Influences of acid precipitation on agricultural cultivars and development of an experimental system of desulphurization

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Abstract

The phenomenon of acid rain has become increasingly problematic due to raise emissions of polluting gases into the atmosphere. Acid rain can be harmful to plant development, especially agricultural cultivars of great importance to human food supplies. We simulated acid rain to determine its impacts on the development of three agricultural species: corn (*Zea mays*), peas (*Pisum sativum*), and beans (*Phaseolus vulgaris*). Solutions of sulfuric acid at three different pH levels (3.5, 4.5, and 5.5) were used to irrigate rows of 12 plants of each species. Acid irrigation was initiated after germination and was repeated three times a week. Corn and beans irrigated with the acid solutions showed lower dry masses than the controls and did not flower. The highest mass losses of corn were observed in rows irrigated with the pH 3.5 solution; beans showed the highest losses at pH 5.5. The peas showed statistical differences in terms of the variables stem diameter and numbers of fruits and seeds when irrigated with pH 3.5 solutions. Simulated acid rain was therefore found to impair the productivities of those plant species. A desulfurization assay was developed to study alternatives to mitigate sulfur dioxide release in atmosphere.

Key words: Agriculture, Acid rain, Desulphurization.

1. Introduction

Since the first Industrial Revolution, due the creation of the steam machine and from the burning of fossil fuels, the emission of pollutant gases into the atmosphere has been growing considerably; and these contribute to the increasing of the occurrence of phenomena known as acid rains [1, 2]. The term "acid rain" was first used by the Scottish chemist Robert Angus Smith to describe the precipitation of acid character, succeeded in the city of Manchester in 1872 [3]. Acid precipitations can be natural or anthropogenic phenomena. Natural acid rains are those caused by gases, such as the SO_2 and other sulfur compounds, emitted by volcanic eruptions and biological processes occurring in soils, marshes and oceans. The anthropogenic acid rain is caused by the burning of fossil fuels, such as coal and petroleum, producing pollutant gases, such as sulfur dioxide (SO_2), nitric oxide (NO) and nitrogen dioxide (NO_2). These gases react with the water vapor present in the atmosphere, forming products as diluted sulfuric acid (H_2SO_4) and nitric acid (HNO_3) [4]. The reactions involved in the acid rain formations are presented:

I – Gas Formation

$$S + O_2 \rightarrow SO_2$$
$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$$
$$N_2 + O_2 \rightarrow 2NO$$
$$2NO + O_2 \rightarrow 2NO_2$$

II – Products Formation

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$$
$$SO3 + H2O \rightarrow H2SO4$$

Normal rain usually has pH around 5.6 (slightly acidic) due to the presence of carbon dioxide in the atmosphere that reacts with water forming the acid carbonic ($CO2 + H_2O \rightarrow H_2CO_3$) a weak acid. However acid rain has pH 4.5 approximately. Acidic precipitation may result in a variety of environmental and economic damages such as soil leaching, absorption of toxic substances by plants and aquatic animals and deterioration of monuments and buildings [5].

In relation to the soils affected by acid rain, the consequences can vary depending on their composition. For example, areas where the soil contains granite or quartz are very affected, since they have a small capacity of neutralization; and soils that have calcium carbonate, can neutralize acidity efficiently [4]. Acid soils, when subjected to frequent acid rains, dissolve substances such as aluminum (Al), lead (Pb) and cadmium (Cd) and these metals can harm the vegetation that lies there. The plants that inhabit this soil can absorb these substances and introduce them into the food chain and, in addition, such substances can interfere in plant germination, development and reproduction [6]. In the water bodies, acid rain also trigger release of high concentrations of the aluminum ion, present in insoluble minerals, such as Al $(OH)_3$, which do not harm aquatic life. This ion, Al^{3+} can cause irritation of the fishes` gills. As a defense, the fish produce mucus to protect gills from irritation. But, as the contact with the toxic ions does not stop, the fish body will produce more mucus what will cause the animal`s death by asphyxiation, since the absorption of oxygen is blocked [7].

