University of Cyprus

Use of biochars for the removal of Volatile Organic Compounds (VOCs)

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24 JUNE 2021

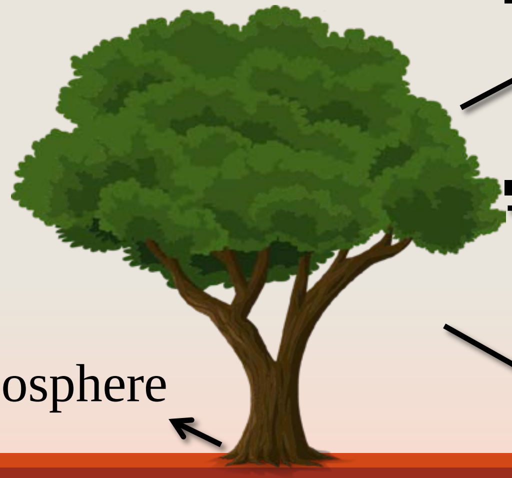
Contents

Volatile organic compounds (VOCs)

Low molecular weight compounds containing mainly carbon and many common characteristics, such as low boiling point, low water solubility, high vapor pressure (≥ 0.01 kPa at 20 ° C).

Biogenic VOCs

- Vegetation
- Plants
- Organs of plant (roots, stem, leaves)

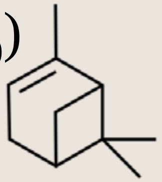


Rhizosphere

Isoprene (C_5)

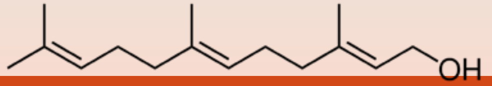
Monoterpenes (C_{10})

e.g., α-Pinene



Sesquiterpenes (C_{15})

e.g., Farnesol



Precursors of:

- O_3 (tropospheric ozone – at ground level)

  (NO_X + *VOC* + *heat & sunlight* = *Ozone*)

- Secondary organic aerosols (SOA)
- Human health

Anthropogenic VOCs

Human daily activity

http://clipart-library.com/clip-art/transparent-background-dog-11.htm
Shen X, Zhao Y, Chen Z, Huang D (2013) Heterogeneous reactions of volatile organic compounds in the atmosphere. Atmos Environ 68:297–314.

Livestock facilities

Decrease property value

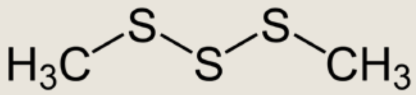
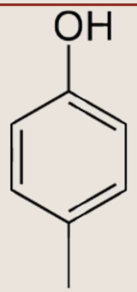
Causes of climate change, air pollution, effect of air quality

- Stress
- Depression
- Fatigue
- Headache
- Respiratory problems
- Eye irritation
- Nausea
- Weakness
- Chest tightness

Ciganek M, Neca J (2008) Chemical characterization of volatile organic compounds on animal farms. 2008:641–651

Decoding the odor of animal waste

Alcohols, acids, amines, aldehydes, hydrocarbons, indoles, ketones, phenols, sulfides, mercaptans

VOC	Structure	Odor threshold (ppm)	Human effects	Odor description
Dimethyl trisulfide (DMTS)		0.003 – 0.006 (AIHA*** 2013)	Skin, eyes, and respiratory irritation (Bp et al. 2009)	Onion/sulfur, fish, rotten cabbage (Rosenfeld et al. 2007)
4-Methylphenol (p-cresol)		0.00005 - 0.009 (AIHA 2013)	Dryness, nasal constriction, throat irritation, effects on gastrointestinal system, blood, liver, kidney (U.S. EPA 2000), HAPs (U.S. EPA 2008)	Sweet, tar, urine (Kamarulzaman et al. 2019)

*U.S. EPA = United States Environmental Protection Agency
**HAPs = Hazardous Air Pollutants
*** AIHA = American Industrial Hygiene Association

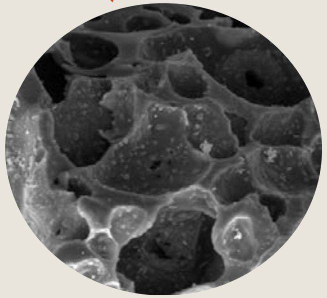
Biochar

International Biochar Initiative (IBI) → Thermochemical conversion of biomass in a low oxygen environment.

