Universal Journal of Agricultural Research 4(2): 42-47, 2016 http://www.hrpub.org
DOI: 10.13189/ujar.2016.040202

Case of Study: Honey without Bees? Chemical Risks Associated to Sugarcane (Saccharum Officinarum) from Belo Horizonte, Brazil

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Abstract Sugarcane is one of the most important of raw materials used in manufactured food products. Its consumption is under public scrutiny for decades, always associated to cavities, obesity and diabetes. Sugary beverage portion sizes have exploded as high as 64 fluid ounces in some fast food chains in the USA. Meanwhile, anthropogenic activities such the application of arsenical pesticides has resulted in elevated (high as 900 $g.g^{-6}$) levels of arsenic (As) in surface soils in many historic sugar cane areas of Hawaii, USA. To quantify simultaneously many elements as possible, it was applied the well-established nuclear analytical technique of Neutron Activation Analysis. Hazardous elements such As, Br, Na, some RREs (rare earth elements), Rb, Sc and U were detected and quantified in the product.

Keywords Arsenic, Uranium, Bromine, Lanthanum, Sucrose

1. Introduction

Sugarcane is a product extracted mainly from the plant *Saccharum officinarum*, belonging to the grass family *Gramineae* [1,2]. Sugarcane offers a very condensed source of calories: an edible portion of 100 grams of sugar cane contains 380 kcal [3]. Due to its sweet and pleasant flavor, the product is an often ingredient used in gum candies, cereal bars, juices, carbonated beverages, energy drinks, baked goods and several breakfast items. Practically everyone in the world consumes one or more forms of refined sugar each meal. Furthermore, sugar cane (as molasses) is plenty used in animal nutrition as an ingredient to increase palatability and energy to the final feed [3].

Eighty percent of the world's sugar supply is derived from sugar cane, cultivated mostly in tropical climates in developing countries. The remaining twenty percent of the world's supply of sugar is derived from sugar beets, mainly cultivated in the northern hemisphere [4].

Brazil is the leading sugar producer and the dominant player in the global trading of sugar. The country is considered the "price setter" on the world sugar market with international sugar prices set by the low production costs associated to produce sugar cane in Brazil [5]. The current forecast shows of Brazilian production of sugar cane within season 2012/13 are 37.66 million tons, 4.72% more than in the previous season, which was 35.97 million tons. Out of this total 69.46% produced in the Southeast Region (including states of São Paulo – major producer, Minas Gerais – the second largest producer), 11.32% in the Northeast, 10.95% in the Midwest Region and 8.13% in the South [6].

The world indicator price for raw sugar experienced a succession of peak and downward movements in 2010 before soaring to a 30-year high of USD $36.08 cents/lb or USD $795.4/t in February 2011. By 2020-2021, the raw sugar price (Intercontinental Exchange) in nominal terms is expected at nearly USD $408/t or USD 18.5 cents /lb [5].

1.1. Health Risk Associated to the Elevating Sugar Consumption

In 2011, the American Heart Association published a statement that warned the fact of Americans consumed 22 teaspoons of sugar in daily basis. The document endorses that *per capita* consumption needs to come down to levels that should not be toxic[7]. The American Heart Association sustains that the best way to maintain a healthy weight and to decrease the risk of heart disease is to eat a healthy diet and to limit added sugar to no more than 100/150 calories a day for women/for men. The limit sounds unrealistic in the era of large size beverages offer: serving cup sizes in fast-food chains are getting larger, leading to an enormous consumption of sugar mainly in infant and teenagers demographics. The trend toward larger portion sizes has occurred together with the prevalence of obesity and people becoming overweight in the west world. Serving sizes of manufacturer-packaged carbonated beverages have exploded – the original bottle size of the world leading soda drink was 6.5 fluid ounces. The same brand is found on market fourfold larger as portion seen on sale nowadays. Beverage portion sizes from the leading fast food (burgers) chains have increased more than fourfold since 1950s, from 7 fluid ounces to 32 fluid ounces. A sugary drink of this size contains 390 calories and almost no nutrients [8,9].

