water

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Supplementary Material

Removal of Herbicides from Landfill Leachate in Biofilters Stimulated by Ammonium Acetate

Nadia Brogård Nord [1], Nils. M. Sevelsted Berthelsen [2], Hasse Milter [2] and Kai Bester [1,*]

[1] Department of Environmental Science, Aarhus University, Frederiksborgvej 399, 4000 Roskilde, Denmark; nadiabnord@envs.au.dk

[2] Region Zealand, Alléen 15, 4180 Soroe, Denmark; nimb@regionsjaelland.dk (N.M.S.B); hmi@regionsjaelland.dk (H.M)

* Correspondence: kb@envs.au.dk

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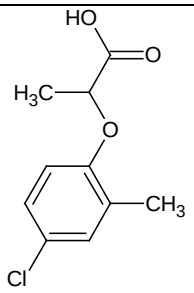
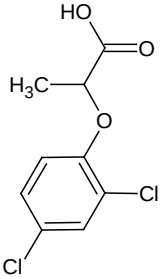
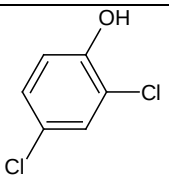
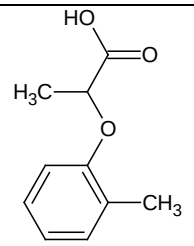
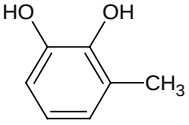
Table S1. Information on compounds, CAS-numbers, structures, and suppliers used for analytical purpose.

Name CAS Number	Structure	$LogK_{ow}$	Supplier
Mecoprop (MCPP) 93-65-2		3.1 (PubChem)	Dr. Ehrenstorfer
Mecoprop-P (*R*-enantiomer) 16484-77-8			Sigma-Aldrich
Mecoprop d3 352431-15-3			Dr. Ehrenstorfer
Dichlorprop (DCPP) 120-36-5		3.4 (PubChem)	Dr. Ehrenstorfer
Dichlorprop-P (*R*-enantiomer) 15165-67-0			Sigma-Aldrich
Dichlorprop d6 Not available			Dr. Ehrenstorfer
2,4-dichlorophenol (2,4-DCP) 120-83-2			Dr. Ehrenstorfer
2-(2-methylphenoxy) propanoic acid (2-MPP) 7345-21-3			Sigma-Aldrich
3-methylcatechol (3-MeCat) 488-17-5			Sigma-Aldrich

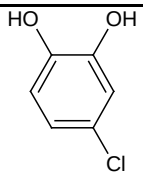
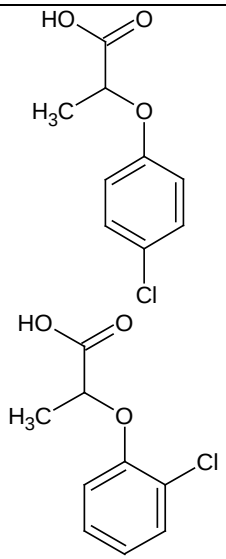
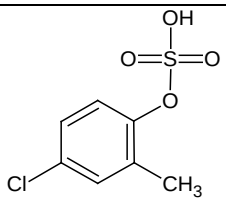
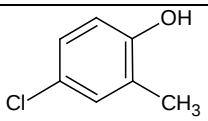
4-chloro catechol (4-ClCat) 2138-22-9		Dr. Ehrensdorfer
2-(2/4-chlorophenoxy) propanoic acid (CPP) 25140-86-7/3307-39-9		Sigma-Aldrich/ Dr. Ehrenstorfer
4-chloro-2-methylphenol sulphate (MCPP sulphate)		TRC
4-chloro-2-methylphenol (4-CloCr) 1570-64-5		Sigma-Aldrich

Table S2. Corresponding compounds of internal standards used in the analytical methods.

Internal Standard (IS)	Internal Standard
Mecoprop d3	MCPP, MCPP sulphate, 4-CloCr, 2-MPP, 3-MeCat
Dichlorprop d6	DCPP, 2,4-DCP, 4-ClCat, CPP

Table S3. HPLC-method for analysis of parents, and metabolites (CPP, MPP, and MCPP sulfate). The MS/MS was operated in negative mode, ion source potential; −4500 V, source temperature; 400 °C, CAD; 10 psig, CUR; 20 psig, GS1; 50 psig, and GS2; 35 psig. Injection volume was 100 μL.

