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INTERNATIONAL CONFERENCE

CONTAMINATED SITES 2018

BANSKÁ BYSTRICA, SLOVAK REPUBLIC, 8 – 10 OCTOBER 2018

The activity has been implemented within the framework of national project
Information and providing advice on improving the quality of environment in Slovakia.
The project is cofinanced by Cohesion Fund of the EU under Operational programme Quality of Environment.

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Biochar Applications to Support Soil Remediation

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Biochar – the Swiss army knife for all remediation problems?

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OUTLINE

- Contaminated sites – a never-ending task?
- How to deal with contaminated sites?
- Mechanisms of interactions between biochar and inorganic pollutants
- Mechanisms with organic pollutants
- Limitations and practical application issues

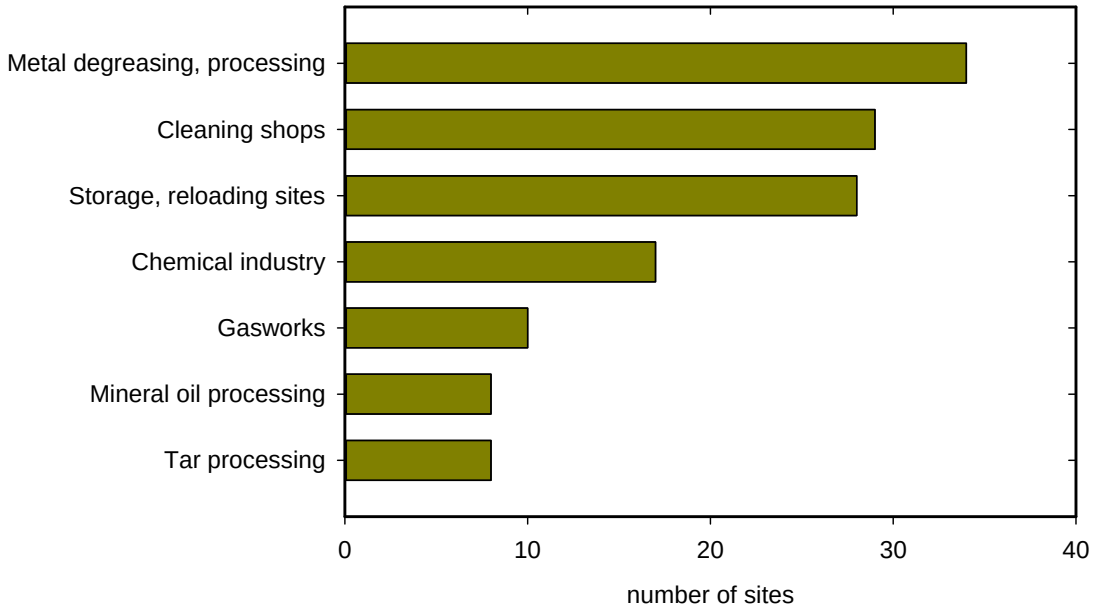
From Landfills and Industry Sites to Contaminated Sites

Austria, 01/2018:

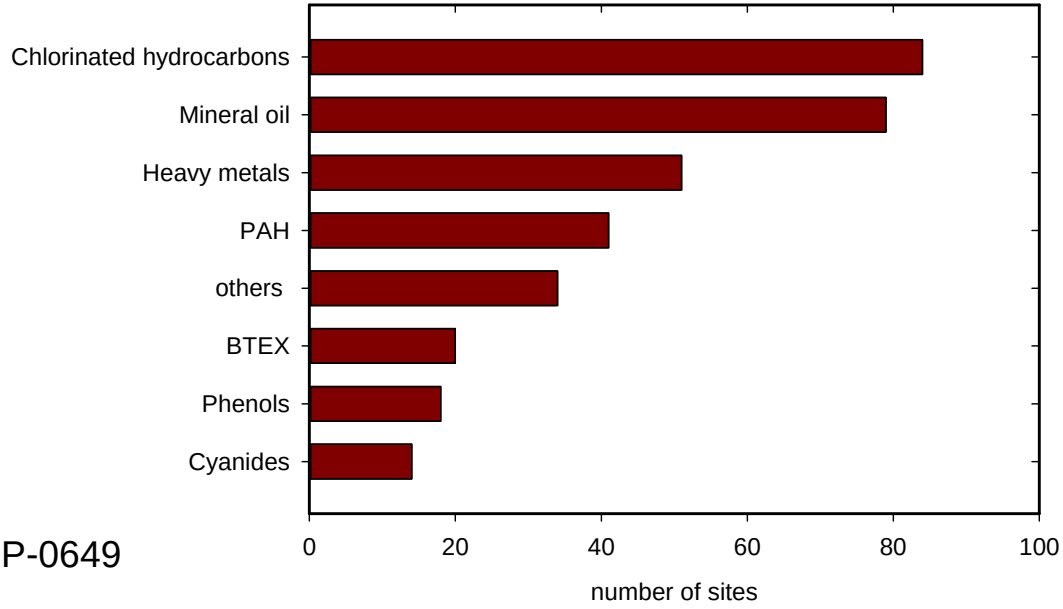
- 68,699 former landfills and potentially contaminated sites are registered
- Thereof 1,896 in the registry of suspected contaminations
- Thereof 293 confirmed as as contaminated sites („significant risk for environment and human health“)
- Thereof 157 already remediated

