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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. The matrices collected were soil, roots, leaves and grains in a corn silage area to investigate which chemical elements are present and their concentrations. The neutron activation analysis (NAA) by k_0 -standardization method was applied on elemental concentration determination. In this technique, the sample is submitted to a neutron flux, in order to produce radioactive isotopes of the nuclei present in the original sample. In the k_0 method, the sample is irradiated together with a neutron flux monitor, usually gold (Au), in the same irradiation position and standards of the interested element are not necessary. Several samples can be irradiated simultaneously when stacked inside the irradiation vessel, intercalated with neutron flux monitors. The 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). In the analysis, 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 were identified in the samples. Although the site studied lacks adequate management of soil fertility and fertilization, Ca, Cu, K, Mo and Zn were determined and their presences are important because they are essential for corn development. Adequate content for the cultivation of silage corn were verified by assessing these nutrients and their translocation in the plant.

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

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28 **1. INTRODUCTION**

29

30 Corn (*Zea mays* L.) is a major crop in Brazil and is the basis of human foods and animal
31 feeds [1]. Growing corn for silage requires advanced technologies and it is low and irregular
32 in Brazil. According to Martin and Pavinato, 2010 [2], production of corn forage is mainly
33 affected by the absorption and translocation of nutrients throughout crop development,
34 interfering in the elemental composition of the product.

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

47

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

57

58 There are several ways of applying the NAA to obtain contents of chemical elements in the
59 sample. The most commonly used is the comparative method, which analyses standards for
60 each element of interest to be determined. The k_0 method is another analytical method that
61 does not use standards of the elements of interest; but uses neutron fluxes monitors. This
62 method is based on the knowledge of spectral parameters in the irradiation position in the
63 reactor, has to perform gamma spectrometry in an absolutely calibrated gamma
64 spectrometer and uses nuclear constants available in the literature. An advantage of the k_0
65 method is that its cost of analysis is low, and laboratory operations are reduced [4].

66

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

71

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

76

77 **2. MATERIALS AND METHODS**

78

79 The soil, roots, leaves and corn grains were sampled on a farm in the municipality of
80 Biquinhas, Minas Gerais State (18°46'58" S and 45°30'08" W), at an average altitude of 629
81 meters in the crop year of 2017.

82

83 The systematic sampling was performed, that is, the soil/plant samples were collected in the
84 first crop row and in zigzag. The collection was carried out in plots based on the harvest
85 period (maturation) of the grains and the variety planted (Agroceres 5055).

86

87 **2.1 Soil sampling and preparation**

88

89 Thirty samples of soil with 150 grams were collected at 15 cm from the roots of the corn
90 plant from 0 to 20 cm. The samples were conditioned in identified plastic bags and sent to
91 preparation at the laboratory at CDTN/CNEN, where the soil was dried at room temperature
92 until reaching a constant weight. Then, the samples were milled in porcelain grains, sieved
93 and packaged in sealed polyethylene bottles, forming a composite sample. Approximately
94 200 mg aliquots were weighed and placed into polyethylene vials suitable for irradiation.

95

96 **2.2 Collection and preparation of corn plant samples**

97

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

101

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

112

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

117

118 **2.3 Preparation of samples for analysis**

119

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

124

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

129 **2.4 Irradiation**

130

131 The irradiations were carried out for 8 hours in the TRIGA MARK-I IPR-R1 nuclear research
132 reactor at CDTN/CNEN, operating at 100 kW. The samples were irradiated at the carousel in
133 the irradiation channel IC-7. In this position, the spectral parameters f (ratio of thermal and
134 epithermal neutron fluxes) and α (distance from the epithermal neutron profile) were 22.32
135 and - 0.0022, respectively, and the thermal neutron flux was $6.35 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ neutrons [9].
136

137 **2.5 Gamma Spectrometry**

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139 After irradiation, the necessary time was waited for the decay of radionuclides with shorter
140 and interfering half-lives. Then, the gamma spectrometry was performed on a HPGe coaxial
141 detector, with 50% of nominal efficiency, model GC 5019 CANBERRA, associated to
142 appropriate electronics and the Genie 2K spectra acquisition program, CANBERRA. The
143 counts were performed on the characteristic gamma energies of the radioisotopes produced.
144 For the analysis of the gamma spectra, the HyperLab program [8,12], was used. The
145 Kayzero for Windows[®] program [13] was applied to calculate the elemental concentrations.
146

147 **2.6 Quality control**

148

149 To verify the method performance, two certified reference materials were analysed: Tomato
150 Leaves (SRM 1573a) and Channel Sediment (BCR-320R) using the same method applied to
151 the samples. The results are displayed in Tables 1 and 2.
152