Step	Total Time (min)	Flow Rate (μL/min)	0.2% FA in HPLC-Water	0.2% FA in Methanol
0	0.00	300	100	0
1	3.00	300	100	0
2	7.50	300	15	85
3	8.00	300	0	100
4	10.00	300	0	100
5	10.50	300	100	0
6	12.00	300	100	0
7	13.00	300	100	0

Table S4. HPLC-method for analysis of metabolites (3-MeCat, 4-CloCr, 4-Clcat, and 2,4-DCP). The MS/MS was operated in negative mode, ion source potential; −4500 V, source temperature; 400 °C, CAD; 10 psig, CUR; 20 psig, GS1; 50 psig, and GS2; 35 psig. Injection volume was 100 μL.

Step	Total Time (min)	Flow Rate (μL/min)	HPLC-Water (%)	Methanol (%)
0	0.00	300	100	0
1	3.00	300	100	0
2	10.0	300	0	100
3	12.0	300	0	100
4	12.5	300	100	0
5	15.5	300	100	0

Table S5. Limit of quantification (LOQ) and detection (LOD) of the analyzed compounds.

Compound	Limit of Detection (μg L^{-1})	Limit of Quantification (μg L^{-1})
Mecoprop	0.03	0.11
Dichlorprop	0.02	0.06
CPP	0.02	0.07
MPP	0.01	0.04
MCPP sulphate	0.02	0.05
(RS)-mecoprop	0.2	0.06
(RS)-dichlorprop	0.2	0.06
2,4-DCP*	-	3.0
3-MeCat*	-	0.3
4-ClCat*	-	1.0
4-CloCr*	-	0.3

Table S6. Total organic carbon (TOC) and nitrogen (TN) for inlet water, and outlet water from the biofilters.

System	TOC (mg L^{-1})	TN (mg L^{-1})
Inlet	13.2 ± 3.2	17.8 ± 1.5
Peat	9.9 ± 1.2	16.3 ± 1.9
Stonewool	10.4 ± 1.7	16.7 ± 1.3
Sand	9.1 ± 0.9 *	16.9 ± 1.1 *

* Sand average outlet excludes samples taken after NH_4Ac addition.

Table S7. Average inlet concentrations from the raw landfill leachate during the experimental period.

	Inlet (μg L^{-1})
MCPP	1.4 ± 0.31
DCPP	0.2 ± 0.03
MPP	0.3 ± 0.13
CPP	3.1 ± 0.68
MCPP Sulphate	<0.05

Table S8. Outlet concentrations of the biofilter. In bold are concentrations below 0.1 μg L^{-1}.

	Mecoprop (μg L^{-1})	MPP (μg L^{-1})	Dichlorprop (μg L^{-1})	CPP (μg L^{-1})
Sand	Outlet	Outlet	Outlet	Outlet
Days				
0	2.30	0.31	0.27	5.44
13	1.33	0.15	0.19	2.83
16	0.73	0.15	0.12	1.31
20	**0.09**	**0.08**	**0.03**	**0.05**
27	**<0.03**	**<0.01**	**<0.02**	**<0.02**
34	1.56	0.41	0.19	3.4
41	0.20	**0.08**	**0.05**	0.14
48	1.78	0.51	0.17	3.35
55	0.57	0.13	**0.08**	1.10
62	0.22	**0.01**	**<0.02**	0.25
69	0.21	**0.02**	**<0.02**	0.24
Stonewool				
Days				
0	1.87	0.20	0.23	3.52
13	1.76	0.21	0.22	3.77
16	1.76	0.19	0.23	3.48
20	1.63	0.32	0.17	2.41
27	**0.05**	0.13	**0.02**	**<0.02**
34	1.26	0.32	0.16	2.77
41	1.16	0.87	0.16	2.99
48	1.32	0.33	0.15	1.50
55	0.97	0.59	0.11	1.41
62	1.49	0.28	0.16	3.52
69	1.55	0.24	0.13	3.11
Peat amended sand				
Days				
0	1.79	0.22	0.24	3.9
13	0.58	**0.09**	**0.08**	0.40
16	0.94	0.19	0.11	1.39
20	1.51	0.43	0.19	3.43
27	**0.1**	0.26	**0.05**	**0.03**
34	1.90	0.34	0.18	2.01
41	1.79	0.42	0.20	3.88
48	1.81	0.64	0.17	3.54
55	1.65	0.97	0.14	3.36
62	0.53	0.21	**0.04**	1.26
69	0.61	0.20	**0.05**	1.42