Several studies have been done on this subject since Robert A. Smith. However, only in the 50s of 19^{th} century, the Nordic scientists, Rodhe and Darmerig first related the burning of fossil fuels with acid precipitations. Shortly thereafter, these two researchers correlated the acidity of the water bodies with the decrease of fish in a region of Scandinavia. With these findings, industrialized countries conducted several studies to check the emission rates of pollutants in the areas most affected by these precipitations. One of the most shocking results, showed that the pollutant gases emitted in England and West Germany were carried by the winds to Sweden and Norway, causing decrease in some aquatic life populations and vanishing others. And in addition, water destined for human consumption was also affected. These results led, in 1969, 39 European countries to sign an agreement to define measures against acid pollution on a large scale. In 1983, the United States of America, the Soviet Union and Canada also signed this agreement [3]. The idea of sustainable development then arose and research in the area intensified.

Alternatives, such as the desulfurization, were created to not compromise the yields in production processes and to avoid slowing down the economic development and at the same time promote the removal of polluting gases. The dessulfurizer is a mechanism that capture in "filters" the SO_2 released by burning fossil fuels in the mills and factories, before it can be discharged into the atmosphere. It works as follows: the SO_2 formed, undergo to calcium hydroxide rain, resulting in calcium sulfate ($CaSO_4$) or calcium sulfite ($CaSO_3$), depending on the amount of oxygen available in the environment. Gases with a very low content in acid oxides are then released by the chimney [7]. Currently, several researches on chemical engineering and biotechnology fields receive an intense investment from public and private sector, aiming the improvement and creation of these and other mechanisms to reduce the emission of pollutant gases.

Therefore, the present work aimed to: study the impacts of acid rain on development and reproduction of vegetables species widely used in agriculture, corn (*Zea mays*), peas (*Pisum sativum*), and beans (*Phaseolus vulgaris*), investigate the occurrence of acid precipitation in Varginha city, Minas Gerais state, Brazil. Experiments were performed simulating industrial desulphurization, through a prototype, to allow understanding of the emission and removal of gas (SO_2) into the atmosphere. This simulation can be used as a didactic model for a better comprehension of the phenomenon and in order to make some proposals for mitigating it.

2. Methods and Materials

2.1. Soil analysis and control of ants and other pests

Previous planting soil analyses were performed and the pesticide Fipronil (Pyrazole) was applied in the study area. For the soil analyzes samples were collected at 20 cm depth at four different points in the experimental area. A composed sample was made with those four subsamples and sent to the laboratory. The soil analyses were performed by Soil Laboratory of the Federal University of Lavras (Minas Gerais state, Brazil).

2.2. Vegetable species and viability of the seeds

The species used in this research were corn (*Zea mays*), Pea (*Pisum sativum*) and Beans (*Phaseolus vulgaris*). They were chosen because they are largely cultivated in the region and have a rapid development. Lots of seeds (Fig. 1) were acquired in the local market and undergo a viability test (seed germination test). The viability test consisted in checking germination of 25 seeds in four independent repetitions. For that filter paper was used as a substrate. The seeds were watered three times a day (morning, afternoon and night) and exposed to a constant illumination.

Figure 1: Samples of seeds used in germination test and in experimental design. Corn, beans and pea (right to left).

2.3. Experimental design

The site to plant crops was chosen to avoid possible anthropogenic interferences within the campus. Twelve pits were made per row; space between them was 1 m (Fig. 2). Four rows of each species were planted, an extra row of maize and pea were used to make a shield to protect crops from strong winds. These two border rows were not considered in the experiment. Each row was irrigated using different pH solutions (pH 3.5; ph 4.5; ph 5.5), and one row was watered with tap water (control lane).

Figure 2: Area used for crops, preparation of pits and soil correction.

2.4. Solutions used in irrigation

The solutions used to irrigate the plants were obtained by diluting pure sulfuric acid in water until desirable pH (3.5, 4.5 or 5.5) was achieved. The volume used for irrigation was defined by the average of annual precipitation distributed during the seven months which experiments were carried out. Irrigation was performed three times per week; 100 ml of the solutions were used in each plant. To supply the lack of water and guarantee the vegetables development, 100 ml of tap water was used to irrigate the plants few hours before irrigating with the acid solutions.

