Biochar substrates for degradation of organic pollutants in soils of former military areas LaTerra

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Status of Inventory: Suspected Contaminated Sites in Germany

Federal State	information stand	Registered Suspected Contaminated Sites		
		Abandoned Waste Disposal Sites	Abandoned Indutrial Sites	Sites in all
Baden-Württemberg	2010	3253	7.766	13.840
Bavaria	2011	10.193	3.737	16.795
Berlin/Brandenburg	2011	7.535	13.764	24.978
Bremen	2011	55	2.910	3.557
Hamburg	2011	420	1.933	1.815
Hessen	2011	316	350	1040
Mecklenburg-Western Pomeria	2010	4.113	7.231	5.835
Lower Saxony	2011	8.976	30.900	93.825
North Rhine Westphalia	2010	18.337	24.642	75.370
Rhineland-Palatinate	2011	10.578	n.d.	12.497
Saarland	2010	1.801	2.442	1.977
Saxony	2011	7.655	22.418	19.785
Saxony-Anhalt	2011	5.985	13.958	16.682
Schleswig-Holstein	2010	2.412	16.096	13.781
Thuringia	2011	5.556	11.094	12.570
Germany				**appr. 315.000**

Situation in the Federal State of BRANDENBURG

Federal Country of Brandenburg:

1989 military occupied area (WGT, NVA):

230.000 ha (8% of the whole country of Brandenburg)

200.000 ha without further military use

PAH **MHC**

Sandy soils with low organic matter

What´s the problem?

Large contaminated areas with high costs for remediation

Competition for area between food crops and energy crops

Project goals

Degradation of organic polutants

Enhancement of soil fertility

Restoration of ecologic and economic potential of

contaminated sites and degraded areas

via application of biochar substrates

on the basis of regional using of biogenic wastes and renewable raw materials

Renewable raw materials

Climate gas reduction CO_2-storage

Closing of regional cycles

Project partner and project structure

Renaturation of post-mining-landscapes

Research for climate and sustainability

Degradation of organic pollutants

Cross-sectional project (HL)
energy and material flow management, value-creation network

Project coordination (FUB)
project coordination quality assurance, actor management, public relation activities

Regional projekt 1 (FUB)
„military conversion areas "
Brandenburg, county Teltow Fläming

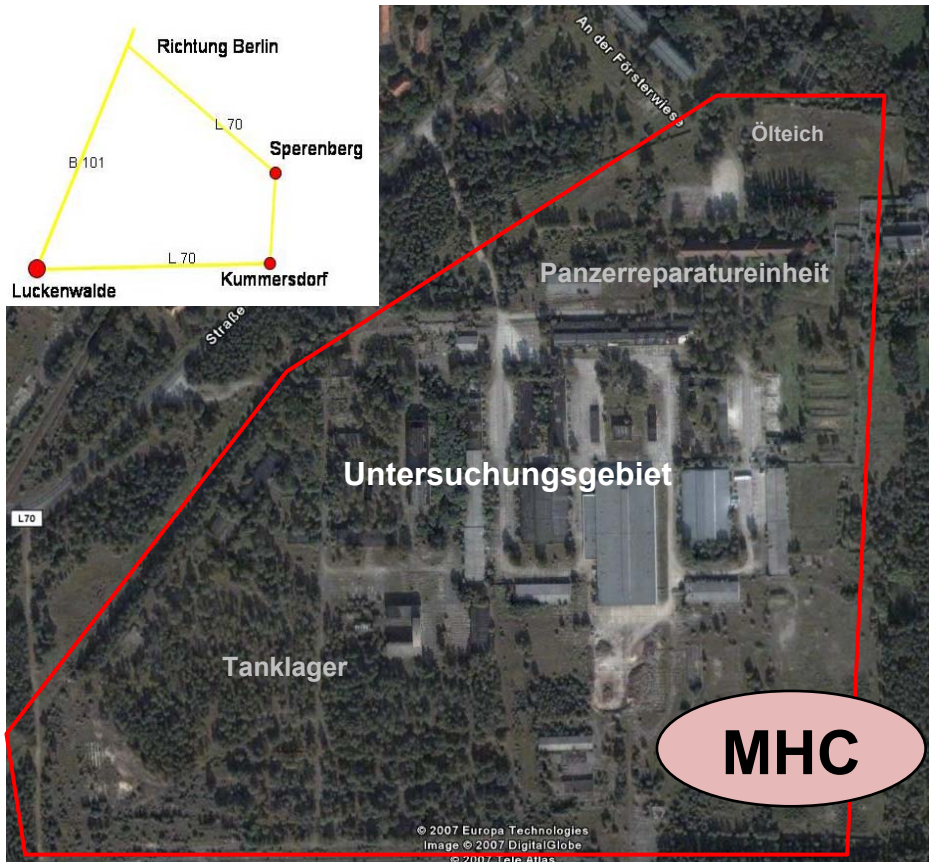
Regional project 3 (Fh-IME)
„forest management"
North Rhine-Westphalia, city of Schmallenberg

Regional project 2 (FIB)
„post mining landscapes"
Brandenburg, counties Oberspreewald-Lusatia, Elbe-Elster

Terra Preta production
Areal GmbH subcontractor

Reforestations of large scale windbreakage areas

Tank repair area and gasstation



Further industrial used area – former tarboard-factory

Examination programme

Contaminated sites (MHC, PAH)

Pot trials	Lysimeter trials	Outdoor tests
2011 - 2014	2012 - 2014	2012 - 2014

- Physical, physico-chemical and chemical examinatons for characterising soils and substrates
- Leaching tests concerning mineral and organic contaminants
-Biological examinations (respiration, nitrification, earthworm, seedling emergence

Pot trials - parameter soil/biochar substrates

- Analysis of soil and the beginning and end of vegetation period

- PAH, MHC
- water content, pH, conductivity, CEC
- C_t, N_t, S_t, N_{min}, KAK_{pot}, P_{avail}, K_{avail}, Mg_{avail} , C_{org}.
- Ca, Mg, K, P, Mn, Cu, Zn, Ni, Cr, Pb, Cd , Hg, As, Tl,
- **Leaching - columns- und shaking - trials**

Biological soil parameters:

- Biomass
- Soil respiration
- Nitrification

Contamination levels

Soil sampling

MHC-contaminations

	MHC-soil	PAH - soil
MHC content mg/kg	**5900**	90
PAH – content mg/kg	0,7	**277**

PAH-contaminations

Very high available content of MHC (89 … 95 %)

The highest amounts of PAH contamination, in the pure PAH-soil are fluoranthen (16 %), pyren (15 %), benzo(a)pyren (10,1 %)

Design of pot trials in 2011

Dipl.-Geogr.
Florian Worzyk
Project-Coordination

MHC, PAH contaminated and non-contaminated soils

With plant

2,8 M.-% substrate
- *with 15 Vol.% BC (A3)*
- *with 30 Vol.% BC (B3)*

14 M.-% substrate
- *with **15 Vol.% BC (A3)***
- *with **30 Vol.% BC (B3)***

Biochar-substrates additions

Without plant

14 M.-% substrate
- *with 15 Vol.% BC (A3)*
- *with 30 Vol.% BC (B3)*

Biochar addition

Amount according to a biochar compostion like 30 Vol.% - 14 M.-% substrate

Production of biochar substrates

Fermentation Pyrochar

Feedstock:

- grass, lop
- biochar (pyrolysis, 15 u. 30 vol.-%)
- + digestate (5 % D.M.; 300 l m^{-3})
- + basalt powder (15 kg m^{-3})

TPS-variant	N	P	K	C_{org}	C/N	pH	Cu	Zn
	M.-%	M.-%	M.-%	M.-%			mg $100g^{-1}$	
TPS Q1 15 Vol.-% biochar	1.28	0.25	1.0	29	23	7.5	26	146
TPS Q2 30 Vol.-% biochar	1.14	0.17	0.8	39	34	7.5	19	124

Biological substrates characterisation / quality assurance

Dipl.-Geogr. Karin Friede

Cress test – phytotoxic gases

Aim: Detection of gaseous phytotoxic substances (Federal Compost Association)

Pitures 4/5: cress test (Karin Friede)

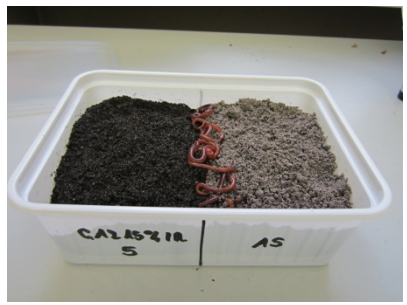
At least 80% of the fresh matter of a reference substrate must be achieved:

LA-TP-A3 = 99,3 %
LA-TP-B3 = 83,8 %

→ Batches are free of phytotoxic compounds

Earthworm avoidance test

Aim: Examination of the effect on the fauna in terms of substrate preference (DIN ISO 17512-1: 2010-06)



Pictures 6/7: eartworm avoidance test (Karin Friede)

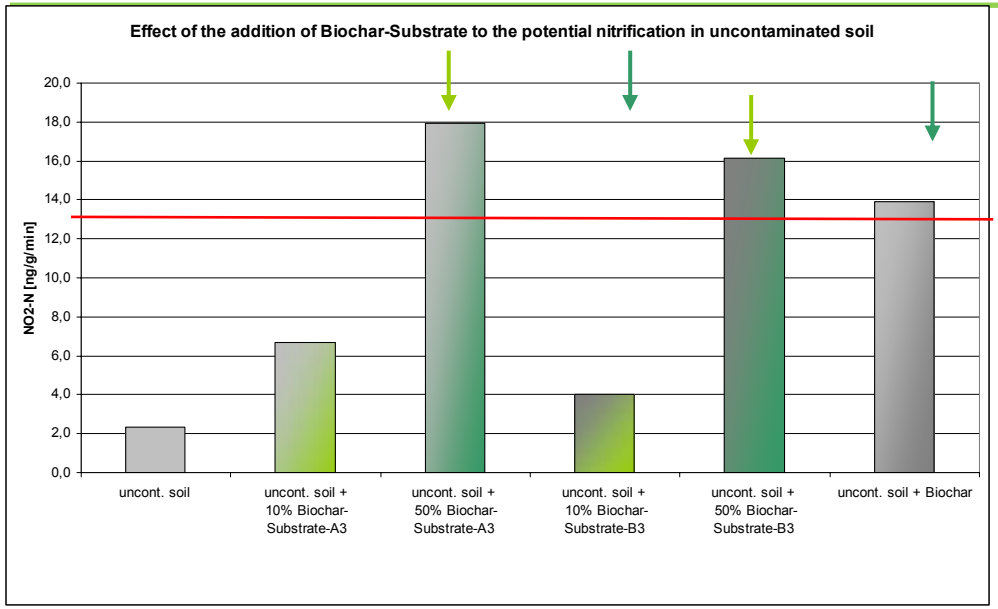
Less than 20% of the total number of worms in Test-Substrate the Habitat function is restricted

GA2 F0% = 6,4 GA2 IR0% = 6,6
GA2 F15% = 3,6 GA2 IR15% = 3,4

→ Biochar-Substrate is not preferred

Pot trial – Nitrification (DIN ISO 15685) – uncont. soil

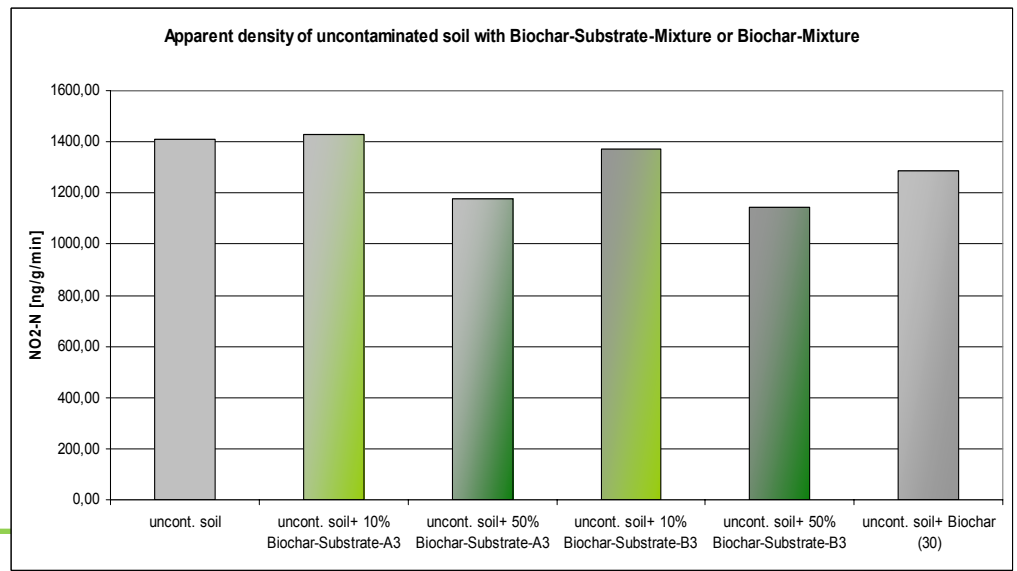
Dipl.-Geogr. Karin Friede



The addition of Biochar-Substrate leads to an increase of the ammonium oxidation potential of the soil.

