Effects of Biochar-amended Tropical Soils on Herbicide Pollution: Column Leaching Studies

Gerardo Ofelio Aldana[1]
Elisa Lopez-Capel[2]
David Werner [2]

Abstract

Biochar is a carbon-rich material that can be used to improve soil quality and reduce herbicide leaching. This study investigated the use of biochar to reduce the leaching of two herbicides, Atrazine and Diuron, from tropical soils in Belize. Column leaching experiments were conducted following the OECD 312 guidelines. Three different soil types were sampled from agricultural sites in Belize and amended with 2.5% (w/w) rice husk biochar. Extreme rainfall events were simulated to present a worst-case scenario of herbicide leaching events. The results showed that the application of biochar to both loam and sandy silt loam soils reduced the leaching of both atrazine and diuron. The column leaching linear Kd (m3/kg) of atrazine in biochar amended loam was 0.15 and for biochar amended sandy silt loam was 0.8. Leachate analysis showed that samples collected from the biochar-amended soils had a much lower herbicide concentration than soils that were not amended with biochar. These results suggest that tropical soils amended with 2.5% rice husk biochar can reduce the leaching of atrazine and diuron, thus protecting human health and the natural environment from water contamination.

Keywords: Biochar, herbicide leaching, tropical soils, Belize

[1] University of Belize

[2] Newcastle University

Corresponding Author: Gerardo Ofelio Aldana, Department of Agriculture, University of Belize, Central Farm, Belize. email: galdana@ub.edu.bz.

Introduction

Extensive herbicide use over the past decades has imposed toxic effects on human health, and terrestrial and aquatic ecosystems (Khorram et al., 2015). According to Castillo et al. (2011), coral reef systems are threatened by upstream anthropogenic activities. The economy of many tropical countries depends on terrestrial and aquatic ecosystems; therefore, it is vital to protect these ecosystems from herbicide contamination. Soils, surface, ground and drinking waters contaminated by herbicides can also cause detrimental effects to human health. The risk of contamination to a non-target site is associated with the physicochemical structure of the compounds, properties of the soil, climatic conditions, land structure and antibiotic and herbicide management practices (Bedmar et al., 2017). A climate-smart and economically feasible technique to reduce herbicide contamination is the *in-situ* application of biochar to soils. Biochar is carbonaceous material produced from the thermochemical conversion of waste biomass in an oxygen-limited environment (Lehmann & Joseph, 2015). Biochar can help reduce soil and water contamination, mitigate climate change, produce energy, and manage agricultural and municipal waste. Therefore, the aim of this study was to determine whether rice husk biochar-amended can reduce atrazine and diuron contamination in tropical soils of different geographical location and texture, under rainfall conditions simulated in column leaching experiments.

Methodology

Biochar, soils, and herbicides

Rice husk biochar used was produced under standardized conditions and provided by the UK Biochar Research Centre (UKBRC) at the University of Edinburgh (www.biochar.ac.uk). Soil samples were collected in Belize from three distinct sites characterized by agricultural activities (Table 1) as per the study from Aldana et al. (2020). The soil-sample sites were located adjacent to natural water bodies that are more prone to herbicide contamination. The soil was collected from the A horizon of the soil profile to a depth of 0-20 cm and air-dried and sieved through a 2 mm sieve and carefully homogenized. The two herbicides used were analytical grade Atrazine (1-Chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine) of 98.9% purity and Diuron (1,1-dimethyl, 3-(3',4'-dichlorophenyl) urea) of 98% purity both purchased from Sigma-Aldrich Ltd., UK.

Table 1. Physicochemical properties of three agricultural soils of Belize

Analysis	Corozal district	Cayo district	Stann Creek district
FAO soil classification	Vertic gleysol	Gleyic cambisol	Gleyic acrisol
Soil Class	Clay loam	Loam	Sandy silt loam
Lime Req. (t/ha)	-	-	5.0

pH	8.2	8.1	6.1
Grid reference	18°13'44.6"N 88°32'07.3"W	17°12'04.4"N 89°00'16.6"W	16°59'40.9"N 88°21'49.0"W
C.E.C. (meq/100g)	69.9	27.5	11.4
Organic matter (%)	5.0	2.9	3.7
Organic Carbon (%)	2.91	1.68	2.15
Silt (%)	37.66	41.37	48.02
Clay (%)	34.93	20.54	15.83
Sand (%)	27.41	38.09	36.15

Abbreviations: FAO, Food and Agriculture Organization; CEC, cation exchange capacity.

