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ScientEvents
ProScience 7 (2020) 47-54

Conference Proceedings
International Meeting of Geohealth Scientists - GHC 2020 - Virtual Meeting

Updating the perception of glyphosate's occurrence in Colombia: a case of high concentrations in a natural reserve in the eastern savannah plains

Carlos Manuel Guío Blanco*, Eduardo Quintero Chavarría

Corporación Geoambiental Terrae, Bogotá,Colombia
**macguiob@gmail.com*

Abstract

Glyphosate has been aerially sprayed in Colombia since decades for the purpose of illicit crop eradication and weed control. Although the most recent illicit crop eradication plan (PECIG) was halted in 2015, its reactivation is being currently attempted by the National Police Anti-Narcotics Directorate, on the grounds of glyphosate's allegedly innocuous nature, low environmental mobility, and well documented practices in Colombia's agroindustry. The lack of glyphosate environmental fate studies in Colombia suggests otherwise. The independent assessment presented here aimed to provide support to low-cost spectrophotometry for glyphosate monitoring, to document the occurrence of glyphosate within a natural reserve, and to provide a preliminary understanding of factors that influence glyphosate dispersion in overflow-savannah soils. Our research site serves as a case study to understand contamination risks to protected areas, regardless of the purpose of glyphosate application. The results show that short-range soil variability conditions a complex distribution of surface and subsurface water pockets, between which glyphosate transport happens. We found concentrations between 0.25 and 2.2 ppm in water samples at eight locations in the natural reserve; four of them in saturated soil horizons at ca. 1 m depth, three among them located at ca. 500 m inwards from the reserve's boundaries. High glyphosate concentrations are related to anomalous sulfate, phosphate, nitrate and ammonium contents in the water. These findings highlight the relevance of independent monitoring to update the perception of glyphosate's environmental impacts in Colombia, and argue for data-based regulatory frameworks and procedures, e.g. in relation to the width of buffer protection zones, and to the inclusion of more comprehensive approaches in monitoring programs, which should take into account -on a case-by-case basis- hydropedological complexities.

Keywords: Glyphosate; Colombia; natural reserve; independent assessment; soils and water; spectrophotometry

ISSN: 2283-5954
Selection and peer-review under responsibility of GeoHealth 2020 Scientific Committee
DOI:10.14644/ghc2020.008

1. Introduction

Glyphosate is a nonselective, post emergence herbicide used in various commercial formulations. Its use in Colombia started officially in 1984, in a massive action to eradicate marihuana, opium poppy and -most notably- coca crops (Moreno, 2015). The most recent eradication plan, known as PECIG, came to a halt in 2015 due to legal complaints asking to enforce the precautionary principle. Nevertheless, in 2019, the National Police Anti-Narcotics Directorate submitted a renewed Environmental Management Plan (PMA, for its Spanish acronym), advocating PECIG's reactivation. The new PMA argues -among other things- that, based on sufficient knowledge about the innocuous nature of glyphosate, its slow mobility in soils, and on well documented practices in Colombia's agroindustry, reactivation should be possible (DIRAN, 2020). The scarce number of glyphosate environmental fate studies in Colombia, and recent evidence of regional health impacts (Camacho & Mejía, 2017), suggest otherwise.

To the best of our knowledge, this is the first published study of impacts of aerially sprayed glyphosate to soils and water in a natural reserve in Colombia. Previous studies have been official assessments that are partially accessible to the public (CORPOICA et al., 2002; IGAC, 2019), a government's commissioned review, complemented by -briefly documented- measurements at five locations (Solomon et al., 2007), and an independent study of glyphosate adsorption at a rice plantation (Bustos, 2012). Our independent assessment aimed to 1) test a low-cost analytical method for glyphosate environmental concentrations, 2) document the occurrence of glyphosate within a natural reserve, and 3) gain a preliminary understanding on soils' influence on glyphosate dispersion, in the overflow-savannah landscape of eastern Colombia.

2. Study area

At the study site, the Natural Reserve of the Civil Society "Aves de Jah", conservation and subsistence farming have been practiced for over two generations. Local concerns about the environmental quality at the natural reserve have been recently raised though, as it is being surrounded by -aerially sprayed- rice plantations, which have spread throughout the region since 2014, in accordance to the official land use capability assessment (Instituto IGAC, 2014). Spraying happens 2 to 3 times per year, between January and April, as a routine step in pre-planting field preparation.