The activity of the ammonium oxidise bacteria increases with increasing substrate additions. A higher Biochar content in the substrate leads to a slight decrease in microbial activity of nitrifies.

—— Wet black soil (reference soil)
NO_2-N=13,3 ng/g/min
(Dreher & Hund-Rinke 2001)

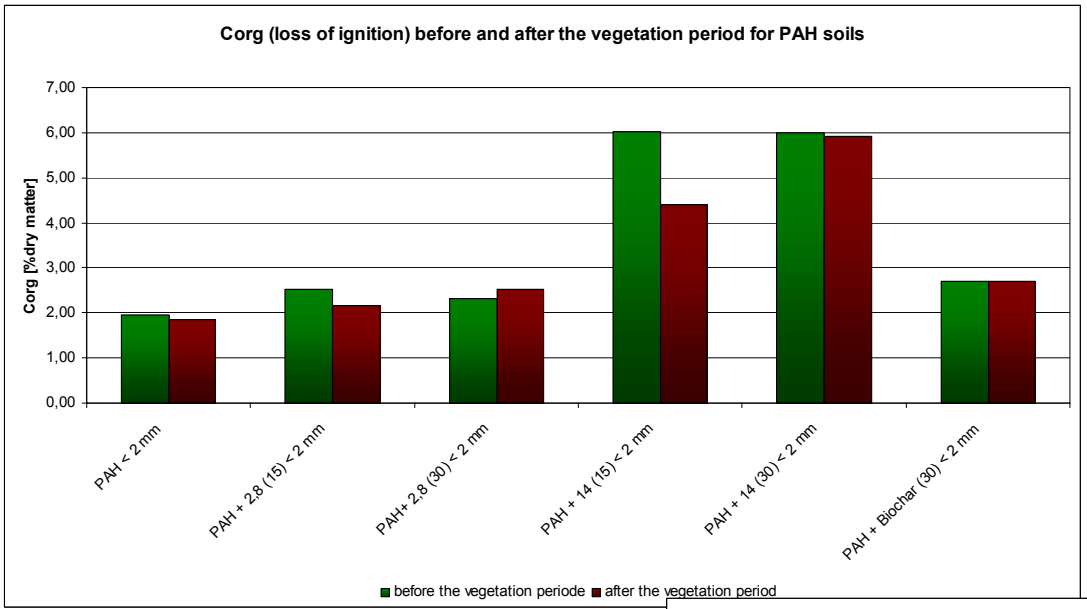


→ **The addition of Biochar-Substrate leads to a decrease of apparent density**

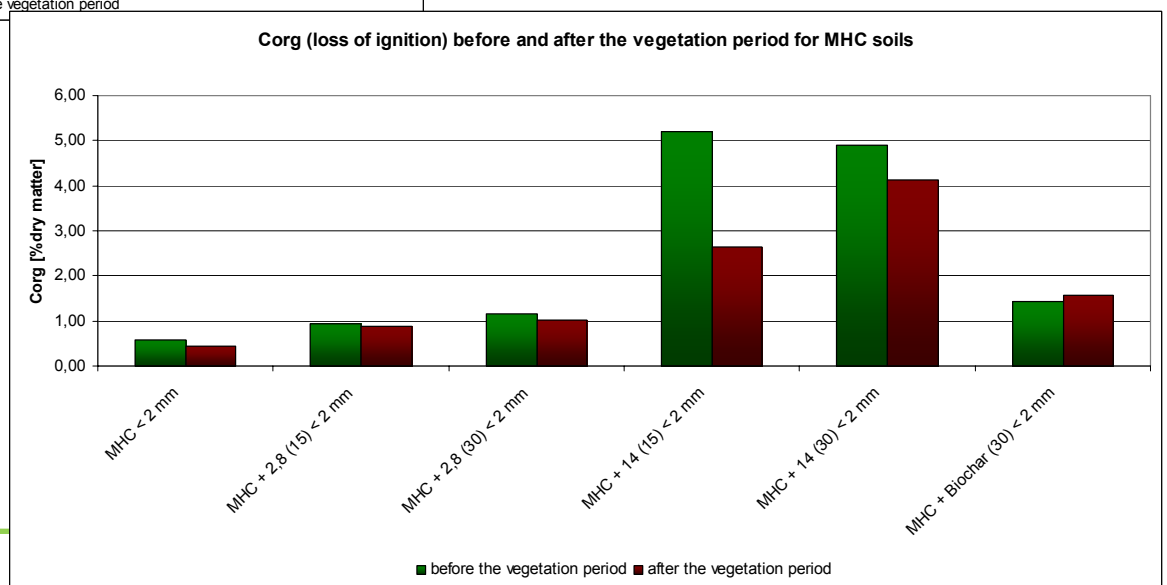
→ **Better permeability of air**

→ **increase in microbial activity of nitrifies**

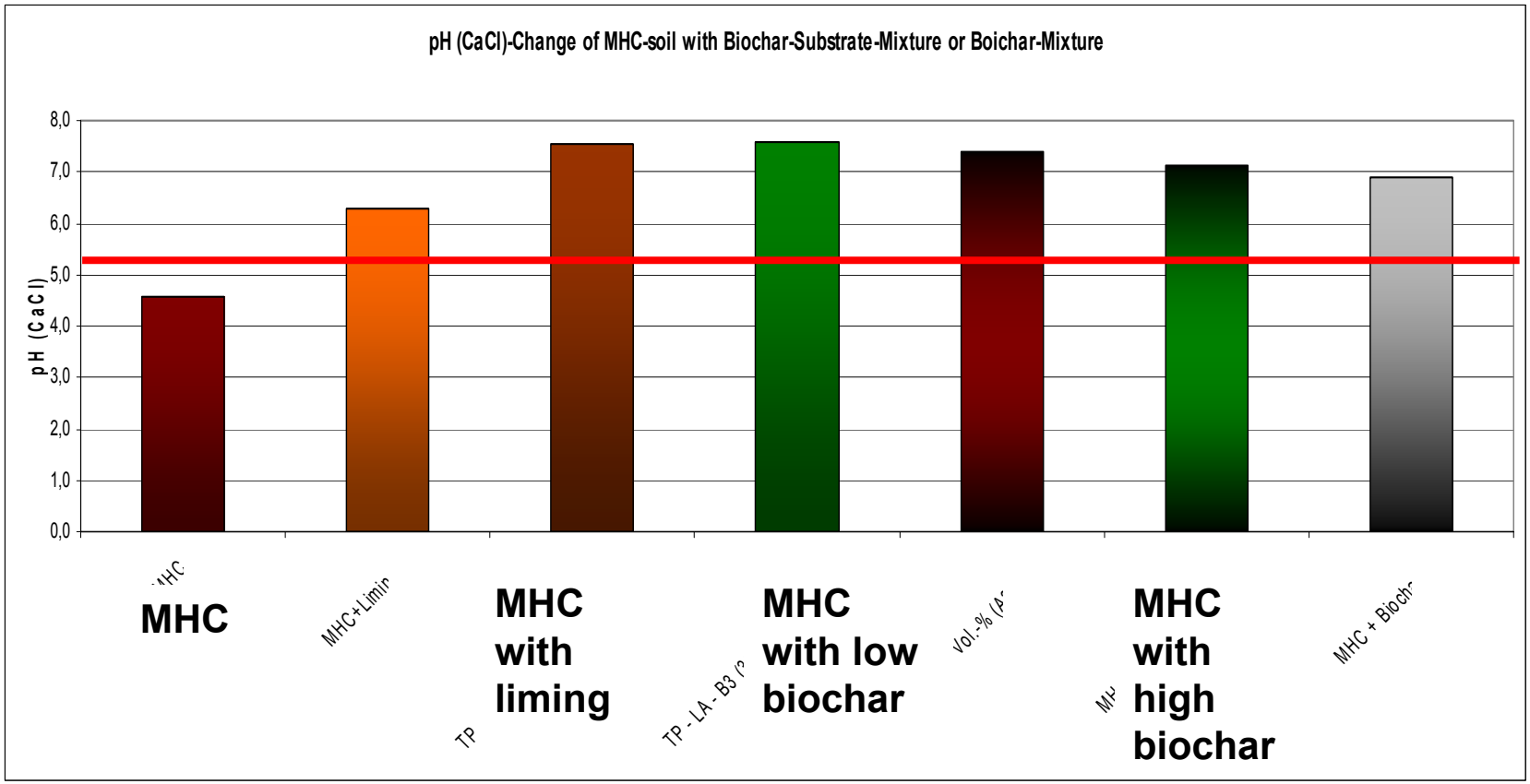
Pot trial – soil carbon



Stable enrichment of soil carbon content

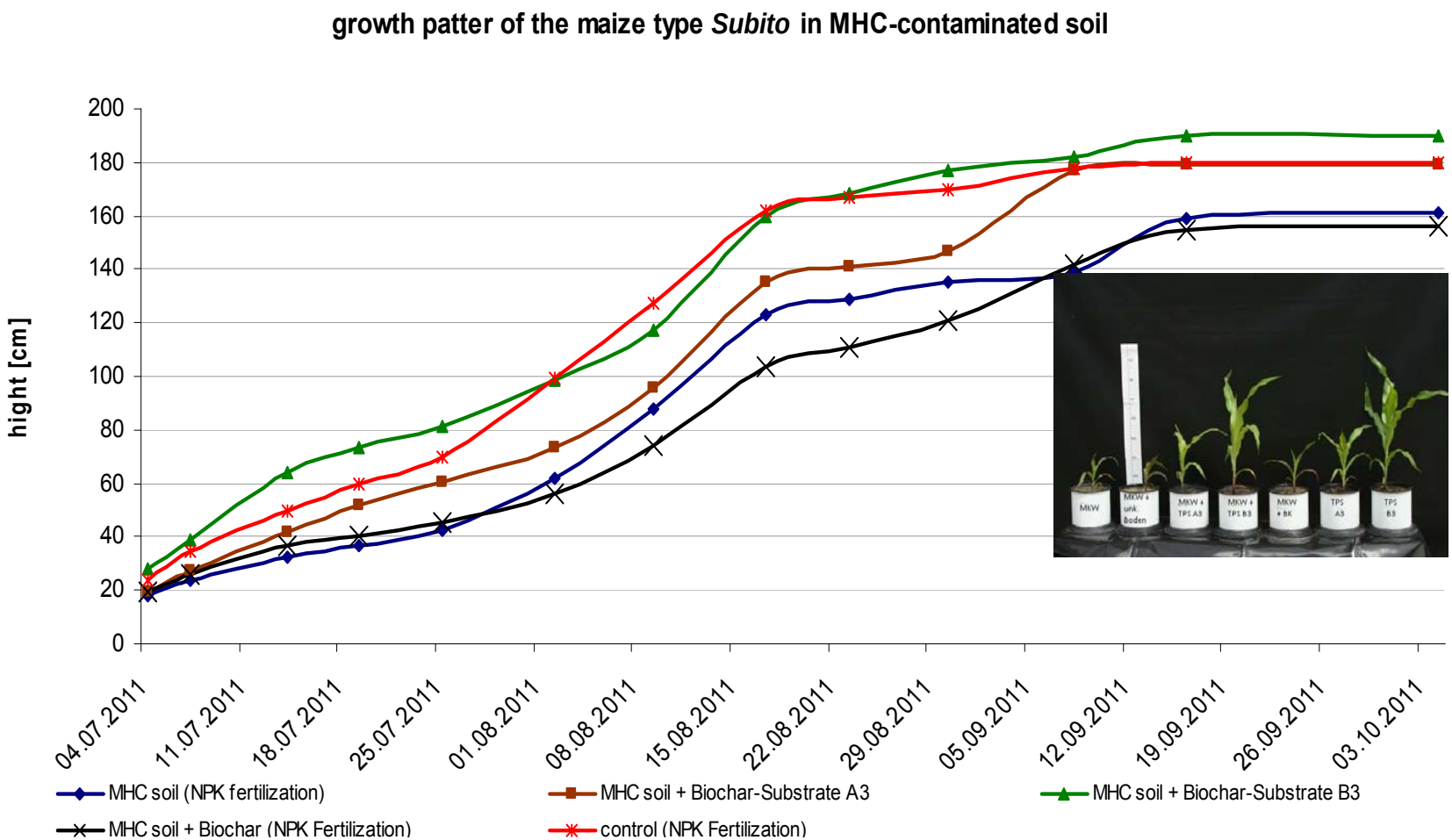


Pot trial – Soil: pH (CaCl) in the MHC - variations



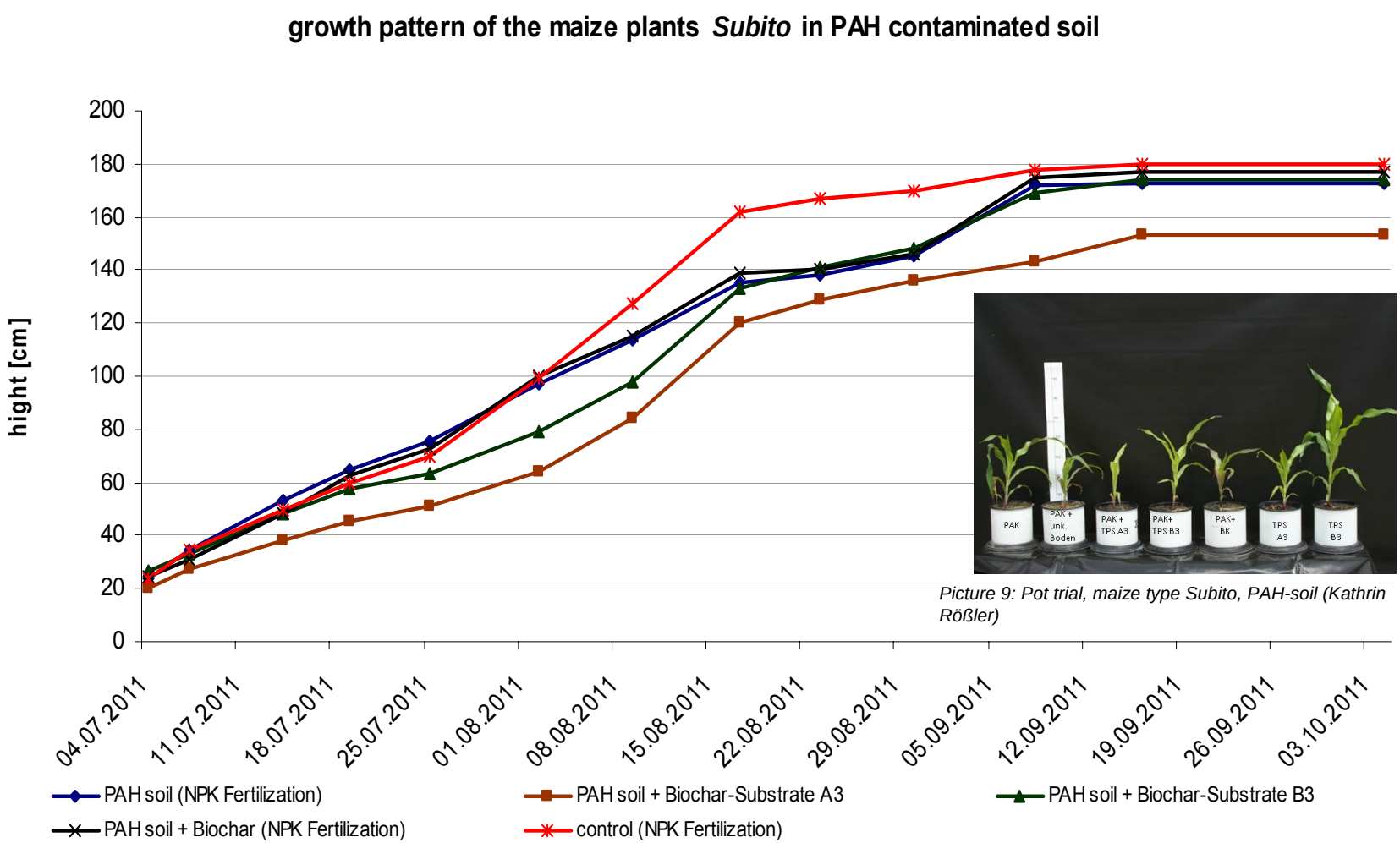
Already by very low biochar (< 1%) amendment huge effect on soil pH!

Pot trial – growth pattern of the maize plants – MHC contamination



