

# **Development and Validation of a Solid-Liquid Extraction with Low Temperature Partitioning (SLE/LTP) Method for Determination of the Herbicide Indaziflam in Brazilian Soils by High Performance Liquid Chromatography (HPLC-UV/Vis)**

**Ana Cecilia Romero Ramírez<sup>1\*</sup>, Matheus F. F. Teixeira<sup>2</sup>,  
Antônio Augusto Neves<sup>1</sup>, Maria Eliana L. R. Queiroz<sup>1</sup>,  
Antonio Alberto da Silva<sup>2</sup>, Ivan Ferreira Furtado<sup>2</sup>  
and André Fernando de Oliveira<sup>1</sup>**

<sup>1</sup>*Department of Chemistry, Federal University of Viçosa, University Campus, 36570000, Viçosa, MG, Brazil.*

<sup>2</sup>*Department of Plant Science, Federal University of Viçosa, University Campus, 36570000, Viçosa, MG, Brazil.*

## **Authors' contributions**

*This work was carried out in collaboration between all authors. Author ACRR designed the study, performed the statistical analysis and wrote the protocol and the first draft of the manuscript. Author MFFT supported work in the laboratory and managed the literature search. Author AAN designed and leded the research. Author MELRQ leaded as Chromatographic analysis. Author AAS reviewed the experimental design and first draft of the manuscript. Author IFF (supported work in the laboratory) and author AFO (supported statistical analysis). All authors read and approved the final manuscript.*

## **Article Information**

DOI: 10.9734/JEAI/2018/39554

### Editor(s):

- (1) Masayuki Fujita, Professor, Dept. of Plant Sciences, Faculty of Agriculture, Kagawa University, Japan.  
(2) Mariusz Cycon, Professor, Department and Institute of Microbiology and Virology, School of Pharmacy, Division of Laboratory Medicine, Medical University of Silesia, Poland.

### Reviewers:

- (1) Jamil Rima, Lebanese University, Lebanon.  
(2) Luis Humberto Mendoza Huizar, Universidad Autónoma del Estado de Hidalgo, Mexico.  
(3) Mahmood Hassan Dalhat, Usmanu Danfodiyo University, Nigeria.

Complete Peer review History: <http://www.sciencedomain.org/review-history/23670>

**Original Research Article**

**Received 23<sup>rd</sup> December 2017**

**Accepted 6<sup>th</sup> March 2018**

**Published 17<sup>th</sup> March 2018**

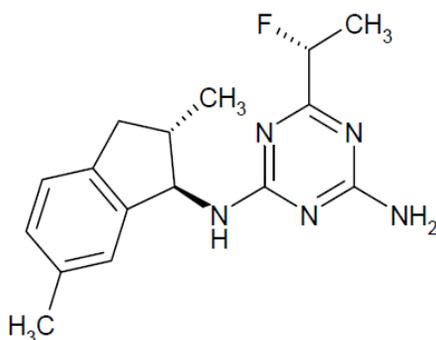
## ABSTRACT

Given the increased use of herbicides in intensive agriculture, it is essential to understand the dynamics of new products in the soil and in the wider environment, in order to avoid problems of contamination. One of the herbicides recently registered in Brazil is indaziflam (C<sub>16</sub>H<sub>20</sub>FN<sub>5</sub>). Although various analytical techniques are available for the determination of herbicides in soils, there have been few studies concerning indaziflam. In the present study, a solid-liquid extraction with low-temperature partitioning (SLE/LTP) method was developed, optimized, and validated for the identification and quantification of this herbicide in the soil by high-performance liquid chromatography with ultraviolet detection (HPLC-UV/Vis). Samples (4 g) of clayey and sandy Red-Yellow Latosol soils were conditioned with charcoal (1% w/w) obtained from the pyrolysis of sugarcane bagasse and were fortified with 2 mg L<sup>-1</sup> of indaziflam. Extraction was performed using 4 mL of ultrapure water (pH 7.0) and 10 mL of acetonitrile (ACN)/ethyl acetate (EtOAc) in a proportion of 8.1:1.9 mL. The mixture was vortexed and then frozen at -20 °C. The supernatant was filtered, evaporated to dryness, and then recovered in 1.5 mL of ACN, prior to analysis by HPLC-UV/Vis. The recoveries of the herbicide were between 79.56 and 106.41% and the coefficients of variation were between 0.9 and 14.4%, in conformity with the parameters established by national regulatory agencies. The method provided selective, efficient, and accurate determination of indaziflam in the soils studied.