The reserve is in the Casanare department, municipality Paz de Ariporo. It covers an area of ca. 660 ha of the eastern overflow-savannah plains. The climate is dry from December to April, and wet from May to November. During the wet season the area is flooded by interconnected wetlands divided by natural levees. During the dry season just a few isolated wetlands (locally known as *esteros*) remain.

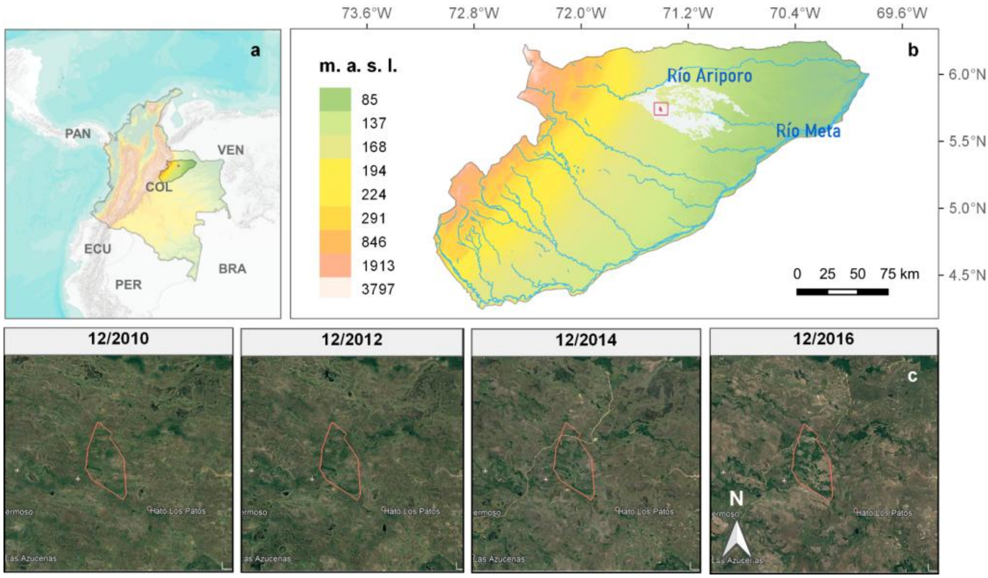

Fig. 1. Research area and environmental context. a) Colombia in northern South America, and Casanare department in the eastern plains, b) The Natural Reserve of the Civil Society "Aves de Jah" (red dot) within an area (light grey) of land capability for rice plantations in the Casanare department. The local drainage flows towards the south-east, into the Meta river. c) Loss of vegetation cover between 2010 and 2016 in the surroundings of the natural reserve reflects the development of rice plantations, were glyphosate is sprayed. Images were acquired with Google Earth Pro V. 7.3.3.7786, from Landsat/Copernicus imagery (accessed on April 15, 2020). Plotted with QGIS V. 3.12.

3. Methods and materials

3.1 Sampling design

Water and soil samples were collected between April and May 2019, at the peak of the dry season. For soils and subsurface water samples (from water-saturated horizons) a stratified random sampling design (SRSD; following Brus, 2019; 2011) was used; for surface water and groundwater samples a convenience sampling design due to accessibility was used.

The SRSD was based on conceptual biogeographical (Mora-Fernández & Peñuela-Recio 2013) and geomorphological (Goosen, 1971) models that supported the selection of environmental covariates, as surrogates for vegetation (NDVI: Tucker, 1979; PSRI: Hatfield and Prueger, 2010) and mineralogy (iron oxide ratio: Sabins, 1999). These covariates were entered into a k-means algorithm (k-means from stats package), in the statistical language R (R Core Team 2019), to compute 6 clusters (strata), whose spatial representation had physical meaning to local farmers (Fig. 2). The resulting strata were unique environmental data combinations that could have contrasting influence on glyphosate's mobility. 15 soil sampling locations and 10 control points were randomly distributed among these strata, in proportion to their surface area. The calculations were performed on 10 m-resolution Sentinel-2 imagery (from April 6, 2019) to account for short-range soil variability.