→ **decrease of plant growth because of MHC – improvement with biochar substrates**

Pot trial – growth pattern of the maize plants – PAH contamination



Picture 9: Pot trial, maize type Subito, PAH-soil (Kathrin Rößler)

→ **no influence of aged PAH on plant growth**

Pot trial - growth pattern

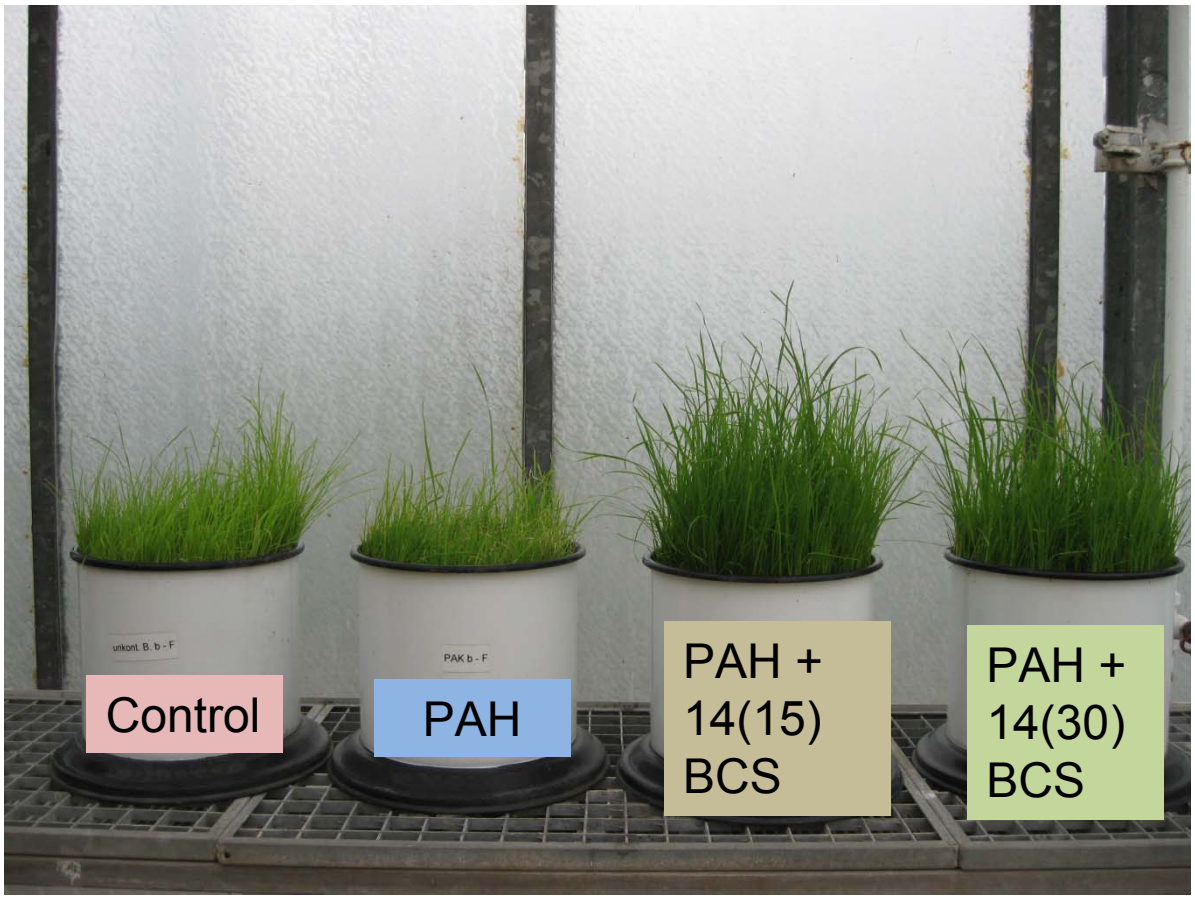
→ Higher growth with 30 Vol-% compared with 15Vol-% Biochar content in the substrates

→ supplementary fertilizer N of the Biochar-Substrates was necessary because the added organic nitrogen was slowly released

→ “not activated Biochar” indicated no positive effects concerning to the growth pattern

→ inhibition of the growth pattern of plants in MHC-contaminated soil was significantly higher then growth pattern of plants in PAH contaminated soil, the reason was the higher amount of available MHC

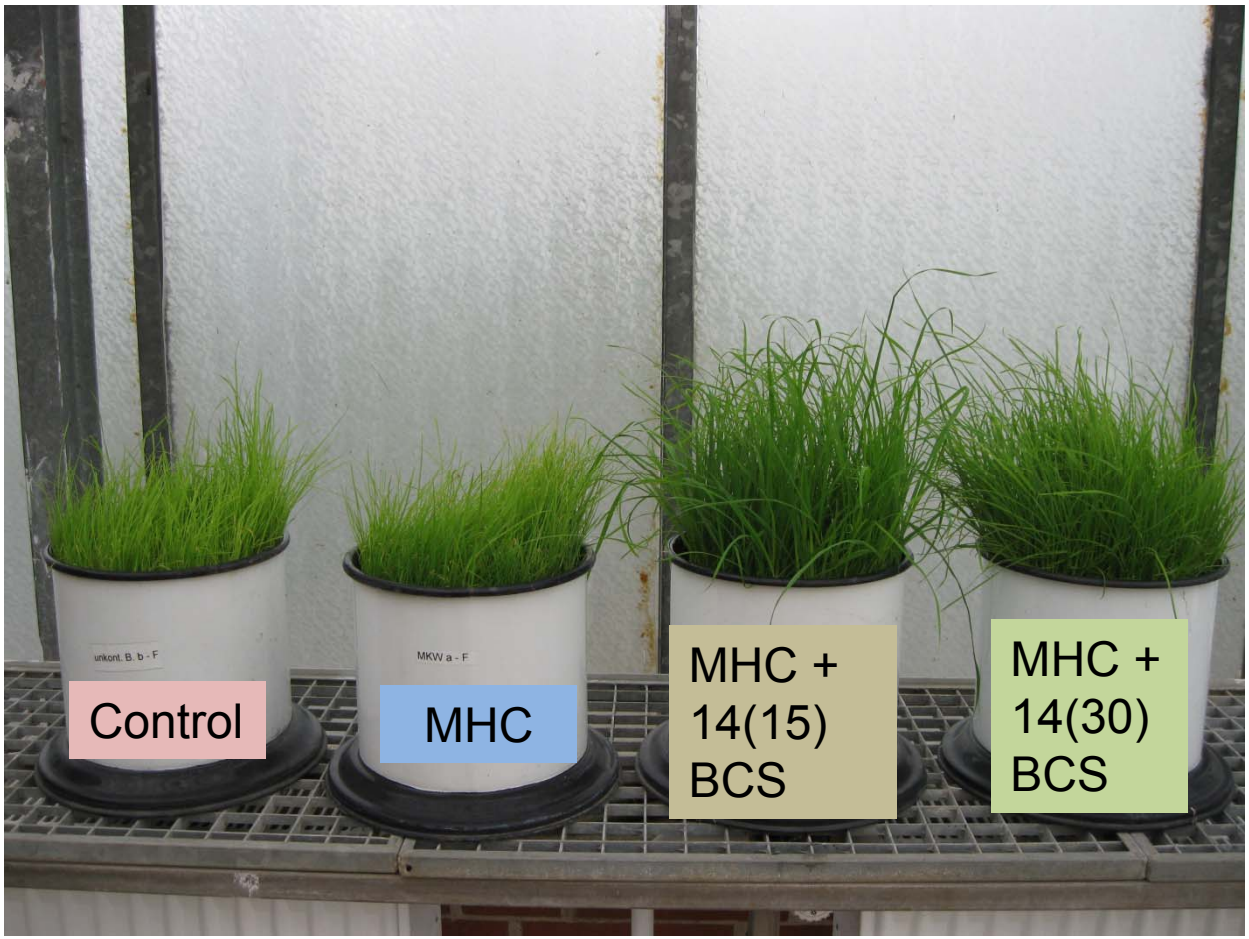
Results of second vegetation period - PAH



