

Sourcing Brazilian marijuana by applying IRMS analysis to seized samples

Elisa K. Shibuya^{a,**}, Jorge E. Souza Sarkis^{a,*}, Osvaldo Negrini Neto^b,
Marcelo Z. Moreira^c, Reynaldo L. Victoria^c

^a *Laboratório de Caracterização Química e Isotópica, Centro de Química e Meio Ambiente, Instituto de Pesquisas Energéticas e Nucleares, IPEN/CNEN-SP, Av. Lineu Prestes 2242, Cidade Universitária, São Paulo, SP, CEP 05508-900, Brazil*

^b *Centro de Exames, Análises e Pesquisas, Instituto de Criminalística/SP, Rua Moncorvo Filho 410, São Paulo, SP, CEP 05567-060, Brazil*

^c *Laboratório de Ecologia Isotópica, Centro de Energia Nuclear na Agricultura, Av. Centenário 303, Piracicaba, SP, CEP 13416-903, Brazil*

Received 24 May 2005; received in revised form 18 August 2005; accepted 19 August 2005

Available online 23 September 2005

Abstract

The stable carbon and nitrogen isotopic ratios were measured in marijuana samples (*Cannabis sativa* L.) seized by the law enforcement officers in the three Brazilian production sites: Pernambuco and Bahia (the country's Northeast known as Marijuana Polygon), Pará (North or Amazon region) and Mato Grosso do Sul (Midwest). These regions are regarded as different with respect to climate and water availability, factors which impact upon the isotope fractionations of these elements within plants. It was possible to differentiate samples from the dry regions (Marijuana Polygon) from those from Mato Grosso do Sul and Pará, that present heavier rainfall. The results were in agreement with the climatic conditions of the suspected regions of origin and this demonstrates that seized samples can be used to identify the isotopic signatures of marijuana from the main producing regions in Brazil.

© 2005 Elsevier Ireland Ltd. All rights reserved.

Keywords: Forensic science; Drug sourcing; Marijuana; Stable isotopes mass spectrometry; Isotope signature

1. Introduction

1.1. Chemical fingerprint and the origin of illicit drugs

According to the United Nations Office on Drugs and Crime (UNODC), last year's global use of illicit drugs rose from 4.3 to 4.7% in the 15-year-old population bracket,

which represents an increase of 200 million-odd users, and a total value of about US\$ 500 billions around the world. Although cocaine and heroin represent the most consequential problems in terms of state welfare, marijuana stands by far as the most produced and consumed drug, involving about 150 million users around the world [1]. It is estimated that the worldwide cultivation ranges from 670,000 to 1,800,000 ha with productivity from 20,000 to 30,000 tonnes a year [2].

Due to its nature of illicit trade, statistics on production, trafficking and drug dealing are mostly based on seized quantities. The UNODC mentions numerous difficulties concerning the reported figures, such as differences in the

* Corresponding author. Tel.: +55 11 3816 9317; fax: +55 11 3816 9322.

** Corresponding author. Tel.: +55 11 3816 9311.

E-mail addresses: eshibuya@usp.br (E.K. Shibuya), jesarkis@ipen.br (J.E. Souza Sarkis).

criteria of reporting information supplied by national governments, and lack of consistent data and information regarding plantation sites, production and trafficking routes [3]. Among these difficulties, the latter is critical for an effective strategic plan against drug traffic [3], and even today most of the information concerning traffic routes is based mainly on unreliable information given by users and drug dealers. For this reason, the development of a methodology to trace these samples to their geographical origin would be extremely helpful as a key element in anti-drug law enforcement.

One of the strategies adopted in order to identify and track down the origin of those materials is based on the concept of chemical fingerprint. This fingerprint is established by determining the organic, inorganic or isotopic profile of the samples, which are associated with plant growth conditions such as climate and availability of elements on the site [4–15].

The relative amounts of the main organic constituents in cannabis plants (THC, tetrahydrocannabinol; CBD, cannabidiol; CBN, cannabinol) vary widely depending on many factors, mainly the genetic variety and the environment in which the plant was grown [16,17]. These parameters are also affected by time and conditions of sample storage once THC was transformed to CBN in these plant tissues. Thus, the use of the organic profile as a chemical tracer is hindered by its complexity, requiring further information related to plant maturity and storage conditions [8,14,17,18].

In comparison to the stable isotopic ratio, the elemental profile of the plants provides further knowledge of the soil. Despite this they cannot establish explicitly their geographic origin and appear rather inconclusive [13–15,19,20]. The carbon and nitrogen isotope ratio on the other hand, reflects the climatic conditions, and consequently, it delimits the potential geographic source when the producing areas present different climates [9,11,12,21–26].

The stable isotopes most commonly used as indicative of global changes are hydrogen, oxygen, carbon and nitrogen, and among them, the variation of stable isotope ratio (δ) of C and N are the most useful for sourcing the geographical origin of plant materials [21,26].