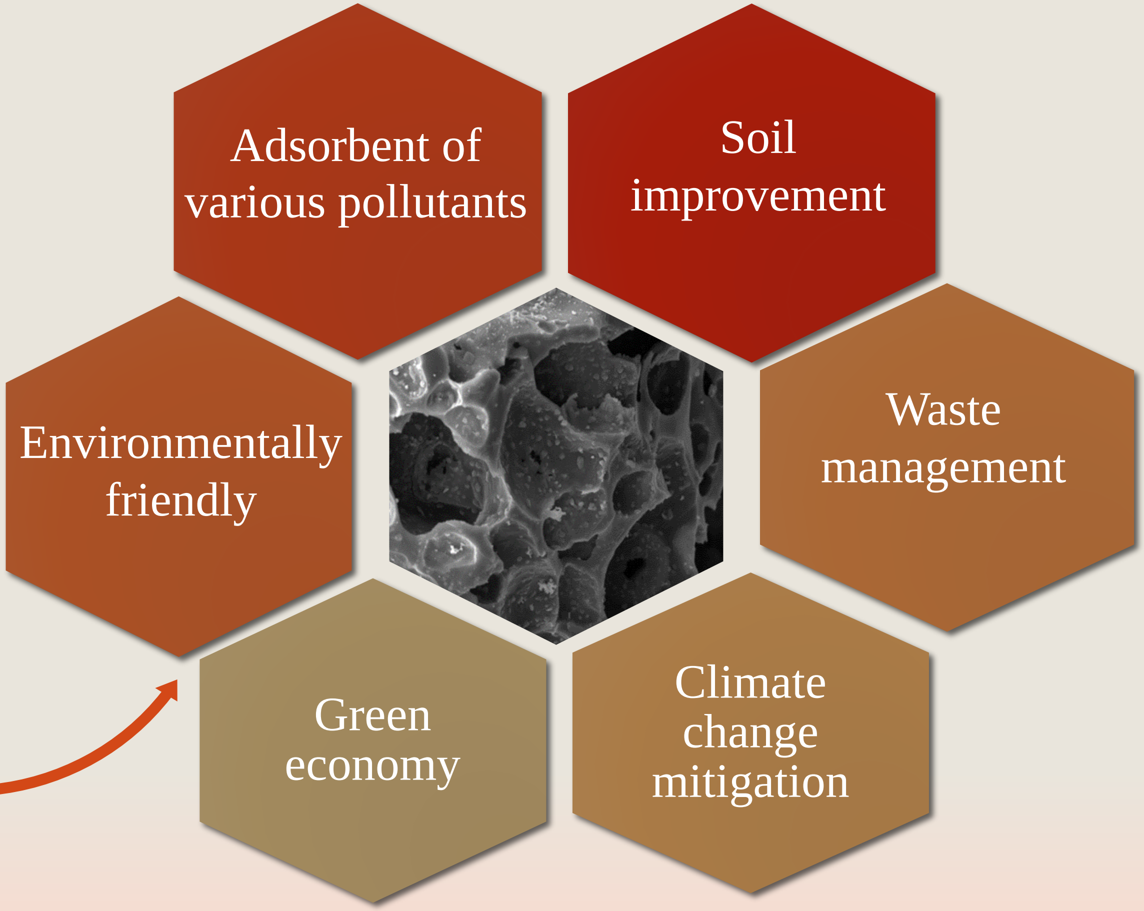
Biomass

Pyrolysis

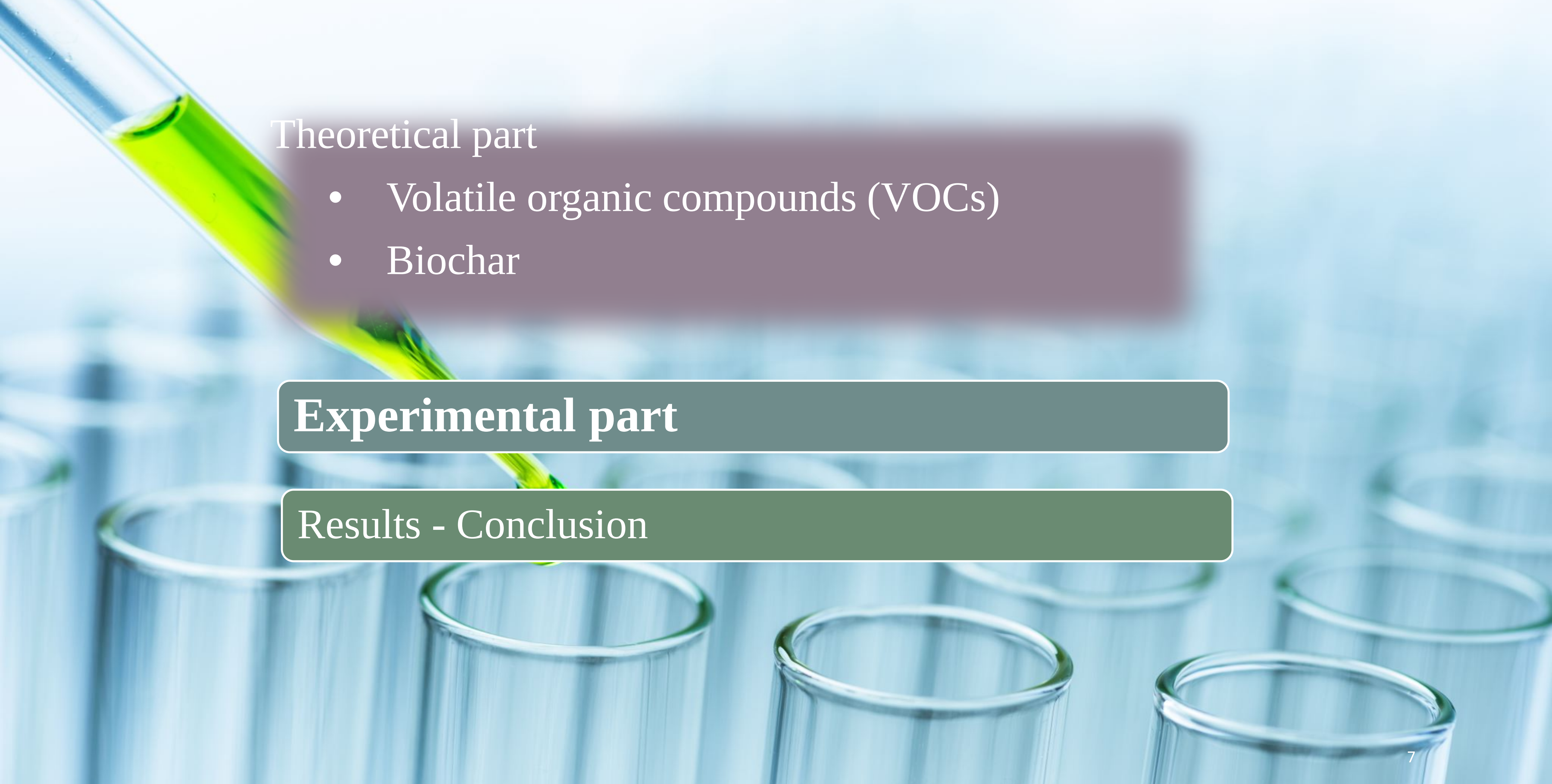
- Slow heating rate
- 100-1000 °C



Biochar



Contents


Theoretical part
• Volatile organic compounds (VOCs)
• Biochar
Experimental part
Results - Conclusion

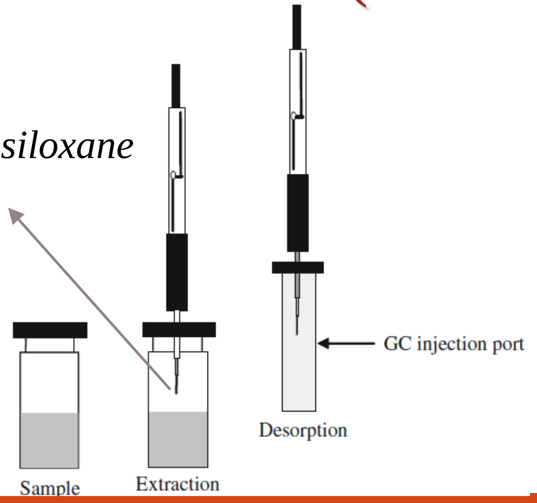
GC-MS system

GC 7890B/MS 5977B, Agilent

GC conditions	Column	SPB-624 (60 m × 0,25 mm i.d. × 1,4 μm film thickness, Supelco)
	Injector	280 °C
	Carrier gas	He (99,999 %)
	Column flow	1.7 mL / min
	Injector	Spitless
MS conditions	Oven temperature program	35 °C (5 min), 4 °C/min to 180 °C (held 20 min)
	MS source	230 °C
	MS quad	150 °C
	Transfer line	250 °C
	Mass range and mode	35-350 m/z, full scan