Source: Granzin and Valtl, 2018; UBA-Report REP-0649

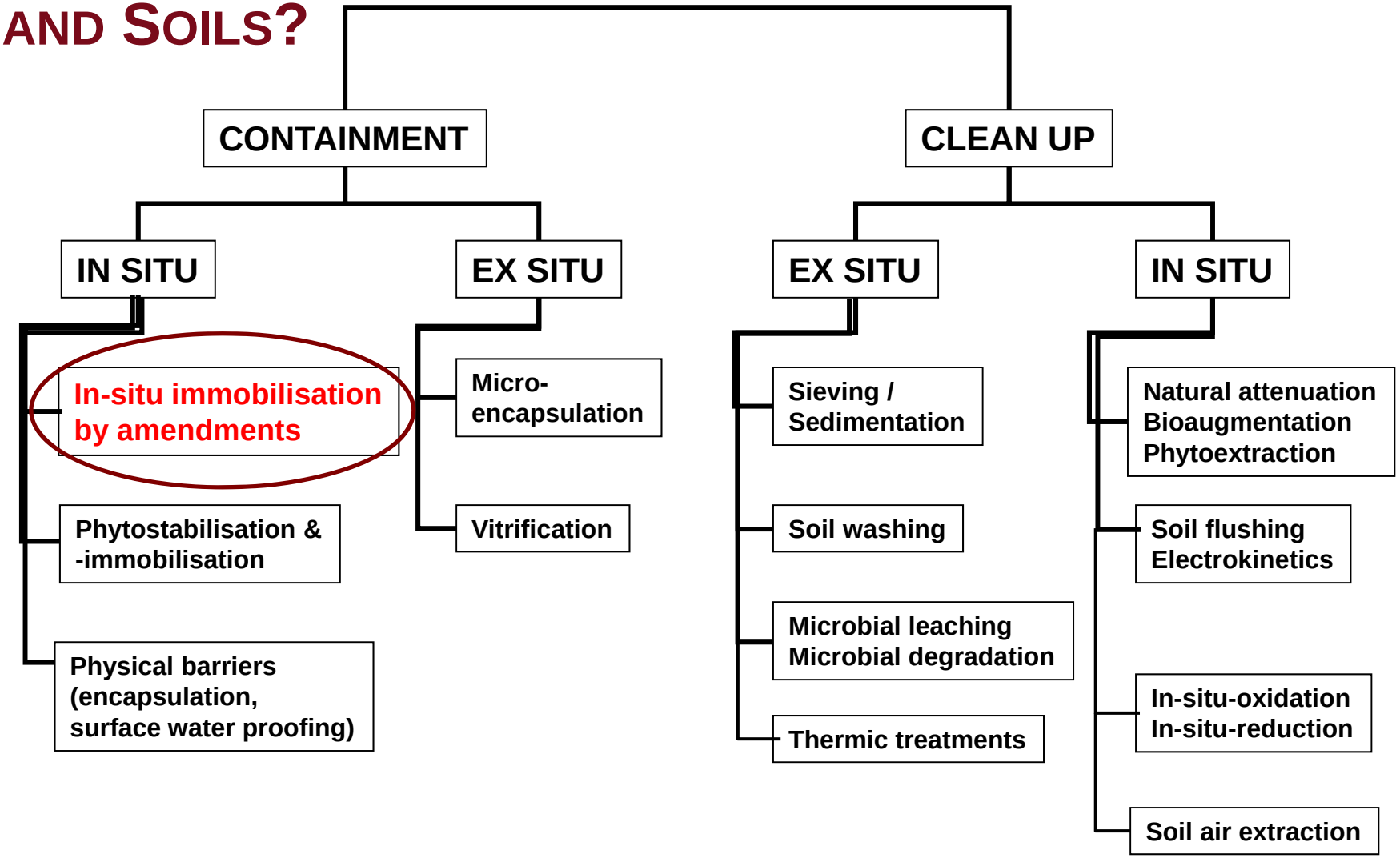
Distribution of industry branches for confirmed contaminated sites



Frequency of pollutants in confirmed contaminated sites



What are the Main Remediation Technologies for Contaminated Sites and Soils?



Source: Lombi et al. (2000) (modified)

IMMOBILISATION-OPTIONS

- Main objective:
  - Leaching and translocation of pollutants should be reduced or prevented
  - Reduction of (bio-)available fractions, but not of total concentrations
- Solidification by
  - mineral binders (gypsum, lime, cement, clay minerals, (synthetic) zeolites
  - organic resins (e.g. urea-formaldehyde-resin)
  - bituminous binders and natural asphalt
- eco-landfill © („diagenetic inertisation“)
  - 67 % landfill material
  - 33 % additives (clay mud, lime, rock flour)
- **Chemical/physical binding with soil amendments**

SOIL AMENDMENTS FOR IMMOBILISATION

1. Ca-rich additives

Lime, gypsum, Ca-apatite, mud from water decalcification

2. Residues from incineration

Fly ash, slag, berengite (Ca-Al-silicate)

3. Silicates

Bentonite, montmorillonit, smektite, zeolite

4. Organic material

Compost, bark mulch, peat etc.

5. Carbonized biomass

***Biochar**, activated biochar, charcoal*

5. Al-, Fe-, Mn-oxides

Red mud, scrap steel, birnessit (Mn-oxide); siderite (Fe-carbonate)