**Keywords:** Indaziflam; method validation; SLE-LTP extraction; HPLC-UV/Vis.

## 1. INTRODUCTION

The herbicide indaziflam (N-[(1R,2S)-2,3-dihydro-2,6-dimethyl-1H-inden-1-yl]-6-[(1R)-1-fluoroethyl]-1,3,5-triazine-2,4-diamine) (Fig. 1) is recommended for the pre-emergent control of weeds in sugar cane, coffee, citrus, eucalyptus, and pine crops [1]. Its mechanism of action is related to the inhibition of cellulose biosynthesis [2], which prevents cell wall formation and therefore paralyzes development of the plant [3]. This herbicide has low water solubility (4.4 mg L<sup>-1</sup> (pH 4), 2.2 mg L<sup>-1</sup> (pH 7), and 2.8 mg L<sup>-1</sup> (pH 9), at 20°C). It is a weak acid with pK<sub>a</sub> 3.5, K<sub>OC</sub> <1.000 mL g<sup>-1</sup> of organic carbon, and log K<sub>OW</sub> of 2.8 at pH 4, 7, or 9 [4]. It is slightly lipophilic [5] and its half-life in soil (t<sub>1/2</sub>) is greater than 150 days [6].



**Fig. 1. Structural formula of the indaziflam molecule**

Given its lengthy persistence in the environment, the use of this herbicide without knowledge of the dynamics of its dissipation in the soil can lead to serious environmental problems, such as carryover [7] as well as the contamination of surface and subterranean water bodies [8]. Recent studies have indicated that conditioning soils with charcoal obtained from biomass by pyrolysis could help to reduce such problems of herbicide contamination [9,10,11]. The charcoal is rich in carbon; it has a high porosity [12] and high cation exchange capacity (CEC) [13]. These characteristics increase herbicides sorption leads to decreased efficacy of soil applied herbicides, avoiding phytotoxicity in the following crops. Besides the biochar decreases a mobility of herbicide and half-life in the soil could reduce leaching of herbicides to groundwater, thus improving overall water quality [14].

Analytical methods including high-performance liquid chromatography (HPLC) and solid-liquid extraction (SLE) have been employed for the determination of herbicides in soils [15,16,17, 18]. However, there have been few studies involving indaziflam. The herbicide has been removed from soil using microwave-assisted extraction with acetonitrile/water (80:20 v/v) [19]. Indaziflam labeled with <sup>14</sup>C has been extracted from a liquid medium using a scintillation spectrometry technique [20].

The aim of this study was to adapt, optimize, and validate a solid-liquid extraction with low-

temperature partitioning (SLE/LTP) method, with analysis using HPLC-UV/Vis, in order to study the behavior of this herbicide in Brazilian soils.

## 2. MATERIALS AND METHODS

### 2.1. Equipment and Reagents

Dry sugar cane bagasse was pyrolyzed for 1 h in a muffle furnace (Linn Elektro Therm, Eschenfelden, Germany), using a heating rate of  $9^{\circ}\text{C min}^{-1}$  and a final temperature of  $500^{\circ}\text{C}$ , as described previously [21,22,23]. The charcoal was triturated and passed through a 150 mesh sieve, resulting in a particle size  $<106\ \mu\text{m}$ .