	MS operation	Electron impact ionization at 70 eV
	Mass analyzer	Quadrupole
	Detector	Electron multiplier
	Library	NIST17

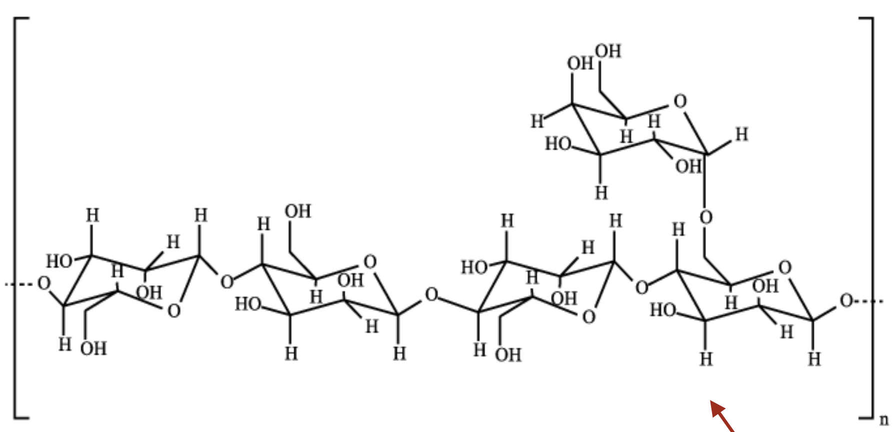
Solid-phase microextraction (SPME)

75-μm Carboxen-polydimethylsiloxane (CAR/PDMS)



Castro R, Natera R, Durán E, García-Barroso C (2008) Application of solid phase extraction techniques to analyse volatile compounds in wines and other enological products. Eur Food Res Technol 228:1–18

Biomass pyrolysis



350 °C

550 °C

Nabertherm GmbH, N_2 100 L/h, 1 bar

Pomegranate peels (PB)

Locust bean gum (LBGB)

Carob (CB)

Prickly pear peels (PPB)

Characterization of biochar

Scanning electron microscopy (SEM)

Elemental analysis (EA)

Brunauer–Emmett–Teller (B.E.T.)