Unlike drugs such as heroin and cocaine, *Cannabis sativa* or marijuana is not processed for consumption and maintains its original elemental and isotopic profiles. Thus, these parameters have been used as an important indicative of its geographical origin [21,26].

Handley et al. evaluated the $\delta^{15}\text{N}$ variation in plants and soil influenced by the following parameters: rainfall, temperature, latitude, altitude and soil pH. Their model excluded samples from regions where atmospheric N_2 was a potentially major source of plant N, sites with anomalous pH values or with very high rainfall (>2500 mm annually), and regions with very low temperatures (high altitude or latitude). It was concluded that rainfall affects foliar $\delta^{15}\text{N}$ values more strongly than whole soil $\delta^{15}\text{N}$, 35 and 8%, respectively [26].

Denton et al. [24] measured the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ levels in marijuana samples seized in Australia, New Guinea and Thailand, with the aim of identifying their provenance. It was not possible to classify the samples according to their origin, but some important conclusions were presented: (1) $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ exhibit low dependence on temperature but present a direct relationship with water availability, particularly in the case of $\delta^{13}\text{C}$; (2) marijuana $\delta^{15}\text{N}$ values strongly reflect the $\delta^{15}\text{N}$ of growth substrate and fertilizer. This methodology also proved to be efficient to identify of indoor-grown sample, producing fairly characteristic $\delta^{13}\text{C}$ values of around -31.8% .

More recently, Galimov et al. [27] proved the potentiality of IRMS technique as a tool to source drugs using samples from different regions of Russia and Ukraine. The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ results for hemp leaves showed a large variation range for $\delta^{15}\text{N}$ (from -3.17 to 9.65%), while for $\delta^{13}\text{C}$ this range was narrow (from -28.38 to -26.43%).

Although these results show the potentiality of the carbon and nitrogen isotopes ratios in assigning the geographic origin of marijuana samples, these studies are scarce in the scientific literature and still do not appear conclusive. The major difficulty reported by the authors in the development of such methodologies lies in obtaining a sufficient number of samples, particularly of recognized origin. Thus, most of these works have been achieved using samples obtained from seizures for which the original geographical origin is unclear [9,15].

The aim of this work was to verify the differences in the stable carbon and nitrogen isotopic compositions for samples seized in the main Brazilian regions of marijuana production and to evaluate the possibility of using these parameters to track the provenance of marijuana samples traded in the country. The first data for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in marijuana samples seized in South America, especially in Brazil will be presented.

1.2. Stable carbon and nitrogen isotopes in plants

The main mechanism of C fixation and fractionation in plants is photosynthesis, whereby absorption of CO_2 from the atmosphere occurs. Plant tissues are deficient in ^{13}C in relation to the atmospheric CO_2 , indicating that there is a discrimination against ^{13}C absorption. This C fractionation is regulated by the plant photosynthetic pathway and is related to both stomatal limitation and enzymatic processes [23].

The three basic C pathways are Hatch–Slack–Kortschak (C4), Benson–Calvin (C3) and Crassulacean Acid Metabolism (CAM). The C3 plants reduce atmospheric CO_2 to phosphoglycerate with low $^{13}\text{C}/^{12}\text{C}$ ratio, presenting $\delta^{13}\text{C}$ average values of around -27% . About 85% of terrestrial plants are comprehended here, including marijuana. For this plant in particular $\delta^{13}\text{C}$ values varying from less than -30% to more than -24% have been reported according to growth conditions [24]. In general, the $\delta^{13}\text{C}$ values decrease with

increased water availability, presenting a small dependence on temperature [24].

Nitrogen fixation occurs via incorporation of nitrated compounds from the soil. Despite the fact that the atmosphere is very abundant in N_2 , plants only can absorb it indirectly through N-fixing bacteria. Decaying organic matter from biomass, manure and fertilizers are also important artificially introduced sources of nitrogen for plants.

In general, the global patterns of soil organic nitrogen in undisturbed ecosystems are mainly the function of annual rainfall. In the same way a strong negative correlation of foliar (leaves) $\delta^{15}N$ and water availability was observed [26]. Unfortunately, for regions with N sources other than soil organic matter, the isotope ratio of this element could be more strongly associated with that source than to climatic conditions [28,29]. To summarize, we have:

- when N is absorbed from the atmosphere by means of N-fixing bacteria or by use of industrial fertilizers, $\delta^{15}N$ values in the soil are low, around 0‰ [30,31];
- when N is absorbed from decayed organic matter fractionation is more significant, with $\delta^{15}N$ values of around 5‰, indicative of fertile soils, abundant in nutrients [31];
- negative values of $\delta^{15}N$ are observed in soils with low ratios of organic matter, in particular dry and sandy soils [32];
- where manure is added as a natural fertilizer, ratios of fractionation are high, with $\delta^{15}N$ above 10‰ [31].