Chromatographic analyses were performed using an HPLC system (Model LC-20AT, Shimadzu) equipped with a UV-Vis detector (Model SPD-20AT, Shimadzu), an auto injector (Shimadzu SIL 10AF) and a stainless steel reverse phase C18 column (VP-ODS, Shimadzu) with a length of 150 mm and internal diameter of 4.6 mm, packed with particles  $4.6 \pm 0.3\ \mu\text{m}$  in diameter. The column temperature was  $30^{\circ}\text{C}$ . The reagents used were HPLC-grade acetonitrile (Sigma-Aldrich, Germany), ethyl acetate (99.5% v/v, Vetec, Brazil), acetic acid (99.7% v/v, Isofar, Rio de Janeiro, Brazil), deionized water obtained from a Milli-Q system, and anhydrous sodium sulfate (99% w/w, Sigma-Aldrich, Germany). A stock standard solution of the herbicide was prepared at a concentration of  $1000\ \text{mg L}^{-1}$  by solubilization of indaziflam BCS-AA10717 (99.5% w/w, Bayer, Brazil) in acetonitrile.

The following equipment and materials were used in the experiments: analytical balances

(Model BP 2215, Sartorius, Gottingen, Germany; Model AY 220, Shimadzu, Kyoto, Japan), vortex mixer (Kasvi K45-2810, Econolab, São Paulo, Brazil), freezer (Consul, Santa Catarina, Brazil), rotary evaporator (Model 802, Fisatom, São Paulo, Brazil) operated at 105 rpm, thermostatic bath (Model TE-184, Technal, São Paulo, Brazil) operated at  $500^{\circ}\text{C}$ , and pH meter (Model DM-22, Digimed, São Paulo, Brazil).

### 2.2 Sample Preparation

Samples of clayey and sandy Red-Yellow Latosol soils were collected from the first 20 cm of the soil profile, in an area free from herbicide applications, in the municipality of Viçosa (Minas Gerais State, Brazil; geographical coordinates:  $20^{\circ}45' 14''\text{S}$ ,  $42^{\circ}52' 55''\text{W}$ ). These samples were used without and with conditioning by addition of 1% (w/w) charcoal. Characterization of the soils was performed in the Viçosa Soil Analysis Laboratory, following the methodology described by Embrapa [24] (Table 1).

### 2.3 Chromatographic Analyses

The optimized chromatographic conditions were as follows:  $20\ \mu\text{L}$  injection volume, mobile phase of acetonitrile/water (60:40), oven temperature of  $30^{\circ}\text{C}$ , and detector wavelength of 190 nm. Under these conditions, the indaziflam peak appeared at a retention time of 4.6 min. Quantification was performed by the external standardization method, with the construction of a standard curve using standards prepared in ACN in the concentration range  $0.2\text{-}4.5\ \text{mg L}^{-1}$ .

**Table 1. Physico-chemical properties of soils**

Soils	pH	P	K	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Al <sup>3+</sup>	H+Al	BS	(t)	(T)	OM
	H <sub>2</sub> O	---mg dm <sup>-3</sup> ---		-----cmol <sub>c</sub> dm <sup>-3</sup> -----							%
RYL <sup>1</sup>	4.60	1.30	13.0	0.40	0.10	0.00	4.90	0.53	1.73	5.48	1.86
RYL <sup>2</sup>	4.70	2.33	41.0	2.20	0.70	0.20	5.61	3.00	3.20	8.61	2.52
			<b>Clay</b>		<b>Silt</b>		<b>Sand</b>		<b>Textural class</b>		
			-----%-----								
RYL <sup>1</sup>			49		12		39		Clayey		
RYL <sup>2</sup>			17		7		76		Sandy		

Analyses performed in the Viçosa Soil Analysis Laboratory, following the methodology of the Brazilian Agricultural Research Company (EMBRAPA, 1997). BS: base saturation; (t): effective cation exchange capacity; (T): total cation exchange capacity; OM: organic matter; <sup>1</sup> clayey Red-Yellow Latosol; <sup>2</sup> sandy Red-Yellow Latosol, pH (H<sub>2</sub>O, KCl, CaCl<sub>2</sub>-Relation 1:2.5). P-K (Mehlich 1 Extractor). Ca, Mg, Al (Extracted KCl 1molL<sup>-1</sup>). H+Al (Extracted Calcium Acetate 0.5 molL<sup>-1</sup> pH:7). OM (Oxidation Na<sub>2</sub>Cr<sub>2</sub>O +H<sub>2</sub>SO<sub>4</sub>).

