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Effect of biochar on pesticide and P sorption and leaching

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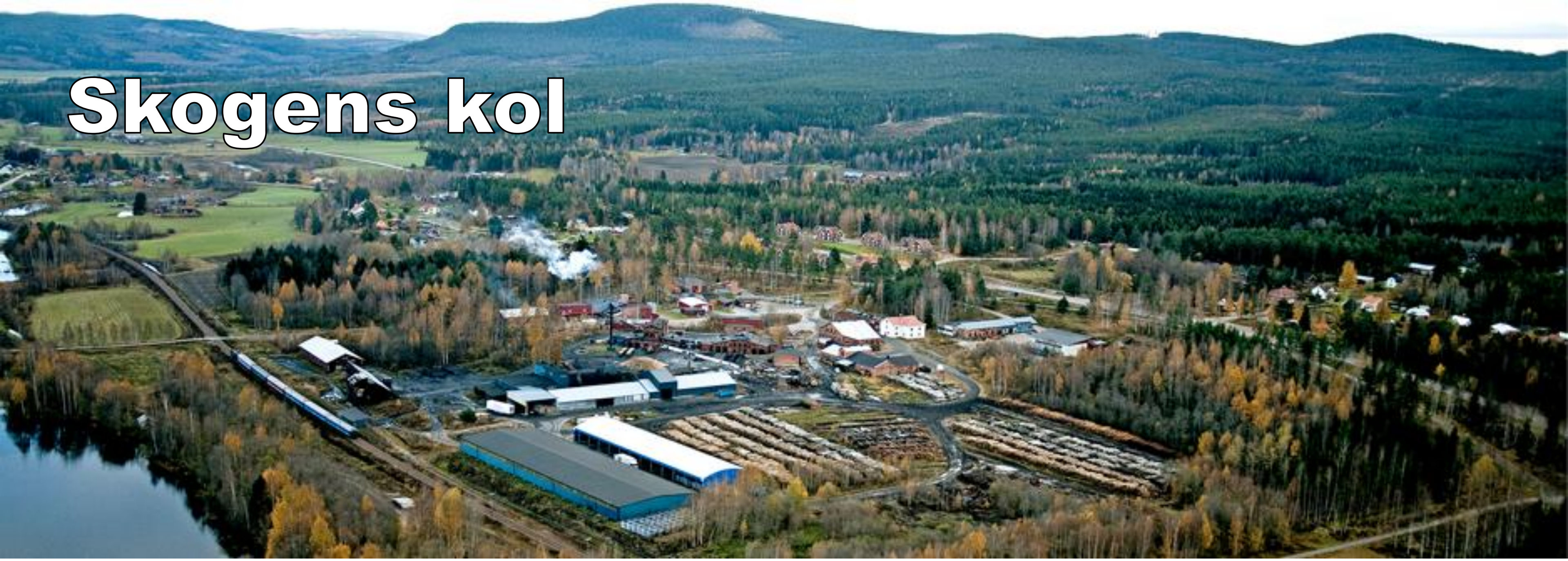
Background

- Pesticides often do not reach their intended target but are transported to groundwater and surface waters
- Diffuse losses of phosphorus from agricultural soils comprise one of the largest contributors of phosphorus to water bodies

Objective

To study how biochars can be used proactively to reduce pesticide and P leaching from sensitive soils

