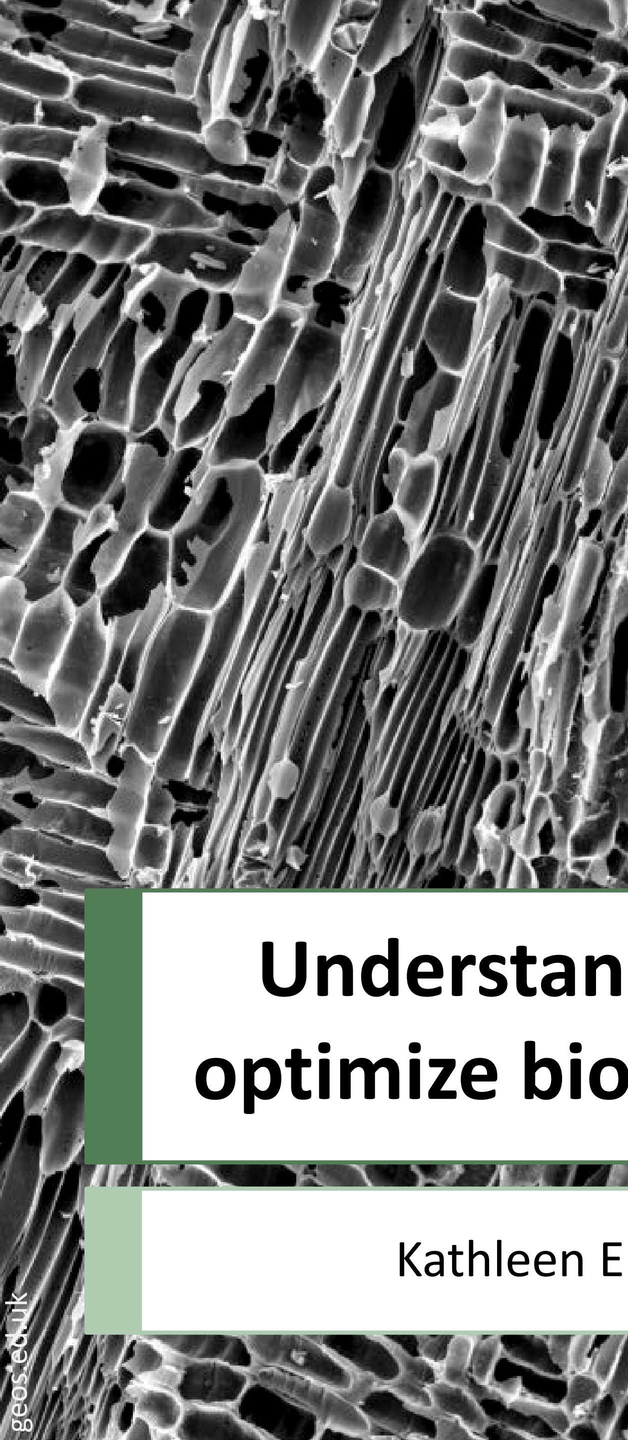

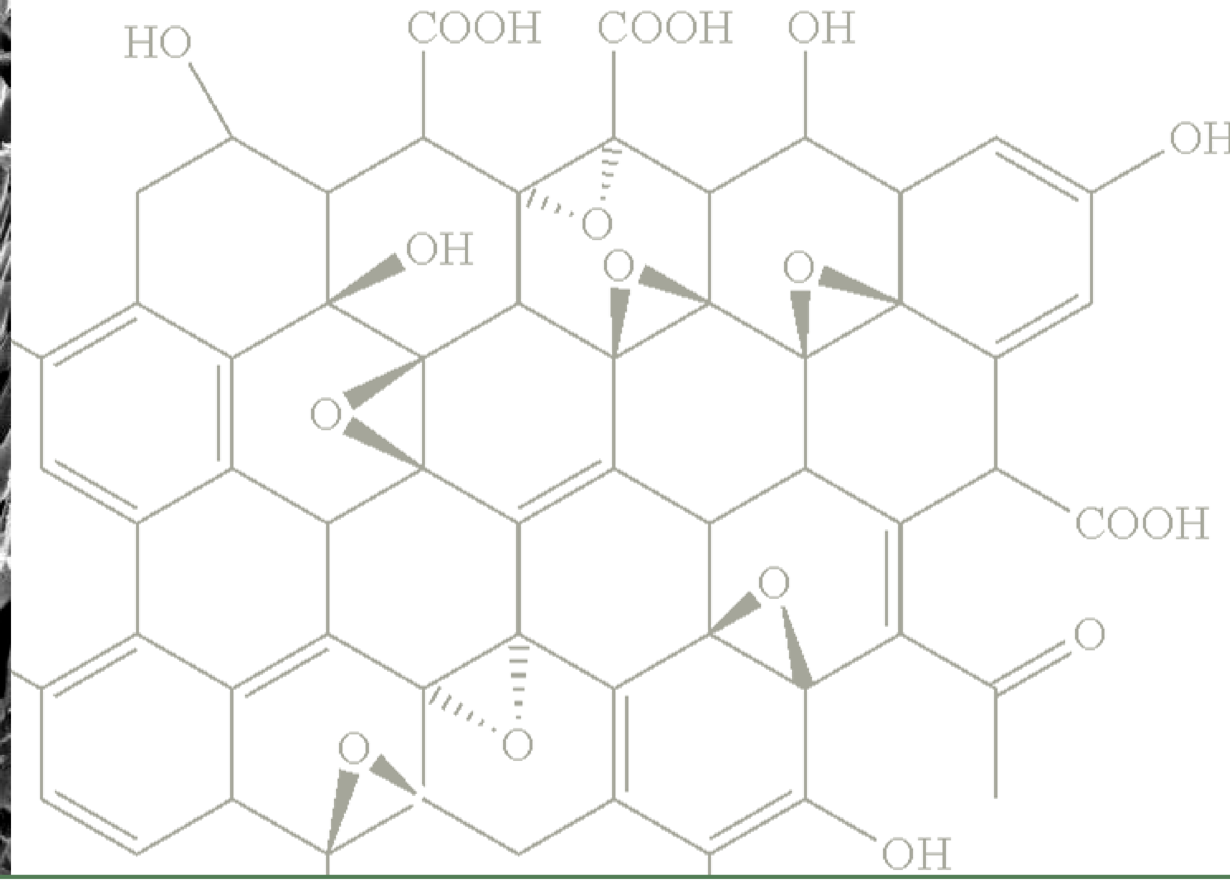

Understanding mechanisms to predict and optimize biochar for sorption of agrichemicals

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Costa Verde
La Coruna
Gijon
Bilbao
San Sebastian
Leon
Pamplona
Vigo
Valladolid
Zaragoza
Barcelona
Costa Dorada
Salamanca
Segovia
Madrid
Minorca
Portugal
Tagus
Toledo
Balearic Islands
SPAIN
Valencia
Mallorca
Olivenza
Albacete
Cordoba
Seville
Granada
Huelva
Malaga
Cadiz
Costa del Sol
Gibraltar (UK)
North Atlantic Ocean


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Biochar as a sorbent

Biochar – pesticide interactions have been widely studied.

Applications

- Filter material
- Water treatment
- Soil remediation

Important to understand these interactions, whether intentional or side effect of alternative applications