## 2.4 Optimization of the SLE-LTP-HPLC-UV/Vis Method

A factorial design with three variables (considering the influence of pH, agitation time, and solvent volume) was employed, with two levels (minimum (-) and maximum (+)). The pH values were 4.0 and 7.0, the agitation times were 1 and 2 min, and the volumes of the acetonitrile/ethyl acetate extractant mixture were 6.5 mL ACN/1.5 mL EtOAc and 8.1 mL ACN/1.9 mL EtOAc. The other experimental conditions were kept constant.

## 2.5 SLE-LTP-HPLC-UV/Vis Method Procedure

Samples of 4.0 g of the clayey and sandy RYL soils, without and with conditioning using 1% (w/w) charcoal, were placed in polypropylene tubes and fortified with 1.0 mL of a solution of indaziflam at a concentration of 2 mg L<sup>-1</sup>; the samples were dried to fresh air by 48 hours. The extraction was then performed by addition of 4 mL of Milli-Q water (at pH 7.0) and 10 mL of a mixture of ACN (8.1 mL) and EtOAc (1.9 mL). The resulting mixture was vortexed for 2 min and was then cooled at -20°C for 4 h in a freezer. The supernatant (organic phase) was passed through a filter containing 1 g of Na<sub>2</sub>SO<sub>4</sub>. The solid phase was then washed with 2 mL of freezing cold acetonitrile, the solvent was evaporated to dryness, and the product was recovered in 1.5 mL of acetonitrile. The HPLC-UV-Vis analysis was performed after filtration of the final extract through a 0.45 µm membrane.

### 2.5.1 Validation of the SLE-LTP-HPLC-UV/Vis method

The method was validated considering the following parameters: selectivity, linearity, limits of detection and quantification, accuracy, precision (repeatability and intermediate precision), enrichment factor, and matrix effects. The validation was performed according to the protocols of the National Health Surveillance Agency [25] and the National Institute of Metrology, Standardization, and Industrial Quality [26].

## 2.6 Statistical Analysis

The data were analyzed using Statistica v.10 software (StatSoft Corp., Tulsa, USA). Analysis of variance (ANOVA) was performed with Origin software [27,28].

## 3. RESULTS AND DISCUSSION

### 3.1 Optimization of the SLE-LTP-HPLC-UV/Vis Method

The extraction percentages obtained for the soils using the SLE/LTP method in the optimization procedure were evaluated by means of Pareto charts (The Pareto Chart Method is a vertical bar graph in which the values of the statistical variables are placed in order of relative frequency, the graph clearly reveals which factors have the greatest impact and presented significant differences) [29]. The Pareto charts showed that for the clayey soil without charcoal addition (Fig. 2A), only the pH had a significant effect on indaziflam extraction (95% confidence level;  $P = 0.05$ ), with a lower solubility of indaziflam at pH 7 than at pH 4. In the case of indaziflam extraction from the same soil with the addition of charcoal (Fig. 2B), the agitation time was the variable with the greatest effect, with improved extraction for longer times, which could have been due to the high adsorption capacity of charcoal.

The pH affected the behavior of indaziflam because the herbicide is classified as a weak acid ( $pK_a = 3.5$ ) [1,4,20]. As the pH increased, the solubility of indaziflam in water decreased, so a greater amount of the compound was extracted into the organic phase. The addition of carbonaceous material like charcoal to a soil increase sorption of herbicides in all cases [14]. This increase sorption is mainly related to their high specific surface area [30] and the presence of functional groups such as carboxyls, hydroxyls, and amines, as well as aliphatic and aromatic structures [31]. Overall, the best experimental conditions found for indaziflam extraction from clayey soil without and with charcoal through the SLE/LTP-HPLC-UV/Vis method were as follows: aqueous solution pH 7, agitation time of 2 min, and 10 mL of extractant solution consisting of 8.1 mL of ACN and 1.9 mL of EtOAc.