In the biochar substrate variants:

- Higher fertilizer efficiency
- Far better growth
- No growth depression

Results of second vegetation period - MHC



In the biochar substrate variants:

- Higher fertilizer efficiency
- Far better growth
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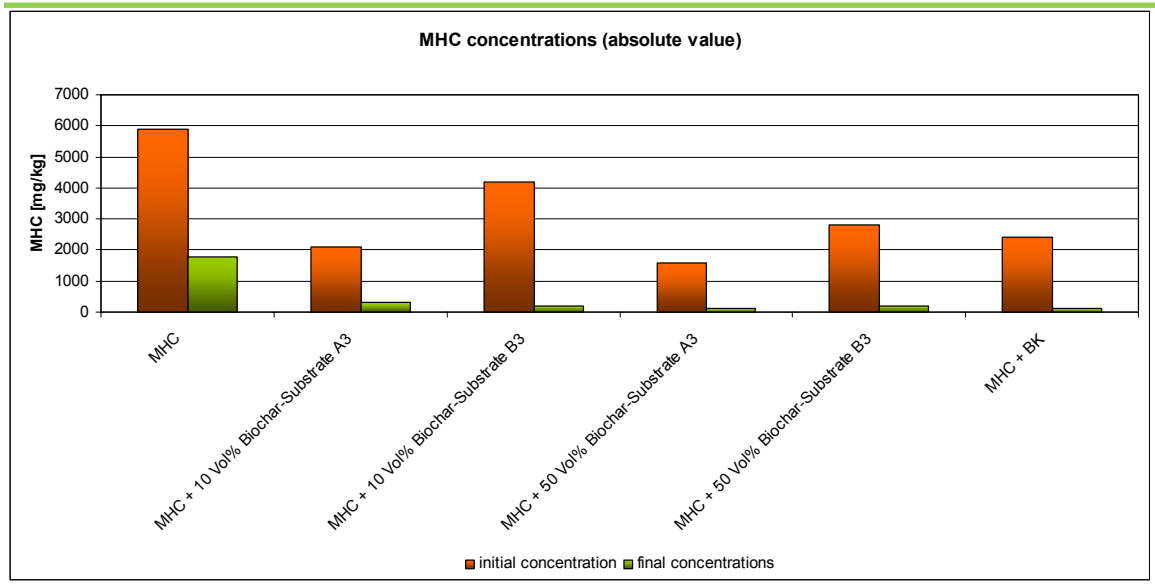
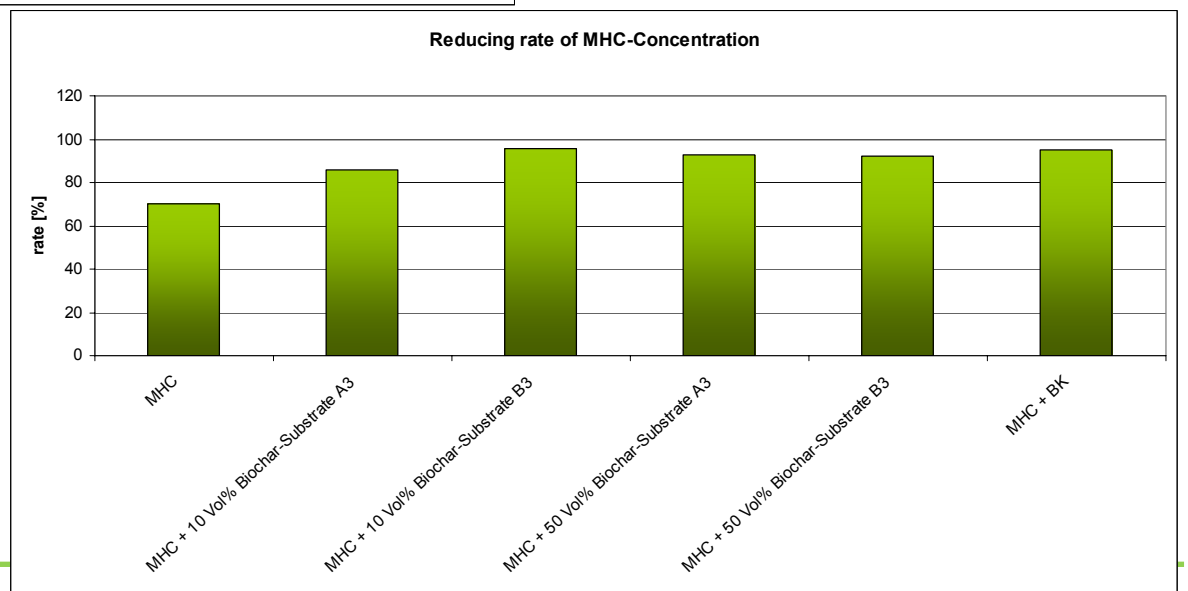
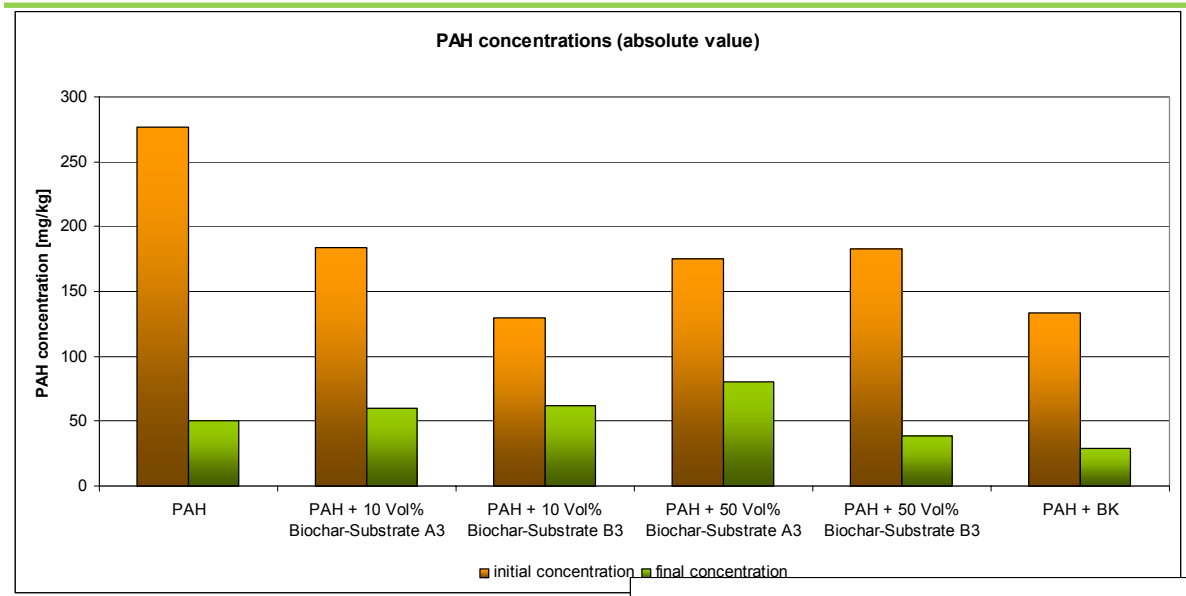
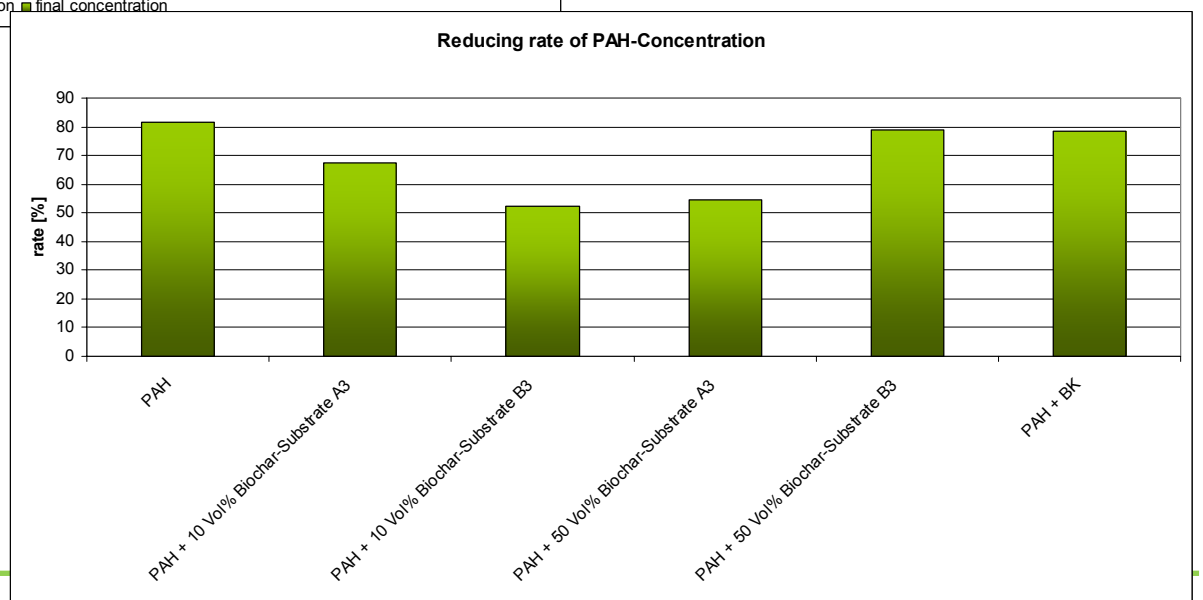
Pot trial – Reduction of the MHC-content



