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Effect of Feedstock and Pyrolysis Temperature on the Retention Capacity of Biochars to Sorb Steroid Hormones and Veterinary Antibiotics

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Introduction

Veterinary antibiotics are administered to animals in order to prevent, treat diseases and also as growth promoters. Their usage in New Zealand amounts to about 60 tonnes per year. After administration up to 80% is excreted in urine and faeces. Additionally, steroid hormones are naturally excreted by dairy cows, and given the land-application of effluent is a common practice in many parts of NZ, there is a concern among regulatory bodies that these contaminants may end up in the receiving environment through soil leaching and may also impact terrestrial organisms. Biochar can contain 60-80% as black carbon, and due to its high surface area, it has been used an effective soil remediation tool [1]. Biochars are often made from different feed stocks and under different heat treatment conditions and these variations may make biochars heterogeneous and therefore may have different contact times with soil components thereby affecting its retention capacity.

Objective

To determine the retention ability of a farm soil amended with biochar obtained from 3 different feed stocks and pyrolytic temperatures (only for Green waste) for an estrogenic steroid hormone (E2), its primary metabolite (E1) and a veterinary antibiotic, sulfamethoxazole (SMO).

Materials

Matawhero silt loam (0-5 cm) was collected from Gisbourne, NZ. Biochars used in this study were produced from green waste (GW) feedstock at 3 different pyrolytic temperatures 350 °C, 450 °C and 550 °C by slow-pyrolysis technique and corncob (CC) by flash carbonization technique, and pine sawdust (PSD) by steam gasification at > 600°C.

Biochar characterization

A range of techniques (Scanning Electron Microscope, X-Ray Diffraction, Fourier Transform Infrared Spectroscopy, ICPMS, 13c-solid-state NMR and EDAX) were used to characterise the biochars [1].

Sorption Experiment

Duplicate air-dried soil samples (2g) amended with above mentioned biochars (1.0% by wt.) were weighed into glass centrifuge tubes. An aliquot of 30 ml of E2 and SMO with 6 concentrations (0.5, 0.75, 1, 2.5, 3.75 and 5 mg/l) in 0.005M CaCl2 were added to the tubes, wrapped in aluminium foil, and shaken for 8-12 hrs to equilibrate in the dark (23°C ± 2). After centrifugation (1750g x 5 min), for SMO: 0.5 ml of supernatant was measured directly by HPLC. For E2/E1, 10 ml of supernatant was extracted with 5 ml of DCM, and the residual soils were extracted with 5 ml dichloromethane. Aliquot (1ml) of extract was evaporated to dryness under N_2, and the residue was reconstituted in 1 ml of 70% methanol + 30% water. Analysis was done by High Performance Liquid Chromatography and UV detector (201 nm for E2 [1]; 275nm for SMO) using a C_{18} column.

Results

All sorption isotherms were highly non-linear for both E2 and E1 in soil amended with the biochars. For SMO, amendment with GW biochars gave linear isotherms whereas for CC and PSD biochar, it was highly nonlinear. Overall, the K_f values for SMO, E2 and E1 in GW amended biochars were similar to soil alone (Table 2), showing the non sorptive nature of GW biochars. When compared to biochars made from different feedstock, E2 and SMO sorption was maximum in the treatment PSD BC + soil,15 folds greater than the control

and 8 fold greater than other biochar amendments for E2. For SMO there was 125 fold increase (PSD) and 15 fold increase (CC) in the sorptive capacity when compared to the control. The higher sorption by PSD derived biochar can be attributed to the level of carbon present and the high BET surface area [1].

Conclusions

The biochar characterization results show that there was not a marked change on the biochar properties due to the different heat treatment except the C content (Table 1). The results from batch sorption studies showed that when same feedstock was used the variations in the pyrolytic temperature had no effect on the sorption characteristics. The soil amended with PSD biochar showed a marked affinity for both SMO, E2 and E1 as compared to other two biochars (CC and GW), presumably due to the higher SSA and C content of PSD biochar as well as due to the presence of abundance of polar functional groups (e.g. – OH) as observed from characterization data [1].

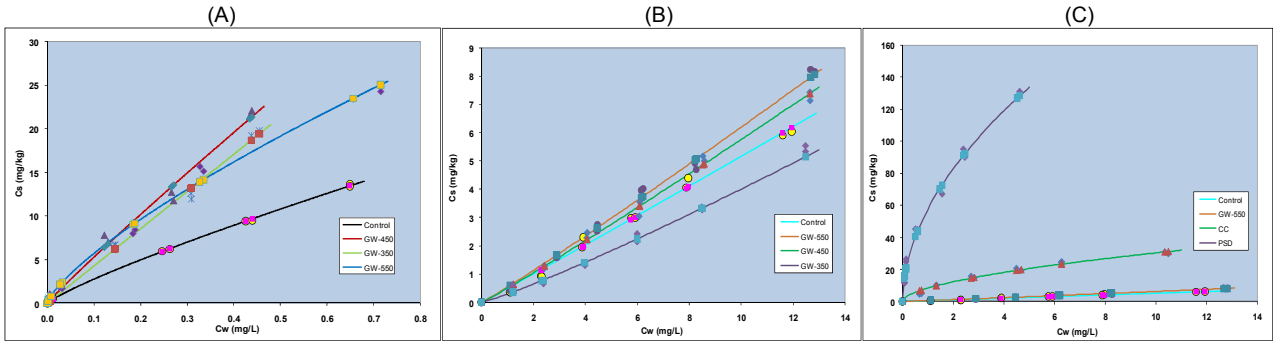

Figure 1. Batch sorption isotherms for E2 (A), SMO (B&C).

Table 1: Chemical properties of Green waste biochar used in sorption studies; *specific surface area was measured by BET nitrogen adsorption; # measured by ICPMS;** experiments in progress.

Biochar	Total C (%)	Total N (%)	Total H	Exchangeable cations# cmol(+)/kg Ca	Mg	K	Na	CEC cmol(+)/kg	Ash (%)	SSA* (m^2/g)
GW-550°C	79.8	0.35	2.83	0.51	0.19	0.77	0.24	1.71	1.61	153
GW-450 °C	71.8	0.31	3.28	0.37	0.13	0.37	0.17	1.04	1.51	**
GW-350 °C	65.2	0.23	4.26	0.21	0.08	0.10	0.05	0.43	1.04	**

Table 2. Summary of sorption parameter Kf derived from the multiple-concentration isotherms in Matawhero soil amended with biochars and in soil alone. Kf in mg $^{1-N}$ L ^{N} kg $^{-1}$

Treatment	SMO	E2	E1
	K_f		
GW +soil	0.45	28.3	63.4
CC +soil	5.95	32.8	34.9
PSD +soil	46.85	262	89.9
Control	0.35	18.4	22.0

Treatment	SMO	E2 [1]	E1
	K_f		
GW-550 °C +soil	0.45	28.3	63.4
GW-450 °C +soil	0.33	29.8	41.1
GW-350 °C +soil	0.33	26.4	43.6
Control	0.35	18.4	22.0

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[1]Sarmah, K. S.; Srinivasan, P.; Smernik, J. R.; Manley-Harris, M.; Antal, J.M; Downie, A; Van Zweiten, 2010. *J. AJSR* 48(6) in press. "*Retention capacity of biochar-amended New Zealand dairy farm soil for an estrogenic steroid hormone and its primary metabolite*"