2.5. Measuring plant development (height, diameter of the lap, number of leaves, fruits, grains and dry mass)

A digital caliper (Mark Ecoffer) was used to measure the diameter of the seedlings lap on the ground. The height of the seedlings was obtained by means of a millimeters ruler (Fig 4). Direct count was performed to determine the number of leaves, fruits and grains of each plant. After that, the aerial part was cut, plants of the same row were put together and identified. The set of each row was placed in oven under 70 º C. Dry mass weight were determined after mass stabilization [8].

Figure 4: Measuring the height and diameter of the plants.

2.6. Rainwater pH

Rainwater in Varginha city was collected during different months of the year. For that a filter paper was coupled to a funnel and this set was put 60 cm above the ground. Samples were analyzed in laboratory using a pH meter (Micronal, Brazil) (Fig. 5).

Figure 5: pH meter used to measure the pH of the rainwater.

2.7. Development of the mechanism of Desulphurization

For better comprehension of the process of emission and absorption of sulfur dioxide into the atmosphere, an experimental model of a dessulfurizer was designed. Under hood, three grams of pure rhombic sulfur (S_8) was put inside a porcelain capsule and the combustion was carried out by heater (a). An upside down funnel (b) was coupled to capsule to capture the SO_2 released, which was conducted through a plastic tube (c) to a kitassato (f-g) tightly closed. The gas was released by a porous stone (h) at the end of the pipe and inside the kitassato where 500 ml of solution of calcium hydroxide [Ca $(OH)_2$] was kept. A vacuum pump (i) was used to drive the gas to Kitassato (Fig 6).

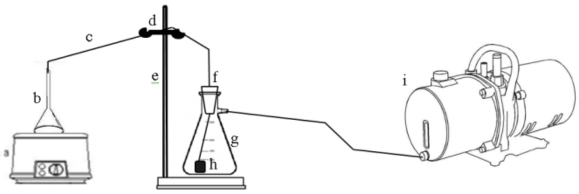

Figure 6: Dessulfurizer prototype.

2.8. Statistical analysis

The statistical analysis of data was performed by analysis of variance (ANOVA) and the comparison of the means was accomplished by the Scott-Knott test, 95% probability. The statistical analyses were carried out in the SISVAR software [9].

3. Results

Evaluation of soil analysis results showed some deficiencies of certain minerals (magnesium, bromine, phosphorus and potassium) and organic matter (Table 1). Bovine manure and fertilizer (Osmocote) was added to soil to supply these limitations and allow proper plant growth.

Table 1: Concentration of nutrients in the soil of the experimental area

Parameter	Soil analyses	Evaluation of concentration*
pH (H_2O)	5.8	Good
P (mg/dm^3)	0.5	Very low
Ca^{2+} ($cmol_c/dm^3$)	0.75	Low
Mg^{2+} (mg/dm^3)	0.13	Very low
Organic matter (dag/kg)	0.49	Very Low
Zn (mg/dm^3)	0.7	Low
Fe (mg/dm^3)	34.3	Good
Mn (mg/dm^3)	16	High
Cu (mg/dm^3)	3.24	High
B (mg/dm^3)	0.04	Very low
S (mg/dm^3)	15.61	Good

* Evaluation based on proper level of nutrients required for plant tissue [10].

The seeds used in viability test displayed germination index of 100% (Fig.7). After that, the seeds were planted in the pits with a mixture of well-balanced minerals, organic matter and soil.

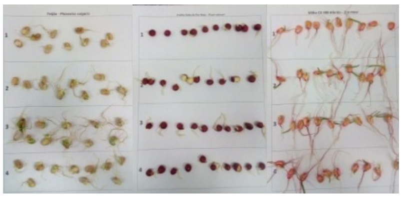

Figure 7: Seeds used in germination test. Beans, corn and pea (right to left) showed 100% viability.

After the germination (about 15 days), the plants were irrigated with solutions of sulfuric acid (pH 3.5; 4.5 or ph 5.5) (Fig. 8). Plants growth was monitored and observed.

Figure 8: Irrigation of seedlings.

Unfortunately just peas grow enough to produce flowers and fruits. Corn and beans plants showed deficient development and reproductive structures were not observed. Despite that, beans and corn plants were cut down to access the dry mass. Results are shown on Table 2. The use of dry weight as a measure of plant growth tends to be more reliable. It was observed lower dry weight in plants irrigated with acid solution in comparison to control plants, therefore acidity has a negative effect on plants development of these two species. Irrigation with acid solution pH 3.5 decreases about fourfold storage of organic matter in these plants. Despite these strong negative effect, acid rain with this pH values were not reported in the literature up to now. Nevertheless plants submitted to the other pH values acid irrigation also displayed reduction in mass.