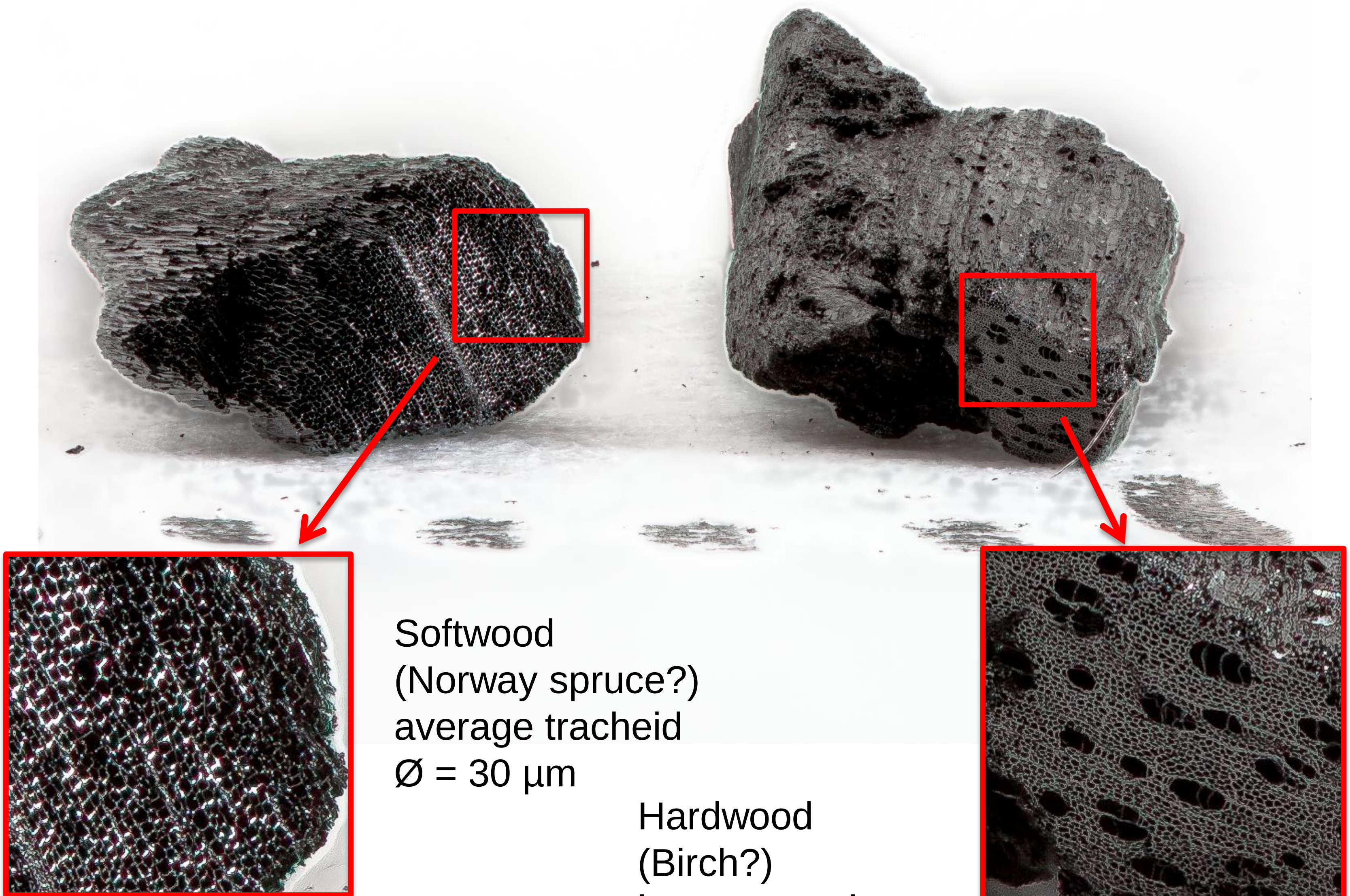
Skogens kol



-wood biochar, produced mainly from Birch (*Betula pendula*) and Norway spruce (*Picea abies*)

- reaching max temp of 390-430 ºC during pyrolysis

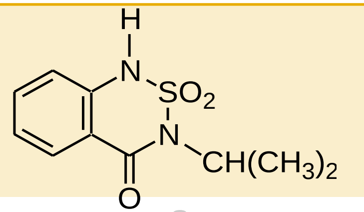
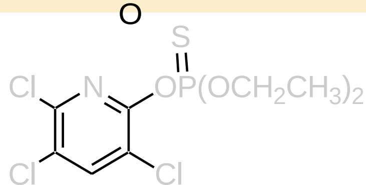
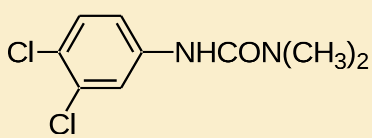
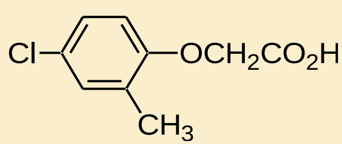
A Material With Large Surface Area And Many Pores



