized forage sorghum, a crop used for cattle feed—where cases of livestock death due to high levels of cyanide or nitrogen-carbon molecules have been documented—and was conducted over two growth periods.

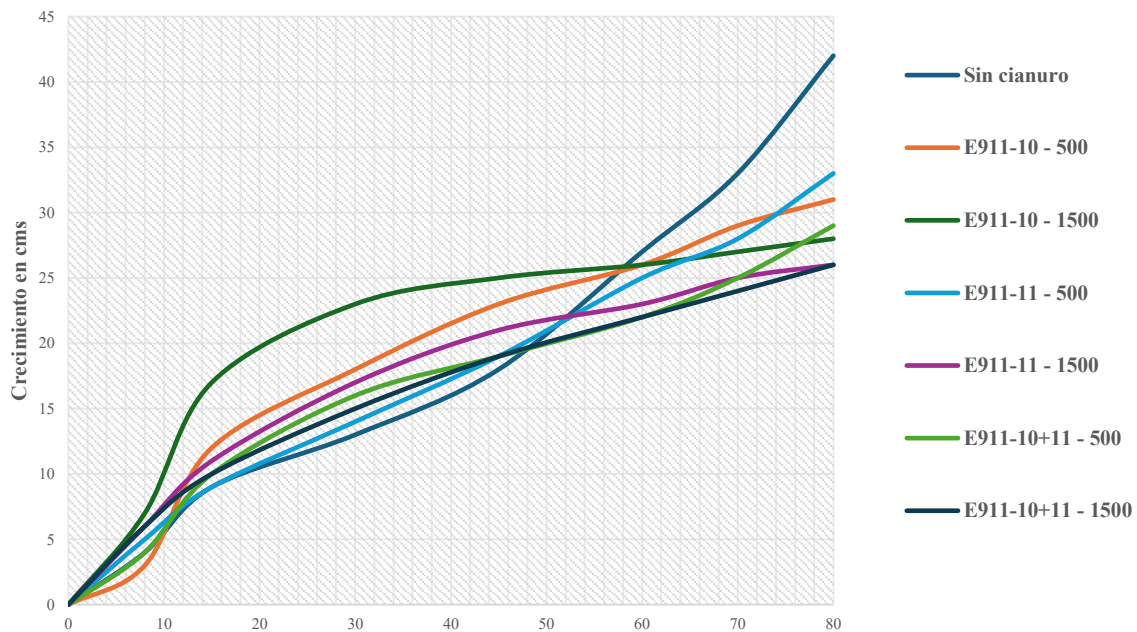
The volatility of the cyanide solution (applied at varying concentrations) interacting with soil moisture triggers a chemical reaction that produces ammonium ions and carbon monoxide at pH levels above 8—conditions typical of gold processing operations. Consequently, the specific cyanide compound is not detected in the soil or plant; instead, the ammonium ion is found. Since ammonium is an inorganic compound naturally consumed by plants for growth, determining the rate of soil removal or plant uptake required measuring total nitrogen and analyzing the relationship between the specific samples taken.

The ammonium ion (NH₄⁺) produced during mineralization in this case study can be converted into NO₂ and NO₃ via nitrification, consumed directly by the plant, or released into the atmosphere as N₂.

Given that ammonium causes weak leaf growth and reduced stem elongation, the findings align with the data in Table (4) regarding average growth (in centimeters). While plants receiving higher cyanide dosages showed

greater growth during the initial 30-day seedling formation stage, a decrease in growth rate became evident after the first month, a trend clearly observed at the 80-day mark (the full duration of seedling growth). Those subjected to higher dosages exhibited lower heights compared to seedlings grown in non-cyanided soils—falling short of the normal growth rate by up to 16 centimeters, which represents a 38% reduction relative to the height achieved under non-cyanided soil conditions, as shown in Figure 3.

Figure 3. Seedling growth trend.



