Examining Biochar Sorption Isotherms, Kinetics, and Thermodynamics of Bentazon; a Preliminary Analysis of Materials

Phoenix Nakagawa, Marufa Fatema, Alistair Brown, Inoka Amarakoon, and Annemieke Farenhorst

Department of Soil Science, University of Manitoba

Introduction

Bentazon (3-isopropyl-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide; Figure 1) is a highly soluble post-emergent, group 6 herbicide used in alfalfa, corn, and soybean production[1]. Bentazon is in the Top 10 most frequently sold herbicides in Canada and among the most frequently detected pesticide in surface waters of Manitoba[2] with concentrations reaching 1444 ng/L (Figure 2).

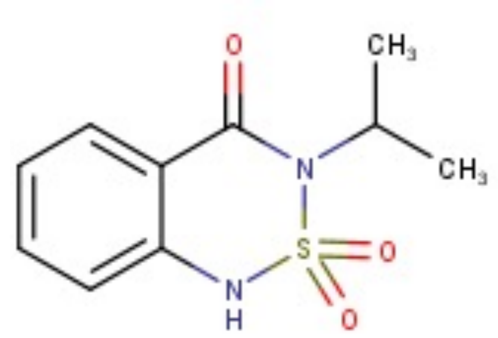

Figure 1. Molecular structure of the group 6 herbicide Bentazon. pKa = 3.51[4]; Kd = 0.72 L/kg[4]; Solubility (Water) = 7112 mg/L @ 20° C[4]

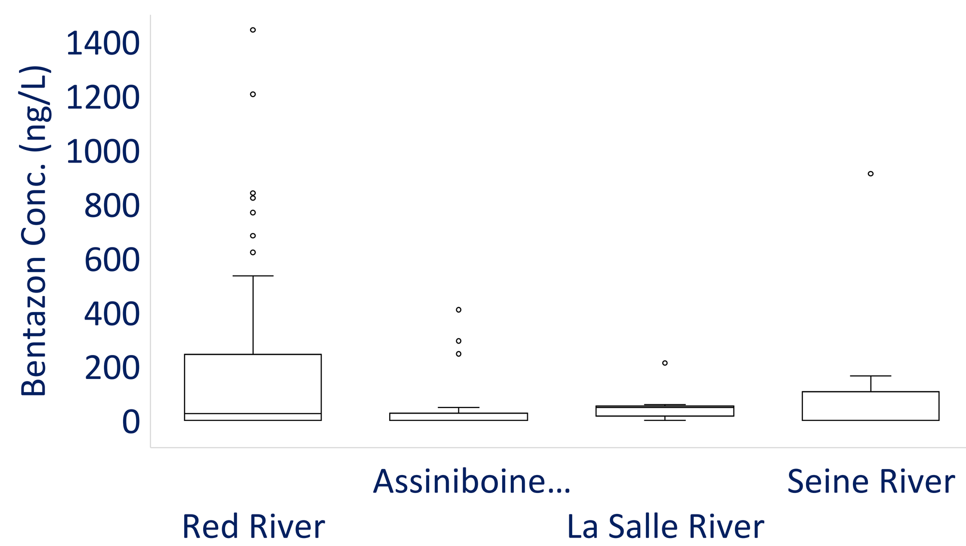

Figure 2. Bentazon concentrations detected in the Red (n = 107), Assiniboine (n = 35), La Salle (n = 9), and Seine (n = 9) from May to August, 2017. From Fatema, M. (Unpublished Thesis).

Biobeds (Figure 3) were invented by a Swedish farmer (Mr. Olsson) to process rinsate through a lignin-rich, high organic matter, slightly acidic biomixture to enhance sorption and degradation of pesticides prior to rinsate, post-spraying rinse water from sprayers, release into the environment[3]. Popular in Europe and Latin America, biobeds are effective at decreasing the concentrations of numerous pesticides, and the broad scale adoption of on-farm biobeds in the Canadian Prairies might be an important strategy to advancing a green economy[2,3]. However, it has been demonstrated that Bentazon is persistent in biobed effluent[4], hence modifications are required to making biobeds more efficient.