Softwood
(Norway spruce?)
average tracheid
Ø = 30 µm

Hardwood
(Birch?)
larger vessels,
smaller fibers

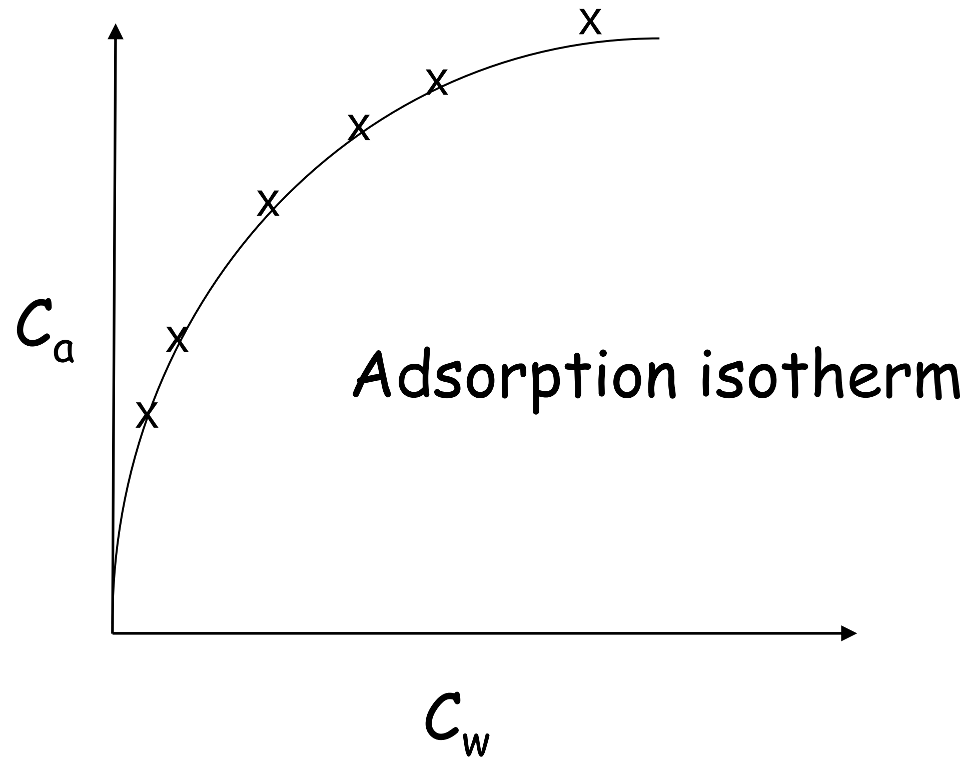
Model Compounds

	Chemical structure	Type	Water solubility*	Soil mobility*
bentazone		herbicide	high (570 mg/L)	mobile
chlorpyrifos		insecticide	very low (1.05 mg/L)	non-mobile -
diuron		herbicide	low (35.6 mg/L)	slightly mobile
glyphosate		herbicide	very high (10 500 mg/L)	slightly mobile
MCPA		herbicide	very high (29 390 mg/L)	mobile

* values from FOOTPRINT PPDB

Measurement Of Adsorption

- Mix biochar with 0.01 M $CaCl_2$ for 24 h
- Add chemical (mixtures of unlabelled and ^{14}C-labelled compounds)
- Mix (often 24 h)
- Measure concentration in solution, C_w
- Calculate concentration on soil (by mass balance), C_a



The Freundlich model

$$C_a = K_f C_w^n$$

K_f: adsorbed amount when $C_W = 1$
$n = 1$ linear; $n < 1$ saturation

Freundlich Parameters

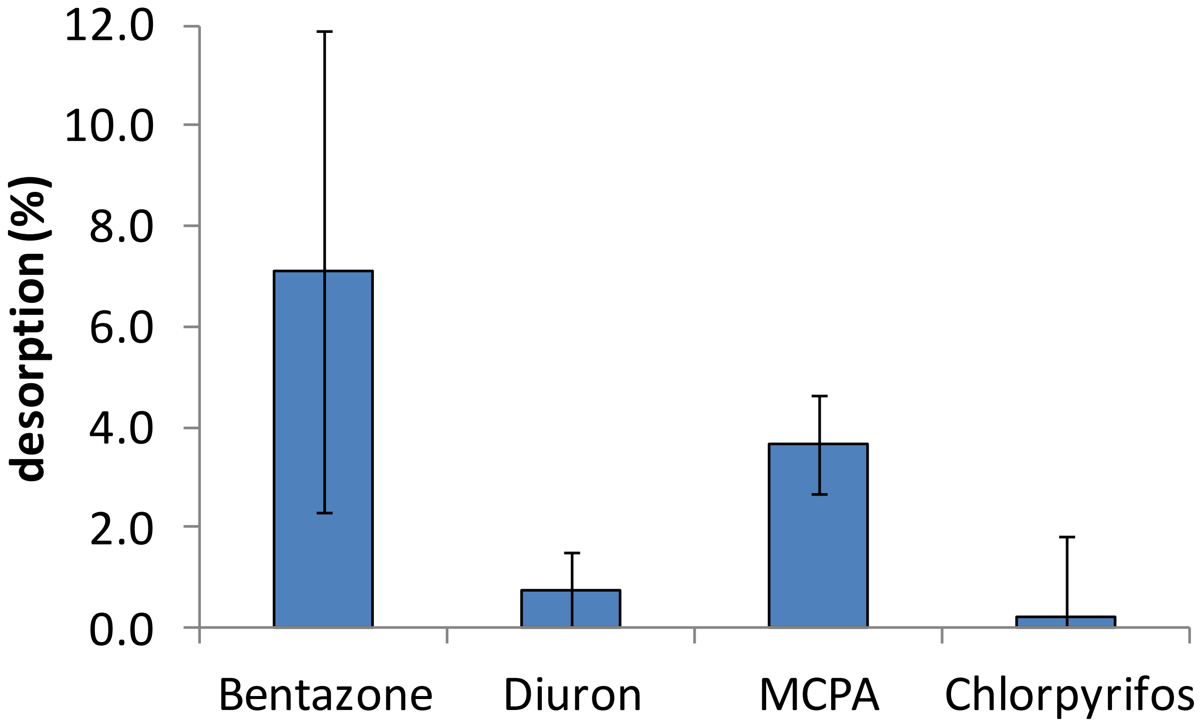
	K_f	n	R^2	Typical K_f on soil*
bentazone	21.6	0.50	0.95	1
MCPA	160	0.51	0.94	1
chlorpyrifos	294	0.81	0.99	No data
diuron	522	0.60	0.96	18
glyphosate	-	-	-	450