In practical terms, soil N may simultaneously originate from different sources [33]. The use of fertilizers in farming tracts, for example, may alter the soil's isotope ratio, and as a result samples obtained from nearby locations may have significantly different isotope signatures. It is believed that this problem will be more pronounced in regions with low amounts of natural nutrients, where the use of fertilizers is necessary. However, although in many instances they may not unequivocally characterize their place of origin regarding climate, the $\delta^{15}N$ values always carry strong individual indications of the planting conditions.

1.3. Marijuana in Brazil

In Brazil, figures for confiscated marijuana have risen significantly in recent years, from about 22 tonnes in 1996 to more than 150 tonnes in 2004 [1]. Those figures reflect not only a rise in production but also the efforts on the part of the Brazilian government to combat drug trafficking. In the South-American continent, Brazil leads in the number of seizures, and is second to Venezuela in terms of consumption.

Official data provided by the Federal Police Department (DPF) for the last years show more than 50% of the marijuana as having been seized in the country's Midwest, which includes the State of Mato Grosso do Sul. However,

Table 1
Eradication and seizures of marijuana in Brazilian regions between January and August 2002

Region	Marijuana (g)	(%)	Plants (eradication)	(%)
Northeast (BA, PE)	16,789,563	22.4	745,534	84.6
Midwest (MS)	32,221,267	43.0	67,033	7.6
North (PA)	969,318	1.3	69,054	7.8
South	15,022,016	20.1	81	0.009
Southeast	9,876,988	13.2	–	
Total	74,879,152	100	881,702	100

Source: Brazilian Federal Police site under Estatística (www.dfp.gov.br available in June 2003).

eradication of plants was higher in the country's Northeast, in the territory of the so-called "Marijuana Polygon", traditionally a major region of production involving the States of Bahia and Pernambuco, mainly in their border region. These data are presented in Table 1. Although indicating a rising trend, seizures in the country's North, in the Pará State, still represent a lower percentage in the national context.

2. Material and methods

2.1. Samples

All samples analyzed in this work were seized in the main producing States of North, Midwest and Northeast Brazilian regions by the State Police Departments (see Fig. 1 and Table 2). According to the local law enforcement officers, they were cultivated near the locales of seizures. Besides, there is no information about the existence of traffic routes between these regions.

The climatic conditions of the main producing zones are described below:

- The Northern region that includes the State of Pará (PA) (see Fig. 1), features equatorial climate, hot and humid with average temperatures ranging from 24 to 26 °C most of the year. With regard to precipitation, however, spatial distribution is not as homogenous as is temperature. Total annual rainfall records exceed 3000 mm along the coast and occidental areas, and drier inland

Table 2
Total of samples analyzed for stable isotope ratios for each state

Region of seizure	Total of samples
Pernambuco (Marijuana Polygon)	27
Bahia (Marijuana Polygon)	20
Mato Grosso do Sul (Midwest)	23
Pará (North)	20
Total	90



Fig. 1. Main regions in Brazil with high level of eradication and seizures.

strips in the state have annual rainfall averages as low as 1500–1700 mm. The annual mean rainfall is 2800 mm, with 1–3 months of dry season, depending on the region.

- (b) The Northeastern States of Pernambuco (PE) and Bahia (BA) are semi-arid climates with annual average temperatures of about 25 °C. Precipitation distribution here is very complex, both in relation to occurrence (which many times may not even take place) and also in its yearly total, ranging from 200 to 2000 mm. The most rainy areas of both states are distributed along the coast. Pernambuco is drier mainly in its interior, which had around 7–9 months of dry season, with annual rainfall of up to 600 mm in the most of the state. Although Bahia has some regions with the same profile, in general its inland climate is less arid, with approximately 4–6 dry months and mean annual precipitation of 800–1000 mm.
- (c) In the Midwestern region, the State of Mato Grosso do Sul (MS), has a predominantly semi-humid tropical climate, with rainy summers and dry winters. Average temperatures are high, from 20 to 25 °C. Yearly rainfall records run from 900 to 1900 mm, a narrower variation as compared to the NE states. This state presents about

3–5 months of dry season depending on the region, with more than 70% of the precipitation occurring in the rainy season.

It is also important to note that Pernambuco and Bahia States include the hydrographic basin of the São Francisco River. These regions are surrounded by irrigated and fertile soils, although rainfall does not exceed 600 and 800 mm annually in PE and BA, respectively, with semi-arid climates and 7–8 months of dry season.

2.2. Samples preparation

The samples are mostly made up of leaves and a few twigs, and some may contain some seeds. In order to develop a quick and useful methodology for the police routine, the analyses were performed using the samples in their entirety. Previously to these analyses, the variability introduced by these tissues in the isotopic composition of the whole samples was evaluated for some samples from Mato Grosso do Sul. They were separated into leaves, seeds and twigs, and then the results were compared to the whole sample.