Column leaching experiment

Column leaching experiments followed the OECD 312 guidelines for testing of chemicals – leaching in soil columns (OECD, 2004). Glass wool was placed at the bottom of four Rotaflo Quickfit CR12/30 Pyrex glass columns of 1 cm inner diameter and 30 cm height to prevent soil loss. Each column was then filled with standard sand (2.54 g/cm^3 solid density) to a height of 5 cm. Two columns were then hand-packed with one soil type, without biochar amendment, to a height of 20 cm. These were labelled as control columns. The other two columns were hand packed with biochar-amended soil at a rate of 2.5% (w/w) to a height of 20 cm. These were labelled as experimental columns. The experiment consisted of three soil types collected from different geographical locations in Belize, as per Table 1 above. The effect of rice husk biochar was tested on atrazine and diuron on each of the soil types. Extreme rainfall events that would occur at each sample location was simulated to present a worst-case scenario herbicide leaching event. Rainfall data was supplied by the National Meteorological Service of Belize. The extreme monthly rainfall recorded between the years of 1966 to 2018 was selected for the simulation. Table 2 shows the simulated scenario, including the rainfall duration and herbicide application rate for each soil-sample site for the column leaching experiments.

Table 2. Rainfall scenarios for column leaching experiments

District/ soil sample site	Soil type	Monthly rainfall (mm)	Duration (days)	Daily rainfall (cm/d)	Daily flow of water in column (mL/d)	Herbicide application rate (kg/ha)	Herbicide concentration in solution (mg/L):
Corozal	Clay Loam	525.4	31	1.7	3	2	3.93
Cayo	Loam	714.1	31	2.3	4	2	2.89
Stann Creek	Sandy silt loam	929.20	30	3.1	5	2	2.15

The simulated rainfall solution was prepared using HPLC grade water concentrated with 0.01 M calcium chloride dehydrate. The columns were manually irrigated with the rainfall solution until the soil reached saturation. The herbicide solution was added for three consecutive days. The column was then daily irrigated with simulated rainfall solution until the end of the experiment. Effluents were stored in 60 mL amber glass vials, in a cold room at 4°C. These samples were analyzed using LC-MS-MS. Soils were also analysed for the presence of herbicides after the experiment. The experiments were conducted in consecutive order and lasted 31, 31 and 30 days for the different three different soil types.

Statistical analysis

Statistical analysis was conducted on sorption data using IBM SPSS Statistics 24. The difference between the measured aqueous concentration in the batch with the absorbent (i.e., soil/biochar/biochar amended soil) and the control batch without the absorbent was statistically determined. The data were evaluated using a paired sample t-test ($P < 0.01$). In addition, the difference between the measured aqueous concentration and zero was statistically determined by calculating the standard error of the mean. When the mean was at least twice as much as the standard error, then the measured aqueous concentration was qualified as statistically significantly different to zero. Only the data points which met both criteria (i.e., statistically significantly different from the control, and statistically significantly different from zero) were used to plot sorption isotherms. Sorption data were fitted to Linear isotherms using least squares regression. Column breakthrough curves were calculated using Matlab R2017a.

Results

Column leaching experiments

Atrazine and Diuron leaching was reduced in biochar-amended loam and biochar-amended sandy silt loam soils, as compared to no amendment. Due to the texture of the clay loam soil, no leachate travelled through the soil column. Therefore, no leaching analysis was further conducted for the clay loam soil.

Column breakthrough curves for atrazine and diuron

Atrazine had a faster breakthrough in the column containing loam without biochar when compared to loam amended with biochar. The effluents of the biochar-amended loam soil contained lower atrazine concentrations as compared to the loam soil without biochar amendment, showing that biochar-amended loam soil was able to reduce the leaching of atrazine. Figure 1 shows that atrazine leaching in loam without biochar was reduced to between 520 to 650 hours but continued after 650 hours. In the biochar-amended loam, the leaching occurred at low concentrations and stayed low once the breakthrough occurred.

As observed in Figure 1, the breakthrough of atrazine in sandy silt loam happened at 500 hours onwards. These results suggest that atrazine would continue to leach in the sandy silt loam soil even after 700 hours if not amended with biochar. However, when the sandy silt loam soil was amended with biochar, atrazine stopped leaching even after 700 hours. The fate of atrazine in sandy silt loam soil was greatly influenced by the presence of biochar.

Diuron did not leach in either the loam soil without biochar amendment or the loam soil with biochar amendment. These results indicate that Diuron may not be a significant threat to groundwater since there is no vertical leaching. However, there can be a threat of Diuron contaminating surface water if no biodegradation occurs in the soil. Diuron had vertical movement in the sandy silt loam and biochar-amended sandy silt loam soil. The overall leaching of Diuron was less in the biochar-amended sandy silt loam soil with biochar amendment (Figure 1).