* PPDB: Pesticide Properties DataBase

K_f: adsorbed amount when concentration in solution = 1
n = 1 linear isotherm; n < 1 indicates saturation

Biochar dramatically increases adsorption of most pesticides (however not for glyphosate)

Desorption



Desorption values after 4 desorption steps summarized

Only small amounts of what is adsorbed will desorb by leaching

Leaching

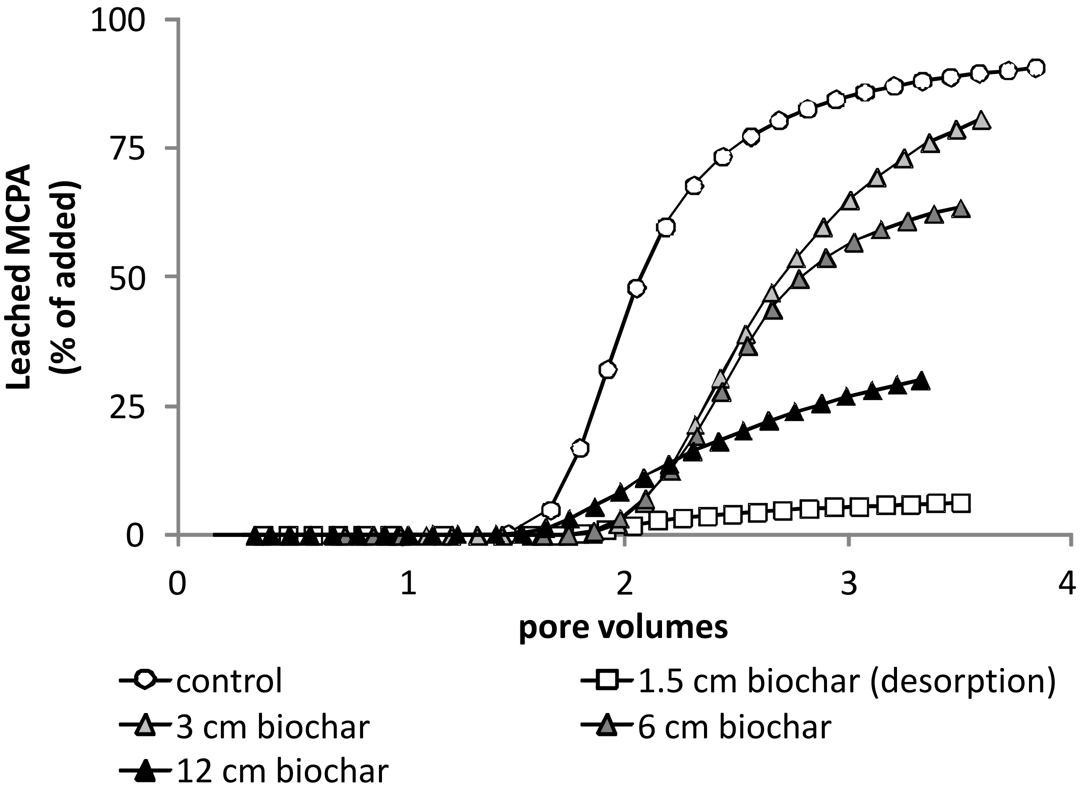
OECD guideline 312:
Leaching in Soil Columns

