Original research papers

Corn Cultivation for Silage: Evaluation of Elemental Composition in the soil and Plants by Neutron Activation Analysis

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ABSTRACT

Corn cultivation for silage requires special soil management and constant applications of fertilizers and agricultural pesticides to achieve satisfactory yield levels. This study was carried out on a farm that has grown corn for several years. The soil does not have adequate management in terms of fertility and fertilization. We collected samples of the soil, roots, leaves and grains in a corn silage area to investigate the chemical elements in the soil and plants. We used the neutron activation analysis (NAA) the k_0-standardization method. This technique consists in subjecting the sample to a neutron flux, in order to produce radioactive isotopes of the nuclei present in the original sample. In addition to the AAN technique, we apply the standardization method k0, which consists of irradiating each sample together with a neutron flux monitor, in the same irradiation position. Several samples can be irradiated simultaneously when stacked inside the irradiation vessel, interspersed with flow monitors. The concentration of the elements is calculated in relation to the monitor which is usually gold (Au), eliminating the need for patterns. Irradiations were carried out in the TRIGA MARK I IPR-R1 research reactor at Nuclear Technology Development Centre/Brazilian Commission for Nuclear Energy (CDTN / CNEN). The NAA technique identified As, Ba, Br, Ca, Ce, Co, Cr, Cs, Cu, Eu, Fe, Hf, K, La, Mo, Na, Nd, Rb, Sb, Sc, Sm, Ta, Tb, Th, U, Yb and Zn, in the samples. Although the site studied lacks adequate management of soil fertility and fertilization, we identified Ca, Cu, K, Mo and Zn, essential for corn development. We detected adequate contents for the cultivation of silage corn by assessing these nutrients and their translocation in the plant.

Keywords: Zea mays L, Nutrients, Neutron activation analysis, Corn, Silage, Absorption, Translocation, Soil, Plants, Method k_0.

1. INTRODUCTION

~~Corn (Zea mays L.) is a major crop in Brazil and is the basis of human foods and animal feeds [1].~~

Corn (Zea mays L.) is a major crop in Brazil and is the basis of human foods and animal feeds [1]. Growing corn for silage requires advanced technologies, and it is low and irregular in Brazil. According to [2], production of corn forage is mainly affected by the absorption and translocation of nutrients throughout crop development, affecting the elemental composition of the product.

The Neutron Activation Analysis (NAA) is one analytical technique that analyzes chemical elements in samples of different matrices, such as soil, plants and foods. It is a multielemental isotopic technique, specific for quantitative and qualitative determination of chemical elements, and is applied in chemical characterization of samples in the most varied fields of applications [3,4]. The NAA is precise and accurate, and capable of determining elemental contents within a wide range, from traces to percentages [5]. It is a non-destructive technique, because sample solubilization is not required, an advantage over other analytical techniques as they require sample solubilization for analysis. As the NAA does not require procedures, such as chemical separation or samples dissolution, it is a more versatile technique, reducing contamination risks and avoiding fractioning or partial recovery of elements [6].

The NAA consists of subjecting a sample to a neutron flux to produce radioactive isotopes of the nuclei in the original sample, a reaction known as activation [7]. The resulting radioisotopes have half-lives, ranging from fractions of seconds to several years, with radioactivity measured by gamma-ray spectrometry, with germanium semiconductor detectors. This type of detector is efficient at gamma radiation and has high resolution. Each radioisotope emits gamma rays with characteristic energies, allowing its identification. The produced spectra are analyzed by software systems that locates, identifies and calculates the area under the gamma peak. The amount of events accumulated in a photopic event of the radioisotope of interest is used to obtain contents of elements in the sample [8].

There are several ways of applying the NAA to obtain contents of chemical elements in the sample. The most commonly used is the comparative method, which analyzes standards for each element of interest to be determined. The k_0 method is another analytical method that does not use standards of the elements of interest; rather, it monitors neutron fluxes. This method is based on the knowledge of spectral parameters in the irradiation position in the reactor, such as thermal and epithermal neutron fluxes, to perform gamma spectrometry in a highly calibrated gamma spectrometer and nuclear constants available in the literature. An advantage of the k_0 method is that it costs of analysis is low, and laboratory operations are reduced [4].

In 2003, the standardized k_0 method was established at the Nuclear Technology Development Centre, Brazilian Commission for Nuclear Energy (CDTN/CNEN), in Belo Horizonte, capital of city Minas Gerais State, Brazil. Since then, it has been used to determine the elemental composition of several matrices [9].