Biochar diversity

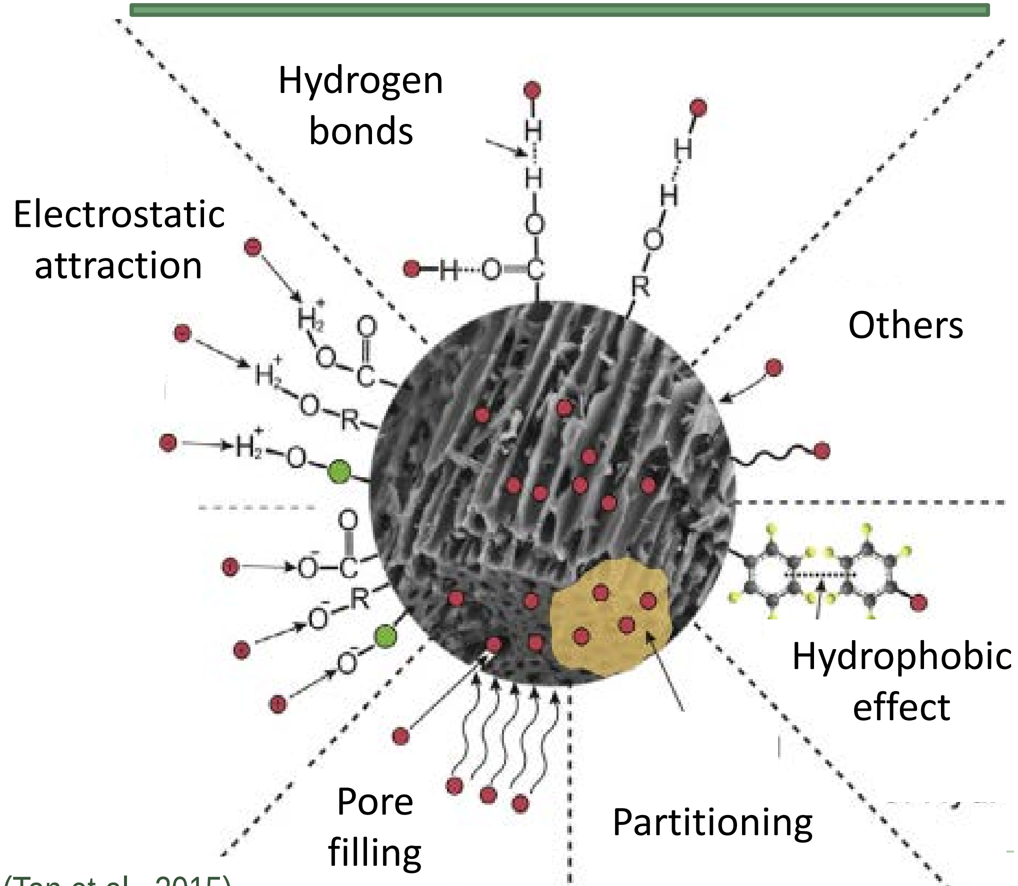
- Available feedstocks and pyrolysis systems

- Differing sorption results limit predictability among biochars
- Limited understanding of the mechanisms driving biochar-pesticide interactions
- There is a need to systematically study chemistry of biochars → greater understanding and optimization

Biochar-pesticide interactions

Sorption depends on both biochar and chemical properties

Proposed mechanisms



(Tan et al., 2015)

- Influenced by biochar surface characteristics
  - Chemical
    - Surface groups
  - Physical
    - Surface area
    - Pore size distribution
- Both can be modified (activation)

Biochar activation

Different techniques include ….

- Heating
- Solvent washing
  - HCl
- Surface oxidation/reduction
  - Steam
  - H_2O_2
  - CO_2
  - H_2SO_4, HNO_3, H_3PO_4

Goals are to increase sorption by increasing SSA and strategically altering functionality

Objectives

1 Activate biochars by a variety of methods to create “normalized” sorbent materials

2 Evaluate the role of biochar surface characteristics on the sorption of select herbicides with different chemistries

Materials - Biochars

Feedstock = Grape wood

Feedstock	**Temp °C**	**Moisture %**	**Ash %**	**Volatile %**	**Fixed C %**	**C %**	**H %**	**N %**	**O %**
Grape wood	350	3.54	10.9	39.5	49.7	66.6	4.0	1.1	17.5
Grape wood	500	3.99	16.8	19.3	64.0	70.4	2.3	0.9	9.6
Grape wood	900	1.31	22.2	6.6	71.1	71.6	0.1	1.0	4.9