6. Combination products, (nano-)composites

Photo: Wolfgang Friesl-Hanl

Binding and Solubility of Heavy Metals in Soil

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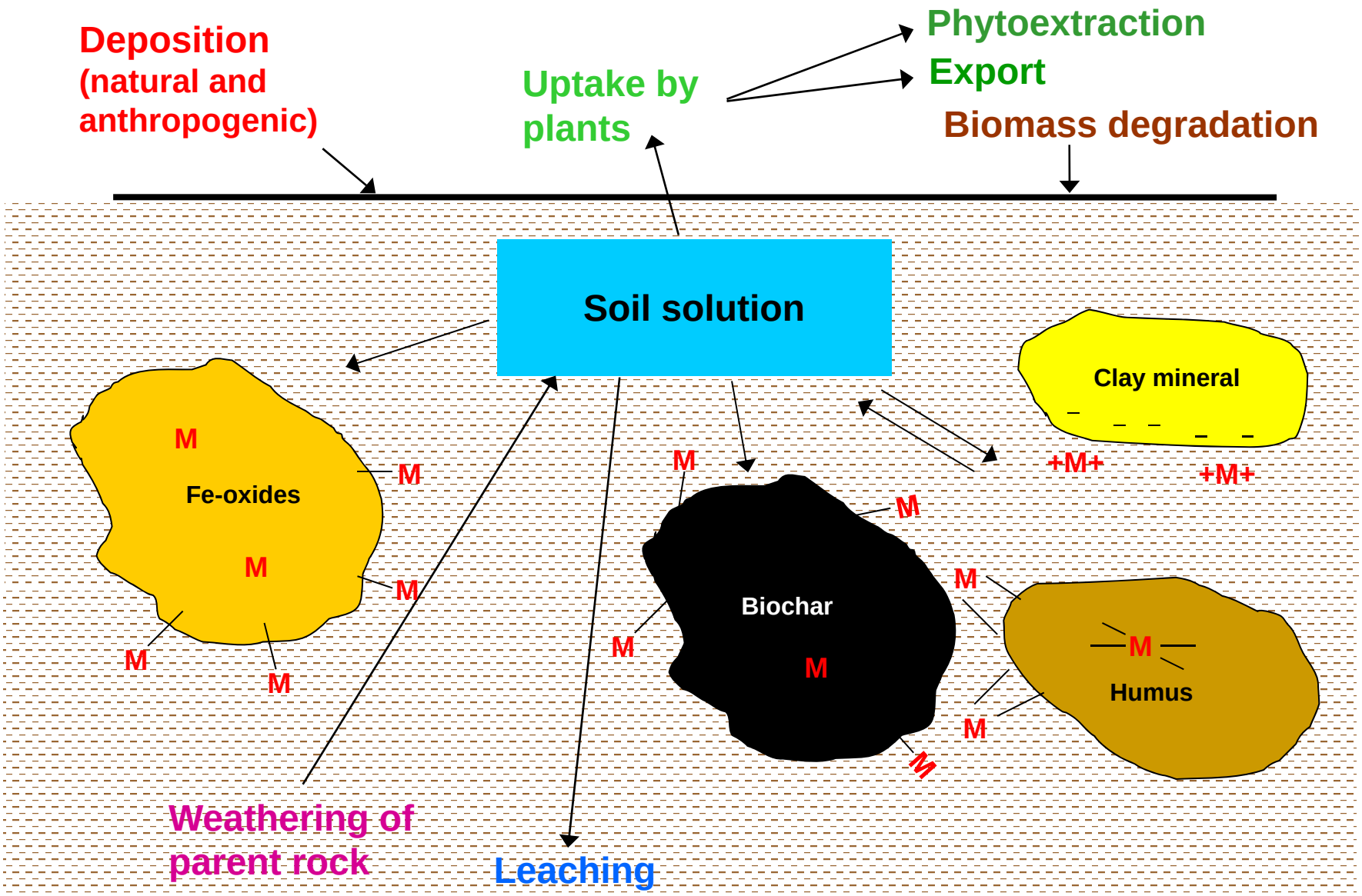

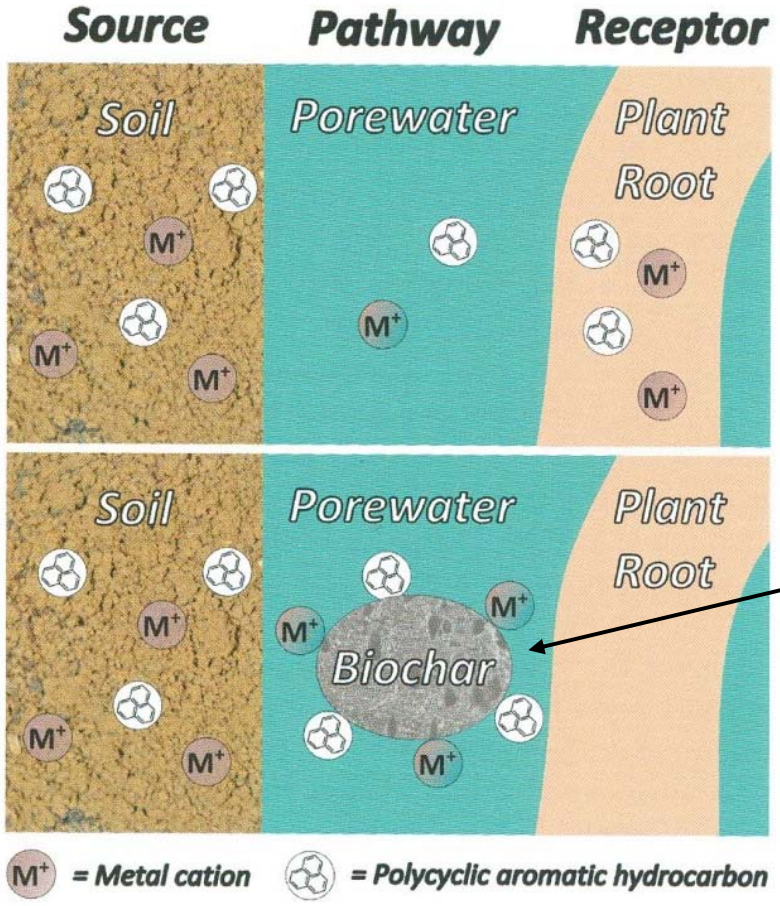

MODE OF ACTION OF BIOCHAR IN THE REMEDIATION OF CONTAMINATED SOILS:

DISRUPTION OF THE CONNECTION FROM THE CONTAMINANT SOURCE (SOIL) TO THE RECEPTOR (PLANT ROOT)

Source: Sizmur et al., 2016 (SSSA Special Publications 63)

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IMMOBILISATION OF HEAVY METALS WITH BIOCHAR: DIRECT MECHANISMS

- Chemical sorption
  - Reaction of functional groups at the biochar surface (e.g. carboxyl-, hydroxyl-, phenol-, carbonyl-groups)
- Physical sorption
  - Elektrostatic interactions between metallic cations and negatively charged biochar surfaces

FROM CELLULOSE AND LIGNIN ….