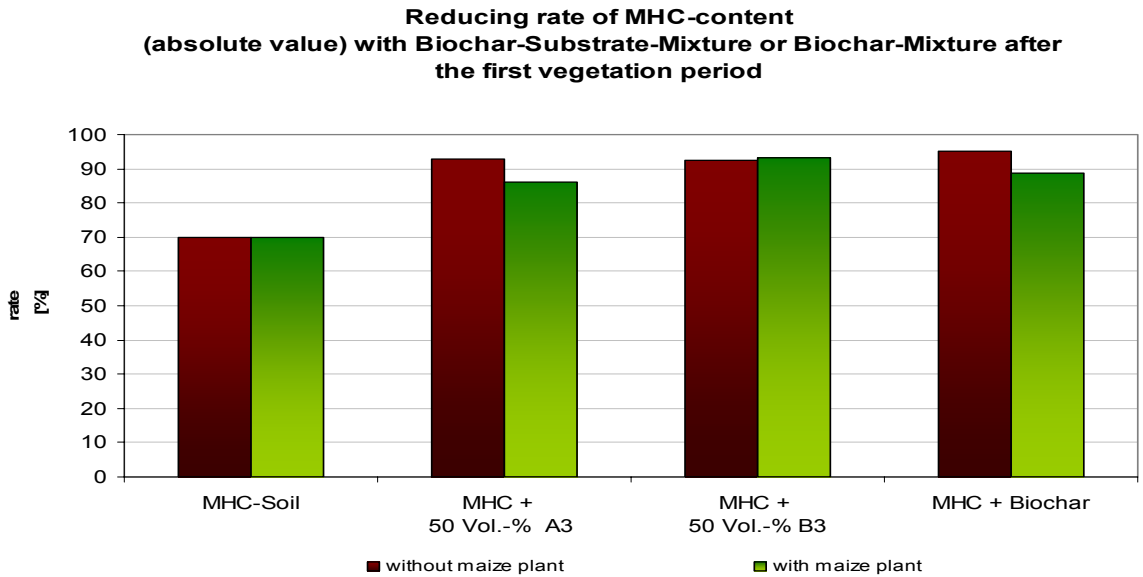


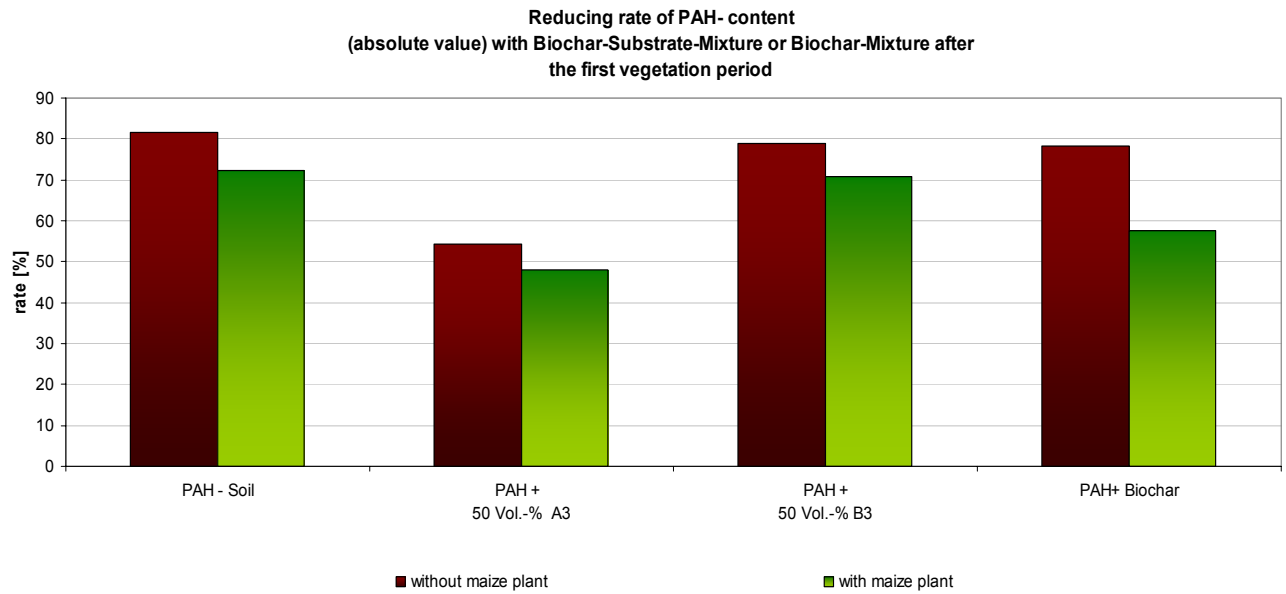
Pot trial – Reduction of the PAH-content





Pot trial – Reducing rate of PAH/MHC content





→ **lower reduction rates with plants - competition**

Leaching tests

Dipl.-Geogr.
Rene
Schatten

Test overview

Batch test

in progress

DIN 19527: 2012-08
DIN 19529: 2009-01

L/S ratio: 2:1 → static test
shaking time: 24h
centrifugation and filtration of the eluate

Column test

planned 2012/13

DIN 19528: 2009-01

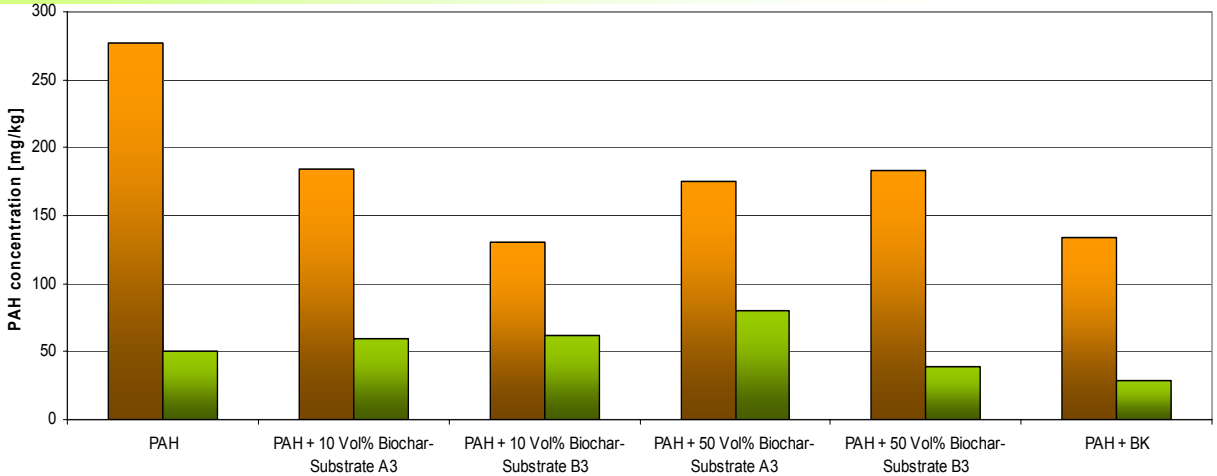
L/S ratio: various (1:1; 2:1; 4:1 etc.)
→ dynamic test
inverse flow direction
(centrifugation and) filtration of the eluate

→ Determination of the leachable contaminants and nutrients of the soil/biochar substrates