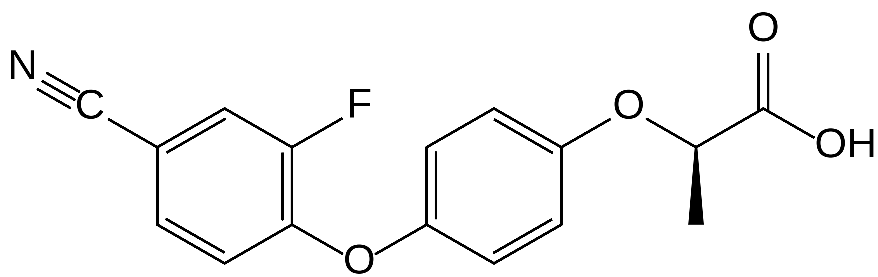
Materials - Biochars

Activations

- **H_2O_2**
- **CO_2**
- HCl
- H_2SO_4
- H_3PO_4
- HNO_3

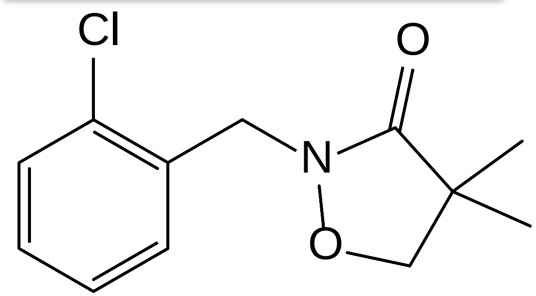
Materials - Pesticides

Cyhalofop



- post-emergence control of grass weeds in rice crops
- weak acid, pKa = 3.9
- Soil Koc = 186

Clomazone



- control of broad-leaved weeds and grasses in a range of crops
- nonionizable (no dissociation)
- Soil Koc = 300