In New York, the former mayor Michael Bloomberg has attempted to limit the size of sugary drinks. Seeking to reduce runaway obesity rates and deaths related to diabetes, the New York City Board of Health approved a ban on the sale of large sodas and other sugary drinks at restaurants, street carts and movie theaters. The rule has intended to bar the sale of sugary drinks in containers larger than 16 ounces [10]. The ban was struck down in March 2013, and remains under debate and appeals in court [11].

1.2. Honey without Bees: An Historical Perspective of Sugar Cane and Slavery

The plant is known to have been cultivated in New Guinea before 1000 BC. After a long journey a semi extensive culture was initiated in India and afterwards in China. The Indians devised the first techniques for extracting sugar from cane and called it "sarkara", a Sanskrit term from which the words for sugar in many European languages originate (açúcar, azúcar sucre, zucker, zucchero). It was in India, between the sixth and fourth centuries BC, that the Persians and the Greeks, discovered the famous "reeds that produce honey without bees" and brought sugar cane to the region from Middle East to Mediterranean Sea [4]. In the 14th Century, Cyprus (followed decades later by Sicily) produced large amounts of sugar cane using labor of Syrian and Arab slaves [12].

Iberians (from the Spanish side) started the modern exploitation of European Islands from the Canary Islands in 1312 by *Malocello*. In the following decades, the Castile Crown sponsored the profitable production of wine, sugar cane, sheep and cattle products in the Canary Islands. The commerce of these items expanded navigation and shipping farther South Atlantic [12].

In the same way, Portuguese Crown copied the Canary´s model based in slave workforce in the *luso* coast of Açores, Madeira, Cabo Verde and São Tomé, to produce wine, sugar cane, sheep and cattle products [12].

By the end of 15th Century, Iberians divided their strategies to expand their colonies: Portuguese searching for an eastward route to Asia and Spanish gambled on a westward route leaded by the Genovese Cap. Christopher Columbus, a sailor who previously worked in sugar cane plantation and slavery in North African Coast. Yet in 1492, date of discovery of America by Columbus, Pope Alexander VI issued a papal bull (*bula pontificia*) establishing the earth as the rightful property of the Roman Catholic Empires divided into regions to Portugal and Spain, accorded by the two Iberian nations in the treat named *Tratado de Tordesilhas* [12].

Afterwards, sugar cane was firstly introduced in Brazilian tropical plantations by the Portuguese Crown in 1530´s. Under Portuguese rule, the African coastline supplied slaves for colonial Brazil's sugarcane plantations. Slavery for Brazilian plantations was responsible for the exodus of millions of African men to South America (mostly to Brazil) in order to keep the sugar cane production running. Those slaves never returned to their homes in Africa. Hence, this exodus was the key fact for the formation of the Brazilian Society. Promptly the number of Africans outnumbered the number of Portuguese and natives. From XVII to XIX centuries, Portuguese men from the work class fathered more offspring with African slaves than with Portuguese women. Nowadays in the Brazilian Southeast, the majority of individuals are mix breed of Europeans, Africans (most of them from the slave heritage) and Indigenous forming the major population group of *mulatos* [12,13].

Slavery was abolished in Brazil only in May 13 1888 ruled by the Princess-Impress Isabel (the last crowned head of Brazil). The *Lei Aurea* (Golden Law) gave an end to the most everlasting slavery in the free world. Additionally, early in the XX Century, coffee temporary replaced sugar cane as the major commodity (in US$) in Brazilian trading [6].