The samples were washed in sonicator for about 30 min in de-ionized water, dried at 40 °C for about 24 h, and ground using an electric mill with ceramic mortar and pestle. About 10 mg of the powdered material was used for isotope analyses.

Samples were analyzed by continuous flow isotopic ratio mass spectrometry (CF-IRMS), employing a Thermo-Finnigan Delta Plus mass spectrometer coupled to a Carlo Erba CHM 1110 elemental analyzer installed at the Isotope Ecology Laboratory, at Center for Nuclear Energy in Agriculture, CENA, University of São Paulo. In brief, organic matter is converted into gases by full combustion, generating N₂ and CO₂. These gases are chromatographically separated and carried by an ultrapure helium flow stream to the mass spectrometer. The ¹⁵N/¹⁴N and ¹³C/¹²C isotope ratios are evaluated after separation of molecules according to isotopic masses, and finally compared to the calibrated gases ratios using international standards as reference: N₂Atm and Pee Dee Belemnite (PDB, standard for C that presents $R = {}^{13}\text{C}/{}^{12}\text{C} = 0.0112372$), respectively. Results are expressed in relative deviations of the isotope ratios as compared to the standards:

$$\delta X_{\text{sample}}(\text{‰}) = \left[\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right] 1000,$$

where R is the ¹⁵N/¹⁴N or ¹³C/¹²C.

2.3. Data analysis

Assessment of results followed the k -means cluster technique, using SPSS program, Version 10.0.5. This statistical tool is used to detect grouping in a data set and is recommended when neither the number nor the members of the groups are known [31]. It separates objects in similar groups taking into consideration two or more variables; the first k cases (where k is the number of clusters defined by the analyst) are used as temporary centers of the clusters. At each step, the samples are assigned in turn to the cluster with the closest center then these centers are recomputed until no further changes occur [34].

3. Results and discussion

In order to verify the variability introduced by the different plant tissues in the C and N isotopic composition of the samples in their entirety, five samples from Mato Grosso do Sul were separated into leaves, seeds and twigs. These results were compared to the MS group (whole samples) using F -test (for variance) and t -test (to test the equality of the means values)—see Table 3. The mean values and variance obtained for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ in the different tissues and in the MS group were equivalent ($\alpha = 0.05$). Although the homogeneity of the data was lower for $\delta^{15}\text{N}$, the variability introduced by the lack of samples grooming was not significant for these studies. The results

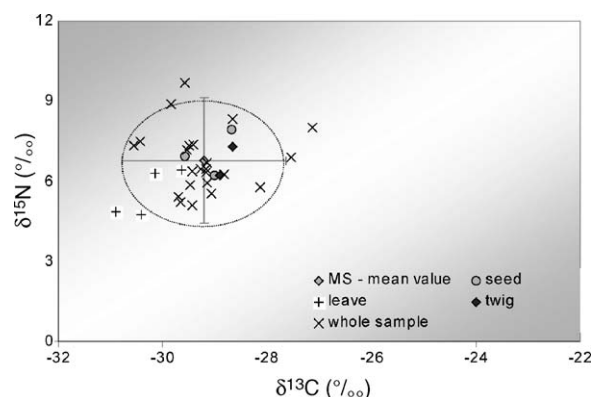


Fig. 2. Isotopic compositions for different cannabis tissues for five samples from Mato Grosso do Sul (leaves, twigs and seeds) in comparison to the mean value of MS group (without grooming). The bars represent 2σ .

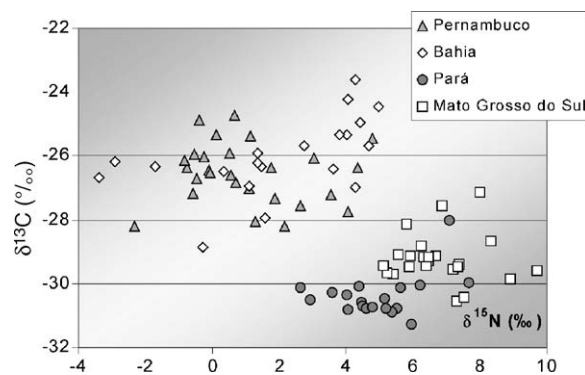


Fig. 3. Isotopic profile obtained for *cannabis* samples from Bahia and Pernambuco (dry regions) and Mato Grosso do Sul and Pará (rainy regions).

are plotted in Fig. 2 in comparison to the values obtained for MS group.

The isotopic profile of samples seized in the dry regions (BA and PE) was distinctly different from those from regions with heavier rainfall (PA and MS)—see Fig. 3.