Column hight of 40 cm,
diameter 40 mm

Flow rate 0.3 mL/min
corresponding to rainfall of
about 14 mm/h

Tested layer thicknesses of
1.5-12 cm

Leaching Of MCPA



- MCPA dose corresponding to 2.25 Kg a.i./ha added to sand or to the biochar (desorption)
- biochar Ø < 2 mm, amounts corresponding to 25, 50, 100 and 200 tonnes/ha
- **23-68% reduction in leaching after 3 pore volumes**
- **94% reduction in leaching after 3 pore volumes when the pesticide is added to the char**

Summary Leaching Tests

- ❑ Leaching decreases with smaller particle sizes

- ❑ Increased retention with increasing layer thickness

- ❑ Decreased leaching when the biochar is in a layer rather than distributed through the sand

- ❑ Very low leaching if the pesticide is first adsorbed to the biochar (90-98% reduction)

Some Needs For A Protective Layer Of Adsorbents To Reduce Leaching

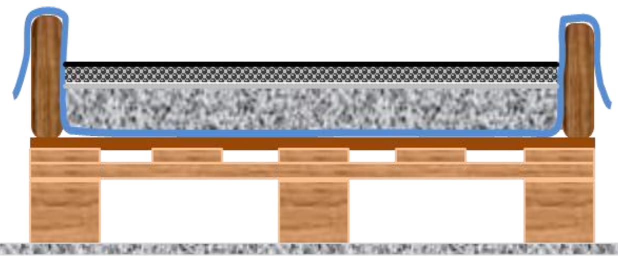
On permeable soils

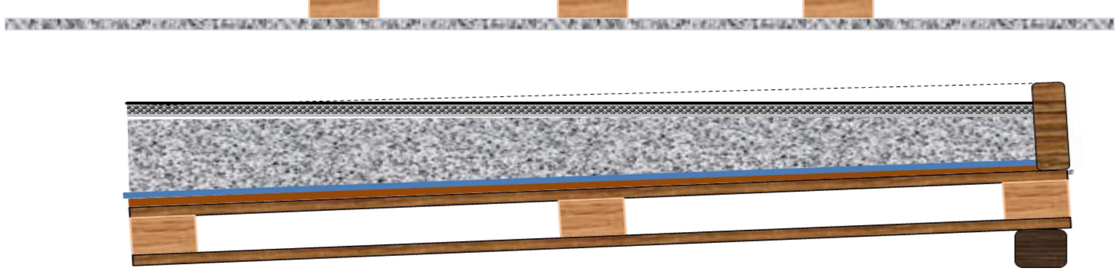
Around inspection wells
of drainage systems

In greenhouses

A Protective Layer Of Different Sorbents In Greenhouses

- Layer of sorbents (thickness 1.5-3.5 cm) placed on sand
- Pesticides sprayed at 4 x recommended dose
- Three mm water per day for two weeks in a greenhouse
- Final heavy watering