### 3.2 Validation of the SLE-LTP-HPLC-UV/Vis Method

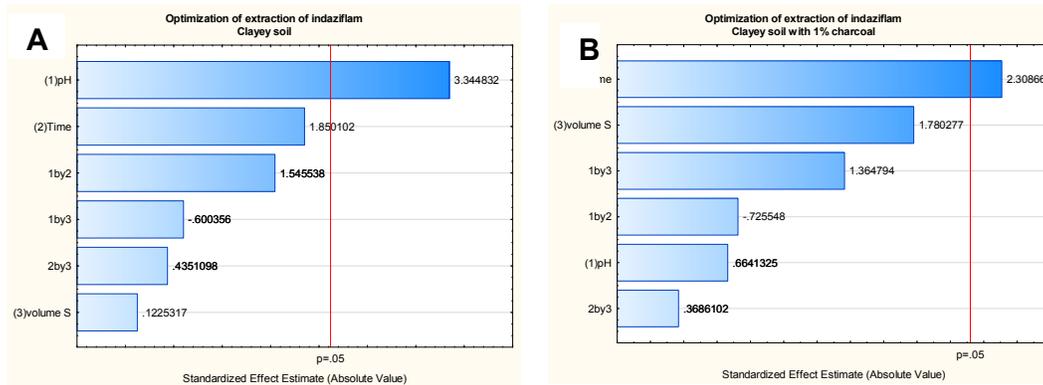
Use of the optimized solid-liquid extraction with low temperature partitioning method for extraction of indaziflam from the soils resulted in extracts that were clear and free from interferents. The chromatograms obtained from extracts of soil samples that were not spiked with indaziflam showed no peaks corresponding to indaziflam, at a retention time of 4.6 min (Fig. 3).

These results confirmed the selectivity of the method and demonstrated that it could be used for chromatographic analysis of the herbicide in soils.

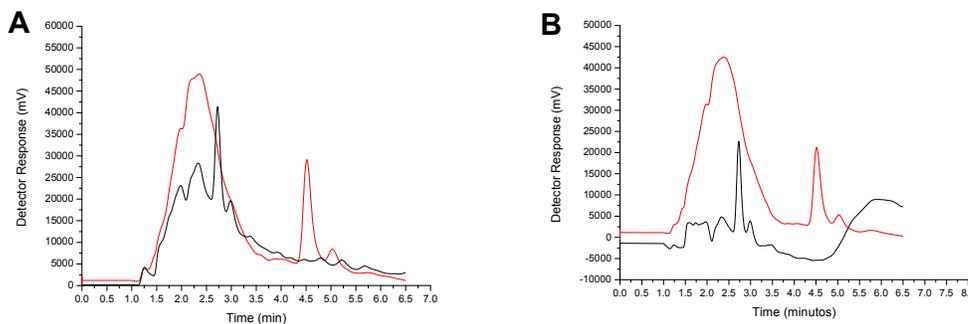
The linearity of the instrumental response was determined using indaziflam standards prepared in acetonitrile, in the concentration range 0.2-4.5 mg L<sup>-1</sup> (Fig. 4A). The coefficient of determination was 0.99 and the residuals showed a random distribution (Fig. 4B), indicative of good linearity and a satisfactory fit. The analytical curve was used to calculate the instrumental limits of detection (LD) and quantification (LQ), with values of 0.15 and 0.44 mg L<sup>-1</sup> obtained, respectively.

The linearity of the response of the method was evaluated for each soil substrate spiked with