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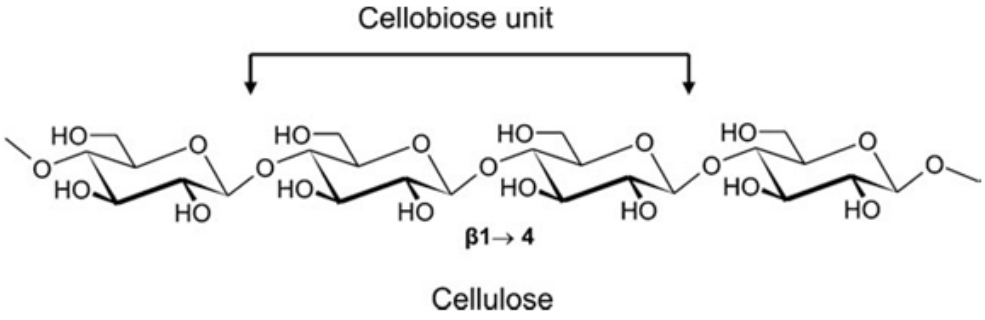
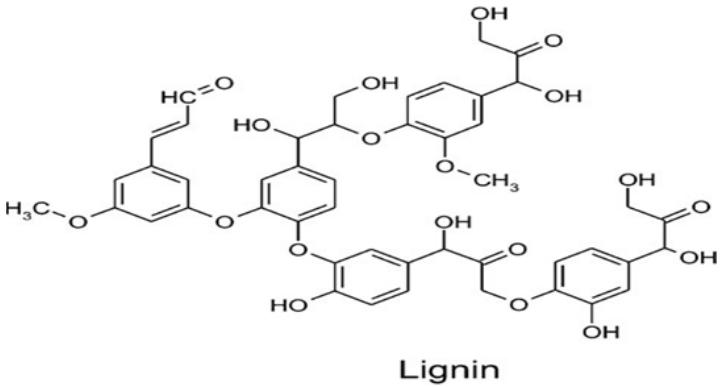
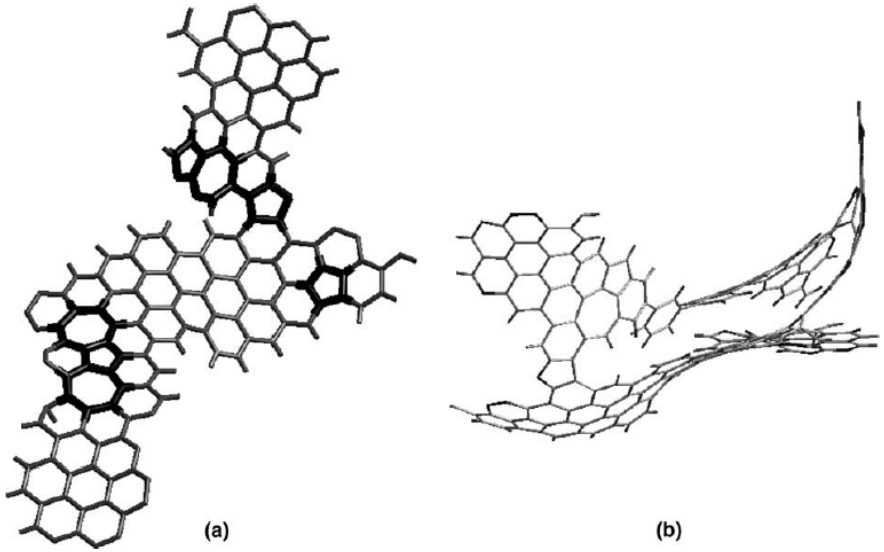
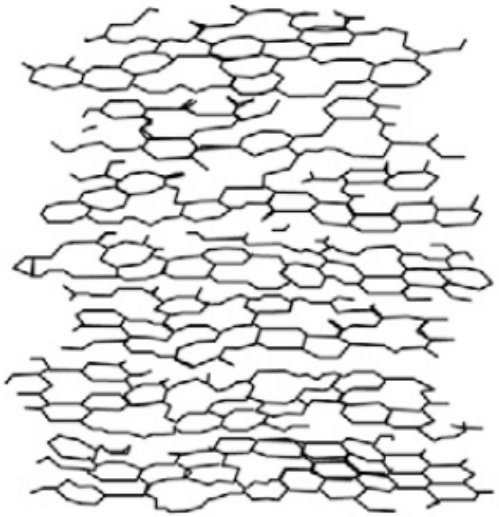




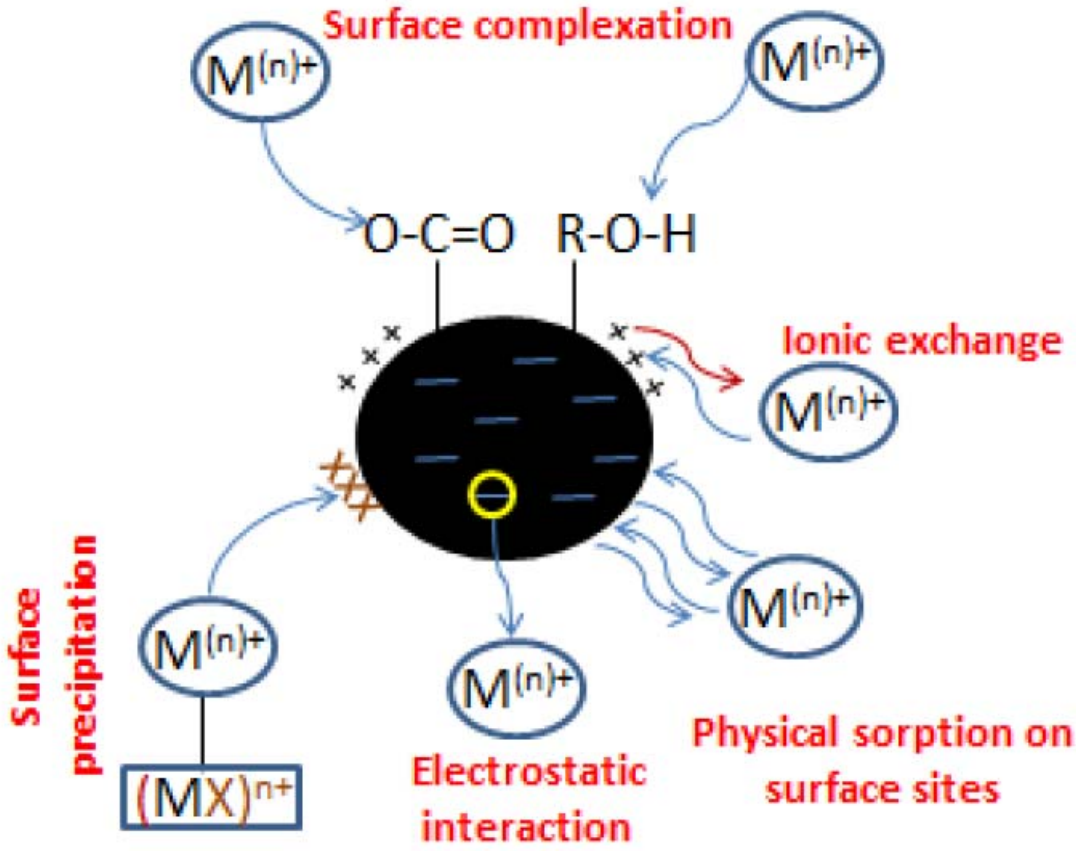
…. DURING PYROLYSIS TO GRAPHENE-LIKE STRUCTURES