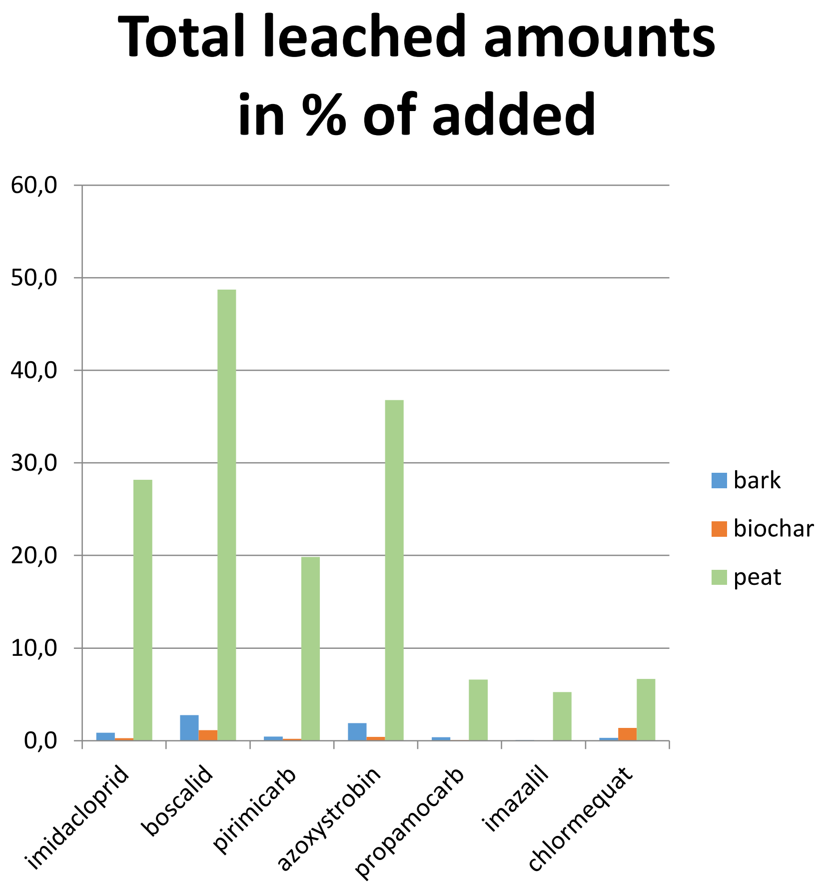


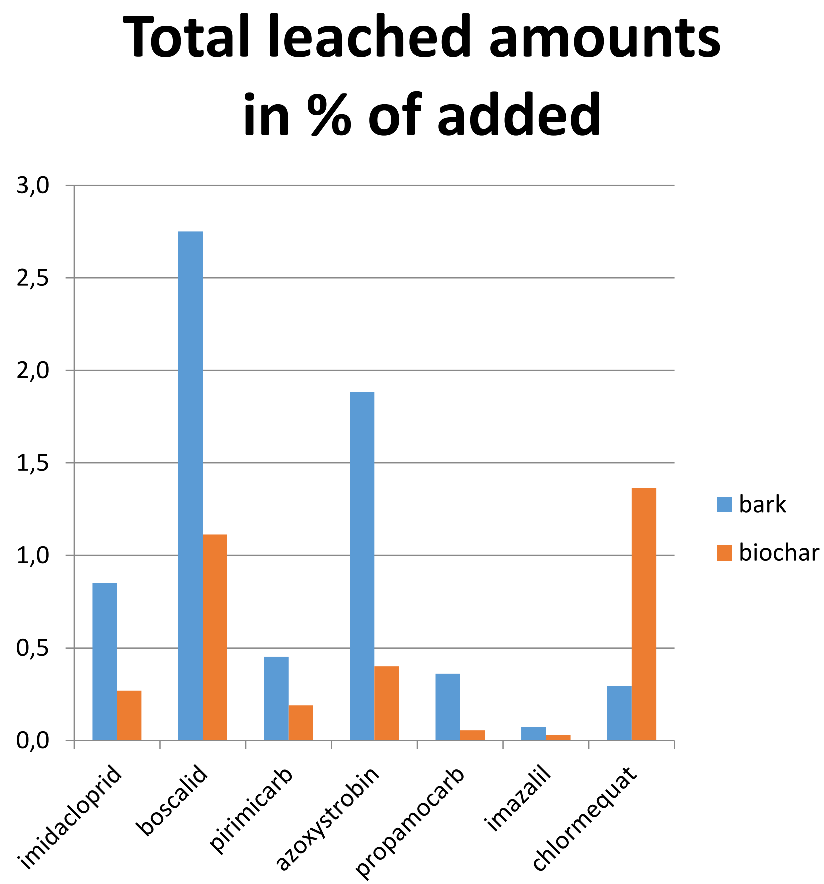
Bark, 3.5 cm

Biochar, 1.5 cm

Peat, 3.5 cm

Leached Amounts Of Seven Commonly Used Greenhouse Pesticides





When Biochar Is Not Efficient

Modifying Biochar

Problem

- Powdered biochar, like powdered active carbon, can be difficult to separate from water after being used as adsorbents
- Most of the traditional engineered carbons (*e.g.* activated carbon and biochar) have limited ability to adsorb P or other anionic nutrients (*e.g.* nitrate)

Solution

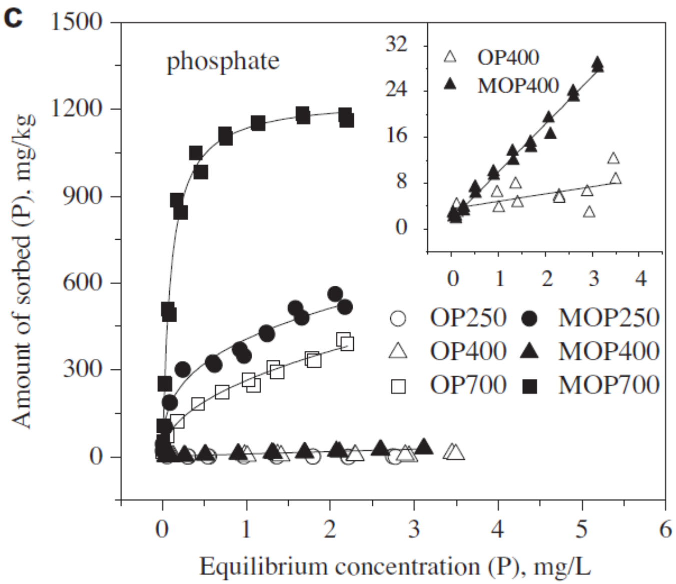
- Magnetic biochar that can be effectively separated by magnetic separating techniques
- Biochar-MgO nanocomposites that bind huge amounts of phosphate P and also nitrate