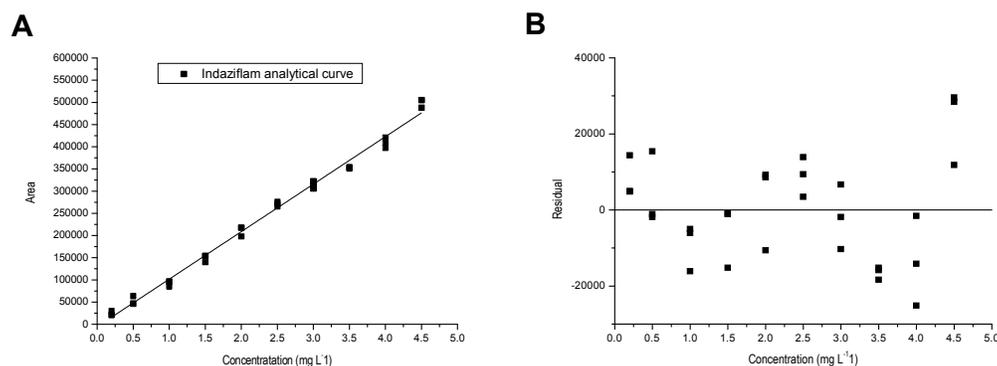
indaziflam at seven levels (0.2, 0.5, 1.5, 2.0, 3.0, 5.0, and 6.0 mg kg<sup>-1</sup>). The analyte peak areas were proportional to the concentrations, with coefficients of determination (R<sup>2</sup>) greater than 0.99. Analysis of the residuals showed a random distribution, demonstrating good linearity and satisfactory quality of the fit. Hence, the analytical curves could be used for quantification of the analyte [25,26,32]. Table 2 shows the results for the analytical curves obtained for the determination of indaziflam in the clayey and sandy soils in the absence or presence of charcoal (at 1% w/w). The limits of detection and quantification were calculated from the ratio of the standard deviation of the analytical response for the blank and the slope of the analytical curve.



**Fig. 2.** Pareto charts of the effects of the factors (1) pH, (2) agitation time, and (3) ratio of the extractant solution volume to the mass of the sample on the extraction of indaziflam from the clayey soil without (A) and with (B) addition of charcoal, using the SLE-LTP-HPLC-UV/Vis method.



**Fig. 3.** Chromatograms for the extracts obtained using the SLE/LTP-HPLC-UV/Vis method: Clayey soil without charcoal (A) and with the addition of 1% charcoal (B), in the absence of the herbicide (black lines) and fortified with indaziflam at 2.0 mg kg<sup>-1</sup> (red lines).



**Fig. 4. Analytical curve for indaziflam in acetonitrile (A), and distribution of residuals of the analytical curve (B)**

**Table 1. Parameters of the linear regression equations of the curves obtained using the SLE-LTP-HPLC-UV/Vis method applied to samples of clayey and sandy soils without and with conditioning by addition of 1% (w/w) sugar cane bagasse charcoal, fortified with indaziflam.**

Matrix	A	b	R <sup>2</sup>	R	LD	LQ
Clayey soil	-24167.63	198822.11	0.9959	0.9979	0.19	0.59
Clayey soil + 1% charcoal	-12536.12	173749.19	0.9954	0.9977	0.21	0.65
Sandy soil	7068.97	164560.59	0.9902	0.9951	0.14	0.43
Sandy soil + 1% charcoal	7504.31	153044.22	0.9944	0.9972	0.16	0.49

a: Linear coefficient; b: angular coefficient; R<sup>2</sup>: coefficient of determination; R: coefficient of correlation; LD: limit of detection (mg kg<sup>-1</sup>); LQ: limit of quantification (mg kg<sup>-1</sup>).

**Table 2. Repeatability, intermediate precision, and recovery for the proposed method applied to samples of clayey and sandy soils without and with conditioning using 1% (w/w) sugar cane bagasse charcoal.**

Matrix	[Indaziflam] (mg kg <sup>-1</sup> )	Recovery (%)	CV (%)		EF	Ra
			Repeatability	Intermediate precision		
Clayey soil	0.5	84.63	1.4	6.9	2.34	2.9
	1.5	87.63	2.8	8.9		
	2.5	96.29	4.9	12.1		
Clayey soil + 1% charcoal	0.5	85.85	2.5	3.5	2.55	2.5
	1.5	90.28	11.0	9.9		
	2.5	88.53	0.9	13.6		
Sandy soil	0.5	88.97	4.9	5.2	2.80	2.4
	1.5	106.41	3.3	5.6		
	2.5	100.86	14.4	12.8		
Sandy soil + 1% charcoal	0.5	86.83	4.0	5.8	2.66	2.2
	1.5	101.60	8.0	7.7		
	2.5	79.56	14.4	10.4		

EF: Enrichment factor; ra: matrix effect ratio.