Batch tests – first results

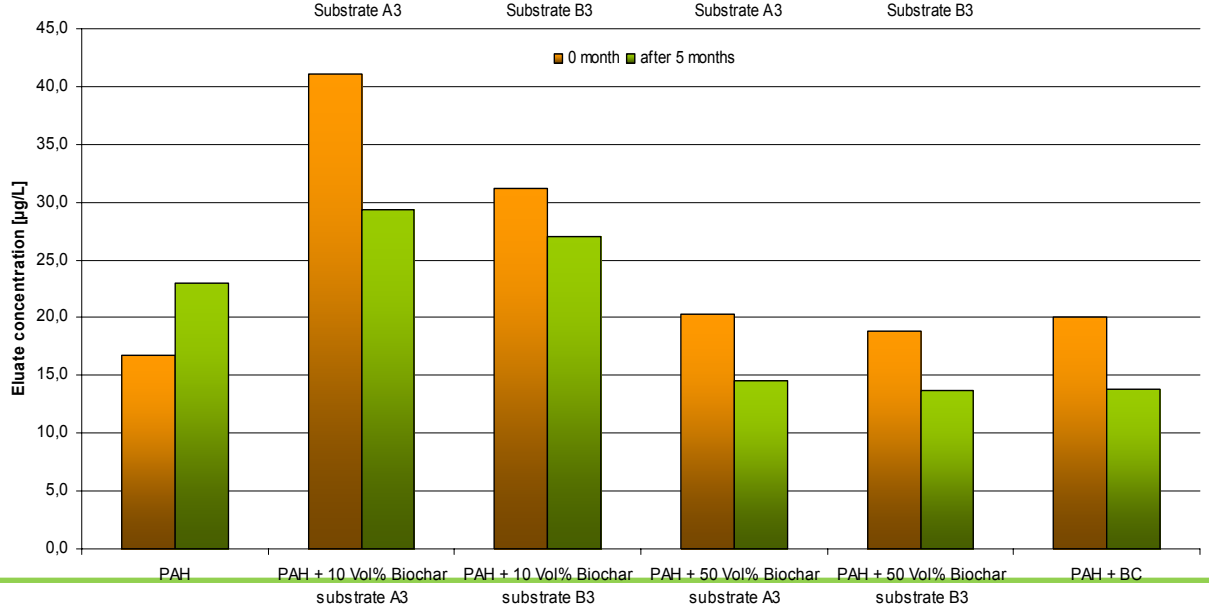
PAH contaminations

PAH
absolute value



High reduction of PAH after 5 months

PAH
eluate concentration

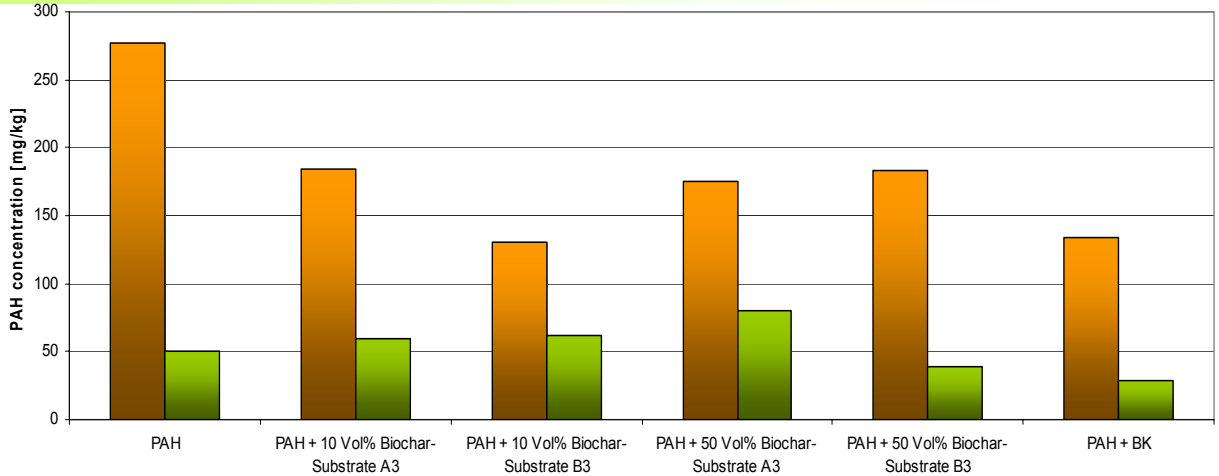


increasing BC leads to decreasing eluate concentrations

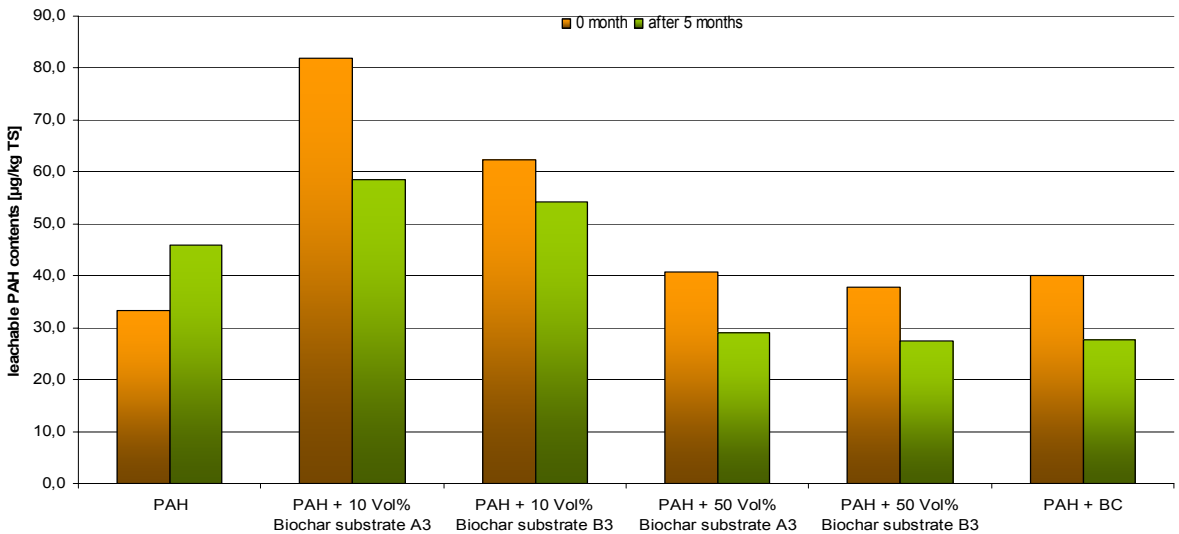
Batch tests – first results

PAH contaminations

PAH
absolute value



leachable PAH
contents regarding
soil sample

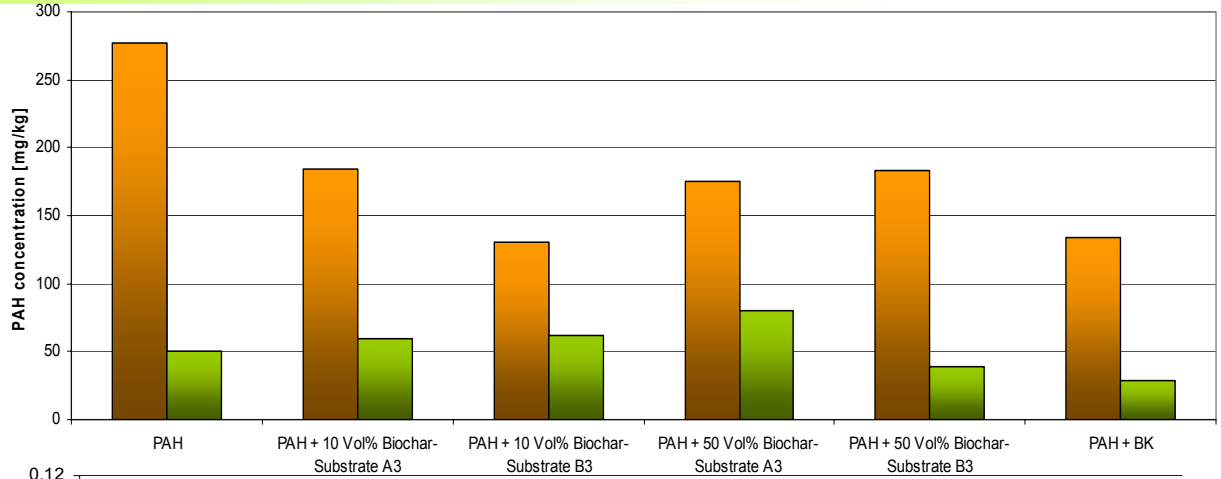


increasing BC leads to decreasing leachable PAH contents

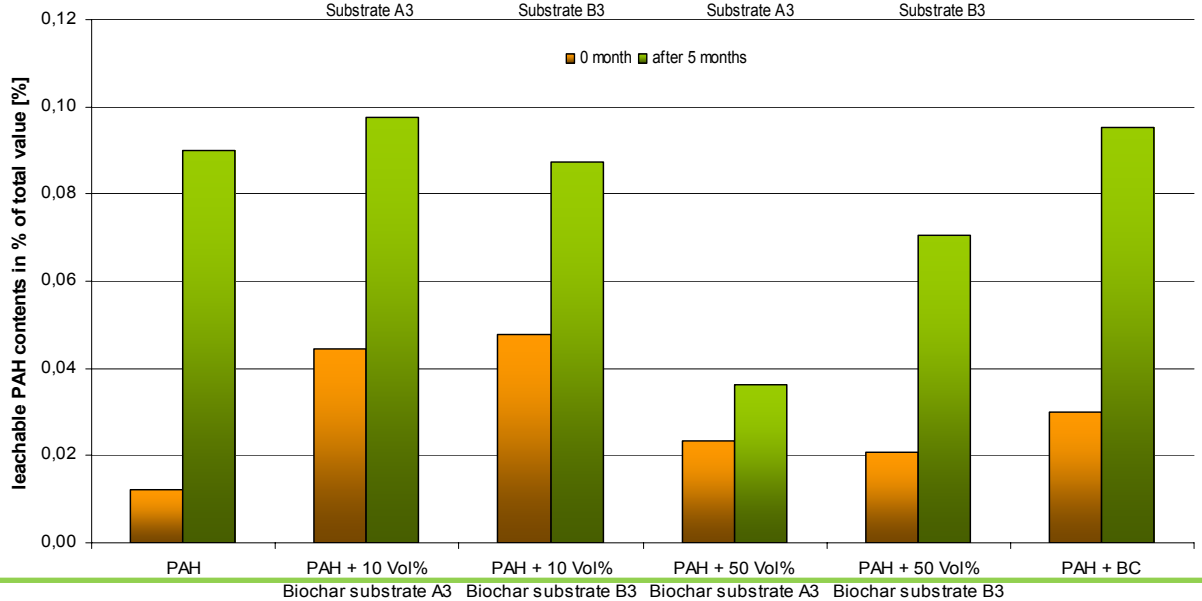
Batch tests – first results

PAH contaminations

PAH
absolute value



leachable PAH
contents regarding
soil total value



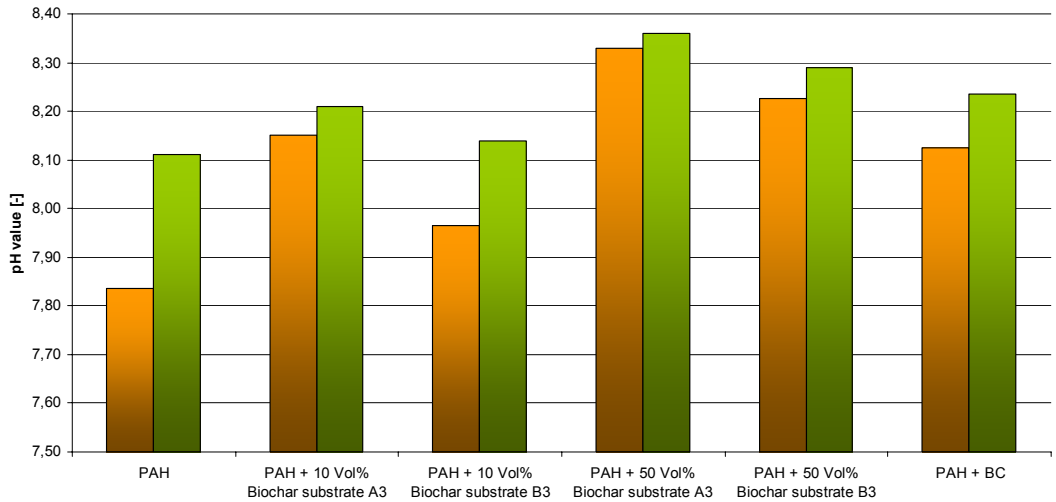
BUT

the leachable
PAH contents regarding
the soil total value in %
are increasing
Note: very low <0,1%!!!

Batch tests – first results

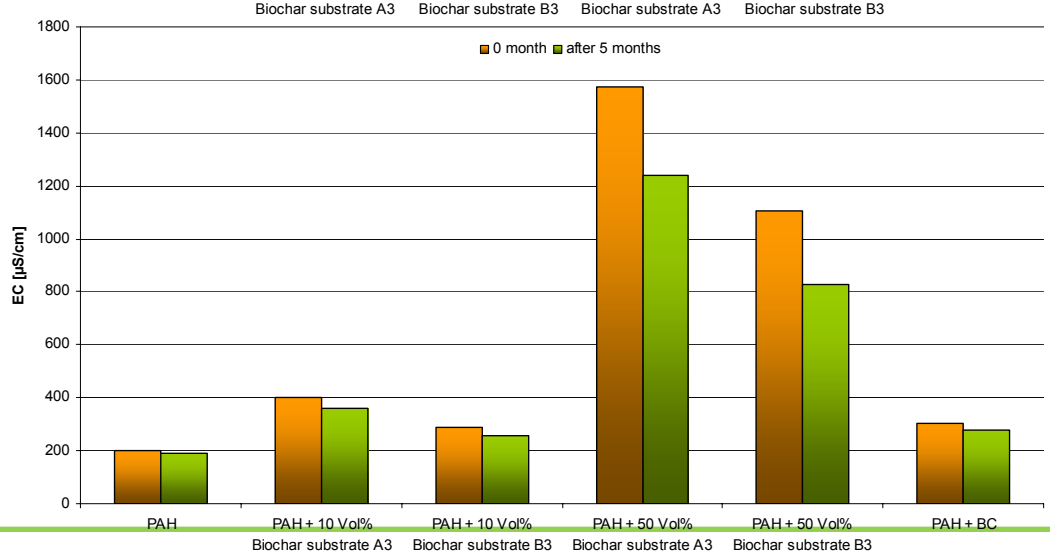
PAH contaminations – eluate parameter

eluate parameter:
pH value



increasing BC leads
to increasing pH value

eluate parameter:
Electric conductivity



increasing BC leads
to decreasing electric conductivity

Batch tests – first results

leachable nutrients

		K	Mg	Mn	P	S	Zn
		Leachable content in % of total value					
PAH	0 month	1,9	0,3	0,3	0,1	4,4	0,2
	After 5 months	0,5	0,5	0,7	0,04	3,7	0,4
PAH + 10 Vol% Biochar substrate A3	0 month	18	1,4	2,9	1,0	1,8	1,9
	After 5 months	25	1,4	2,6	0,2	3,6	1,2
PAH + 10 Vol% Biochar substrate B3	0 month	17	1,3	2,0	1,3	2,9	1,2
	After 5 months	15	1,2	2,0	0,1	2,6	0,8
PAH + 50 Vol% Biochar substrate A3	0 month	36	1,6	1,8	3,3	5,5	1,4
	After 5 months	37	1,9	1,6	0,8	7,5	1,2
PAH + 50 Vol% Biochar substrate B3	0 month	28	1,4	1,4	2,5	2,7	1,0
	After 5 months	22	1,4	1,3	0,5	4,5	1,1
PAH + BC	0 month	15	0,5	0,8	0,8	3,8	0,7
	After 5 months	26	1,0	2,1	0,1	4,1	1,2

mit steigender TPS-Gabe steigt die Verfügbarkeit der Nährstoffe, aber nicht immer mit steigendem BC-Gehalt bei gleicher Gabe
nach 5 Monaten i.d.R. weniger eluierbar, aber nicht verallgemeinerbar
Kalium sehr hoch eluierbar (bis zu 37% vom Gesamtgehalt!)

Batch tests – first results

leachable nutrients

- Elutionsverhalten von biokohlesubstratet sehr differenziert; Einfluss der Kohle erkennbar
- zum einen führen steigende BC-Gehalte zu sinkenden Eluatkonzentrationen, aber in Bezug zu den proz. Anteil vom Gesamtgehalt zeigt sich manchmal ein anderes Bild (vor/nach Gefäßversuch)
- PAK werden sehr gering eluiert (<0,1%), da gealterte PAK sehr schwer desorbierbar sind
- Nährstoffe/anorg. Elemente werden erwartungsgemäß leichter mobilisiert (Kalium!)
- laut Literatur können Schad-/nährstoffe an Kohlepartikel festgelegt werden, aber genauso gut mit feinen Partikeln ausgewaschen werden

- Batch test für Boden/TPS-Substrate gut durchführbar und liefert reproduzierbare und vergleichbare Ergebnisse
- interessant ist zudem die Elution von „reinen“ Biokohlesubstraten (TerraBoGa) → Methodenanpassung

Local project No. 2 – renaturation of post-mining-landscapes

In regional project 2 (Western Lusatia, county Oberspreewald-Lusatia) reclamation and renaturation of post-mining-landscapes is first priority. In this case, the project seeks for an upgrade of devastated soils for plant production as well as for restoration of soil functions and setup of organic soil substances.