Magnetic Biochar

Chen et al., 2011 A novel magnetic biochar efficiently sorbs organic pollutants and phosphate. Bioresource Technology 102(2):716-723

Magnetite formation and biochar preparation in one-step

- Chemical co-precipitation of Fe^{3+}/Fe^{2+} on orange peel powder followed by pyrolysis
- Binds 1.2 g P/Kg when pyrolyzed at 700 °C
- Formation of magnetite (iron(II,III) oxide, $Fe^{2+}Fe^{3+}{}_2O_4$) gives a magnetic biochar



OP: orange peel biochar
M: magnetic

- Interesting application: Removal of pharmaceuticals from wastewater effluents using magnetic biochar

Biochar-MgO nanocomposites

Removal of phosphate from aqueous solution by biochar derived from anaerobically digested sugar beet tailings (Yao et al., 2011a and 2011b)

- Biochar made from biogas residue from sugar beet tailings (DSTC)
- Surface area: 449 m^2/g (comparable to that of many commercial activated carbon adsorbents)
- Large amount of colloidal and nano-sized periclase (MgO) on the surface
- 133 g of phosphate per Kg is comparable to or even larger than that of commercial phosphorus fertilizers

Table 2
Summary of the Langmuir maximum capacity of phosphate removal by different adsorbents.

Adsorbent	Q ($mg\,kg^{-1}$)	Reference
Activated coir-pith carbon	5100–7262	[15,16]
Hydroxy-aluminum, hydroxy-iron, and hydroxy-iron–aluminum pillared bentonites	10,500–12,700	[37]
Functionalized nanoporous sorbent (FE-EDA-SAMMS)	43,300	[38]
Iron impregnated coir pith	70,920	[39]
Alunite	118,000	[2]
La(III)-, Ce(III)-, and Fe(III)-loaded orange waste	42,700	[40]
Metal loaded skin split waste	21,650–72,000	[41]
Slag and treated slag	32,900–60,700	[19]
Magnetic orange peel biochars	219–1240	[26]
DSTC	133,085	This work

133 g/Kg!!

Table 1
Elemental analysis of raw and digested sugar beet tailings, and their associated biochars, STC and DSTC, respectively (mass%)[a].

Sample	C	H	O[b]	N	P	S	Ca	Mg	K	Fe	Al	Zn	Na	Cu
Digested Tailing	33.94	4.53	46.89	2.35	0.34	0.28	9.68	1.20	0.79	–[c]	–	–	–	–
Raw Tailing	36.06	3.43	55.82	1.23	0.16	0.09	1.80	0.53	0.88	–	–	–	–	–
DSTC	30.81	1.38	39.87	2.74	2.18	0.46	9.78	9.79	1.97	0.75	0.24	0.03	–	–
STC	50.78	2.08	36.70	1.83	0.35	0.05	4.41	1.53	1.04	0.59	0.64	–	–	–

[a] Expressed on a total dry weight basis.
[b] Determined by weight difference assumed that the total weight of the samples was made up of the tested elements only.
[c] Below 0.01%.