In this work, we used the standardized k_0 method of neutron activation [4,9] to analyze the elemental composition of the soil, roots, leaves and corn samples. The objective was to determine the chemical elements in samples in a corn growing area for silage and evaluate these nutrients in terms of the cultivated area and planted species.

2. MATERIALS AND METHODS

We sampled the soil, roots, leaves and corn grains on a farm in the municipality of Biquinhas, Minas Gerais State (18º46'58" S and 45º30'08" W), at an average altitude of 629 meters in the crop year of 2017.

We performed systematic sampling, that is, we sampled soil/plant randomly on the first crop row and in zigzag. The collection was carried out in plots based on the harvest period (maturation) of the grains and the variety planted (Agroceres 5055).

2.1 Soil sampling and preparation

Thirty samples consisting of 150 grams of soil were collected at 15 cm from the roots of the corn plant from 0 to 20 cm. The samples were conditioned in identified plastic bags and sent to preparation at the laboratory at CDTN/CNEN, where the soil was dried at room temperature until reaching a constant weight. Then, the samples were milled in porcelain grains, sieved and packaged in sealed polyethylene bottles, forming a composite sample. Approximately 200 mg aliquots were weighed and placed into polyethylene vials suitable for irradiation.

2.2 Collection and preparation of corn plant samples

The plants were cut close to the ground~~,~~ and separated into roots, leaves and corn cobs. The samples were stored in plastic bags, tagged, and sent to the preparation at the laboratory at CDTN/CNEN.

The soil aggregated to the roots was removed. The roots were washed in running water, deionized water and dried with paper towel. Then, the samples were packaged in plastic beakers and placed in the freezer for further freeze-drying. Regarding the leaves, whole parts in the opposite position and below the first spike were collected. The samples were stored in plastic bags and tagged. In the laboratory, the samples were washed in running and deionized water to remove any soil particles from the leaves. They were wrapped in plastic beakers and place in the freezer. One corn ear was collected per plant. The samples were then placed in plastic bags, tagged and sent to the laboratory at CDTN/CNEN, where they were threshed, and the grains were washed in running and deionized water and then placed in the freezer.

After reaming in the freezer for a minimum of 12 hours at -10ºC, the samples were freeze-dried and weighed to obtain the moisture percentage. Root and leaf samples were ground in a Grindomix GM 200 knife mill and packed in a bottle with a lid. The corn kernels were packed without crushing.

2.3 Preparation of samples for analysis

For irradiation, aliquots of 150 mg of root and leaves were weighed and packed in a polyethylene sample holder. The corn samples were weighed in triplicate and stored in the sample holders with masses of 2.5 g. These~~is~~ sample masses were in agreement with the methodology of analysis of large samples, recently established at CDTN [10].

For the application of the k_0 method, the samples were conditioned in a larger sample vial, intercalated by neutron monitors, disks (6 mm diameter and 1 mm thick) [11] of Al-Au (0.1%), IRMM-530RA, supplied by the Institute for Reference Materials and Measurements (IRMM), Belgium.

2.4 Irradiation

The irradiations were carried out for 8 hours in the nuclear research reactor TRIGA MARK-I IPR-R1 in at CDTN/CNEN. The samples were irradiated at the carousel in the irradiation channel IC-7, with the reactor operating at 100 kW. In this position, the spectral parameters f (ratio of thermal and epidermal neutron fluxes) and α (distance from the epithermal neutron profile) were 22.32 and - 0.0022, respectively, and the thermal neutron flux was 6.35×10^{11} cm^{-2} s^{-1} neutrons [9].

2.5 Gamma Spectrometry

After irradiation, we waited the necessary time for the decay of radionuclides of shorter and interfering half-~~-~~lives and, then, gamma spectrometry, was performed on a HPGe coaxial detector, with 50% of nominal efficiency, model GC 5019 CANBERRA, associated to appropriate electronics and the Genie 2K spectra acquisition program, CANBERRA. The counts were performed on the characteristic gamma energies of the radioisotopes produced. For the analysis of the gamma spectra, we used the HyperLab program [8,12], which is specific for this analysis, while for the calculation of the elemental content, we used the Kayzero for Windows® [13] program.

2.6 Quality control

To verify the method performance, two certified reference materials were analyzed: Tomato Leaves (SRM 1573a) and ~~a~~ sediment (BCR-320R) using the same method used for the corn samples (Tables 1 and 2).