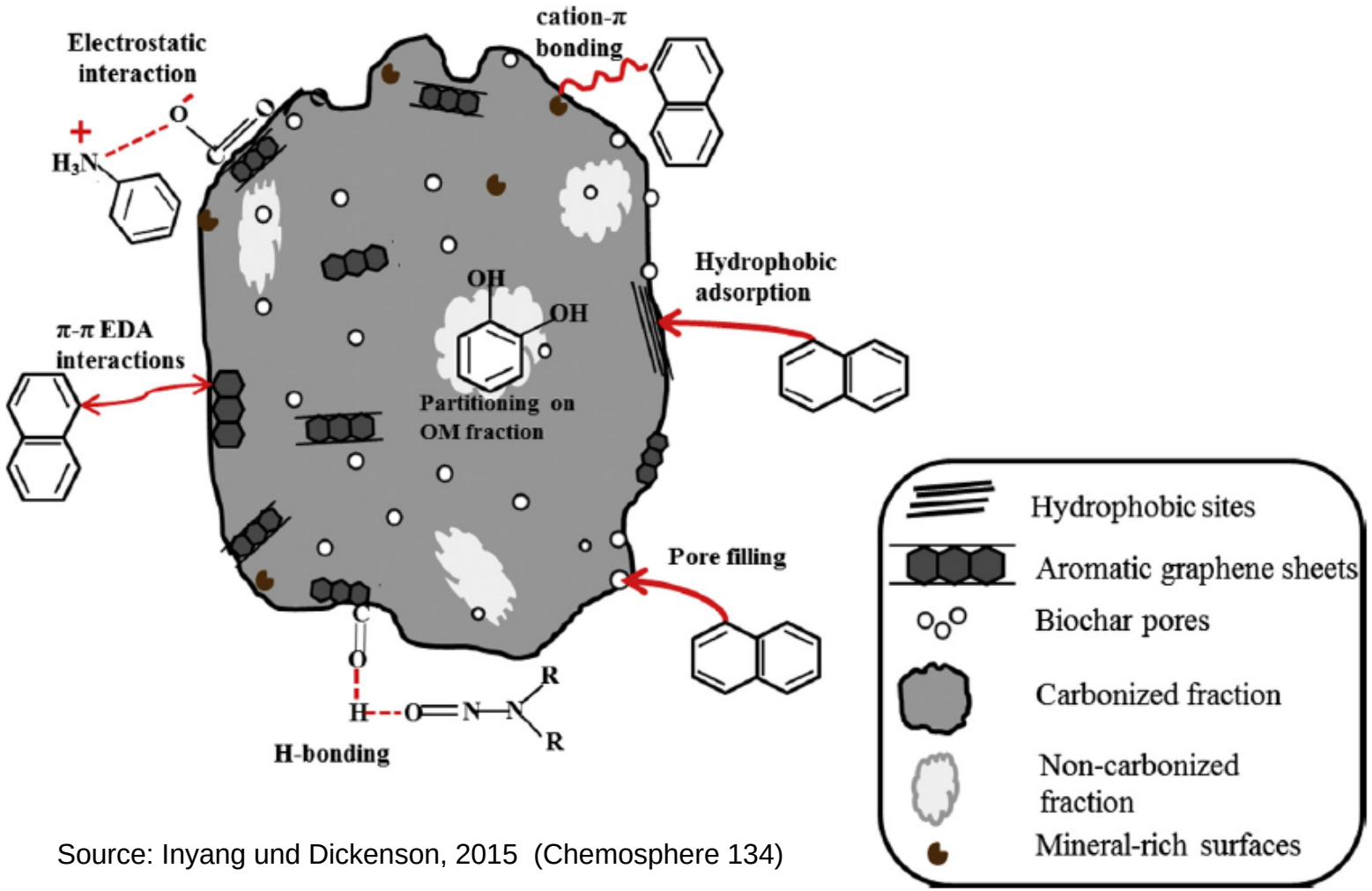
Sources: http://usmle.biochemistryformedics.com/role-of-dietary-fibre/
Kumar et al., 2005; Schimmelpfennig & Glaser, 2012