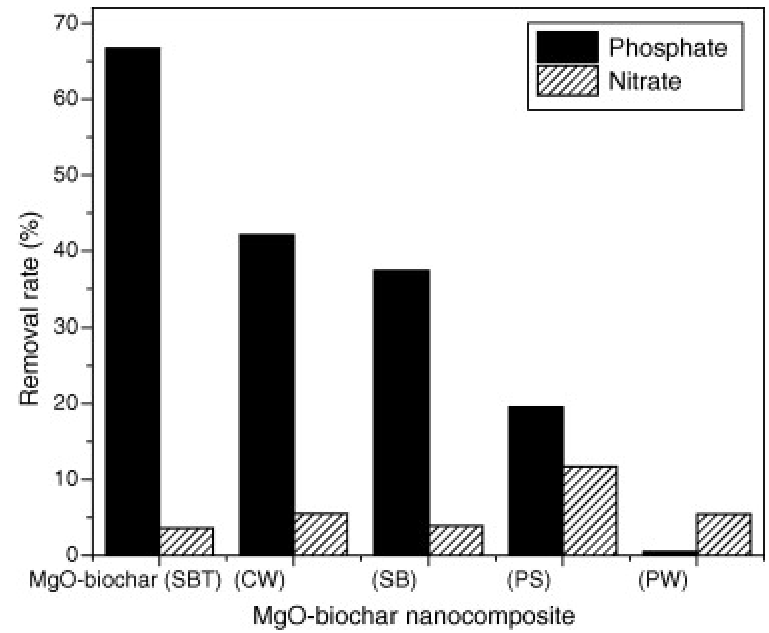
Biochar-MgO nanocomposites

Zhang, M., et al. 2012. Synthesis of porous MgO-biochar nanocomposites for removal of phosphate and nitrate from aqueous solutions. Chemical Engineering Journal 210:26-32

Production of biochar-MgO nanocomposites

- Feedstock immersed in $MgCl_2$ solution for 2 h
- Pyrolyzed up to 600 °C for 1 h
- Formation of biochar-MgO particles (nanocomposites) in the biochar matrix
- Nanocomposites made from sugar beet tailings and peanut shells had the best adsorption capacities (835 g phosphate/Kg and 95 g nitrate/Kg)
- Much higher than previously reported values of other carbon based and commercial adsorbents (< 20 g phosphate/Kg)
- A phosphate and nitrate superadsorbent!

Removal efficiencies to aqueous phosphate (20 ppm) and nitrate (20 ppm)
After 24 h, 50 ml solution, 0.1 g of adsorbent



Feedstock

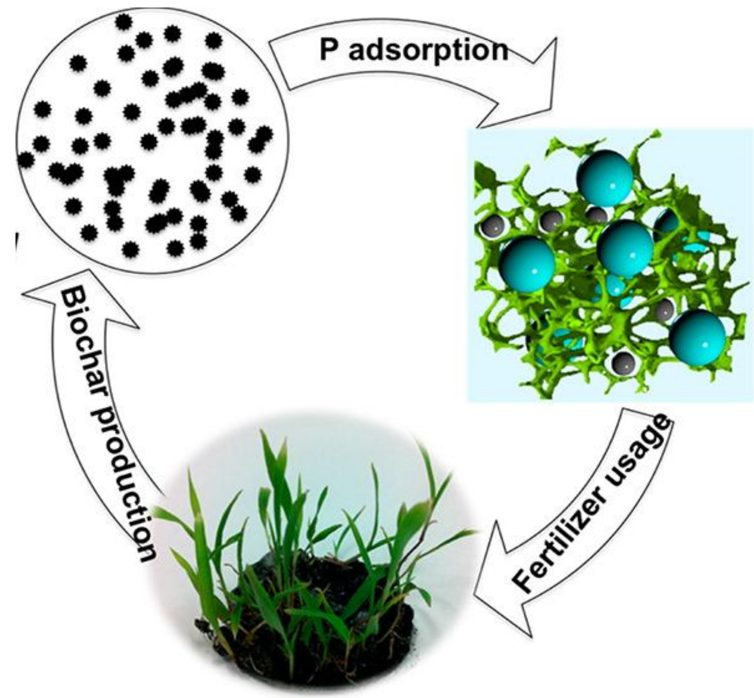
SBT: Sugar beet tailings
CW: Cottonwood
SB: Sugarcane bagasse
PS: Peanut shells
PW: Pine wood

Summary
Removal Of Phosphates

	P binding capacity g/Kg	Remark	Ref
Magnetite formation on biochar by cooking	0.5	Magnetic Binds glyphosate	Our work
Magnetite formation during pyrolyisis	1.2	Magnetic No competition with binding of organic pollutants	Chen et al., 2011
Periclase formation during pyrolyisis of biogas residue from sugar beet tailings	133		Yao et al., 2011a and 2011b
Periclase formation during pyrolyisis of $MgCl_2$-enriched feedstock	835 !	Also adsorbs nitrate (95 g/Kg)	Zhang et al. 2012.

Summary

- Leaching of most pesticides can be substantially reduced by a thick layer of biochar (some dm)
- Very low leaching if the pesticide is first adsorbed to a thin layer of biochar (90-98% reduction)
- Possible to modify the biochar for increased pesticide binding (e.g. glyphosate) and recovery (e.g. biochar-magnetite)
- Biochar-periclase (MgO) nanocomposites have a very large phosphate and nitrate binding capacity
- Such P- and N-enriched biochars can potentially be used as slow-release fertilizers



Yao et al., , 2013

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Thank you for your attention!