The samples seized in BA and PE merge, with high dispersion ratios (as listed in Table 4), due to the proximity of both states and the high spatial and temporal variability

Table 3
Mean values and variance for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ for *cannabis* tissues and whole samples for samples from Mato Grosso do Sul

	$\delta^{13}\text{C}$ (‰)		$\delta^{15}\text{N}$ (‰)	
	Tissues	Whole sample	Tissues	Whole sample
Mean (‰)	-29.55	-29.21	6.33	6.78
Variance (‰)	0.65	0.61	1.08	1.38

Table 4
 $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ mean value and standard deviation for samples from Pernambuco, Bahia, Mato Grosso do Sul and Pará

State	$\delta^{15}\text{N}$		$\delta^{13}\text{C}$	
	Mean (‰)	S.D. (‰)	Mean (‰)	S.D. (‰)
Dry regions				
PE	1.04	1.78	-26.53	0.96
BA	1.99	2.55	-26.03	1.22
Regions with high water availability				
MS	6.78	1.17	-29.21	0.78
PA	5.00	1.28	-30.32	0.71

of their precipitation records. Since PE and BA are neighboring states, many samples may have been grown in borderline areas, and those seized in PE may have been grown in BA or vice versa. Carbon and nitrogen isotopic composition cannot separate samples from these regions and then these states must be grouped as a single producing region.

Although samples from MS and PA presented overlapping, the isotopic profile obtained for Pará group pointed to heavier rainfall. The dispersion of results is slightly lower, indicating more homogenous groups particularly with respect to $\delta^{13}\text{C}$ for PA, which may reflect a more uniform rainfall pattern in that state throughout the year.

The most significant considerations are:

- $\delta^{13}\text{C}$ values of BA and PE samples ranged from -23‰ to -29‰, and $\delta^{15}\text{N}$ values went from -3.38‰ to nearly 5‰, a high degree of variability in comparison to the other two groups.
- $\delta^{13}\text{C}$ mean values of PA and MS samples were -30.5‰ and -29‰, respectively, typical values for regions with high rainfall.
- MS samples showed average $\delta^{15}\text{N}$ values higher than those of PA (around 7‰ and 5‰, respectively), consistent with local rainfall values [23].
- These results are in agreement with the climatic condition of the locales of samples seizures.

Aiming at a better understanding of the samples behavior and in an effort to verify the existing clusters for each one of the regions, the *k*-means technique was employed in groups from humid and dry regions separately. In order to represent the number of the state for each cluster and to evaluate the potentiality of this statistical tool in the discrimination of the groups, *k* = 2 was adopted in both cases. The samples from the Northeast were classified (see Fig. 4), as follows:

Group 1: Samples with $\delta^{15}\text{N}$ values in the neighborhood of 0‰. These values suggest samples from plants growing in soils not exceedingly rich in nutrients, where nitrogen may be generated by the action of N-fixing bacteria, which may

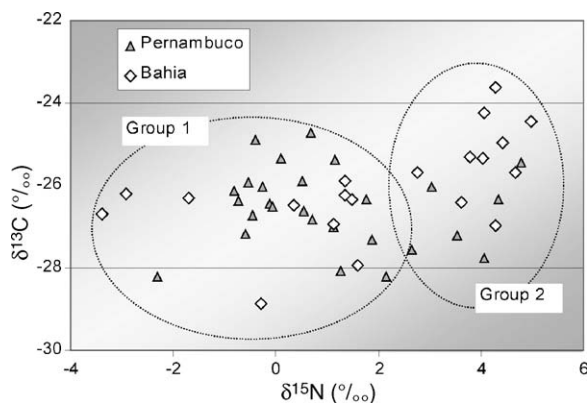


Fig. 4. Samples from Bahia and Pernambuco classified by *k*-means technique. Group 1 presents $\delta^{15}\text{N}$ around 0‰ (regions with low levels of nutrients) and Group 2 around 4‰ (regions with high soil fertility).

also indicate the use of industrial fertilizers. Three samples from BA and one from PE showed $\delta^{15}\text{N}$ values of less than -1.7‰, pointing to dry and sandy soils as their probable locale of growth. About 68% of these samples were seized in PE.

Group 2: These samples had $\delta^{15}\text{N}$ values higher than 2.6‰ and an average value in the neighborhood of 4‰. Such values denote samples probably grown in fertile soils, with decaying organic matter and rich in nutrients. About 63% of these samples were seized in BA.

It is known by the police that marijuana in Pernambuco State is cultivated together with leguminous plants with a view to increasing the absorption of atmospheric N_2 and the availability of this nutrient in the soil. The results reinforce this theory, since $\delta^{15}\text{N}$ values for this state were mostly around 0‰. Results for Group 2 may be associated with the São Francisco Basin, which is bordered by fertile soils and presents low annual rainfall with 7–8 months of dry season. Consistently with the semi-arid climate, some samples show extremely high $\delta^{13}\text{C}$ values, of around -24‰.