SORPTION MECHANISMS FOR METALS TO BIOCHAR



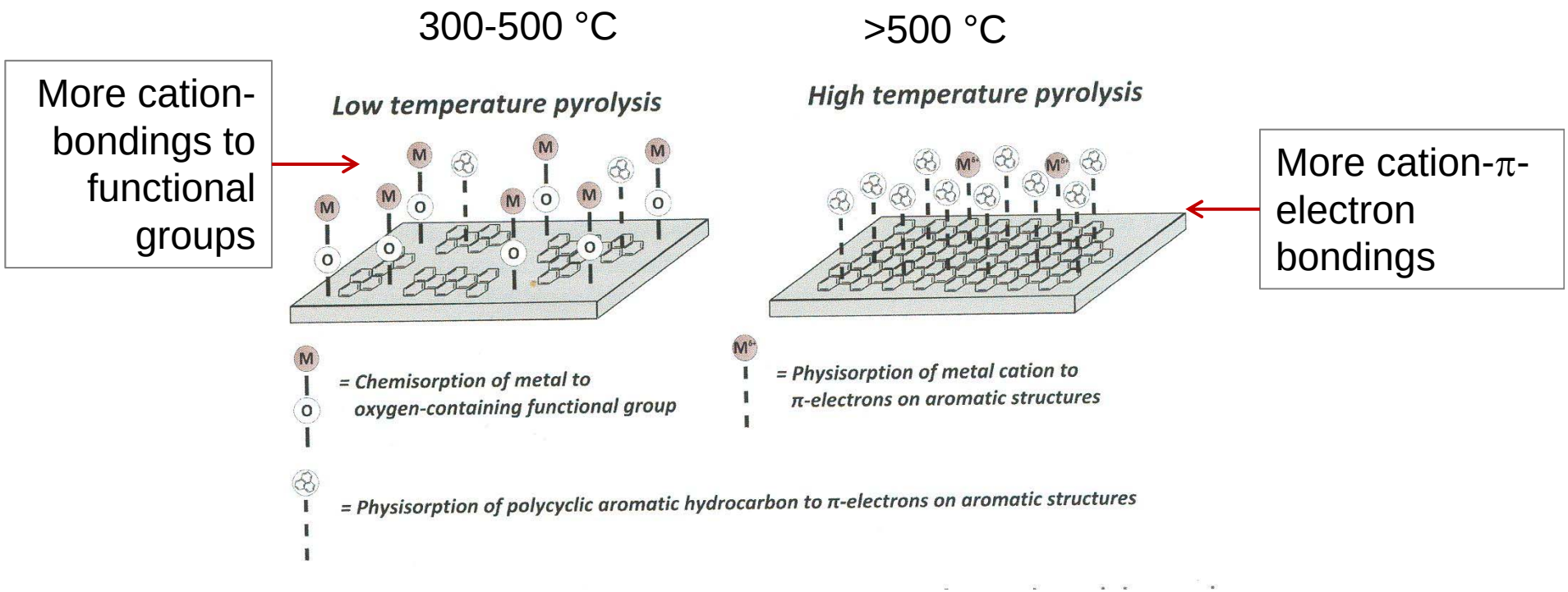
Source: Inyang et al., 2015 (Critical Reviews in Environmental Science and Technology)

SORPTION MECHANISMS FOR ORGANIC CONTAMINANTS TO BIOCHAR



Source: Inyang und Dickenson, 2015 (Chemosphere 134)

DOMINATING BONDING MECHANISMS OF POLLUTANTS TO DIFFERENTLY PRODUCED BIOCHARS



Source: Sizmur et al., 2016 (SSSA Special Publications 63)

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BONDING MECHANISMS OF HEAVY METALS TO BIOCHAR: INDIRECT MECHANISMS

- Change of pH
  - High pH of biochar reduces the solubility of metals by the formation of metal hydroxides
- Increase of organic matter in soil
  - Biochar increases DOC – some metals preferably form complexes with organic matter (e.g. Cu)
- Interactions with phosphate
  - Some heavy metals can be precipitated as phosphates (e.g. Pb). However, As may be mobilized by P!
- Change of redox-conditions
  - By changing the oxidation-state of redox-sensitive metals their speciation may change

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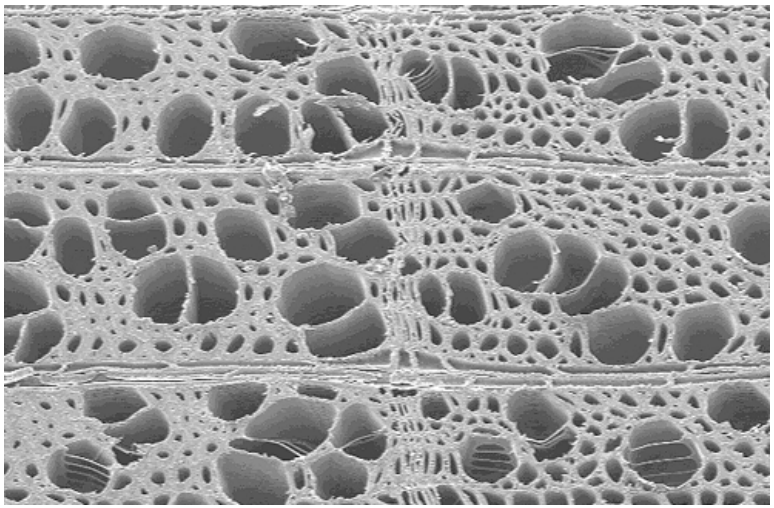
INCREASE OF SPECIFIC SURFACE AREA DURING CARBONIZATION OF PLANT BIOMASS BY CREATING ADDITIONAL PORES