Post-mining-landscapes Welzow

Application of biochar substrates

Production of artificial Terra Preta Materials (TPS)

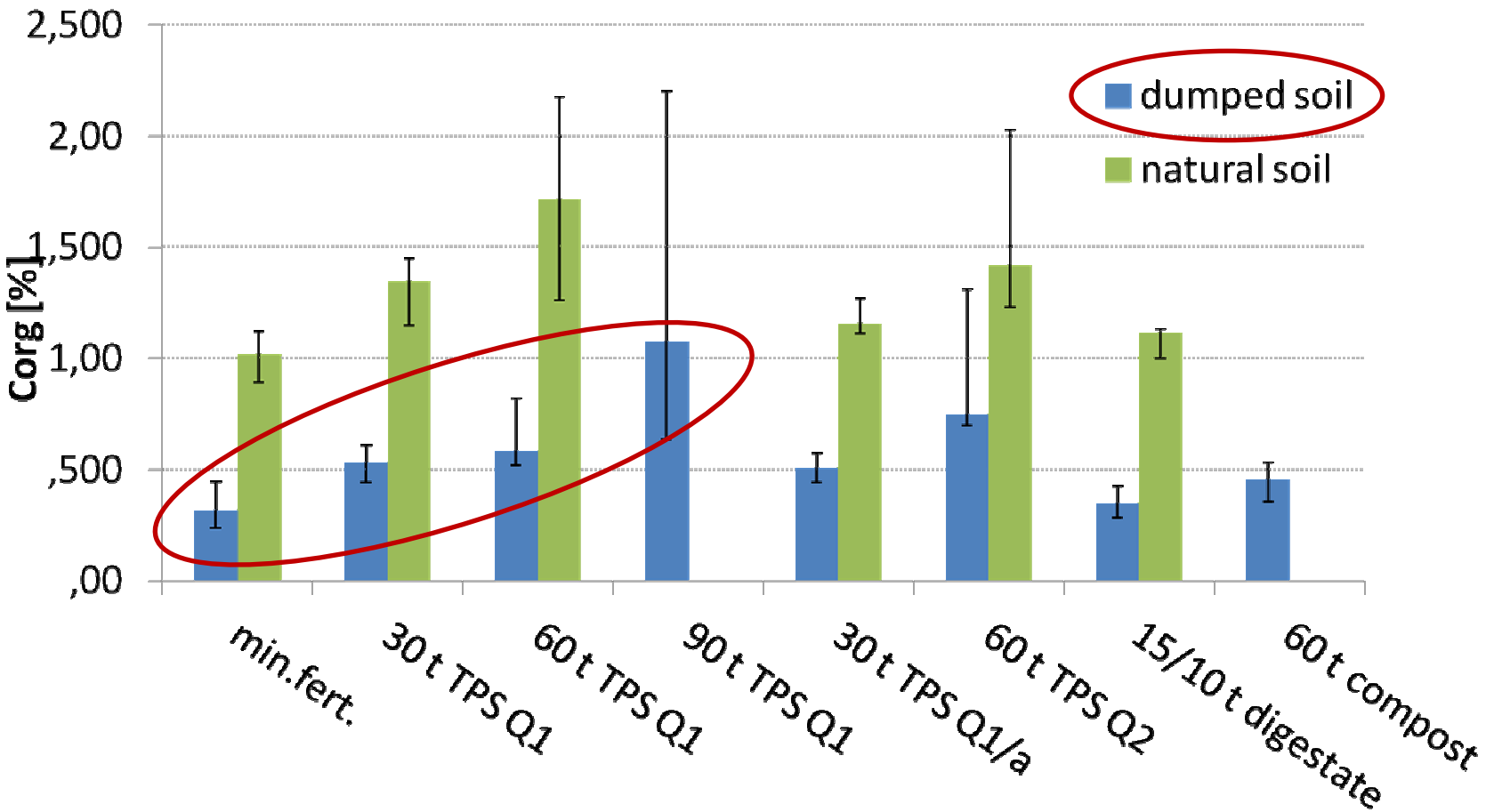
Feedstock:

- grass, lop
- biochar (pyrolysis, 15 u. 30 vol.-%)
- + digestate (5 % D.M.; 300 l m^{-3})
- + basalt powder (15 kg m^{-3})

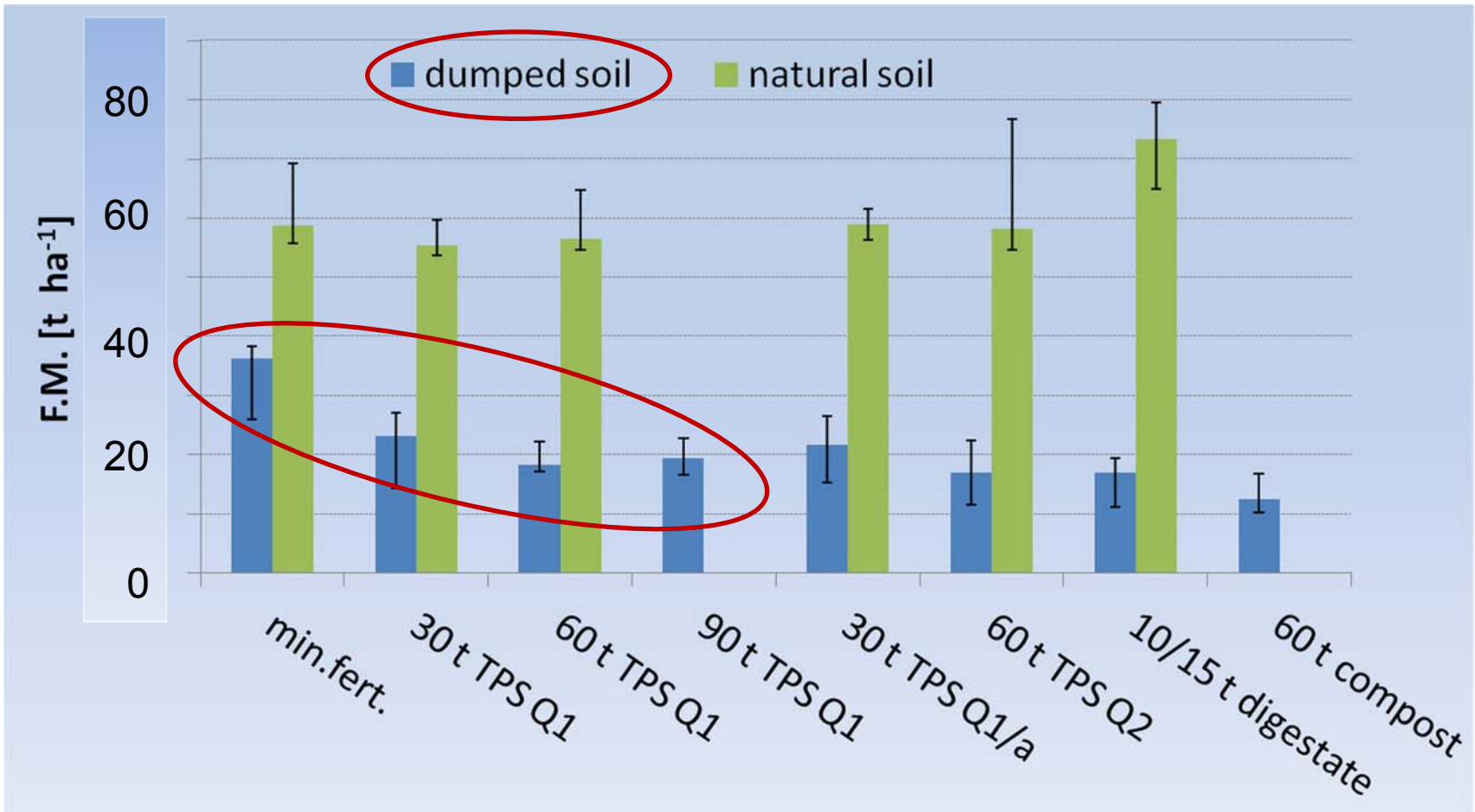
TPS-variant	N	P	K	C_{org}	C/N	pH	Cu	Zn
	M.-%	M.-%	M.-%	M.-%			mg 100g^{-1}	
TPS Q1 15 Vol.-% biochar	1.28	0.25	1.0	29	23	7.5	26	146
TPS Q2 30 Vol.-% biochar	1.14	0.17	0.8	39	34	7.5	19	124

limit BioAbfV (30 t): 70
300

C_{org}-contents in topsoils treated with Terra Preta Materials (TPS)

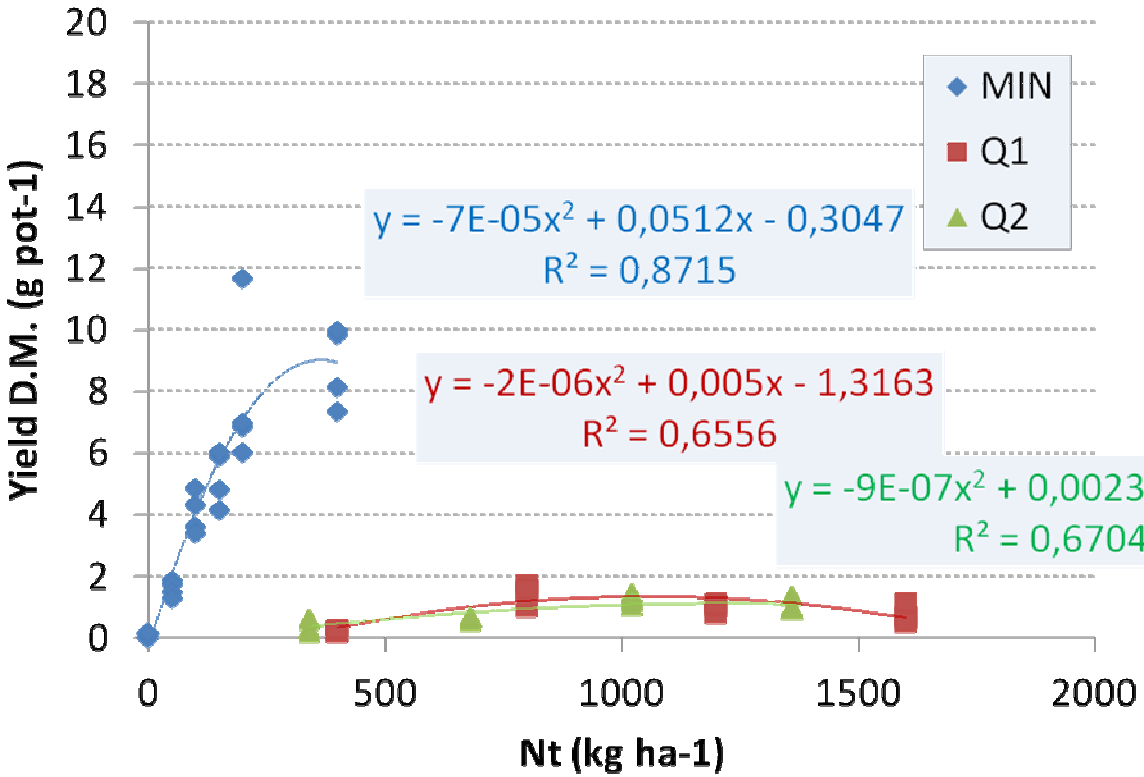


Corn yields after application of biochar-substrates



Pot experiment: “Fertilizing capacity of biochar substrates”

Dry matter yields of *Dactylus glomerata L.* depending on N_t - application on a dumped soil, first cut



=> Mineral N fertilizer equivalent < 5 %

Conclusions

- Reduction of organic pollution works
- Full effect development of biochar-substrates needs time, patience and a good feeling for all components and the local circumstances where the substrates are applied
- Design of substrates for special problems and conditions on site – guidance for transfer of results

Thank you very much for the attention!