The method provided accurate and precise determination of indaziflam in samples of soils without or with charcoal conditioning, fortified with the herbicide at three concentration levels (0.5, 1.5, and 2.5 mg kg<sup>-1</sup>) and analyzed using seven replicates (Table 3). The recovery

percentages were between 79.6 and 106.4%, while the coefficients of variation were between 0.9 and 14.4%. These values were in compliance with established guidelines for residue analysis [25,26,32], which stipulate that recoveries should be in the range 70-120%, with coefficients of

variation below 20%. The experimental enrichment factors (EF) were close to the theoretical value (2.66), and no trends were observed for the physico-chemical properties of the herbicide and the soils. The matrix effect ratios were higher than 1, indicating a substantial effect of the matrix [16].

#### 4. CONCLUSIONS

The SLE/LTP-HPLC-UV/Vis method optimized and validated was selective, efficient, precise, and accurate to the determination of indaziflam in samples of clayey and sandy Red-Yellow Latosol soils without and with conditioning using charcoal obtained from sugar cane bagasse.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

#### REFERENCES

1. Tompkins J. Pesticide Fact Sheet Indaziflam; 2010. Available: [https://www3.epa.gov/pesticides/chem\\_search/reg\\_actions/registration/fs\\_P C-080818\\_26-Jul-0.pdf](https://www3.epa.gov/pesticides/chem_search/reg_actions/registration/fs_P C-080818_26-Jul-0.pdf).
2. Trigo C, Koskinen WC, Kookana RS. Sorption-desorption of indaziflam and its three metabolites in sandy soils. *Journal of Environmental Science and Health, Part B*. 2014;49(11):836-843.
3. Guerra N, De Oliveira Jr. RS, Constantin J, Antonio Mendes de Oliveira Neto, Guilherme Braga Pereira Braz. Aminocyclopyrachlor and indaziflam: Selectivity, control and environmental behavior. *Revista Brasileira de Herbicidas*. Portuguese. 2013;12(3):285-295.
4. IUPAC; 2010. Available: <http://sitem.herts.ac.uk/aeru/iupac/Reports/1663.htm>
5. Rittenhouse J. Sorption-Desorption, Leaching, and Bioavailability of Aminocyclopyrachlor and Indaziflam in Minnesota Soils. Retrieved from the University of Minnesota Digital Conservancy. 2015;64. Available: <http://hdl.handle.net/11299/178918>.
6. Brosnan JT, McCullough PE, Breeden GK. Smooth crabgrass control with indaziflam at various spring timings. *Weed Technology*. 2012;25(3):363-366.
7. Soltani N, Mashhadi RH, Mesgaran MB, Cowbrough M, Tardif FJ, Chandler K, Swanton CJ, Sikkema PH. The effect of residual corn herbicides on soybean injury and yield seeded in the same season. *Canadian Journal of Plant Science*. 2011; 91(3):571-576.
8. Székács A, Mörtl M, Darvas B. Monitoring pesticide residues in surface and ground water in Hungary: Surveys in 1990–2015. *Journal of Chemistry*. 2015;15. Article ID 717948.
9. Loganathan VA, Feng Y, Sheng GD, Clement TP. Crop-residue derived char influences sorption, desorption and bioavailability of atrazine in soils. *Soil Science Society of America Journal*. 2009; 73(3):967-974.
10. Sun K, Kanga M, Kyoung S, Libra JA, Zhao Y, Xing B. Variation in sorption of propiconazole with biochars: The effect of temperature, mineral, molecular structure, and nano-porosity. *Chemosphere*. 2016; 142:56–63.
11. White PM, Potter TL, Lima IM. Sugarcane and pinewood biochar effects on activity and aerobic soil dissipation of metribuzin and pendimethalin. *Industrial Crops and Products*. 2015;74:737–744.
12. Lehmann J, Joseph S. Biochar for Environmental management: Science and technology. 2009;23(2):17-23.
13. Mukherjee A, Zimmerman AR, Harris W. Surface chemistry variations among a series of laboratory-produced biochars. *Geoderma*. 2011;163(3-4):247-255.
14. Mesa AC, Spokas KA. Impacts of biochar (Black Carbon) additions on the sorption and efficacy of herbicides. *Herbicides and Environment*. 2011;1985:315–340.
15. Costa AI, Queiroz ME, Neves AA, De Assis RC, Dos Soares CE, Da Silva AA, D'antonino I, De Oliveira AF, Bellato CR. Mobility and persistence of the herbicide fomesafen in soils cultivated with bean plants using SLE/LTP and HPLC/DAD. *Environmental Science and Pollution Research*. 2015;22(5):3457–3466.
16. De Aragão NM, Veloso MC, De Andrade JB. Validation of chromatographic methods of analysis - an easy experiment application- using high performance liquid chromatography (HPLC) and the principles of "green chemistry" for determination methylxanthines in beverages. *Quimica Nova*. Portuguese. 2009;32(9):2476-2481.