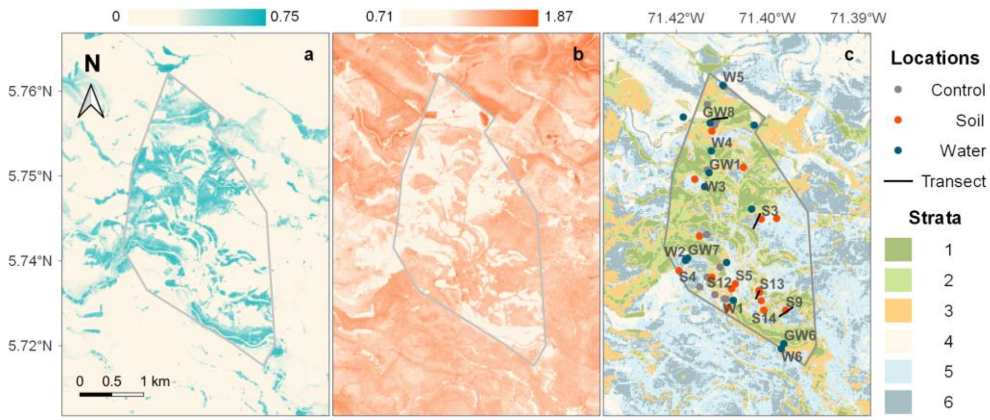

Fig. 2. Two covariates used in the SRSD and locations. a) NDVI, b) iron oxide ratio, c) k-means strata and studied locations. The labelled points correspond to sites sampled for glyphosate analysis. Sentinel-2 images were acquired from Copernicus Open Access Hub and pre-processed using SNAP V. 7.0.0. Plotted with QGIS V. 3.12

3.2 Field methods

Soil profiles were excavated at 15 locations, in accordance to the SRSD. We recorded soil properties according to Schoeneberg et al. (2012); among them: vegetation cover and type, texture, bioturbation, wetness, redoximorphic features, structure and pH.

At each location, we collected a 2.5 kg composite sample of 5 topsoil -0 to 20 cm depth- subsamples from the corners and center of a 25 m^2 square centered at the pit. Where saturated soil horizons were found, we collected 500 mL of water in opaque PET bottles. We collected the same volume from streams, wetlands, and wells during the last day of fieldwork; at the last sampling location, a bottle was filled with deionized water to use it as blank. All samples were kept in Styrofoam boxes with refrigerating gels until laboratory analysis.

Electrical resistivity and induced polarization tomographies were recorded along four transects, following Binley & Kemna (2005). A Wenner-type arrangement was used with 2.5 and 5 m spacings over 300 m. With this setting, a maximum resolution of 1 m, down to maximum 40 m depth, was achieved. The data were recorded in an ABEM 1000 equipment, adapted to an arrangement of 24 cables, and processed with the software RES2DIV.

3.3 Analytical procedures

The method to quantify glyphosate has been described elsewhere in detail (Waiman et al., 2012; Felton et al., 2018). Summarized, it consists of three steps: 1) derivatization of glyphosate with 9-fluorenylmethoxycarbonyl chloride (Sigma Aldrich-USA, 1 g in 1 L acetonitrile) for 2 hours, 2) removal of surplus with dichloromethane, and 3) analysis with UV-vis spectrophotometry at 265 nm (SpectronicBioMate 3 UV-vis Thermo). 50 mL from each of the 18 samples were filtered (0.5 µm) by vacuum pump and analyzed in this way at the “Soils” and “Weed control” laboratories, Universidad Nacional de Colombia (Bogotá). In the remaining volume of each sample major ions were measured with colorimetry, turbidimetry (anions) and flame atomic absorption spectroscopy (cations). For our study, a calibration curve with a linear relationship (R^2 0.97) between glyphosate concentration and absorbance was determined. The detection limit was 2.5 ppm. For the 15 topsoil samples, the laboratory PRIMORIS was commissioned with extraction and analysis of glyphosate using LC-MS/MS 2D (detection limit 10 ppb).

3.4 Data analysis

Field-data from soil profiles were quantitatively processed using the aqp package (Beaudette et al., 2013) in R: a soil profile collection was created; Munsell colors were converted to RGB codes (for each horizon and redoximorphic features); the most abundant nodules and redox enrichments per horizon were converted to volume fractions; glyphosate and water-saturated horizons were located by depth; and profiles were grouped into landforms, based on vegetation types and relative distances to permanent water bodies.

The data of major ions were screened with boxplots and histograms, which showed a positive skew in all cases. Therefore, the data were log-transformed, standardized and centered (Güler et al., 2002), before principal component analysis (`stats` package from R).

4. Results and discussion

Glyphosate was detected in 8 from the 18 water samples analyzed with spectrophotometry, at concentrations between 0.25 and 2.2 ppm (Table 1); the highest in *esteros*. These concentrations are two to three orders of magnitude higher than average occurrences from several countries (Van Bruggen et al., 2018), and thus contradict the official perception of low or absent environmental impacts in Colombia (DIRAN, 2020).