153 To evaluate the method efficiency, the E_n -score [14] test was applied, which takes into
154 account for the calculations, the expanded uncertainty of the experimental and certified
155 values with a coverage factor $k = 2$ (95% confidence interval). This means that true results
156 are 95% likely to be within the confidence interval.
157

158 The following equations were used in the E_n : calculations:
159

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

160

161

162 where exp means experimental, U_{exp} means the expanded uncertainties with $k = 1$, of the
163 experimental results and $U_{certified}$ is the certified values, $k = 2$.
164

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

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166

167 u_{AREA} is the net area uncertainty of the peak gamma studied and u_{method} is the total
168 uncertainty of method k_0 established as 3.5% in the CDTN.
169

170 The method performance was evaluated by the criterion $|E_n| \leq 1$, meaning that the
171 performance was satisfactory, that is, the results of the method are within the 95%
172 confidence interval. If $|E_n| > 1$, indicating the unsatisfactory performance of the method.
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Table 1. Experimental results and certified values for SRM 1573a, Tomato Leaves, and statistical evaluation, E_n -score.

Elements	Experimental Results	SRM 1573a Certified Values	E_n -score
	$k=1$ mg kg ⁻¹	$k=2$ mg kg ⁻¹	
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

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

Elements	BCR-320R, Channel Sediment		E_n -score
	Experimental Results, $k=1$ mg kg ⁻¹	Certified Values $k=2$ mg kg ⁻¹	
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

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The values of E_n -score pointed out that the method produced results with 95% of possibility to be inside a range of values that correspond to the true values.

3. RESULTS AND DISCUSSION

The results for the elements in the different matrices studied (soil, roots, leaves and corn grains) with their respective uncertainties 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 analysed.

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Table 3. Chemical elements determined in soil, root, leaf and corn grains samples (dry mass).

Elements	Concentration (mg kg ⁻¹)			
	Soil	Root	Leaf	Corn 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.

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3.1 Elements in soil samples

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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, N₂ fixation and electron transfer through the cycling between Fe²⁺ and Fe³⁺. 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].

Zn content was 42 ± 4 mg kg⁻¹ in the soil sample. According to Broadley and partners, 2007 [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 increased by prolonged cultivation, especially in sandy soils and in the Cerrado region [18].

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220 Cr was also identified in the soil at content $100 \pm 4 \text{ mg kg}^{-1}$. For [19] reported that lettuce
221 plants grown in a soil supplemented with $200 \text{ mg kg}^{-1} \text{ Cr}^{3+}$ showed a content of 11.1 mg kg^{-1}
222 in the tissue and a 60% reduction in dry matter weight 60 days after application, in relation to
223 the control samples.
224

225 Br contents varied according to samples with the highest value found in the roots at 20 ± 1
226 mg kg^{-1} . Most toxic elements are found in the roots, as the plants attempt to contain the toxic
227 effect they cause to metabolism. Br is not considered an essential chemical element for
228 plants and animals; however, its excessive consumption can be harmful to human health
229 [20]. In the soil, Br contents range from 5 to 40 mg kg^{-1} , confirming the data obtained in this
230 study.
231

232 Ce, Eu, La, Nd, Sc, Sm, Tb, Yb are rare elements and were detected in the soil samples.
233 Ce, La, Sc and Nd had the highest contents, below the toxic limit for the plants, also
234 confirming the data obtained by Uchida and partners, 2007 [21].
235

236 **3.2 Elements in root samples**

237
238 Table 3 shows the elements found in the roots of corn plants. Fe, K and Na showed higher
239 content, indicating greater absorption of these elements by the roots.
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241 Br, Co, Cr, Cs, Hf, Rb, Sb, Ta, Th, and Zn were also found in the roots and the number of
242 elements absorbed by the roots is smaller than in the soil. This is because the plant may
243 have blocked these toxic elements to avoid absorption. In addition, plants have root
244 exclusion mechanisms and when none of these mechanisms is sufficient, they have
245 physiological mechanisms to contain their toxic effect on metabolism [22]. There was Br
246 accumulation in the root, $20 \pm 1 \text{ mg kg}^{-1}$, since Br content in the soil is smaller, $5.9 \pm 0.2 \text{ mg}$
247 kg^{-1} .
248

249 Rare earth elements, namely Ce, La, Sc and Sm, were also identified in the root samples, at
250 contents much lower than in soil samples.
251

252 **3.3 Elements in leaf samples**

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254 Fe, K and Na were detected in the leaf samples. Ca, which was not detected in the other
255 samples, was found in the leaf sample at a content $6.8 \pm 0.6 \text{ g kg}^{-1}$. For [23] states that the
256 suitable range for Ca, in nutritional terms, for corn plants is 2.5 to 8.0 g kg^{-1} .
257