To evaluate the method efficiency, the E_n [14] test was applied, which takes into account for the calculations, the expanded uncertainty of the experimental and certified values with a coverage factor k = 2. This means that true results are 95% likely to be within the confidence interval.

The following equations were used in the calculation of E_n:

$$E_n = \frac{Valor_{\exp} - Valor_{\text{certified}}}{\sqrt{U_{\exp}^2 + U_{\text{certified}}^2}} \quad (1)$$

where~~,~~ exp means experimental, U_{exp} means the expanded uncertainties with k = 1, of the experimental results and $U_{\text{certified}}$ is the certified values, k = 2.

$$U_{\exp} = 2 \cdot U_{exp\_Comb} \text{ where: } U_{\exp\_Comb} = \sqrt{u^2{}_{AREA} + u^2{}_{method}} \quad (2)$$

u_{AREA} is the net area uncertainty of the peak gamma studied and u_{method} is the total uncertainty of method k_0 established as 3.5% in the CDTN.

The method performance was evaluated by the criterion $|E_n| \leq 1$, meaning that the performance was satisfactory, that is, the results of the method are within the 95% confidence interval. If $|E_n| > 1$, indicating the unsatisfactory performance of the method.

Table 1. Experimental results and certified values for SRM 1573a, Tomato Leaves, and statistical evaluation, En-score.

	SRM 1573a		
	Experimental Results, k=1	**Certified Values k=2**	
Elements	**mg kg^{-1}**	**mg kg^{-1}**	**E_n-score**
Ca	47180 ± 1922	50500 ± 900	-0.84
Co	0.55 ± 0.02	0.57 ± 0.02	-0.43
Fe	378 ± 12	368 ± 7	0.41
K	27190 ± 492	27000 ± 500	0.17
Na	133 ± 2	136 ± 4	-0.49
Rb	15 ± 1	14.89 ± 0.27	-0.22

Sb	0.063 ± 0.003	0.063 ± 0.006	0.03

Table 2. Experimental results and certified values for BCR-320R, Channel Sediment, and statistical evaluation, E_n-score.

	BCR-320R, Channel Sediment		
	Experimental Results, k=1	Certified Values k=2	
Elements	**mg kg^{-1}**	**mg kg^{-1}**	**E_n-score**
As	24 ± 1	21.7 ± 2	0.94
Co	11 ± 1	9.7 ± 0.6	0.61
Cr	67 ± 6	59 ± 4	0.58
Fe	27825 ± 6833	25700 ± 1300	0.28
Hg	1.01 ± 0.07	0.85 ± 0.09	0.95
Sc	6 ± 1	5.2 ± 0.4	0.21
Th	6 ± 2	5.3 ± 0.4	0.08
U	1.6 ± 0.5	1.56 ± 0.2	0.00
Zn	352 ± 124	319 ± 20	0.13

3. RESULTS AND DISCUSSION

The chemical elements were analyzed based on their nuclear characteristics, that is, their respective radioisotopes, energies and half lives.

The results for the elements in the different matrices studied (soil, roots, leaves and corn grains) with their respective standard deviations are shown in Table 3. Six essential elements for plant growth, namely Cu, Fe, Mo and Zn as well as Ca and K were determined (Table 3). Co and Na, beneficial elements for the plants, were also analyzed.

3.1 Elements in soil samples

Fe content in the soil samples was higher than in the other samples (root, leaves and corn grains). Fe is considered an important element for energy transformation in plants [15]; however, it is not usually available for absorption due to the low solubility in its oxidized form. In the plants, Fe is related to several metabolic activities, participating in the formation of some enzymes, besides it is indispensable in the processes of respiration, photosynthesis, N_2 fixation and electron transfer through the cycling between Fe^{2+} and Fe^{3+}. Thus, Fe availability is linked to crop yield. However, in Brazilian soils, responses of corn crops to Fe applications are practically non-existent. Fe contents in soils of the Cerrado region in Brazil is satisfactory for the development of the plants [16].

Table 3. Elements determined in the soil samples; root, leaf and corn grains (dry mass).