Figure 3. The two-celled biobed that become operational at the Ian Morrison Research Farm in Carman, MB in 2020

Biochars are aromatic porous materials produced through the pyrolysis of organic matter that have been shown to be effective at sorbing high concentrations of pesticides[5] and can be utilized within biobed effluent tubes to retain remaining Bentazon. However, before beginning biochar sorption experiments to test biochar efficacy, centrifuge tubes and extraction filter papers used in the biochar sorption study must first be analyzed for possible ancillary sorption of Bentazon themselves[6].

Objectives

Determine whether the Whatman® 542 filter paper (WFP) or polytetrafluoroethylene (PTFE), fluorinated ethylene propylene (FEP), and borosilicate glass (BSG) centrifuge tubes sorb Bentazon when used in biochar sorption experiments.

Methods and Materials

Sorption

Solutions of Bentazon were made with 18 MΩ MilliQ water and 0.01 M $CaCl_2$. 50 mL PTFE and FEP and 30 mL BSG centrifuge tubes were used for tube sorption experiments while WFP was used for filter sorption. All samples in triplicate with;

- 20 mL of 7.5 and 75 µg/L Bentazon in PTFE, FEP, or BSG tubes; rotated 24 hours.
- 30 mL of 7.5 and 75 µg/L Bentazon gravity filtered through WFP.
- 40 mL undisturbed control solutions of 7.5 and 75 ppb Bentazon.

Sample Extraction

50 µg/L Bentazon-d_7 spike → Oasis® HLB 3cc SPE extraction → 3 mL MeOH elution → N_2 Evaporation @ 42° C → Recon. 1 mL 50:50 MeOH: MilliQ → Syringe Filtered to LC-MS Vial

LC-MS/MS Quantitative Analysis

Chromatography via Aquity UPLC® HSS T3 column (2.1 mm x 50 mm, 1.8 µm) with MeOH and MilliQ binary gradient over 9 mins:

- 6% MeOH 0-0.5 mins; ramp to 95% MeOH to 4.00 mins and hold to 5 mins; re-equilibrate at 6% MeOH until 9 mins.
- Bentazon retention time: 2.7 mins.
- Samples were analyzed in negative mode electrospray ionization (ions in Table 1) and quantified using an 8-point internal calibration curve.

Statistical Analyses

SAS version 9.4 for Windows (SAS Institute 2013). Tube sorption was analyzed using paired TTEST comparing PTFE, FEP, and BSG to control solutions for both Bentazon (7.5 & 75 µg/L) concentrations. Filter sorption was also analyzed using paired TTEST, comparing WFP with control solutions for both Bentazon (7.5 & 75 µg/L) concentrations.

Table 1. The qualifier (q) and quantifier (Q) ions used to quantify Bentazon and Bentazon-d_7.

Compound Name	Precursor Ion	Product Ion
Bentazon-d_7 (q)	246.09	182.1
Bentazon-d_7 (Q)	246.09	132
Bentazon (q)	239.05	197
Bentazon (Q)	239.05	132.1

Results

BSG and FEP tubes were found to sorb Bentazon significantly while PTFE tubes did not sorb any Bentazon (Table 2). The WFP was not found to sorb significantly at 7.5 ug/L; however, at 75 ug/L it sorbed significant amounts of Bentazon (Figure 4).