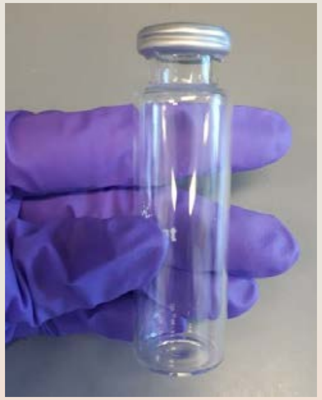
Determination of VOCs in manure

HS-SPME/GC-MS

In-house made glass jars (250 mL) + fresh cattle manure (100 g)

Calibration curves

- Dimethyl trisulfide (DMTS)
- p-Cresol



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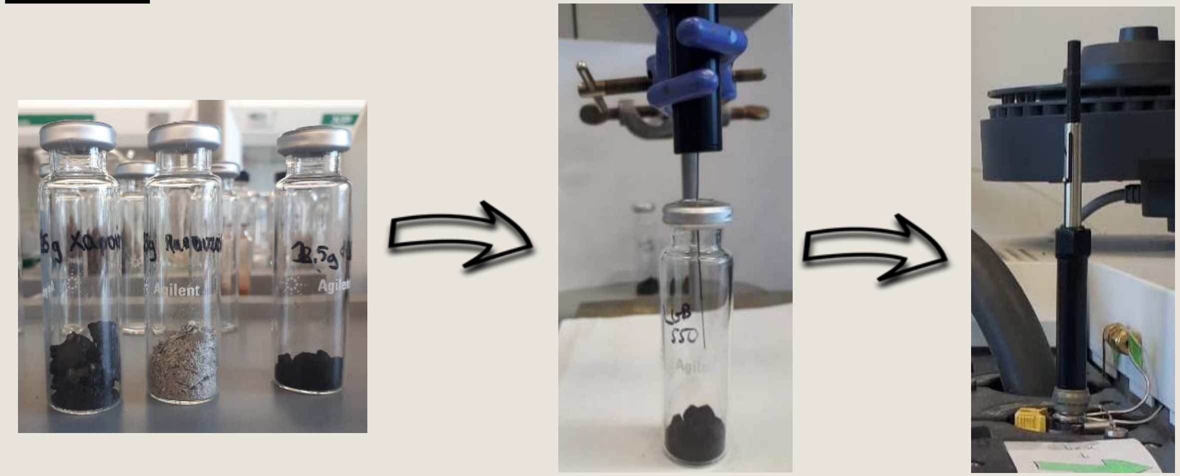
VOCs removal experiments



A) Effect of contact time (n ≥ 3)

p-Cresol

Biochars (1 g)	Contact time (min)
PB (350, 550 °C)	30 - 480
CB (350, 550 °C)	30 - 480
PPB (350, 550 °C)	30 - 480
LBGB (350, 550 °C)	30 - 360

DMTS

Biochars (1 g)	Contact time (min)
PB (350, 550 °C)	30 - 480
CB (350, 550 °C)	30 - 480
PPB (350, 550 °C)	30 - 780
	30 - 480
LBGB (350, 550 °C)	30 - 240

B) Effect of VOCs concentration (n ≥ 3)

p-Cresol: 100 - 1000 ppb_v

DMTS: 50 - 900 ppb_v

Contents

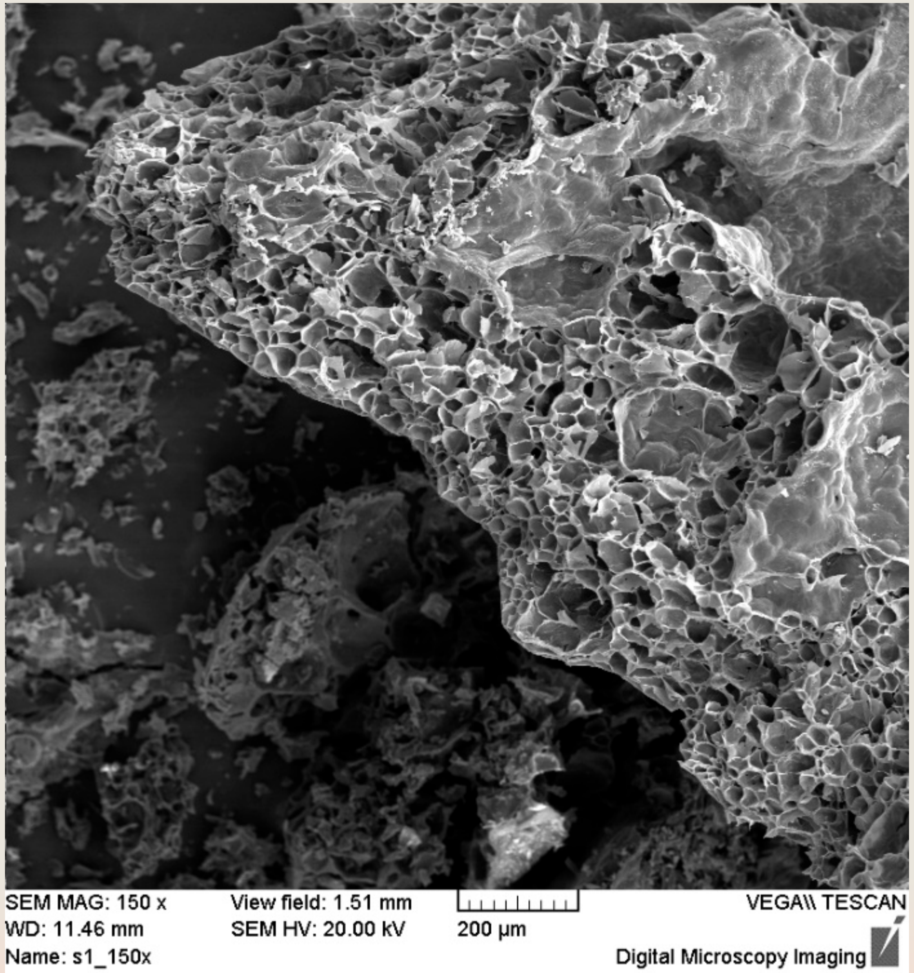
Results of Elemental Analysis (EA) and yield of biochars