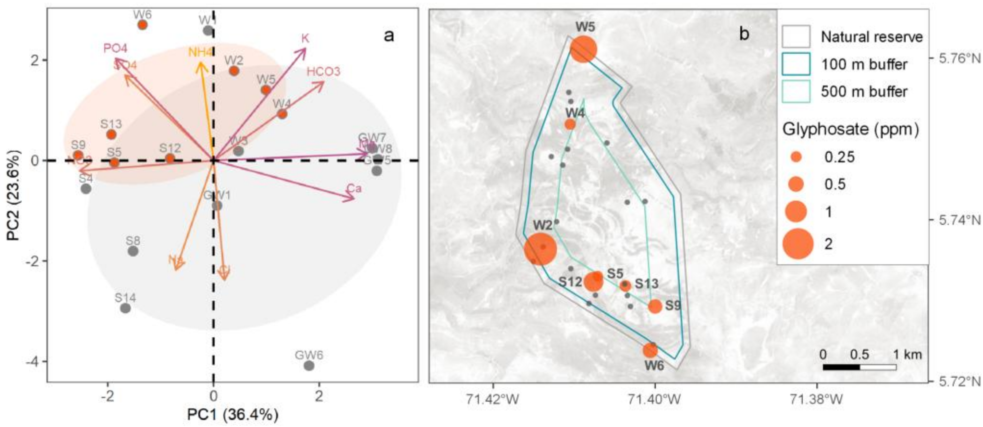

Fig. 3. a) PCA biplot. Dots represent samples with (orange) and without (grey) glyphosate. The ellipses have 70% coverage. Arrows represent major ions. Plotted with facto extra. b) Spatial distribution of glyphosate occurrence. Grey dots include topsoil sampling locations. Blue lines are hypothetical buffer zones. Plotted with QGIS V. 3.12

Fig. 3a and Table 1 show relatively high concentrations of sulfate, nitrate and phosphate related to glyphosate in saturated soil horizons, and ammonium related to glyphosate in *esteros*. Since these anomalous concentrations are not similarly present in all samples that had glyphosate detected, these relationships might reflect different land management practices, e.g. the application of fertilizers and/or other pesticides, which supply anions that facilitate glyphosate mobility due to competition for adsorption sites in soil particles.

Table 1. Major anions and glyphosate measured in groundwater (GW), surface water (W) and water from saturated soil horizons (S). All concentrations are given in ppm. Values above the upper quartile are in bold. Outliers with *.

ID	HCO_3	Cl	SO_4	NO_3	PO_4	NH_4	Glyphosate
GW1	14.4	**3.23**	1.54	0.09	0.08	0.26	*< 0.25*
GW5	**46.6**	2.18	1.99	0.1	0.05	0.24	*< 0.25*
GW6	21.1	**7.06***	0.14	0.65	0.06	0.4	*< 0.25*
GW7	**39.8**	2.44	4.21	0.11	0.04	0.59	*< 0.25*
GW8	**40.8**	2.09	1.52	0.15	0.07	0.21	*< 0.25*
W1	31.2	1.48	18.2	0.47	1.1	**3.5***	*< 0.25*
W2	**36.0**	2.62	14.6	0.75	**1.16**	**4.69***	*2.21*
W3	15.1	2.7	13.2	0.28	0.63	0.57	*< 0.25*
W4	21.8	2.35	12.7	0.19	0.65	**0.86**	*0.26*
W5	**34.2**	2.27	12.4	0.72	0.9	0.75	*1.57*
W6	18.5	1.74	8.83	**1.09**	**4.13***	**1.46**	*0.48*
S4	10.2	**2.79**	**29.2**	0.86	0.8	**1.12**	*< 0.25*
S5	15.6	2.35	**40.9**	**1.35**	**1.38**	0.58	*0.24*
S8	16.8	**3.49**	1.44	**1.13**	0.28	0.35	*< 0.25*
S9	15.0	**3.66***	**148***	0.65	**2.33**	0.3	*0.43*
S12	15.6	2.7	**129***	0.72	**1.84**	0.12	*0.82*
S13	13.2	1.38	**42.8**	**1.29**	0.9	0.55	*0.28*
S14	0.72	2.44	0.23	**1.04**	0.04	0.35	*< 0.25*

At four sites, glyphosate was found in water samples from saturated soil horizons, at ca. 1 m depth (Fig. 4), at concentrations between 0.25 to 0.82 ppm; three among them located at ca. 500 m inwards from the reserve's boundaries (Fig. 3b). LC-MS/MS on topsoil samples did not detect glyphosate at any sampling location. These findings, which suggest interflow transport into the natural reserve, contradict previous assertions (Solomon et al., 2007) about its low mobility in Colombian soils. As shown here, subsurface occurrences and transport beyond 100 m can happen, but are not acknowledged in the terms of reference for the PMA (ANLA, 2019), nor in the PMA's protection measures and procedures.