17. Kemmerich M, Bernardi G, Adaime MB, Zanella R, Prestes OD. A simple and efficient method for imidazolinone herbicides determination in soil by ultra-high performance liquid chromatography–tandem mass spectrometry. *Journal of Chromatography A*. 2015;1412:82-89.
18. Passos AB, Freitas MAM, Torres LG, Silva AA, Queiroz ME, Lima CF. Sorption and desorption of sulfentrazone in Brazilian soils. *Journal of Environmental Science and Health, Part B*. 2013;48(8):646-650.
19. González-Delgado AM, Ashigh J, Shukla MK, Perkins R. Mobility of indaziflam influenced by soil properties in a Semi-Arid Area. *PLoS ONE*. 2015;10(5):1–12.
20. Alonso DG, Koskinen WC, Oliveira Jr. RS, Constantin J, Mislankar S. Sorption–desorption of indaziflam in selected agricultural soils. *Journal of Agricultural and Food Chemistry*. 2011;59:13096-13101.
21. Henkel C, Muleya PD, Abdollahi KK, Marculescu C, Boldor D. Pyrolysis of energy cane bagasse and invasive Chinese tallow tree (*Triadica sebifera* L.) biomass in an inductively heated reactor. *Energy Conversion and Management*. 2016;109:175–183.
22. Heitkoetter J, Marschner B. Interactive effects of biochar ageing in soils related to feedstock, pyrolysis temperature, and historic charcoal production. *Geoderma*. 2015;245:56–64.
23. Inyang M, Gaoa B, Pullammanappallil P, Ding W, Zimmerman AR. Biochar from anaerobically digested sugarcane bagasse. *Bioresource Technology*. 2010; 101(22):8868–8872.
24. Embrapa. Manual of soil analysis methods. National Center Soils Research (Rio de Janeiro RJ). 2th ed. 1997;212.
25. ANVISA. National Health Surveillance Agency. Resolution RE n 899, May 29, 2003. Portuguese. 2003;1-15.
26. INMETRO - National Institute of Metrology, Standardization and Industrial Quality. Guidelines on Validation of Methods of Chemical Testing, DOQ-CGCRE-008. Portuguese;2003.
27. Mendham J, Denney RC, Barnes JD, Thomas MJK. Quantitative chemical analysis. Vogel, LTC, 6th ed. Rio de Janeiro, R.J. Portuguese; 2002.
28. Miller JC, Miller JN. Statistics for analytical chemistry. Addison-Wesley Iberoamericana, Wilmington, Spanish; 1993.
29. Neto BB, Scarminio IS, Bruns RE. Planning and optimization of experiments. Publisher of Unicamp, 2nd ed. Campinas, SP, Portuguese; 1996.
30. Saijun Li, Jinhong Lü, Tao Zhang, Yueqian g Cao, Jianfa Li. Relationship between biochars' porosity and adsorption of three neutral herbicides from water. *Water Science and Technology*. 2016; wst2016535.
31. Production of char from vacuum pyrolysis of South-African sugar cane bagasse and its characterization as activated carbon and biochar. *Journal of Analytical and Applied Pyrolysis*. 2012; 96:24-32.
32. Ribani M, Bottoli CBG, Collins CH, Jardim IC, Melo LF. Validation of chromatographic and electrophoretic methods. *Quimica Nova*. Portuguese. 2004;27(5): 771-780.

© 2018 Romero et al.; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

*Peer-review history:*  
The peer review history for this paper can be accessed here:  
<http://www.sciencedomain.org/review-history/23670>