The classification of MS and PA samples by the *k*-means technique is shown in Fig. 5. Group 3 basically refers to samples seized in PA (84%, but includes three samples from MS), while Group 4 basically refers to MS samples (83%, but includes four samples seized in PA). Results obtained for samples from MS presented a high degree of dispersion (see Table 3) and can be related to the local and seasonal variation of rainfall. Some samples from MS and one sample from PA presented $\delta^{13}\text{C}$ values similar to those obtained for dry regions, and are in agreement with rainfall variation. The $\delta^{15}\text{N}$ results for these states also are in agreement with rainfall extent, with values for PA lower than those for MS. The overlap observed between these

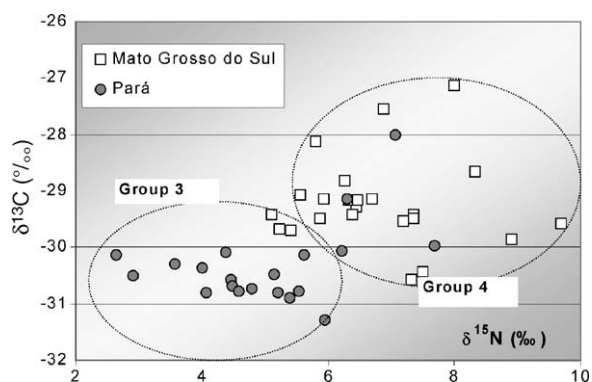


Fig. 5. Samples from Mato Grosso do Sul and Pará classified by *k*-means technique.

groups is related to similar climatic conditions and cannot be eliminated.

The behavior of samples may be more clearly observed in the histograms of Figs. 6 and 7. With the exception of Fig. 7a, the distribution of $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ reveal the climatic conditions of marijuana growth, allowing identification of samples from semi-arid and rainy regions. Values of $\delta^{15}\text{N}$ of dry regions are more complex (see Fig. 7a), and indicate the use of fertilizers and other resources in an effort to optimize crops.

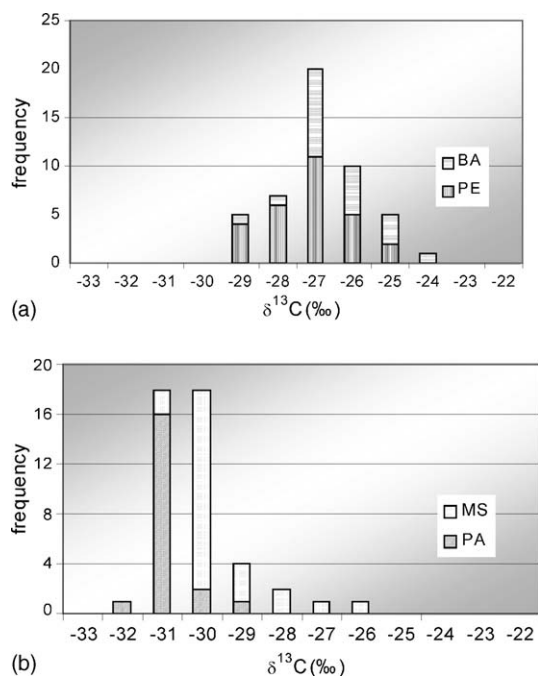


Fig. 6. (a and b) Histogram of $\delta^{13}\text{C}$ for samples seized in semi-arid regions and in rainy regions, respectively (BA, PE, MS and PA represent Bahia, Pernambuco, Mato Grosso do Sul and Pará, respectively).

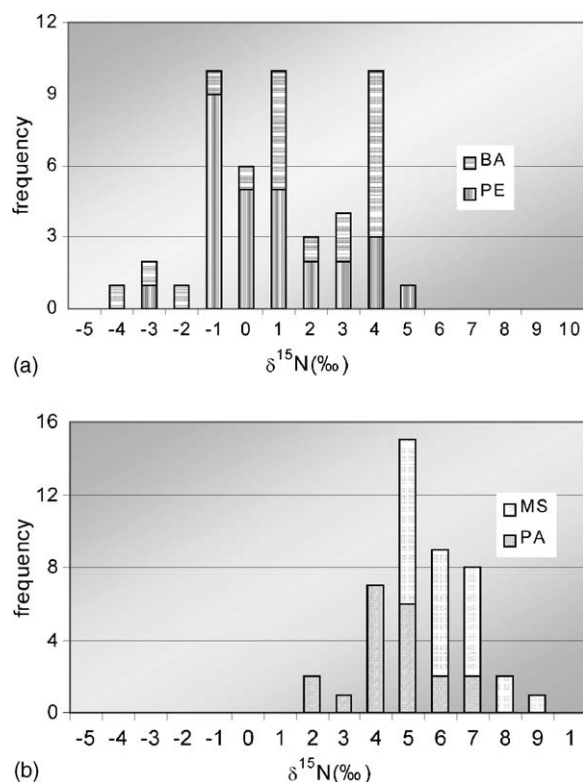


Fig. 7. (a and b) Histogram of $\delta^{15}\text{N}$ for samples seized in semi-arid regions and in rainy regions, respectively (BA, PE, MS and PA represent Bahia, Pernambuco, Mato Grosso do Sul and Pará, respectively).