	Content (mg kg^{-1})			
Elements	**Soil**	**Root**	**Leaf**	**Grains**
Ag	< 1	< 0.2	< 0.08	< 0.02

As	6.9 ± 0.3	< 0.1	< 0.08	< 0.08
Ba	267 ± 12	< 10	< 4	< 2
Br	5.9 ± 0.2	20 ± 1	7.0 ± 0.3	0.30 ± 0.06
Ca	< 2*	< 1.0*	7.0 ± 0.6*	< 0.2*
Ce	81 ± 3	2.0 ± 0.1	0.36 ± 0.06	< 0.1
Co	4.5 ± 0.2	0.30 ± 0.02	< 0.008	0.010 ± 0.001
Cr	100 ± 4	3.8 ± 0.2	0.71 ± 0.07	< 0.1
Cs	7.5 ± 0.3	0.2 ± 0.01	0.08 ± 0.01	< 0.005
Cu	< 3	< 1	< 0.7	388 ± 31
Eu	1.2 ± 0.1	< 0,01	< 0.004	< 0.002
Fe	44 ± 2*	0.78 ± 0.03*	83 ± 5	13 ± 1
Hf	17 ± 1	0.20 ± 0.01	< 0.008	< 0.006
Hg	< 0.7	< 0.1	< 0.08	< 0.3
K	16.9 ± 0.6*	24 ± 1*	21 ± 1*	3.0 ± 0.4*
La	21.9 ± 0.8	0.60 ± 0.02	0.60 ± 0.02	< 0.001
Mo	< 1	< 0.8	< 0.5	0.30 ± 0.01
Na	0.50 ± 0.02*	0.105 ± 0.004*	50 ± 2	6 ± 1
Nd	16.7 ± 2	< 0.9	< 0.8	< 0.4
Rb	124.0 ± 5.0	27 ± 1	26 ± 1	4.4 ± 0.4
Sb	1.2 ± 0.05	0.07 ± 0.01	< 0.02	< 0.002
Sc	17.4 ± 0.6	0.31 ± 0.01	0.010± 0.001	< 0.0003
Se	< 2,0	< 0.2	< 0.2	< 0.08
Sm	4,2 ± 0,2	0.089 ± 0.004	0.030 ± 0.001	< 0.001
Ta	2.0 ± 0.1	0.04 ± 0.01	< 0.01	< 0.003
Tb	0.70 ± 0.03	< 0.02	< 0.01	< 0.003
Th	17.9± 0.6	0.31 ± 0.01	< 0.02	< 0.01
U	4.4 ± 0.2	< 0.5	< 0.3	< 0.01
Yb	3.8 ± 0.2	< 0.05	< 0.04	< 0.01
Zn	42± 4	8.5 ± 0.6	14 ± 1	22 ± 4

(g kg^{-1}) *; <, smaller than.

Zn content was 42 ± 4 mg kg^{-1} in the soil sample. According to [17], its share in soil contents ranges from 60 to 89 mg kg^{-1} depending on the rock of origin and deposition sources. Zn deficiency is augmented by prolonged cultivation, especially in sandy soils and in the Cerrado region [18].

Cr was also identified in the soil at content 100 ± 4 mg kg^{-1}. For [19] reported that lettuce plants grown in a soil supplemented with 200 mg kg^{-1} Cr^{3+} showed a content of 11.1 mg kg^{-1} in the tissue and a 60% reduction in dry matter weight 60 days after application, in relation to the control samples.

Br contents varied according to samples with the highest value found in the roots at 20 ± 1 mg kg^{-1}. Most toxic elements are found in the roots, as the plants attempts to contain the toxic effect they cause to metabolism. Br is not considered an essential chemical element for plants and animals; however, its excessive consumption can be harmful to human health [20]. In the soil, Br contents range from 5 to 40 mg kg^{-1}, confirming the data obtained in this study.

Ce, Eu, La, Nd, Sc, Sm, Tb, Yb are rare elements and were detected in the soil samples. Ce, La, Sc and Nd had the highest contents, below the toxic limit for the plants, also confirming the data obtained by [21].

3.2 Elements found in roots samples

Table 3 shows the elements found in the roots of corn plants. Fe, K and Na showed higher content, indicating greater absorption of these elements by the roots.

Br, Co, Cr, Cs, Hf, Rb, Sb, Ta, Th, Zn were also found in the roots, and the number of elements absorbed by the roots is smaller than in the soil. This is because the plant may have blocked these toxic elements to avoid absorption. In addition, plants have root exclusion mechanisms, and when none of these mechanisms is sufficient, they have physiological mechanisms to contain their toxic effect on metabolism [22]. There was Br accumulation in the root, 20 ± 1 mg kg^{-1}, since Br content in the soil is smaller, 5.9 ± 0.2 mg kg^{-1}.