Recently Phillips[14] wrote in *The Guardian* (London) regarding the sugar cane cutters labor situation in São Paulo State, Brazil, 2007 ` Inside the prison-like construction are the *cortadores de cana* - sugar cane cutters - part of a destitute migrant workforce of about 200,000 men who help prop up Brazil's ethanol industry. (…) The "*cortadores*" - cane cutters - are effectively slaves and complain that Brazil's cane industry is, in fact, a shadowy world of middle men and human rights abuses. (…) That includes working 12-hour shifts in scorching heat and earning just over US$ 1 per ton of sugar cane cut, before returning to squalid, overcrowded "guest houses" rented to them at extortionate prices by unscrupulous landlords, often ex-sugar cutters themselves. (…)`. This modern slavery encountered nowadays in sugar cane plantations of Brazil and in South Asia is a conjunction of psychological manipulation and debt bondage, by which unfair loans to pay the subsistence and the worker round-trip to the farm keeping them perennially bonded to their employers [15].

1.3. Hazardous Substances in Sugar Cane Plantations

Anthropogenic activities such the application of arsenical pesticides has resulted in elevated (high as 900 $g.g^{-6}$) levels of arsenic (As) in surface soils in many historic sugarcane areas of Hawaii, USA [16].

Rock phosphates applied as fertilizers in many crops present essential elements: calcium, phosphorus, manganese, selenium, sodium, and also hazardous elements such as uranium, thorium, arsenic, fluoride and elements with role to be determined such rubidium and the rare earth elements (the called RREs) [17].

2. Objective

To assess the concentration of multiple elements, including the most hazardous element in the world arsenic, in sugar cane *Saccharum officinarum* produced and commercialized in Brazil in order to verify the levels of essential, hazards and also of elements with role yet to be defined.

3. Material and Methods

3.1. Analytical Technique

The instrumental neutron activation analysis (INAA) technique is based on nuclear properties of the nucleus of the atom, radioactivity, and the interaction of radiation with matter. The simplest description of the technique says that when one natural element is submitted to a neutron flux, the reaction (neutron, gamma) occurs. The radionuclide formed emits gamma radiation, which can be measured by suitable equipment. About 70% of the elements have nuclides possessing properties suitable for neutron activation analysis. At the Nuclear Technology Development Centre (CDTN), Belo Horizonte, Brazil, it is located the nuclear reactor Triga Mark I IPR-R1 that allows the application of this technique [18,19].

3.1.1. Sampling

It was taken randomized 5 commercial packs of sugar cane from local brands in local stores in Belo Horizonte, Minas Gerais State, Brazil. To quantify simultaneously many elements as possible, it was applied the well-established nuclear analytical technique of Neutron Activation Analysis [18,19]

The sugar cane samples were freeze-dried and lyophilized for 24 hours to eliminate their water content. Samples of each pack were isolated, weighed around 250 mg and stored into polyethylene irradiation vials. They were irradiated in the reactor IPR-R1 (CDTN/CNEN operating at 150 kW the thermal neutron flux is 6.6×10^{11} neutrons cm^2 s^{-1}. The samples were irradiated simultaneously with gold foil comparators and reference material. Elemental contents were determined through two schemes of sample irradiations: 8 hours of irradiation to detect calcium, rubidium and uranium contents[16], 4 hours of irradiation to detect the remaining elements cited herein [17] accordingly their half-lives as seen in Table 1.

After suitable decay time, the gamma spectroscopy was performed in a HPGe detector (hyper pure germanium semiconductor detector), 10% of efficiency, FWHM 1.85 keV and ^{60}Co, 1332 keV, connected to a multichannel analyzer. The calculations were processed using the Solcoy/KayZero Software [18,19].

3.1.2. Quality Control

Triplicates of reference material Rice Flour (SRM 1568a, from National Institute of Standards and Technology, USA) were analyzed in order to verify the efficiency of the method and the traceability of element level determinations. Triplicates were weighed around 250 mg (same mass of the samples) into polyethylene irradiation vials in order to be irradiated in the same batch of the sugar samples and monitors, each triplicate for an irradiation scheme (4 or 8 h).