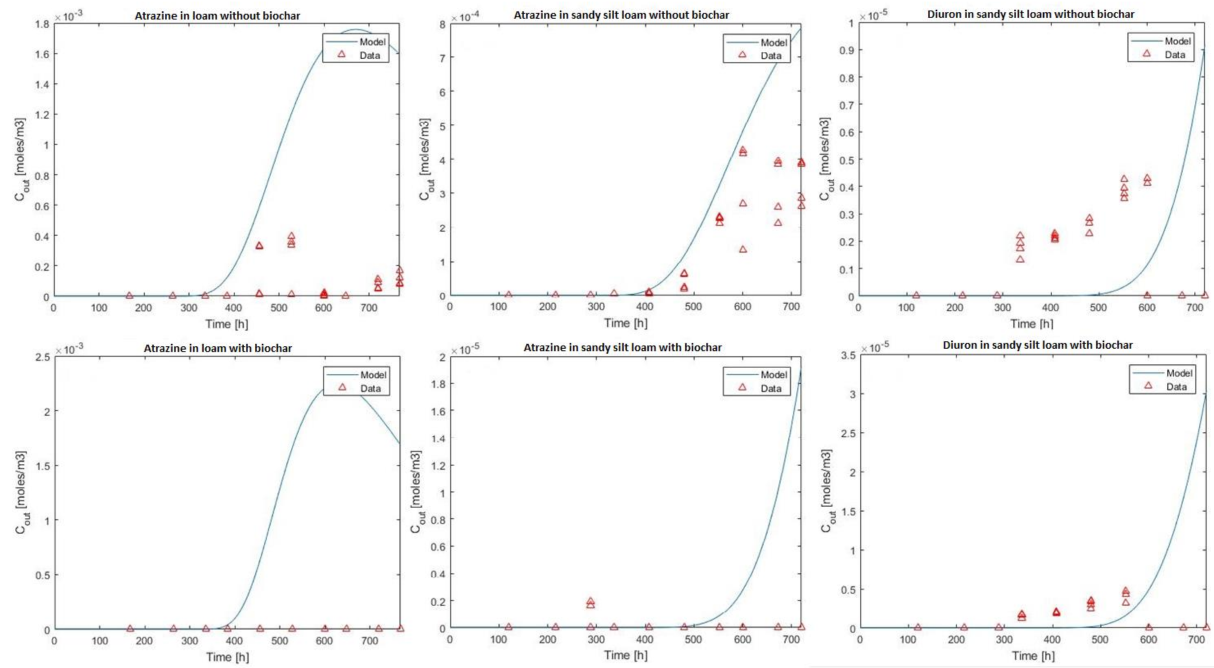

Figure 1. Breakthrough curves for Atrazine and Diuron in different soil mixtures.

Comparison of batch microcosm and column leaching studies

In Table 3 below, the linear K_d of the soil and amended soil mixtures obtained from the batch sorption experiments were compared to the linear K_d of the soil and biochar-amended soil mixtures from the soil column leaching experiments.

Table 3. Comparison of linear K_d observed in the batch microcosm and column leaching studies.

Soil mixtures	**Batch microcosm linear K_d (m^3/kg)**	**Column leaching linear K_d (m^3/kg)**	
		Soil	*Biochar*
ATR + L	0.0781	0.0045	-
ATR + L + BC	1.3394	0.0045	0.15
ATR + SSL	0.0636	0.008	-
ATR + SSL + BC	0.8455	0.008	0.8
DIU + SSL	0.0000625	0.02	-
DIU + SSL + BC	7.9573	0.02	0.5

Abbreviations: ATR = atrazine; DIU = diuron; L = loam; SSL = sandy silt loam; BC = biochar

Discussion

Herbicide behavior in soils amended with biochar

The application of rice husk biochar to both loam and sandy silt loam soils reduced the leaching of Atrazine and Diuron. The presence of biochar increased sorption sites in the soil matrix, that stopped the Atrazine and Diuron from leaching. These results coincide with a study conducted by Martin et al., (2012), where it was found that the introduction of fresh biochar to the soil led to a notable enhancement in the soil's sorption capacity for atrazine and diuron, in contrast to soils without amendments. Yavari et al. (2021) discovered that the non-amended soil exhibited the greatest leaching of two herbicides, imazapic and imazapyr, followed by soils amended with rice husk biochar. The top part of the soil columns (7.5 cm) retained higher quantities of the herbicides, with biochar-amended soils demonstrating the highest retention rates, exceeding 95%. In this study, other factors that reduced Atrazine and Diuron leaching were clay particles and organic matter in the soil. The presence of biochar in soil may have also stimulated microbial growth, therefore increasing the biodegradation of Atrazine in the soil (Jablonowski et al., 2013). However, some biodegradation uncertainties must be considered since neither the microbial population nor the nutrient concentrations in the soil supplied by biochar were measured in this study. Worrall et al., (2001) suggested that although organic matter can absorb herbicides and prevent its leaching, there might be a small risk that the absorbed herbicide may leach later. Martin et al. (2012) also explains that sorption potential of biochar is determined by the biochar application rate and age in the soil. In this case, however, the herbicides were absorbed, and the presence of biochar may have assisted with the biodegradation process. As for the clay loam soil, the water did not leach through the clay loam column with and without biochar amendment. Therefore, no leaching analysis was further conducted for this soil type. However, because water did not leach through the clay loam soil, the leaching of Atrazine and Diuron in clay loam would not be a problem for groundwater leaching. However, the stagnant water containing Atrazine and Diuron could be a problem for surface water runoff.