Source: E.V. Kultikova, 1999



Pyrolysis

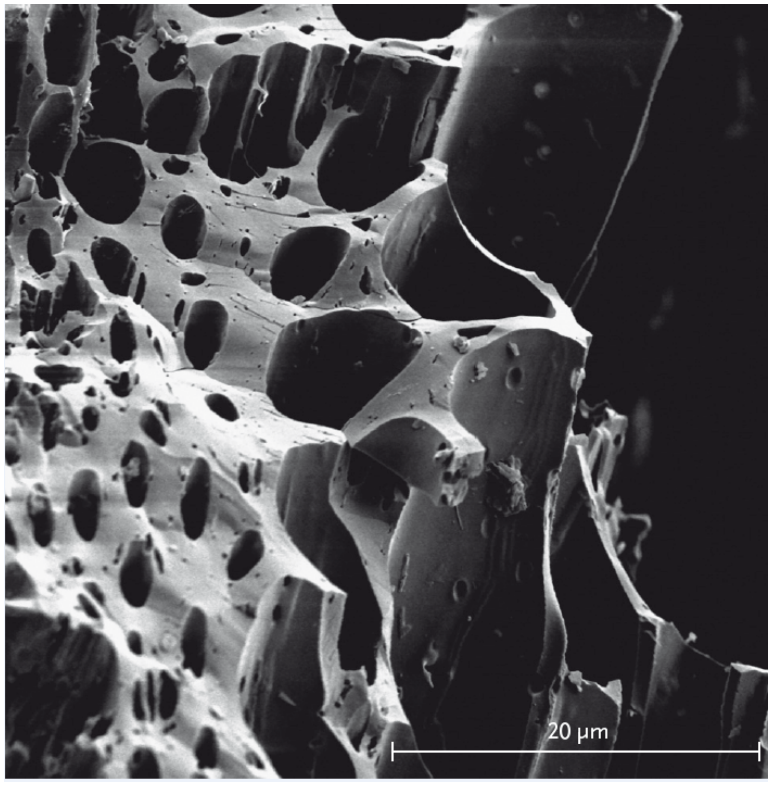


Photo: Martin Brandstetter

Biochar in soil remediation: Meta-analysis of pollutant sorption to biochar

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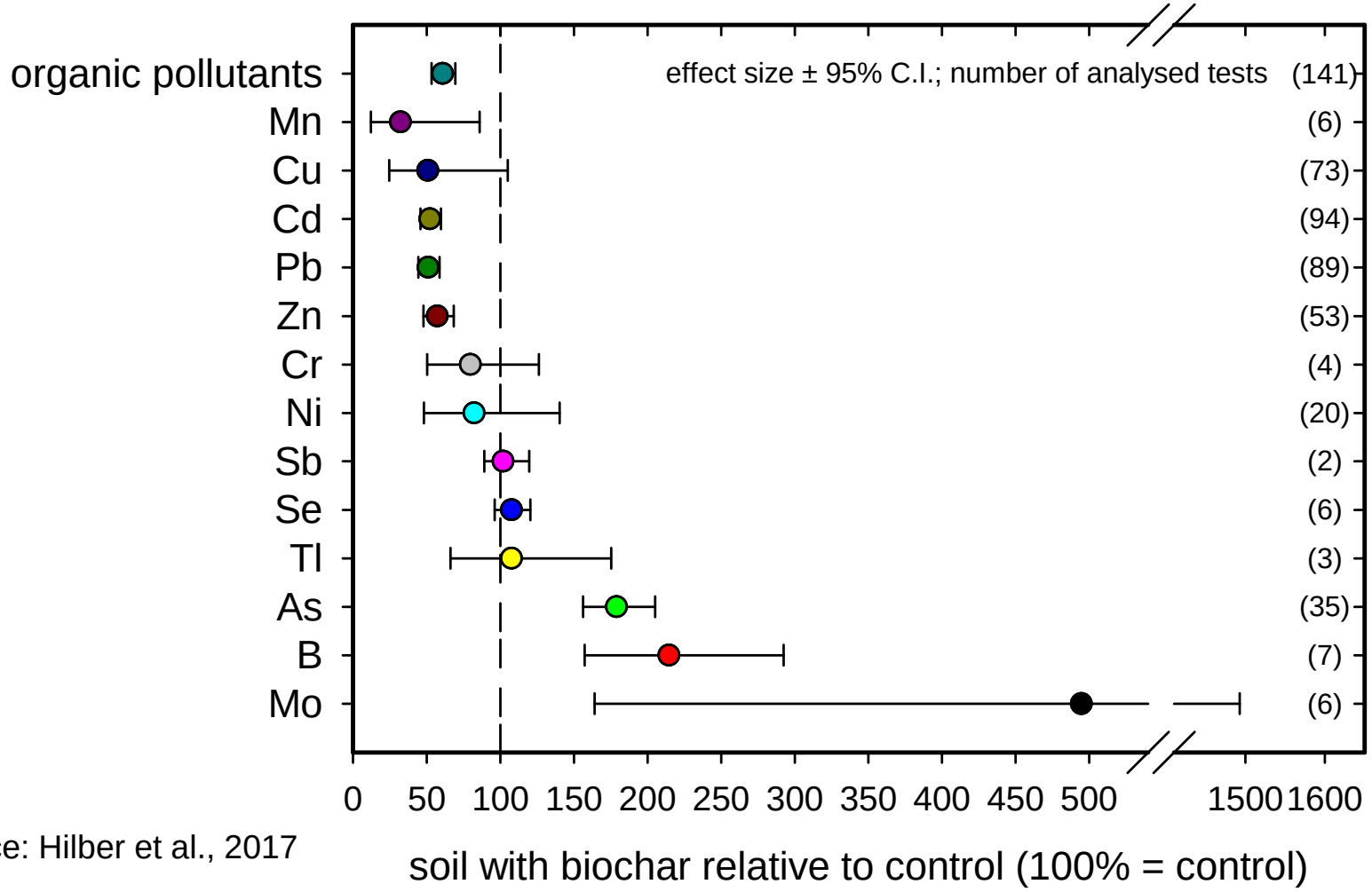
Differences between contaminants in availability from soil in reaction to biochar application

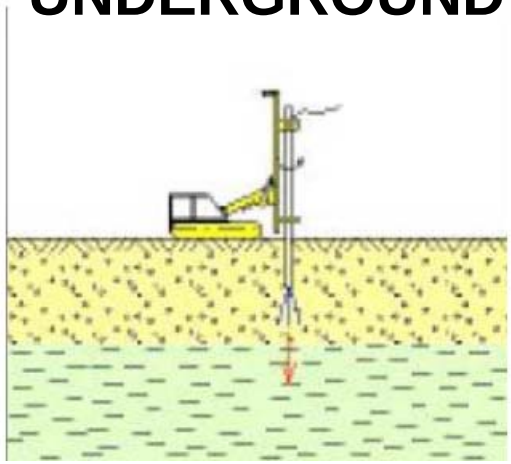


Source: Hilber et al., 2017

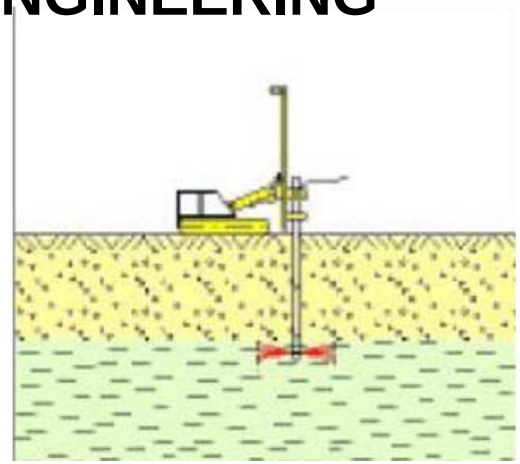
Options for Counter-measures: Modification of the feedstock for pyrolysis or of the biochar product

- „Building bridges“ (between biochar surface and the sorbate)
  - Fe-, Mn- modified biochar binds anionic substances better
- (Partial) oxidation of biochar
  - H_2O_2 etc.
- Increase the attached functional groups
  - E.g. by weak organic acids
- „Activated“ biochar (in analogy to activated charcoal)
  - Water vapour activation, strong acids or bases
- Composites with clay minerals
  - Zeolites etc.