4. Results: Presence of Some Selected Hazardous Elements in Sugarcane from the Local Market of Belo Horizonte, mMnas Gerais, Brazil

Quality Control

For QA/QC purposes, a selected reference material: Rice Flour Reference Material SRM 1568a see data on Table 2 were used as three replicates (each irradiation batch was formed of 32 bone samples, samples of phosphate and one replicate of each SRM and k0-INAA standards). Batches were irradiated ways on Monday morning for 3 weeks in a row. SRM were analysed in order to verify the efficiency of the method and the traceability of element level determinations.

Table 1. Elemental composition of sugar cane from Brazil. N=5, dry weight

Element	Activation Product	Product Half Life	Elemental Concentration [$g.g^{-6}$]
Arsenic	^{76}As	1.097 days	0.81 ± 0.10
Bromine	^{82}Br	1.471 days	16.8 ± 1.54
Calcium	^{47}Ca	4.536 days	848 ± 79
Lanthanum	^{140}La	1.679 days	0.53 ± 0.06
Sodium	^{24}Na	0.621 days	262 ± 30
Rubidium	^{86}Rb	18.660 days	31.7 ± 6.2
Scandium	^{46}Sc	3.410 days	0.34 ± 0.04
Samarium	^{153}Sm	1.816 days	0.12 ± 0.02
Uranium	^{239}Np	2.355 days	0.31 ± 0.05

Table 2 data quality assessment: summarizes the concentrations for calcium, arsenic, rubidium and sodium determined in the certified reference material, Rice Flour (NIST-SRM 1568a) from National Institute of Standards and Technology, Gaithersburg, USA. A good agreement was found between the experimental and certified values.

Table 2. Elemental composition of Rice Flour Reference Material SRM 1568a. N=3, dry weight

Element	Certified Value [$g.g^{-6}$]	Experimental Value [$g.g^{-6}$]
Arsenic	0.29 ± 0.03	0.25 ± 0.04
Calcium	118 ± 6	112 ± 19
Rubidium	6.14 ± 0.09	6.59 ± 0.45
Sodium	6.6 ± 0.8	6.1 ± 1.5

5. Discussion

The FDA Food and Drug Administration (USA) has published results on arsenic in apple juice (ready to drink) of domestic (North American) market: five percent of the 94 apple juice samples were above 10 $g.g^{-9}$ of total arsenic, data obtained using ICP-MS (Inductively coupled plasma mass spectrometry). In a memorandum from the Department of Health and Human Services - Chemical Hazard Assessment Team, Office of Food Safety (HFS-301), FDA affirms that the chronic consumption of apple juice products containing over *the level of concern* (*LOC* = 23 $\mu g.L^{-1}$ or $g.g^{-9}$) *of total arsenic* would represent a potential health risk [20]. The same LOC could be applied for different types of juices and beverages, for instance pear juice. In a different survey from 2008 using ICP-MS some samples of concentrated pear juice show up to 70 $\mu g.L^{-1}$ of total arsenic [21]. If it compared a cup of coffee prepared with a 100 mg of hot water, 1 rounded tablespoon (7.5 grams with less than 1.0 gram passing the paper filter) of coffee and 2 rounded tablespoon 15.0 grams of sugar cane from this study, considering a hypothetical amount of 0.0 $g.g^{-9}$ arsenic in both water and coffee, this hypothetical cup of coffee would present 13 $\mu g.L^{-1}$ (or $g.g^{-9}$) of inorganic arsenic only due to sugar cane, half of the LOC = 23 $\mu g.L^{-1}$ or $g.g^{-9}$ of total arsenic.

The odd presence of uranium and rare earth elements such lanthanum and samarium in sugar cane could be explained due the fact of phosphate fertilizers (monazite and rock phosphate for instance) are used in crop yielding; these rock fertilizers present significant amounts of uranium and RREs [17]. Apparently, metabolism of some nutrients in plants is increased by rare earth elements. RREs are responsible for the transfer of N from inorganic to organic form, which is beneficial for protein synthesis and regulation of nutrient balance in plants [22].