4. Conclusions

This work demonstrates the potentiality of IRMS technique as an important tool in tracking the provenance of marijuana samples seized in different Brazilian regions. The isotopic profile was in agreement with the climatic conditions of the locales of seizures, confirming the law enforcement officer information that most of them were cultivated in the same region where they were seized. As expected, due to the geographical proximity, it was observed a large overlap between samples from Pernambuco and Bahia. The overlapping of some samples from Pará and Mato Grosso do Sul can be related to the climatic similarity of these regions. In both cases, the use of complementary analytical techniques such as gas chromatography, gas chromatography mass spectrometry or even inorganic analysis, such as inductively coupled plasma atomic emission or mass spectrometry can be used to assess additional information. In spite of this, the results show a clear difference between samples from the humid and dry regions.

Based on this work, it will be possible to evaluate the possibility to create a national database of isotopic signature of Brazilian marijuana using stable isotope measurements of

seized samples, which in future can also be used to source the provenance of the marijuana seized in the main centers of consumption, as the city of São Paulo.

Acknowledgments

Institutes of Criminalistics (IC) and State Police Departments (SSP) of Bahia, Mato Grosso do Sul, Pará and Pernambuco that provided the samples. This work was supported by Fapesp and FINEP/PADCT.

References

- [1] Office on Drugs and Crime (UNODC), Global Illicit Drugs Trends 2003, United Nations Publications, New York, 2003.
- [2] United Nations Office for Drug Control and Crime Prevention (UNDCP), Global Illicit Drugs Trends 1999, United Nations Publications, New York, 1999.
- [3] United Nations Office for Drug Control and Crime Prevention (UNDCP), Global Illicit Drugs Trends 2000, United Nations Publications, New York, 2000.
- [4] Moreda-Piñero, A. Fischer, S.J. Hill, The classification of tea according to region of origin using pattern recognition techniques and trace metal data, *J. Food Comp. Anal.* 16 (2003) 195–211.
- [5] M.J. Martín, PablosF, A.G. González, Characterization of green coffee varieties according to their metal content, *Anal. Chim. Acta* 358 (1998) 177–183.
- [6] R.S. Schwartz, L.T. Hecking, Determination of geographic origin of agricultural products by multivariate analysis of trace element composition, *J. Anal. At. Spectrom.* 6 (1996) 637–642.
- [7] M. Desage, R. Guilluy, J.L. Brazier, Gas chromatography with mass spectrometry or isotope-ratio mass spectrometry in studying the geographical origin of heroin, *Anal. Chim. Acta* 247 (1991) 249–254.
- [8] M. Stefanidou, A. Dona, S. Athanaselis, I. Papoutsis, A. Koutselinis, The cannabinoid content of marihuana samples seized in Greece and its forensic application, *Forensic Sci. Int.* 95 (1998) 153–162.
- [9] J.R. Ehleringer, D.A. Cooper, M.J. Lott, C.S. Cook, Geolocation of heroin and cocaine by stable isotope ratios, *Forensic Sci. Int.* 106 (1999) 27–35.
- [10] F. Besacier, H. Chaudron-Thozet, M. Rousseau-Tsangaris, J. Girard, A. Lamotte, Comparative chemical analyses of drug samples: general approach and application to heroin, *Forensic Sci. Int.* 85 (1997) 113–125.
- [11] J.R. Ehleringer, J.F. Casale, M.J. Lott, V.L. Ford, Tracing the geographical origin of cocaine, *Nature* 408 (6810) (2000) 311–312.
- [12] F. Besacier, R. Guilluy, J.L. Brazier, H. Chaudron-Thozet, J. Girard, A. Lamotte, Isotopic analysis of ^{13}C as a tool for comparison and origin assignment of seized heroin samples, *J. Forensic Sci.* 42 (3) (1997) 429–433.
- [13] R.J. Watling, Sourcing the provenance of cannabis crops using inter-element association patterns ‘fingerprinting’ and laser ablation inductively coupled plasma mass spectrometry, *J. Anal. At. Spec.* 13 (1998) 917–926.