Methods

Biochar characterization

- ATR - FTIR
- Zeta potential
- Surface area
- pH
- % moisture

Sorption characterization

- Batch equilibration method
- HPLC analysis
- % sorbed

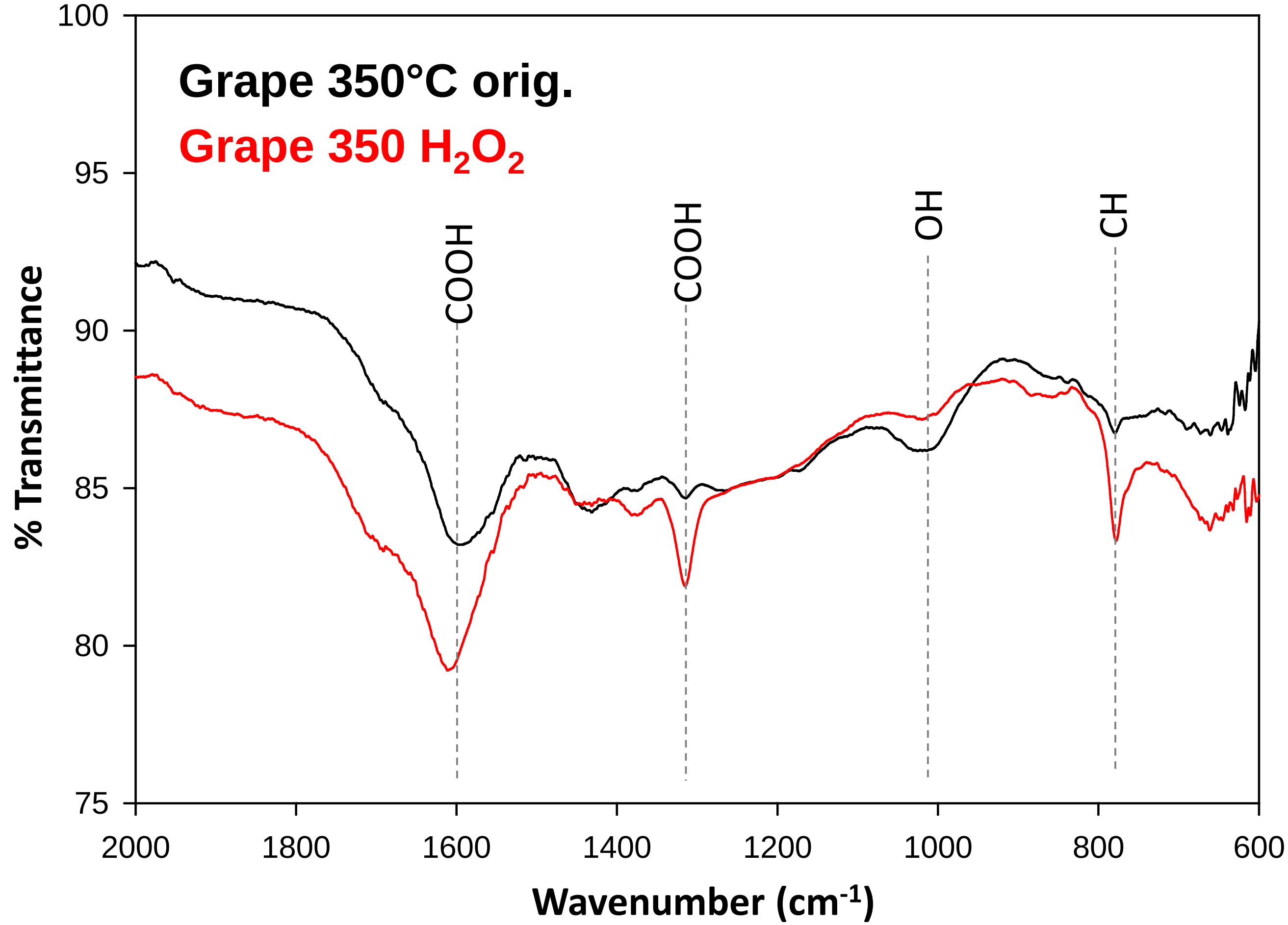
Results – Pesticide sorption

	Cyhalofop (H_2O)		**Clomazone** (H_2O)	
Biochar	**% sorbed**[a]	**pH**	**% sorbed**[a]	**pH**
Grape 350	**6.3**	7.9	**65.0**	7.9
Grape 500	**11.0**	9.8	**47.5**	9.7
Grape 900	**99.1**	11.6	**99.7**	11.6

[a] average CV = 0.1

- Greater sorption of clomazone on all biochars
- Lower clomazone sorption at 500°C than 350°C

Results – H_2O_2 activation



Visible changes in surface chemistry with activation

Results – Pesticide sorption

	Cyhalofop (H_2O)		**Clomazone** (H_2O)	
Biochar	**% sorbed**[a]	**pH**	**% sorbed**[a]	**pH**
Grape 350	**6.3**	7.9	**65.0**	7.9
Grape 350 H_2O_2	**35.4**	4.8	**70.3**	4.8

[a] average CV = 0.1

- Increase with activation more pronounced for cyhalofop
- Greater fraction of cyhalofop in molecular form at low pH
- This emphasizes the influence of pH for weak acid pesticides compared to nonionizable compounds
- pH could be due to added functional groups or alternative alterations