Many studies such the USDA Data Library [3] point out the fact of sugar is not an important source of any essential element or vitamins. Results strength the term 'empty calories` what often is used to refer sugar (and solid fats) [23]. One example of the lack of essential elements in sugar cane is the low concentration found for calcium (one of the most important element in man and animal lives), Ca = 84.8 ± 7.9 mg/100 g in sugar, which is in accordance with the value of 83.0 mg/100 g as calcium concentration in the sugar brown reported in the *Basic Report from the National Agricultural Library* NAL [3]. Sodium concentration observed in this study (Na = 262 ± 30 $g.g^{-6}$ in sugar) is in compliance with NAL USDA data Na = 280 $g.g^{-6}$ in sugar brown [3]. In fact, Na is an essential element with a limited ingestion up to 2400 $mg.day^{-1}$ (equivalent to 8 kilograms of sugar or 6.0 grams of table salt *Sodium Chloride*) to be considered as safe. Upper values are associated to heart and kidney diseases [7]. Hence, sugar is not a major source of sodium in a healthy diet.

For different commodities like rice (what is not an empty calorie itself), fortification programmes are already a reality. Muthayya [24] point out` There are opportunities to fortify a significant share of rice that comes from large mills supplying centralized markets and national welfare programs in major rice-growing countries. (…) The cost of fortifying rice is only 1.5% to 3% of the current retail price of rice. Countries that mandate rice fortification have the strongest evidence for achieving wide coverage and impact [24].

In fact, the role of sugar as an efficient vehicle for fortification with vitamin A is already a well-stablished technology [25]. Concerning mineral fortification of sugar, there are different conclusions for different initiatives. In Guatemala during the mid-1970s, a trial on fortification of sugar with NaFeEDTA was carried out. At the time, the product appeared to be promising, showing an apparent absorption of 3% to 8%. Sugar was fortified by directly adding 1 g of the chelate per kilogram of sugar. However, after four years of consumption of this fortified sugar in three selected communities, the change in iron nutrition was only marginal. Significant increase in the urinary excretion of zinc, copper, and iron was observed. Recently, iron tris-glycine chelate, a new tasteless chelate in which iron is chelated with three molecules of glycine has been used successfully to fortify sugar in Brazil. With the tris-glycine chelate, there are no organoleptic changes, to the point that it can be used in caster sugar [26].

6. Conclusions and Recommendations

Sugar cane is really an 'empty calories' food additive, in terms of essential elements (such calcium) in man and animal nutrition. It should be discussed among public and private stakeholders how pertinent and reliable could be the adoption of policies like fortification of sugar with minerals, policy proposed and reported during the WHO – World Health Organization - Global Nutrition Policy Review (GNPR) 2009-2010 [27].

Nevertheless, fortification programmes to improve mineral properties on sugar should not promote increased consumption of sugar itself, since sugar cane presents hazardous elements as observed in this study, besides the fact of high consumption of sugar leads to obesity and diabetes.

When we ingest a food or drink, the nutrients contained are released from a complex matrix, absorbed into the bloodstream and transported to their respective target tissues. However, not all nutrients can be utilized to the same extent. In other words, they differ in their bioavailability. Understanding nutrient bioavailability helps optimize diet formulations and set appropriate nutrient recommendations. Regarding main human health, the bioavailability of a nutrient is governed by external and internal factors. External factors include the food matrix and the chemical form of the nutrient in question, whereas gender, age, nutrient status and life stage (e.g., pregnancy, labor, exercising) are among the internal factors.

Because aspects such as nutrient status also determine whether and how much of a nutrient is actually used, stored or excreted.

Acknowledgements

This project is partially supported by: by the Minas Gerais state-owned Scientific supporter Agency FAPEMIG. We appreciate every effort from CDTN/CNEN during Mr. Avelar´s Post-Doc internship at the institute in order to carry-out the nuclear analyses.

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