Saturated soil horizons were sporadic, even at pits that were only few meters apart. A "pocket-like" distribution of low-resistivity soils, seen in most geoelectric transects (not shown here), suggests poorly connected saturated horizons at the time of sampling. If composite samples had been collected, we would have likely found lower concentrations of glyphosate. Its presence at depth in transitional landforms, i.e. upper-basins and splays (Fig. 4), in spite of fine soil textures, could be explained by root-related macropores and swellshrink fractures, as seen in other studies (Vereecken, 2005). Since glyphosate was just found -sporadically- in some subsoils and lentic water bodies, its occurrence could be linked to trans-seasonal transport and accumulation cycles, involving soils, *esteros* and interflows.

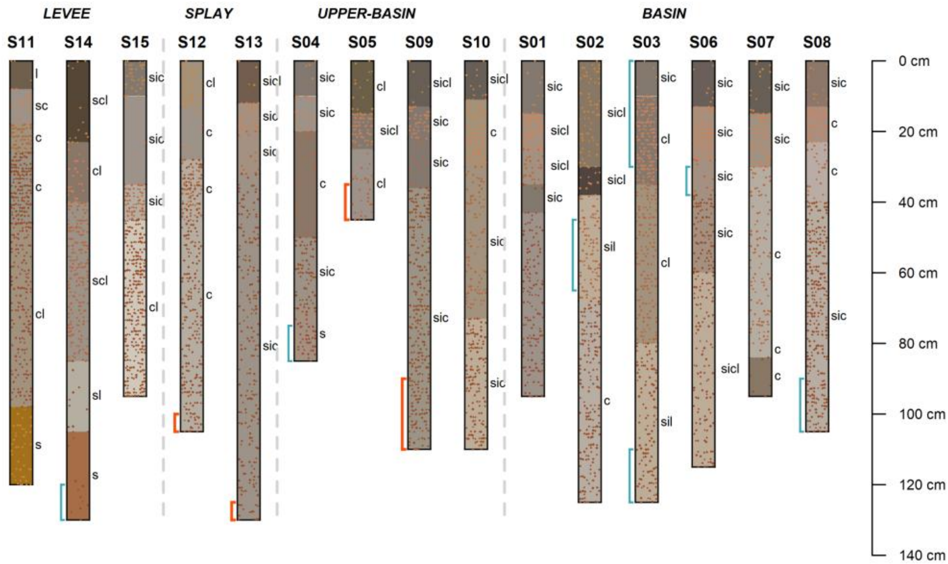

Fig. 4. Soil profiles model and depth locations of saturated water horizons with (orange brackets) and without (blue brackets) detected glyphosate. Redoximorphic features are mostly nodules that do not reflect the current hydrology and do not affect glyphosate's occurrence. Horizon labels are texture codes according to Schoeneberg et al. (2012)

5. Conclusions

A low-cost analytical UV-vis spectrophotometry approach was useful due to the occurrence of glyphosate at high concentrations in subsoils and lentic water. The official perception of "low environmental impacts" in Colombia is biased: our case showed that even natural reserves are at risk of contamination. Measures such as the width of buffer protection zones, should be reviewed and supported by data on a case-by-case basis, considering also subsurface transport mechanisms. Composite sampling in existing monitoring programs should be critically assessed against evidence of short-range soil variability. Further research on surface-subsurface connectivity in the overflow-savannah, and toxicologic studies of local species –inhabiting transitional landforms and *esteros*- , are needed.

6. Acknowledgements

This study was funded by a grant-giving institution who wishes to remain anonymous. Access to the grant was facilitated by AIDA (https://aida-americas.org/). We acknowledge the collaboration of Julio Fierro and Juan Francisco Diaz from Corporación Geoambiental Terrae, the student Eduart Murcia, as well as Ramiro Tellez – and his friends and family- from Reserva Aves de Jah, for their involvement in discussions, field work and logistics.

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