258 K and Ca had the highest contents in the leaf samples and Ca accumulation in leaves is due
259 to its low mobility in the phloem [24].
260

261 Br, Cr, Cs, Rb and Zn were also detected in the leaf samples; however, the elements were
262 detected at lower contents than in the root samples. Except for Zn, which showed a larger
263 translocation from roots to leaves.
264

265 Cr changed its content from $3.8 \pm 0.2 \text{ mg kg}^{-1}$ in the roots to $0.71 \pm 0.07 \text{ mg kg}^{-1}$ in the
266 leaves, in agreement with Moral and partners, 1995 [25]. The authors explain that, in plants,
267 most Cr is retained in the roots and only a small portion is transported to the shoots.
268

269 Rare elements (Ce, La, Sc and Sm) continued to be translocated to the leaves at levels
270 much lower than in the root samples. As these elements are absorbed by the plants, their
271 distribution among different organs differs considerably. Research has shown that contents
272 of rare elements in the roots are higher than in the other plant organs. Cunha and partners,

273 2010 [26] showed that rare earth elements decrease towards roots> leaves> stems>
274 flowers> fruits or grains in various crops, such as corn, wheat and rice.

275

276 **3.4 Elements in corn grains**

277

278 Fe, K and Na were also detected in samples of corn grains, however, Ca was determined at
279 detection limit. K content was lower in soil, root and leaf samples, the opposite to data
280 obtained by Marschner and partners, 2011 [15]. The authors reported that higher Ca
281 contents increase grain production. Higher transport and storage of photo assimilation in
282 corn grains increase K content since K participates in the transport of sucrose and photo
283 assimilation from the source to the drain [15].

284

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

289

290 Trace elements were also found in samples of corn grains, such as Co, Mo, Rb and Zn. Co
291 was detected at a low content. Figliolia and partners, 1992 [28] reported that Co could be
292 absorbed as Co²⁺, transported from the roots to shoots by the xylem, via the transpiratory
293 current. The authors report that the highest contents are found in the roots, followed by the
294 leaves, and the lowest contents are found in the stems. Mo also had a low content at 0.30 ±
295 0.01 mg kg⁻¹. Pereira and partners, 2012 [29] showed that approximately 0.08 mg kg⁻¹ of Mo
296 in corn seeds are sufficient to allow normal growth and development of plants.

297

298 **3.5 General evaluation of the elements found**

299

300 The high Zn contents found in the samples must be related to its greater absorption and
301 storage in plant organs with later translocation to the grains. According to Fahad and
302 partners, 2015 [30], the Zn concentration in plant organs are proportional to translocation
303 and accumulation of this element in grains. Foliar applications become a more effective
304 strategy to increase Zn contents in the grain [31] since Zn is absorbed by the leaf epidermis,
305 remobilized and transferred to the grain through the phloem.

306

307 Rare earth elements were not detected in corn samples, as expected, due to their low
308 solubility and bioavailability to reproductive organs. Oliveira, 2012 [32], describes that not all
309 elements are equally retained in the roots of different species, suggesting that tolerance to
310 an element does not necessarily guarantee tolerance to another.

311

312 Therefore, the most important elements, based on contents found in the soil, root, leaves
313 and corn grains, were Fe, with high content in the soil, along with Br, K, Na, Rb and Zn,
314 since all these elements were detected in all the samples studied. Several toxic elements
315 and rare earth elements were also detected in soil samples, roots and leaves; nevertheless,
316 their concentrations were below the threshold established by the Brazilian legislation [33].

317

318 **4. CONCLUSION**

319

320 The neutron activation analysis, *k₀*-method, determined many elements, namely As, Ba, Br,
321 Ca, Ce, Co, Cr, Cs, Cu, Eu, Fe, Hf, K, La, Mo, Na, Nd, Rb, Sb, Sc, Sm, Ta, Tb, Th, U, Yb,
322 and Zn in the samples, despite the different matrices.

323

324 Although the studied site did not have adequate management of soil fertilization, six
325 essential elements were identified for crop development. The evaluation of contents of these

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326 nutrients and translocations in the plant showed the nutrients have adequate contents for the
327 cultivation of corn for silage.

328

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336

337 **COMPETING INTERESTS**

338

339 Authors have declared that no competing interests exist.

340

341 **AUTHORS' CONTRIBUTIONS**

342

343 "Author 1" designed the study, performed the statistical analysis, wrote the protocol. "Author
344 2" managed the analyses of the study (k_0 method) and "Author 3" managed the bibliographic
345 research. All the authors read and approved the final manuscript. "

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