Source: Prepared by the author

Nitrogen (N) accumulation over time in plants grown in non-cyanided soils follows a sigmoid (S-shaped) pattern: growth is initially relatively slow due to low N accumulation, followed by a period of increased growth—implying higher N consumption—up to day 70; finally, towards the end of the growth stage (which lasts 80 days for sorghum), the trend flattens out, suggesting reduced N consumption.

In contrast, sorghum seedlings grown under cyanidation conditions exhibit accelerated growth between days 8 and 12 (the germination phase), followed by a period of peak N uptake between days 16 and 60, accompanied by moderate growth; towards the end of the growth stage, the curve tends to stabilize, showing growth values lower than those of seedlings grown in non-cyanided soils.

Regarding soil moisture, a comparison reveals that non-cyanided soils had a moisture content of 7.36%, whereas soils contaminated with cyanide solution showed moisture levels of 0.7% (at 500 ppm) and 1.31% (at 1500 ppm). This indicates a significant reduction in water content compared to non-cyanided soils; thus, it can be inferred that the chemical reaction of cyanide in the presence of water—once the soil is exposed to solar radiation and the atmosphere—reduces soil moisture and generates higher concentrations of ammonium ions (NH_4) and carbon dioxide (CO_2).

Ammoniacal nitrogen (NH_4^+) in soils is readily converted into nitrate nitrogen (NO_3); consequently, it does not accumulate in the soil—where levels typically range from 2 to 10 ppm in natural or non-cyanided soils—and the plant-absorbed inorganic nitrogen accounts for approximately 15% of the total nitrogen. Specifically, in the sample with a 0% non-cyanided concentration, inorganic nitrogen represents 0.0126% of the sample. In contrast, for samples with dosed concentrations of 500 ppm and 1500 ppm, the total nitrogen content during plant growth can be considered to consist primarily of inorganic nitrogen; this is due to the oxidation of cyanide in the presence of water and sunlight, which leads to the formation of the ammonium ion—a component of most fertilizers.

Given that the measured pH levels (9 to 11) are unsuitable for microorganism growth, it can be inferred that the inorganic nitrogen percentage is nearly identical to the total nitrogen value (0.08% and 0.17%, respectively); thus, the inorganic nitrogen levels in the cyanided samples are high compared to those found in non-cyanided soils. High concentrations of NH_4 can be absorbed and incorporated by the plant, accumulating in the roots at moderate to high toxicity levels. This is evidenced by impaired plant development—inferred from growth data and total nitrogen levels found in the sorghum plants—showing concentrations of 0.018% for plants grown in non-cyanided soil; 0.7% for plants in soil with 500 ppm cyanide and 1% for those in soil with 1500 ppm cyanide (after 80 days); and 2.9% for plants in soil with 1500 ppm cyanide (after 30 days). These findings align with Figure 2, "Seedling growth trend," which shows a steeper slope during the initial days of growth.

CONCLUSIONS

The hypothesis of the research study was successfully verified; however, it is important to pursue additional study parameters that enhance the use of sorghum—or other hyperaccumulator plants—in the remediation of contaminated soils, with the ultimate goal of ensuring their safety for crops intended for human and animal consumption.

Most soils, particularly those in mining areas, act as water filters due to the high sand content in their matrix; while toxic molecules and compounds may remain in the soil, substances like cyanide tend to persist in aqueous media, as water serves as the vehicle allowing them to retain their physicochemical properties for extended periods. Consequently, mining industries must focus their efforts on managing and remediating the industrial wastewater generated during their processes before it impacts other abiotic components of the surrounding environment.

This research demonstrated that hyperaccumulator plants like sorghum can exhibit similar growth patterns in both favorable and unfavorable environments; although development was reduced by nearly 40% compared to plants grown in non-cyanide-contaminated soil, it is noteworthy that these plants were able to grow and develop despite the hazardous conditions under which the experiment was conducted.

Declarations

This manuscript is derived from research conducted for the Master's degree in Sustainable Development and the Environment at the University of Manizales, Colombia.

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