- [14] C.B. Coffman, W.A. Gentner, Cannabinoid profile and elemental uptake of *Cannabis sativa* L. as influenced by soil characteristics, *Agron. J.* 67 (1975) 491–497.
- [15] S. Landi, Mineral nutrition of *Cannabis sativa* L., *J. Plant Nutr.* 20 (1997) 311–326.
- [16] P.S. Fetterman, E.S. Keith, C.W. Waller, O. Guerrero, N.J. Doorenbos, M.W. Quimby, Mississippi-grown *Cannabis sativa* L. Preliminary observation on chemical definition of phenotype and variations in tetrahydrocannabinol content versus age, sex and plant parts, *J. Pharm. Sci.* 60 (1971) 1246–1249.
- [17] A. Ohlsson, C.I. Abou-Chaar, S. Agurell, I.M. Nilsson, K. Olofsson, F. Sandberg, *Bull. Narcotics*, vol. XXIII, United Nations Publications, 1971, pp. 29–32.
- [18] M.J.F. Maunder, A comparative evaluation of the D-tetrahydrocannabinol content of cannabis plants, *J. Assoc. Public Analysts* 8 (1970) 42–47.
- [19] K.E. Janzen, L. Walter, A.R. Fernando, Comparison analysis of illicit cocaine samples, *J. Forensic Sci.* 37 (1992) 436–445.
- [20] J.G. Ensing, C. Racamy, R.A. Dee Zeew, A rapid gas chromatographic method for fingerprinting of illicit cocaine samples, *J. Forensic Sci.* 37 (1992) 446–459.
- [21] G.R. Stewart, M.H. Turnbull, S. Schmidt, P. Erskine, ^{13}C natural abundance in plant communities along a rainfall gradient: a biological integrator of water availability, *Aust. J. Plant Physiol.* 22 (1995) 51–55.
- [22] R. Amudson, A.T. Austin, Schuur EAG, K. Yoo, V. Matzek, C. Kendall, A. Uebersax, D. Brenner, W.T. Baisden, Global patterns of the isotopic composition of soil and plant nitrogen, *Global Biogeochem. Cy.* 17 (1) (2003) 31–31-10.
- [23] G.D. Farquhar, M.H. O’Leary, J.A. Berry, On the relationship between carbon isotope discrimination and the intercellular carbon dioxide concentration in leaves, *Aust. J. Plant Physiol.* 9 (1982) 121–154.
- [24] T.M. Denton, S. Schmidt, C. Critchley, G.R. Stewart, Natural abundance of stable carbon and nitrogen isotopes in *Cannabis sativa* reflects growth conditions, *Aust. J. Plant Physiol.* 28 (10) (2001) 1005–1012.
- [25] M.H. O’Leary, Carbon isotopes in photosynthesis, *Bioscience* 38 (1988) 328–336.
- [26] L.L. Handley, A.T. Austin, D. Robinson, C.M. Scrimgeour, J.A. Rave, Heaton THE, S. Schmidt, G.R. Stewart, The ^{15}N natural abundance ($\delta^{15}\text{N}$) of ecosystem samples reflects measures of water availability, *Aust. J. Plant Physiol.* 26 (1999) 185–199.
- [27] E.M. Galimov, V.S. Sevastyanov, E.V. Kulbachevskaya, A.A. Golyavin, Isotope ratio mass spectrometry: $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ analysis for tracing the origin of illicit drugs, *Rapid Commun. Mass Spectrom.* 19 (2005) 1213–1216.
- [28] P.D. Erskine, D.M. Bergstrom, S. Schmidt, G.R. Stewart, C.E. Tweedie, J.D. Shaw, Subantarctic Macquarie Island—a model ecosystem for studying animal-derived nitrogen sources using ^{15}N natural abundance, *Oecologia* 117 (1998) 187–193.
- [29] W.J. Choi, S.M. Lee, H.M. Ro, K.C. Kim, S.H. Yoo, Natural ^{15}N abundance of maize and soil amended with urea and composted pig manure, *Plant Soil* 245 (2002) 223–232.
- [30] T. Yoneyama, K. Fujita, T. Yoshida, T. Matsumoto, L. Kambayashi, J. Yazaki, Variation in natural abundance of ^{15}N among plant parts and in $^{15}\text{N}/^{14}\text{N}$ fractionation during N_2 fixation in legume-rhizobia symbiotic system, *Plant Cell Physiol.* 27 (1986) 791–799.

- [31] I.D. Clark, P. Fritz, *Environmental Isotopes in Hydrogeology*, Lewis Publishers, New York, 1997, pp. 148–151.
- [32] L.A. Martinelli, M.C. Piccolo, A.R. Townsend, P.M. Vitousek, E. Cuevas, W. McDowell, G.P. Robertson, O.C. Santos, K. Treseder, Nitrogen stable isotopic composition of leaves and soil: Tropical versus temperate forests, *Biogeochemistry* 46 (1999) 45–65.
- [33] P. Högberg, ^{15}N natural abundance in soil-plant systems, *New Phytol.* 137 (1997) 179–203.
- [34] W.O. Bussab, E.S. Miazaki, D.F. Andrade, Introdução a Análise de Agrupamentos, in: 9^o Simpósio Nacional de Probabilidade e Estatística, Associação Brasileira de Estatística, São Paulo, 1990.