Biochar	C (%)	N (%)	Yield (%)
PB 350 °C	79.7	0.5	23.4
PB 550 °C	67.3	0.0	19.3
CB 350 °C	59.5	0.8	40.3
CB 550 °C	89.3	0.3	22.6
PPB 350 °C	75.2	0.2	8.0
PPB 550 °C	95.6	0.0	2.9
LBGB 350 °C	69.2	0.7	30.4
LBGB 550 °C	59.8	0.4	22.4
Pomegranate peels	37.3	0.3	-
LBG	62.1	1.0	-
Carob	42.0	0.5	-
Prickly pear peels	37.4	0.4	-

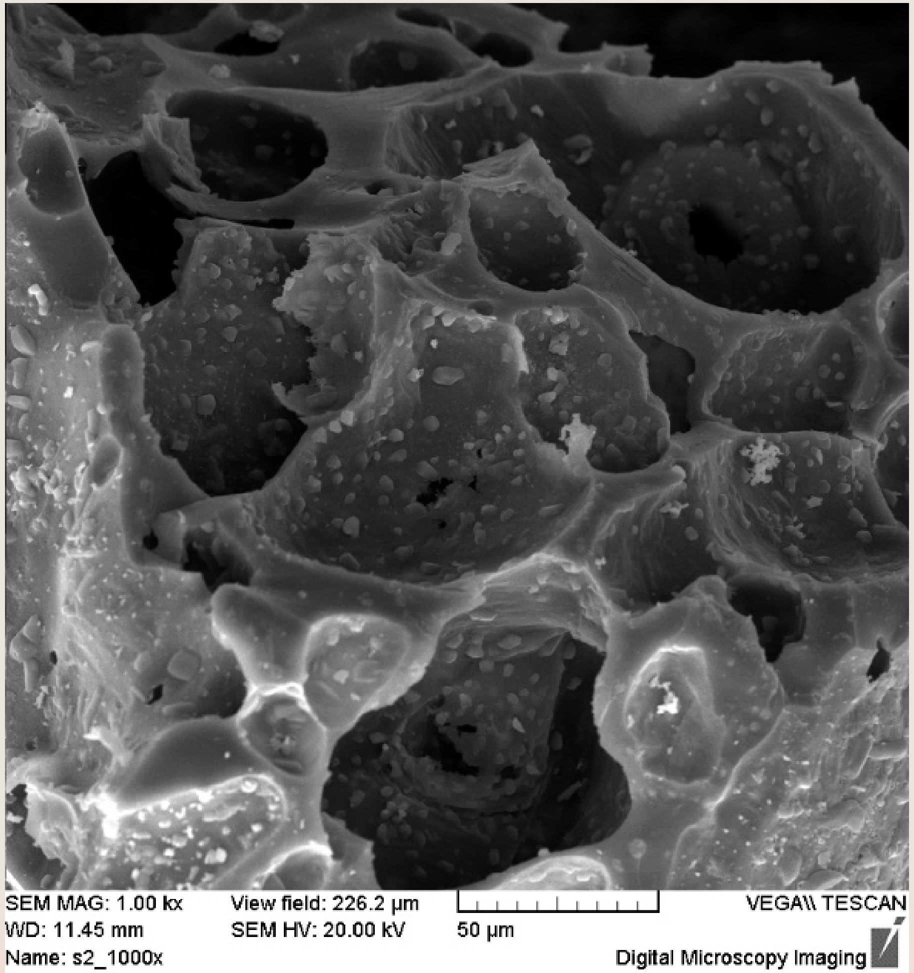
Raw materials (Pomegranate peels, LBG, Carob, Prickly pear peels)