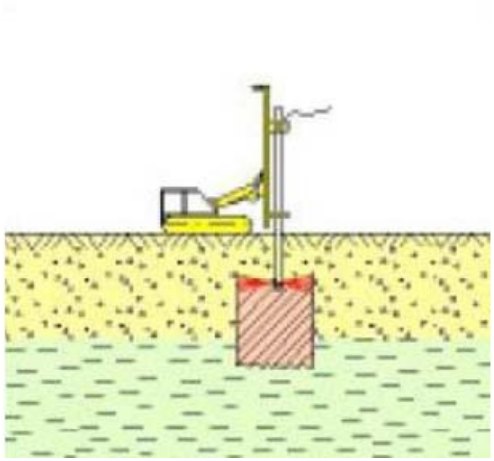
For (future) real-world biochar applications in contaminated sites: Techniques from underground engineering



Drilling



Change to injection

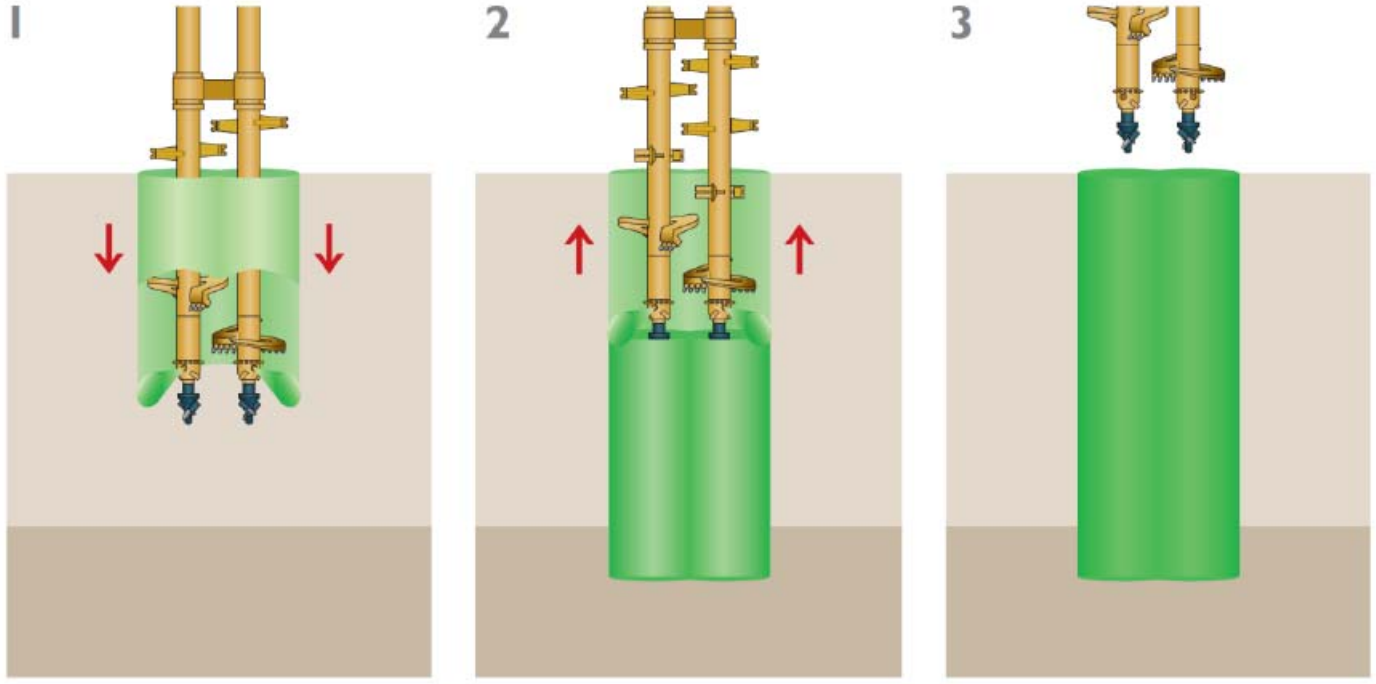


injection under high pressure

Different denominations: „Jet-Grouting“, high pressure injection (HDI), High pressure cement stabilization (HDBV), SOILCRETE-technique, SOILJET-technique, RODINJET-technique, …
Up to depths of 15-25 m.

Source: Friesl-Hanl et al., 2012

Alternatives from underground engineering: Deep-Soil-Mixing



Achievable depths: 16-24 m.
Suspensions could be injected.

Quelle: Friesl-Hanl et al., 2012

Biochar as Swiss army knife for environmental problems?

→Yes, but – you have to select between different Swiss army knives

Source: http://www.schweizer-messer.eu/

→ Yes, but – Swiss army knives, too, may take advantage of modifications

Pimp my biochar ....

SUMMARY / CONCLUSIONS

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- **Biochar for stabilization / immobilization of soil pollutants**
  - Aim: Reduction of (easily) available fraction
  - Less leaching, less plant uptake
- **Treatable pollutants**
  - Heavy metals / metalloids
  - Persistent organic pollutants (PAH, PFC, …)

For extensive contaminations with low to moderate concentrations

- **Different direct and indirect bonding mechanims**
  - Heavy metals: Reaction with functional groups, electrostatic interactions, precipitation; pH-shift ….
  - Organic pollutants: interactions of π-electrons, (nano-)pore filling, hydrophobic adsorption, …..
- **Anionic pollutants require modified biochar**
  - Fe-/Mg-modification, clay-mineral composites, water vapour activation …..
- **Incorporation technique as challenge**
  - Pollutant and biochar must get into contact!
  - Occasionally techniques from underground engineering may help

Thanks for your attention

(… and wishing you a happy charring …)

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