Rare earth elements, namely Ce, La, Sc, and Sm, were also identified in the root samples, at contents much lower than in soil samples.

3.3 Elements in leaf samples

Fe, K and Na were detected in the leaf samples. Ca, which was not detected in the other samples, was found in the leaf sample at a content 6.8 ± 0.6 g kg^{-1}. For [23] states that the suitable range for Ca, in nutritional terms, for corn plants is 2.5 to 8.0 g kg^{-1}.

K and Ca had the highest contents in the leaf samples and Ca accumulation in leaves is due to its low mobility in the phloem [24].

Br, Cr, Cs, Rb and Zn were also detected in the leaf samples; however, the elements were detected at lower contents than in the root samples. Except for Zn, which showed a larger translocation from roots to leaves.

The Cr changed its content of 3.8 ± 0.2 mg kg^{-1} in the roots to 0.71 ± 0.07 mg kg^{-1} in the leaves, confirming [25]. The authors explain that, in plants, most Cr is retained in the roots and only a small portion is transported to the shoots.

Rare elements (Ce, La, Sc, and Sm) continued to be translocated to the leaves at contents much lower than in the root samples, as these elements are absorbed by the plants, their distribution among different organs differs considerably. Research has shown that contents of rare elements in the roots are higher than in the other plant organs. For [26] showed decreases in contents of rare earth elements towards roots> leaves> stems> flowers> fruits or grains in various crops, such as corn, wheat and rice.

3.4 Elements in samples of corn grains

Fe, K and Na were also detected in samples of corn grains, while Ca was at its detection limit. K content was lower in the soil, root and leaf samples, contrary to data obtained by [15]. The authors reported that higher Ca contents increase grain production. Greater transport and storage of photo assimilation in corn grains increase K content, since K participates in the transport of sucrose and photo assimilation from the source to the drain [15].

Na contents ranged from 500 mg kg^{-1} in the soil to 6 mg kg^{-1} in the grains. No reference value was found for this mineral in the literature; however, it is known that Na can partially replace K when Na contents are low in the soil. Still, Na is essential for some species, usually grasses, which photosynthesize via C-4 metabolism [27].

Trace elements were also found in samples of corn grains, such as Co, Mo, Rb and Zn. Co was detected at a low content. For [28] reported that Co could be absorbed as Co^{2+}, transported from the roots to shoots by the xylem, via the transpiratory current. The authors report that the highest contents are found in the roots, followed by the leaves, and the lowest contents are found in the stems. Mo also had a low content at 0.30 ± 0.01 mg kg^{-1}. For [29], approximately 0.08 mg kg^{-1} of Mo in corn seeds is sufficient to allow normal growth and development of plants.

3.5 General evaluation of the elements found

The high Zn contents found in the samples must be related to its greater absorption and storage in plant organs with later translocation to the grains. According to [30], the higher the Zn content in plant organs, the greater the translocation and accumulation in the grains. Foliar applications become a more effective strategy to increase Zn contents in the grain [31]~~,~~ since Zn is absorbed by the leaf epidermis, remobilized and transferred to the grain through the phloem.

Rare earth elements were not detected in the corn samples, as expected, due to their low solubility and bioavailability to reproductive organs. For [32], describes that not all elements are equally retained in the roots of different species, suggesting that tolerance to an element does not necessarily guarantee tolerance to another.

Therefore, the most important elements, based on contents found in the soil, root, leaves and corn grains, were Fe, with high content in the soil, along with Br, K, Na, Rb and Zn, since all these elements were detected in all the samples studied. Several toxic elements and rare earth elements were also detected in soil samples, roots and leaves; nevertheless, all contents were below the threshold established by the Brazilian legislation. Essential elements detected were absorbed and moved to all plant parts, except for corn roots, which limited translocation of toxic elements (Co, Hf, Sb, Ta and Th) to the shoots.

4. CONCLUSION

The neutron activation analysis, the k_0-method, identified and quantified many elements, namely As, Ba, Br, Ca, Ce, Co, Cr, Cs, Cu, Eu, Fe, Hf, K, La, Mo, Na, Nd, Rb, Sb, Sc, Sm, Ta, Tb, Th, U, Yb, and Zn in the samples, despite the different matrices.

Although the studied site did not have ~~an~~ adequate management of soil fertilization, we identified six essential elements for crop development. The evaluation of contents of these nutrients and translocations in the plant showed the nutrients have adequate contents for the cultivation of corn for silage.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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