Results of SEM

PB 350 ℃



PB 550 ℃



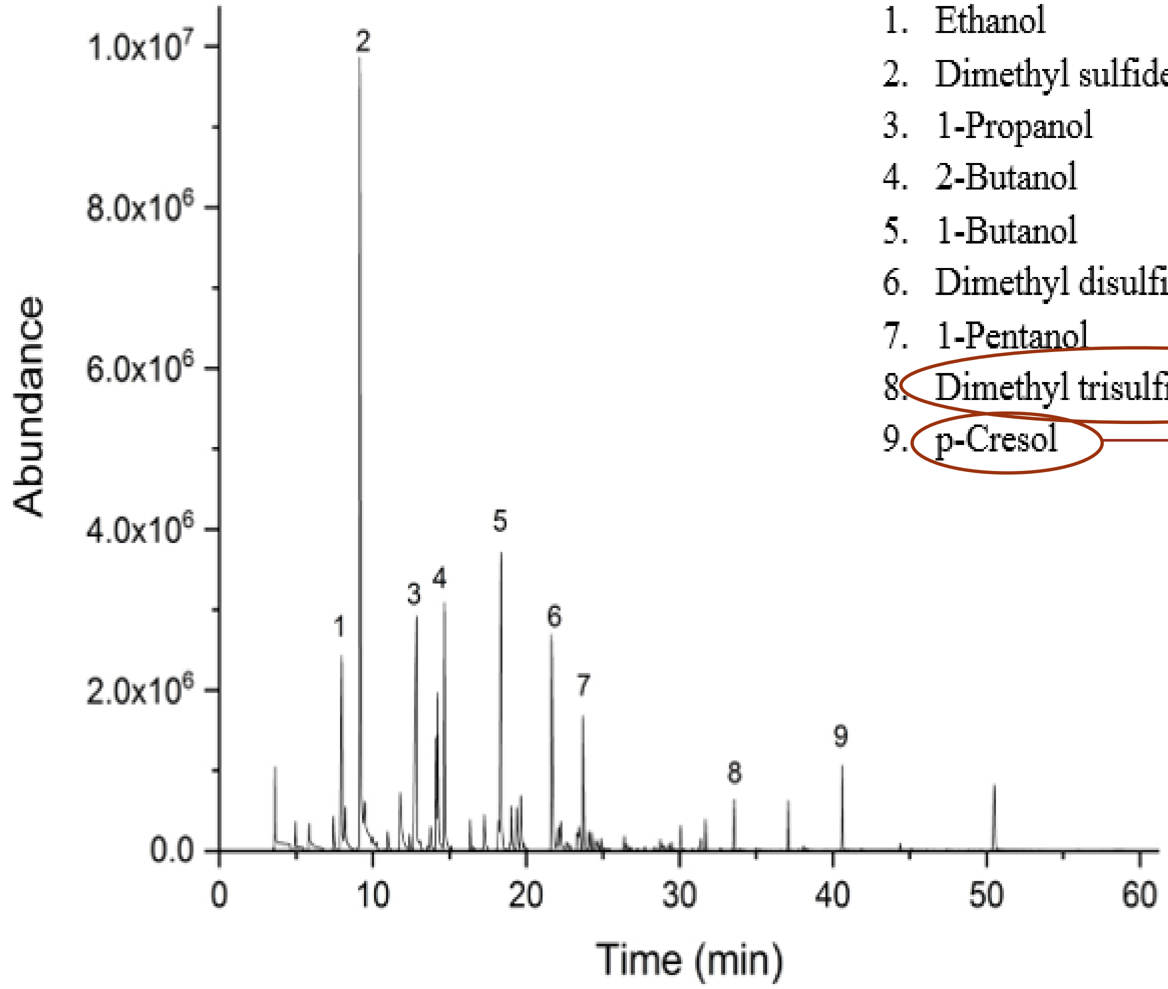
Results of BET

Biochar	Specific surface area (m^2 / g)
PB 350 °C	0.79
PB 550 °C	8.27
CB 350 °C	1.63
LBGB 350 °C	0.83
LBGB 550 °C	2.11
Manure biochar (Stylianou et al. 2020)	14.03

Stylianou M, Christou A, Dalias P, et al (2020) Physicochemical and structural characterization of biochar derived from the pyrolysis of biosolids, cattle manure and spent coffee grounds. J Energy Inst 93:2063–2073.

Identification of VOCs of cattle manure

HS-SPME-GC-MS chromatogram



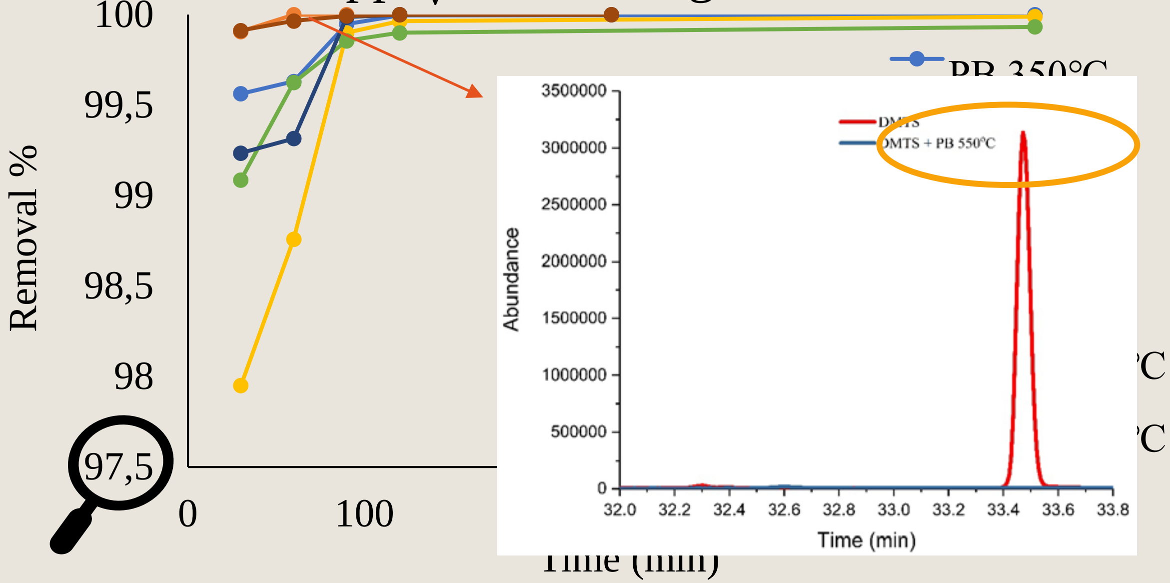
1. Ethanol
2. Dimethyl sulfide (DMS)
3. 1-Propanol
4. 2-Butanol
5. 1-Butanol
6. Dimethyl disulfide (DMDS)
7. 1-Pentanol
8. Dimethyl trisulfide (DMTS)
9. p-Cresol