Part of working group Geoecology

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GEFÖRDERT VOM Bundesministerium für Bildung und Forschung

Substrates characterisation / quality assurance

Dipl.-Geogr. Rene Schatten

Compare of Biochar-Substrates batches – nutrients

Biochar-Substrates	TP - LA - A3	TP - LA - A3	TP - LA - B3	TP - LA - B3
Parameter	Small batch	Big batch	Small batch	Big batch
Dry matter [%]	50,8	45,2	52,5	46,9
pH (CaCl2)	8,1	7,5	7,4	7,6
Total carbon [%]	25,5	28,2	31,5	33,5
Total nitrogen [%]	1,2	1,2	1,2	1,0
Total phosphor [mg/kg dry matter]	2581	3435	2597	2388
Total potassium [mg/kg dry matter]	13865	13005	14200	9227
NO3-N [mg/l fresh matter]	11,1	1,2	31,5	1,2
NH4-N [mg/l fresh matter]	7,3	2,6	7,4	0,8

Table 1: Compare of Biochar-Substrate batches (own design)

→ the total of C, N, P, K between Small batch and Big batch is comparable

→ the soluble N in the Big batch is much lower then in the small batch → lack of nitrogen (maize)

Pot trials - Soil- and Substrates characterisation

Chem.-physic. Parameter of the Biochar-Substrates batches and the used soils

Biochar-Substrates/Soil / Parameter	TP - LA - A3 total	TP - LA - B3 total	uncontaminated soil < 2 mm	MHC < 2 mm	PAH < 2 mm
Dry matter [% fresh matter]	45,5	54,5	92,9	93,8	95,42
Water content [% fresh matter]	51,5	48,5	7,1	6,2	4,58
pH (CaCl2)	7,53	7,60	6,35	4,57	7,12
Salt content (fresh) [g/l]	3,50	1,94	0,3	0,02	0,28
Apparent density (fresh) [g/l]	772,8	688	1411,1	1553	1432,1
Apparent density (dry) [g/l]	355	329	1311	1457	1367
Maximum water holding capacity [Vol.-%]	71,8	77,5	39,4	41,3	39,5
Corg (loss of ignition) [% dry matter]	27,4	30,0	1,7	0,6	1,97

Table 3: chem.-physic. Parameter of Biochar-Substrates batches and used soils (own design)

Pot trials - Soil- and Substrates characterisation

NPP-contents of Biochar-Substrates batches and used soils

Parameter \ Böden	TP - LA - A3 total	TP - LA - B3 total	uncontaminated soil < 2 mm	MHC < 2 mm	PAH < 2 mm
Total nitrogen [%]	1,2	1,0	0,07	0,04	0,08
Total phosphor [mg/kg dry matter]	3435	2387	347	529	369
Total potassium [mg/kg dry matter]	13005	9227	391	447	679

Table 4: NPP-contents of Biochar-Substrate batches and soil (own design)

→ Nutrients content of uncontaminated and contaminated soils are comparable

→ Phosphorus and potassium increased in the Biochar-Substrate-A3, compared to B3

Substrates characterisation / quality assurance

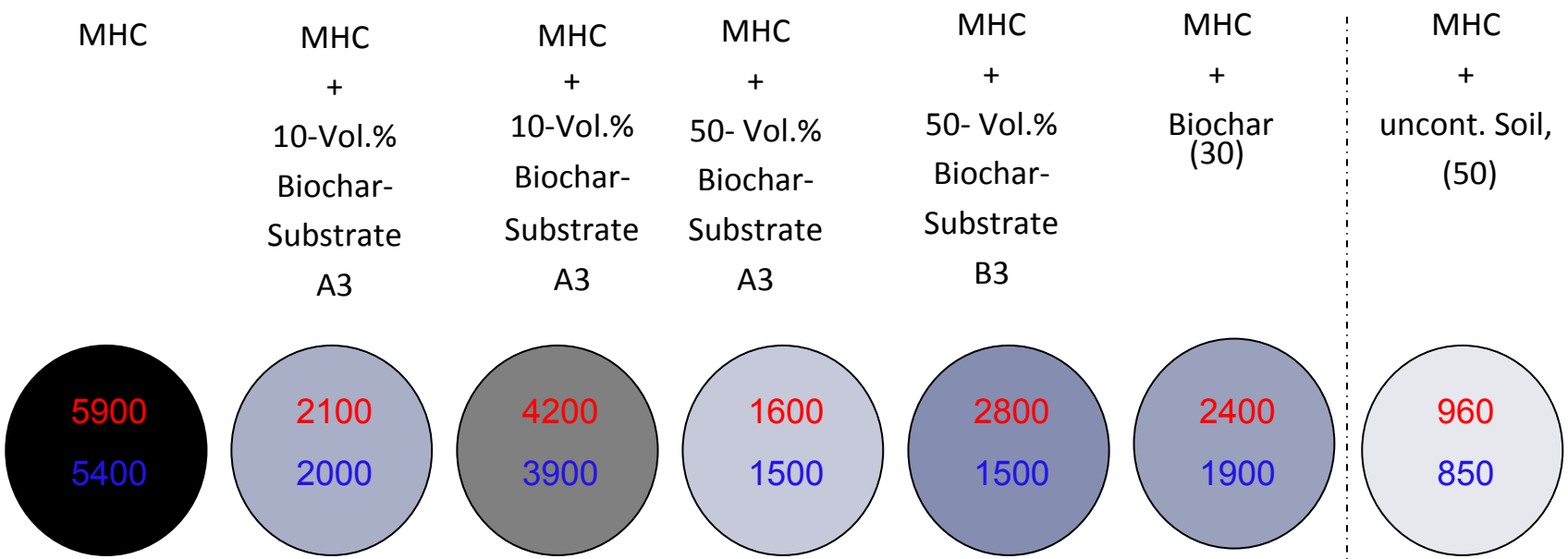
Compare of Biochar-Substrates batches – inorganic & organic pollutant

Biochar-substrates	**TP - LA - A3**	**TP - LA - A3**	**TP - LA - B3**	**TP - LA - B3**	***Bio waste Ordinance***
Parameter	Small batch	Big batch	Small batch	Big batch	***30 t/ha***
PAH 16 [mg/kg dry matter]	0,15	0,65	0,10	0,75	
Cadmium [mg/kg dry matter]	0,33	< 0,1	0,30	< 0,1	*1*
Chromium [mg/kg dry matter]	39,0	42,7	38,7	34,2	*70*
Copper [mg/kg dry matter]	47,3	36,2	41,2	28,6	*70*
Nickel [mg/kg dry matter]	58,9	29,4	40,5	30,8	*35*
Plumb [mg/kg dry matter]	13,2	18,1	13,3	8,0	*100*
Zinc [mg/kg dry matter]	161,7	151,2	149,7	143,3	*300*

Table 2: Compare of Biochar-Substrate batches (own design)

→ PAH-content low increase; non-hazardous
→ the total of inorganic pollutant between Small batch and Big batch is comparable
→ All data are under the critical value of the Bio waste Ordinance (including Ni)

Pot trial – MHC contents

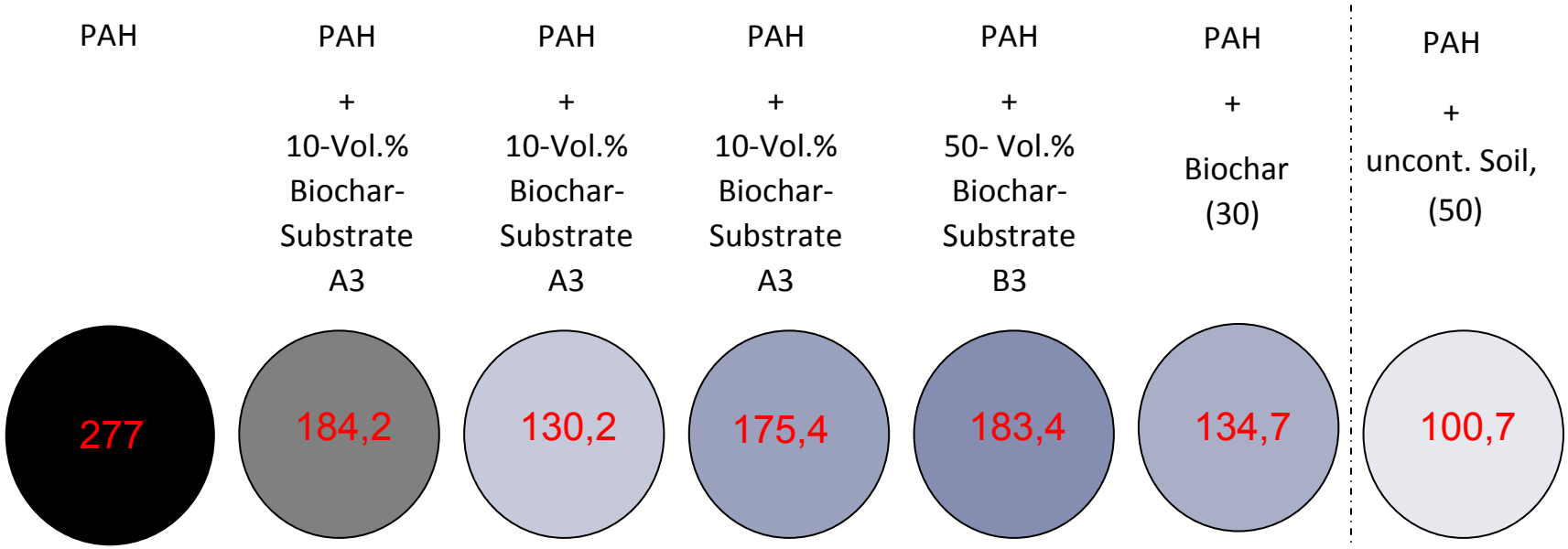


MHC contents in mg/kg dry matter, red: total contents C10 – C40, blue: availed content C10-C22

→ MHC contents in the mixtures: 960 – 4200 mg/kg dry matter (there was no influence between the amount of interferences and the MHC contents)

→ Very high available content of MHC contents: 89 and 95 %, exception: MHC + 14(30) with 53,6 %

Pot trials - PAH-contents

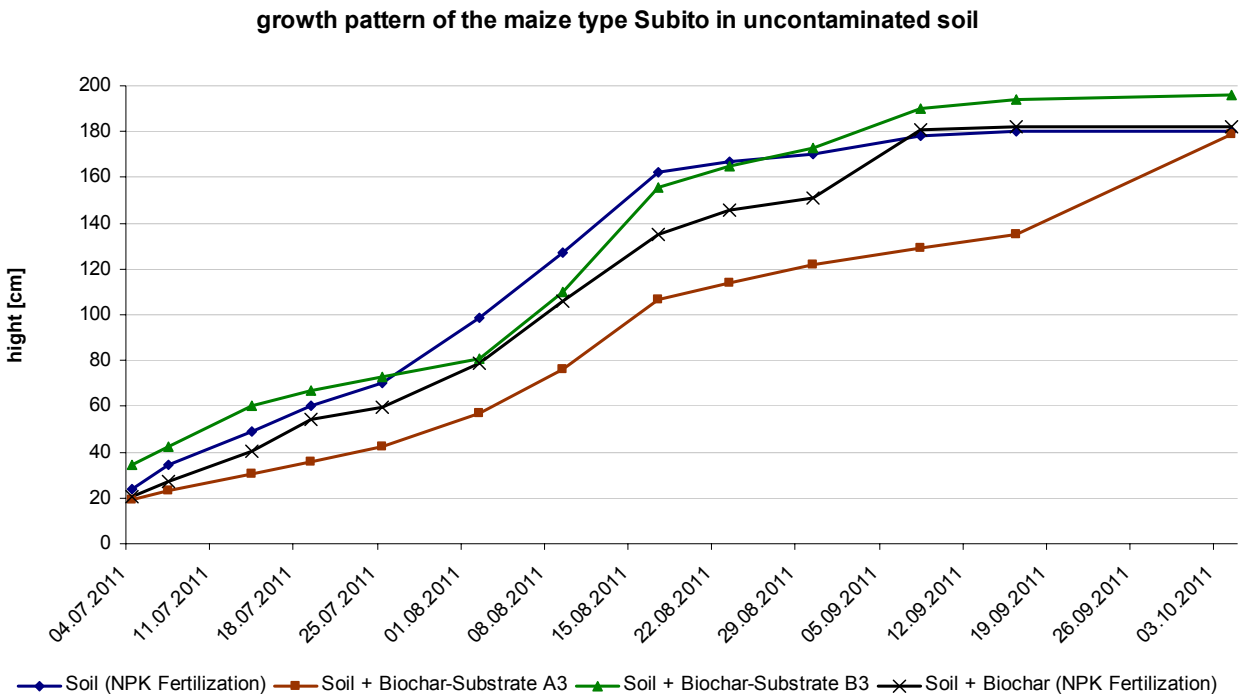


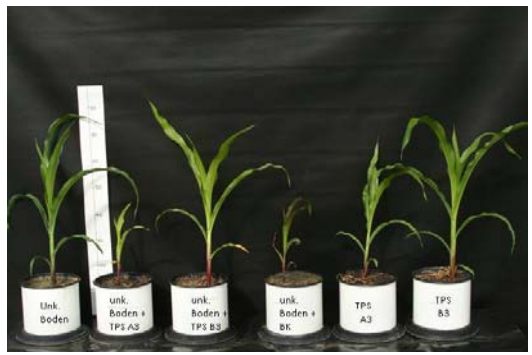
PAH-content in mg/kg dry matter

→ PAH contents in the mixtures : 130,2 – 184,2 mg/kg TS (there was no influence between the amount of interferences and the PAH contents)

→ The highest amounts of PAH contamination, in the pure PAH-soil are fluoranthen (16 %), pyren (15 %), benzo(a)pyren (10,1 %)

Pot trial – growth pattern of the maize plants





Picture 10: Pot trial, maize type Subito, uncontaminated soil (Kathrin Rößler)