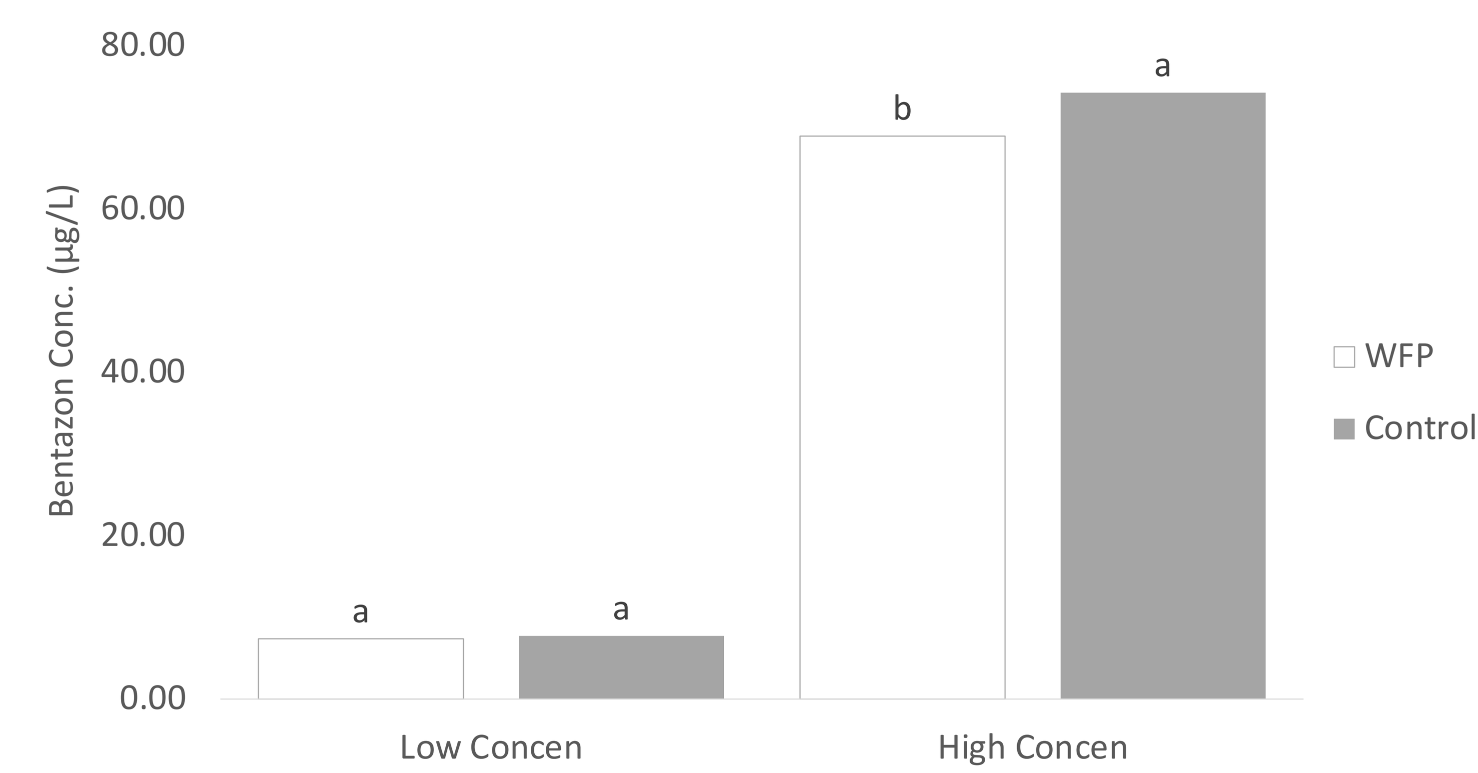

Figure 4. Comparison of filtrate from WFP and control solutions of Bentazon. Different letters represent a significant difference between samples (α = 0.05);

Conclusions and Future Works

PTFE tubes should be used in future Bentazon sorption experiments since it does not sorb Bentazon. Another filter paper should be found and tested for sorption due to WFP sorbing at high concentrations. Future work will involve testing biochar sorption isotherms, kinetics, and thermodynamics as well as column leaching, hydraulic conductivity, and in-field trials of biochar filters with Bentazon.

Table 2. Comparison of PTFE, BSG, and FEP to control solutions after rotating for 24 hours. Different letters represent a significant difference between samples (α = 0.05); values are (Mean ± SE).

Treatment	Low Concentration (µg/L)	High Concentration (µg/L)
Control	7.74 ± 0.04 a	74.25 ± 0.62 a
PTFE	8.42 ± 0.31 a	74.11 ± 0.57 a
BSG	5.06 ± 0.03 b	50.41 ± 0.28 b
FEP	0.51 ± 0.45 b	22.85 ± 13.71 b

Acknowledgements; Thank you to the NSERC-USRA and Dr. J.A. Garland Summer Research Award for funding PN during the summer work term under AF. PN would also like to thank her ancestors, the Indigenous Amami peoples of Tokunoshima, for raising her and ensuring her existence today.

References

1. Lewis et al. (2016). Human Eco. Risk. Assess. 22, 1050-1064., *2.* Fatema, M. (Unpublished Thesis)., *3.* Castillo et al. (2008). J. Agri. Food Chem. 56, 6206-6219., *4.* Braul et al. (2018). AAFC. , *5.* Uchiyama et al. (2012). J. Agri. Food Chem. 60, 2989-2997., *6.* Sharom and Solomon. (1980). Can. J. Aquat. Sci. 38, 199-204.