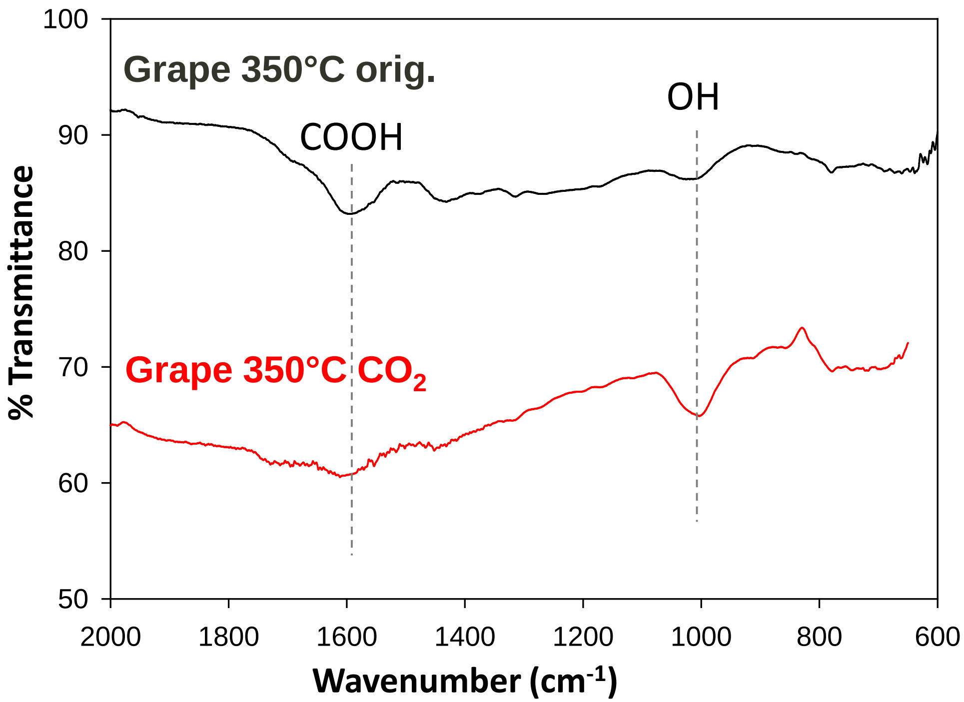
Results – Pesticide sorption

	Cyhalofop (H_2O)		**Cyhalofop** (0.01 M $CaCl_2$)	
Biochar	**% sorbed**[a]	**pH**	**% sorbed**[a]	**pH**
Grape 350	**6.3**	7.9	**19.5**	7.5
Grape 350 H_2O_2	**35.4**	4.8	**55.2**	4.5

[a] average CV = 0.1

- Higher sorption in $CaCl_2$
- Sorption increased **6 x** and **3 x** with activation in H_2O and $CaCl_2$, respectively
- 3 unit pH decrease in both H_2O and $CaCl_2$ with activation

Results – CO_2 activation



	Cyhalofop (0.1 M $CaCl_2$)	
Biochar	**% sorbed**	**pH**
Grape 350	19.5	7.5
Grape 350 CO_2	13.1	7.2

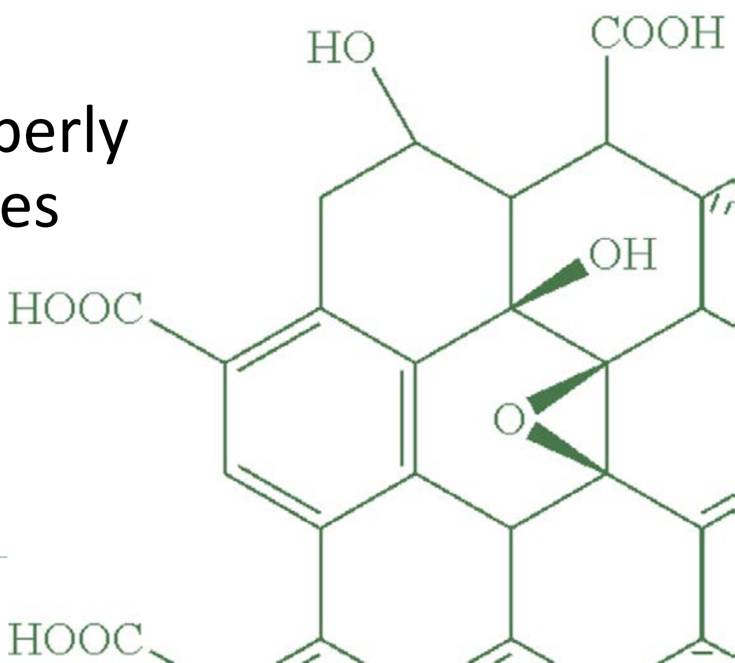
- CO_2 activation decreased cyhalofop sorption
- Lost carboxyl groups correspond to decreased sorption
- Supports role of carboxylic group being important to sorption

Conclusions

- Activation can customize biochars for desired sorption properties

- Biochar activation is a useful tool in studying binding mechanisms of organic contaminants

- This information can be used to properly select biochars for intended purposes and environments



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