Table 2. Dry mass of corn and bean plants

Lane	Mass Dry
Corn (control)	33.16
Corn (pH 3.5)	8.9
Corn (pH 4.5)	21.29
Corn (pH 5.5)	12.47
Bean (control*)	2.6
Bean (3.5)	0.58
Bean (4.5)	1.16
Bean (5.5)	0.27

* plants irrigated with tap water

The biometric data of the pea irrigated using different sulfuric acid pH solution shows statistical difference among some parameter. The results are presented in Table 2. It was observed significant differences in diameter of the lap, number of fruits and number of seeds in plants watered with solution pH3.5. This result points to differences in growth and productivity of these seedlings with the decreases of the pH of the solution, pH 3.5 impairs the plants development considerably.

Despite this work showed only extreme acid conditions interfere in pea, bean and corn development, it is important to mention that more experiments are required to check long term damages. Because acid precipitation has a number of potential effects on terrestrial ecosystems including acidification of soils, altered nutrient supply, increased mobilization of aluminum and other shifts from acid sensitive to acid tolerant species of soil flora and fauna population, altered rates of decomposition of organics and nitrogen fixation [11].

Table 3: Biometric data to evaluate pea plant development

pH	Lap Diameter (mm)	Height (cm)	Number: Leaves	fruits	seeds
3.5	2.61^{b*}	48.41^{a}	52.36^{a}	0.67^{b}	2.08^{b}
4.5	3.18^{a}	50.71^{a}	50.00^{a}	1.08^{b}	4.42^{a}
5.5	3.25^{a}	50.38^{a}	55.50^{a}	1.58^{a}	6.00^{a}
Control	3.28^{a}	51.33^{a}	52.50^{a}	1.42^{a}	5.17^{a}

*Means followed by the same superscript letter are not significantly different by Scott-Knott test (95% probability)

The prototype of dessulfurizer worked properly. The heater caused the combustion of the sulfur present into capsule through the sublimation process. The oxygen present in the system reacts with sulfur forming sulfur dioxide (SO_2). As soon as the sulfur combustion was visually perceived, the vacuum pump was turned on. The gas began to be sprinkled by the porous stone, allowing the sulfur dioxide react with calcium hydroxide to produce calcium sulfite and calcium sulfate ($CaSO_4$ + $CaSO_3$) and water. After total sulfur burning the pump was shutdown and salts decant in the solution. All process was documented and it is shown on Fig 9-11.

Figure 9: Experimental model of desulphurization.

Figure 10: S_2 combustion and SO_2 capture (A), gas sprinkled inside Kitassato (B).

Figure 11: Sulphite and calcium sulphate decanting on the bottom of the Kitassato.

Samples of rain were collected in different months of year 2017, and brought to laboratory to check pH and therefore the occurrence of acid precipitation in Varginha city. Most of the sample had neutral pH, despite acidity was identified in two days of precipitation in May (drought season).

Table 4: pH of the rain in different Month

Analyzed sample	pH
May 1*	5.32
May 2*	7.15
May 3*	5.32
June	6,95
August	7,75
September	7,78
October	6,93

*Different days in the same month.

4. Conclusion

The experimental conditions employed in this work can state that the decrease in the pH of water used for irrigation harms and decreases corn, pea and beans growth and productivity. Rain is still an important parameter for agriculture yield and acid precipitation can negatively influence the availability of these important grains used in human and animal subsistence. Plants submitted to acid irrigation of pH 3.5 were the most damaged, whereas the pH ranges between 4.5 and 5.5 did not differ statistically from the natural pH of the precipitation.

Measures to decrease emission of sulfur dioxide should be adopted to avoid occurrence of acid precipitations, an alternative is desulfurization. The experimental model showed that it is possible to remove sulfur dioxide before its release into atmosphere. Hence it is possible to accomplish reduction of pollutants at the same time generate valuable downstream products as calcium sulfate, widely used in civil construction, chalk production and in agribusiness to produce fertilizer. The desulfurization, in addition, can be used as a didactic model in various subjects for instance chemistry and biology.

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