Comparison of batch microcosm and column leaching studies

The results in Table 3 shows that the K_d of the batch sorption experiments compared to our previous study (Aldana et al., 2020) were much higher than the K_d of the soil column leaching experiments. In the batch sorption experiments, the herbicides had a higher contact time to soil or biochar-amended soil mixtures than in the column study. The soil column leaching experiments were a closer representation of what would occur in an actual environmental scenario, thus catering for preferential flow and other soil hydrological parameters.

Conclusions

The column leaching studies showed that tropical soils such as loam, clay loam and sandy silt loam amended with 2.5% (w/w) rice husk biochar, reduced the leaching of both Atrazine and Diuron. Even at worse-case rainfall scenarios, 2.5% rice husk biochar played an important role in reducing herbicide leaching. Diuron was even reduced to non-detectable levels in the column leachates. Utilizing biochar for pesticide leaching reduction holds promise for transforming agricultural practices and safeguarding water bodies. By minimizing the leaching of pesticides into groundwater and surface water, biochar not only lessens the environmental impact of these chemicals but also promotes sustainable farming. Ultimately, the use of biochar emerges as a holistic approach that benefits both farmers and the broader ecosystem by mitigating environmental risks, preserving water quality, and fostering economic sustainability. Additional research is needed to explore how microbial populations in biochar-amended soil influence the fate of pesticides by participating in degradation and transformation processes.

References

Aldana, G.O., Hazlerigg, C., Lopez-Capel, E. and Werner, D. (2020). 'Agrochemical leaching reduction in biochar-amended tropical soils of Belize', European Journal of Soil Sciences, 72(3), pp. 1243-1255. Doi: https://doi.org/10.1111/ejss.13021.

Bedmar, F., Gimenez, D., Costa, J.L. and Daniel, P.E. (2017). 'Persistence of acetochlor, atrazine, and s-metolachlor in surface and subsurface horizons of 2 typic argiudolls under no-tillage', Environmental Toxicology and Chemistry, 36(11), pp. 3065–3073. doi: 10.1002/etc.3874.

Castillo, K., Ries, J. and Weiss, J. (2011). Declining coral skeletal extension for fore reef colonies of *siderastrea siderae* on the mesoamerican barrier reef system, Southern Belize. PLoS ONE 6(2): e14615. https://doi.org/10.1371/journal.pone.0014615

Jablonowski, N.D., Borchard, N., Zajkoska, P., Fernández-Bayo, J.D., Martinazzo, R., Berns, A.E. and Burauel, P. (2013). 'Biochar-mediated [14C]atrazine mineralization in atrazine-adapted soils from Belgium and Brazil', Journal of Agricultural and Food Chemistry, 61(3), pp. 512–516. doi: 10.1021/jf303957a.

Khorram, M., Zhang, Q., Lin, D., Zheng, Y., Fang, H. and Yu, Y. (2015). 'Biochar: a review of its impact on pesticide behavior in soil environments and its potential applications', Journal of Environmental Sciences, 44, pp. 269–279. doi: 10.1016/j.jes.2015.12.027.

Lehmann, J. and Joseph, S. (2015). Biochar for environmental management. 2nd edn. New York, NY 10017: Routledge.

Martin, S., Kookana, R., Van Zweiten, L. and Krull, E. (2012). Marked changes in herbicide sorption-desorption upon ageing of biochars in soil. Journal of Hazardous Materials, 231– 232 (2012) 70– 78.

OECD. (2004). 'Leaching in Soil Columns', OECD Guidelines for the testing of chemicals, pp. 1–15.

Worrall, F., Fernandez-Perez, M., Johnson, A.C., Flores-Cesperedes, F. & Gonzalez-Pradas, E. (2001). 'Limitations on the role of incorporated organic matter in reducing pesticide leaching', Journal of Contaminant Hydrology, 49 (3–4), 241–262.

Yavari, S., Asadpour, R., Kamyab, H., Yavari, S., Kutty, S., Baloo, L., Manan, T., Chelliapan, S. and Sidik, A. (2021). Efficiency of carbon sorbents in mitigating polar herbicides leaching from tropical soils', Journal of Clean Technologies and Environmental Policy (2022) 24:251–260, https://doi.org/10.1007/s10098-021-02113-z.