Calibration curves

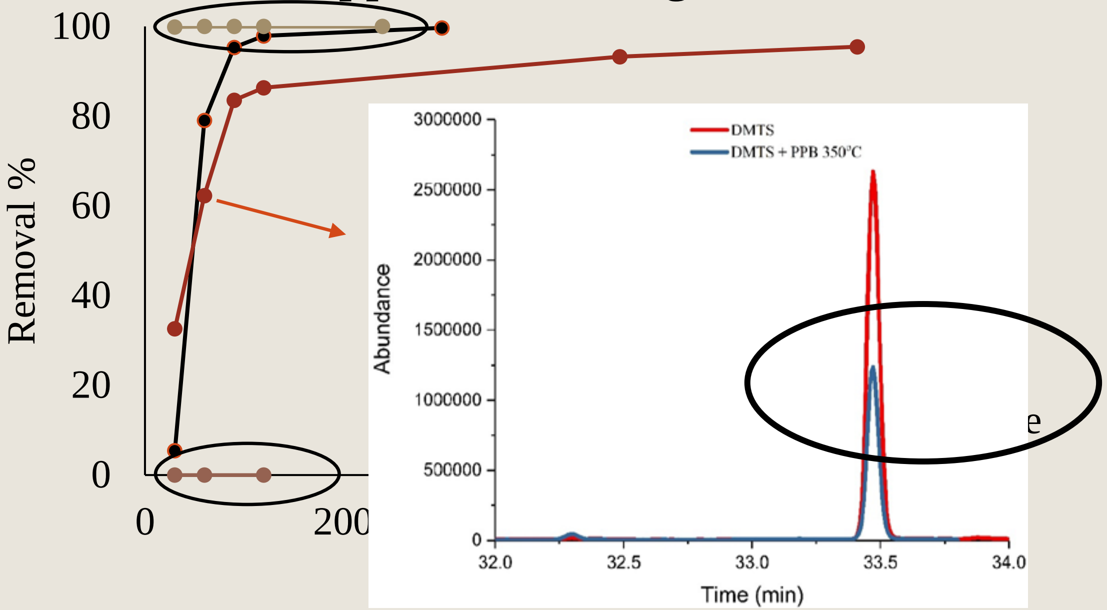
Results of targeted-VOCs removal experiments

Effect of contact time (n ≥ 3)

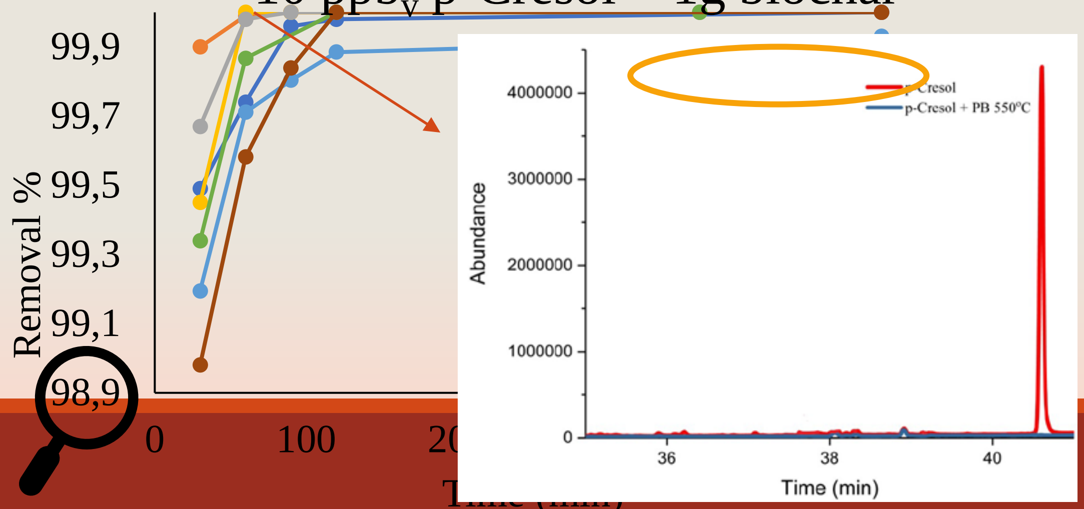
10ppb$_v$ DMTS + 1g biochar



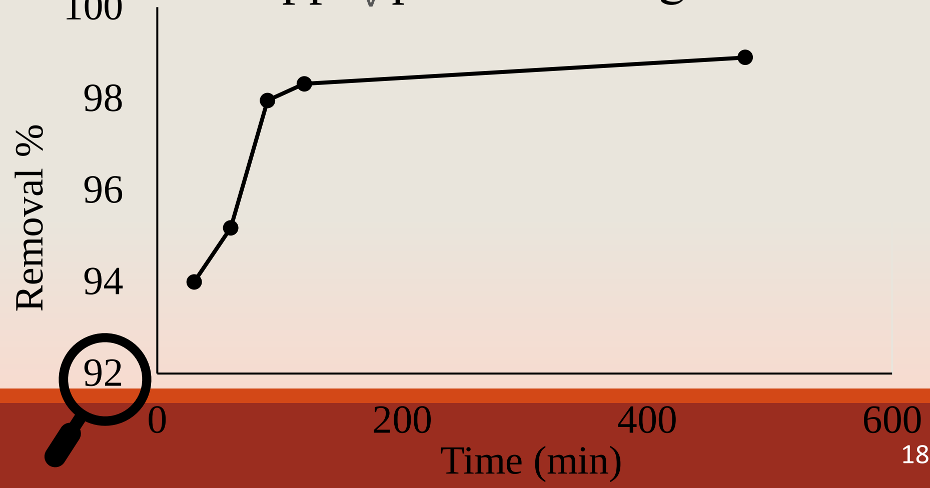
10ppb DMTS + 1g biochar



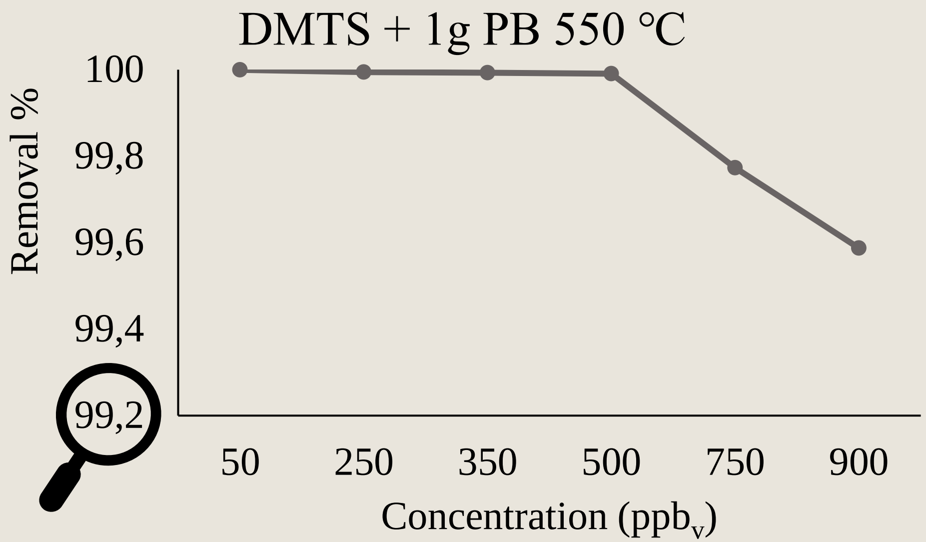
10 ppb$_v$ p-Cresol + 1g biochar

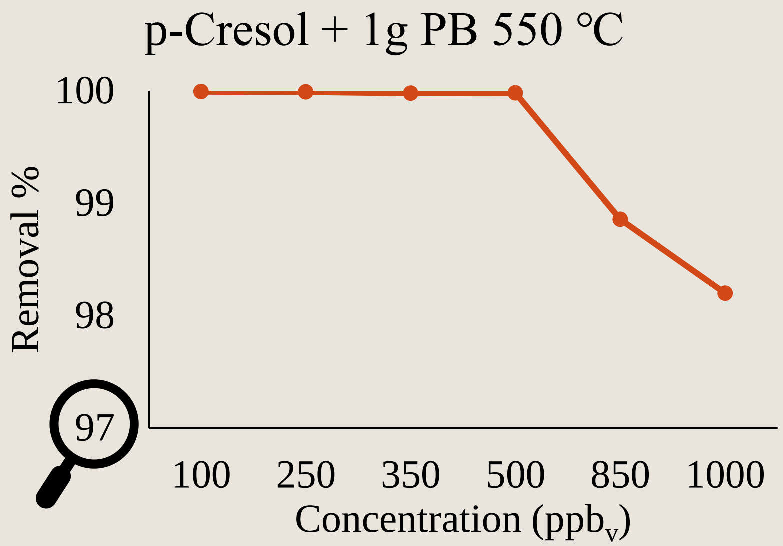


10 ppb$_v$ p-Cresol + 1g PPB 350°C



Effect of VOCs concentration (n ≥ 3)





Conclusions

1. Good removal of target -VOCs from all biochars.
2. SEM microstructure of PB 550 °C indicate rough honeycomb pattern with many cavities.
3. Increase of the T of pyrolysis ⟶ increase the specific surface area of the biochars (SSA)
4. The targeted -VOCs (DMTS, cresol) were removed from PB 550 °C in a short time (in most cases at 60 min).

Conclusions

5. The order of increasing ability for the total removal of VOCs from biochars for 60 min contact is as follows:

   PPB 350 ℃ < CB 350 ℃ < PPB 550 ℃ < CB 550 ℃ ≤ LBGB 350 ℃ ≤ PB 350 ℃ < LBGB 550 ℃ < PB 550 ℃

6. Effect of contact time: Ideal biochar = PB 550 ℃

7. Effect of VOCs concentration: Decrease of removal ability

Thank you!