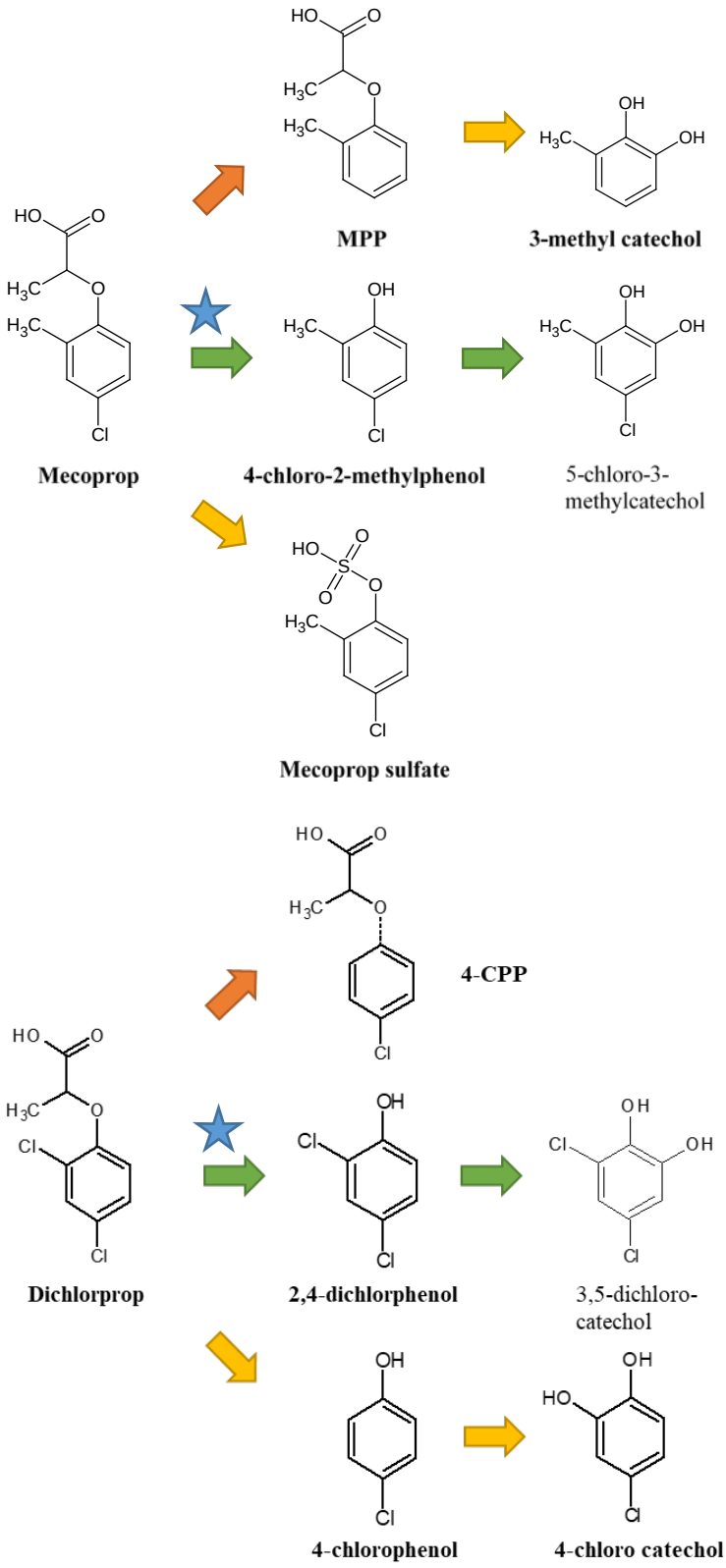


Figure S1. Proposed degradation pathway of mecoprop and dichlorprop. Green arrows shows aerobic degradation, orange is anaerobic, and yellow is neutral/unknown. Compounds in bold are included in our analysis. The blue star indicates the enantioselective pathway. Based on reviews by Buss et al., [7] and Müller and Kohler [13].

Figure S2. Filling of the sand biofilter (**left**) and the stonewool biofilter from the top (**right**).

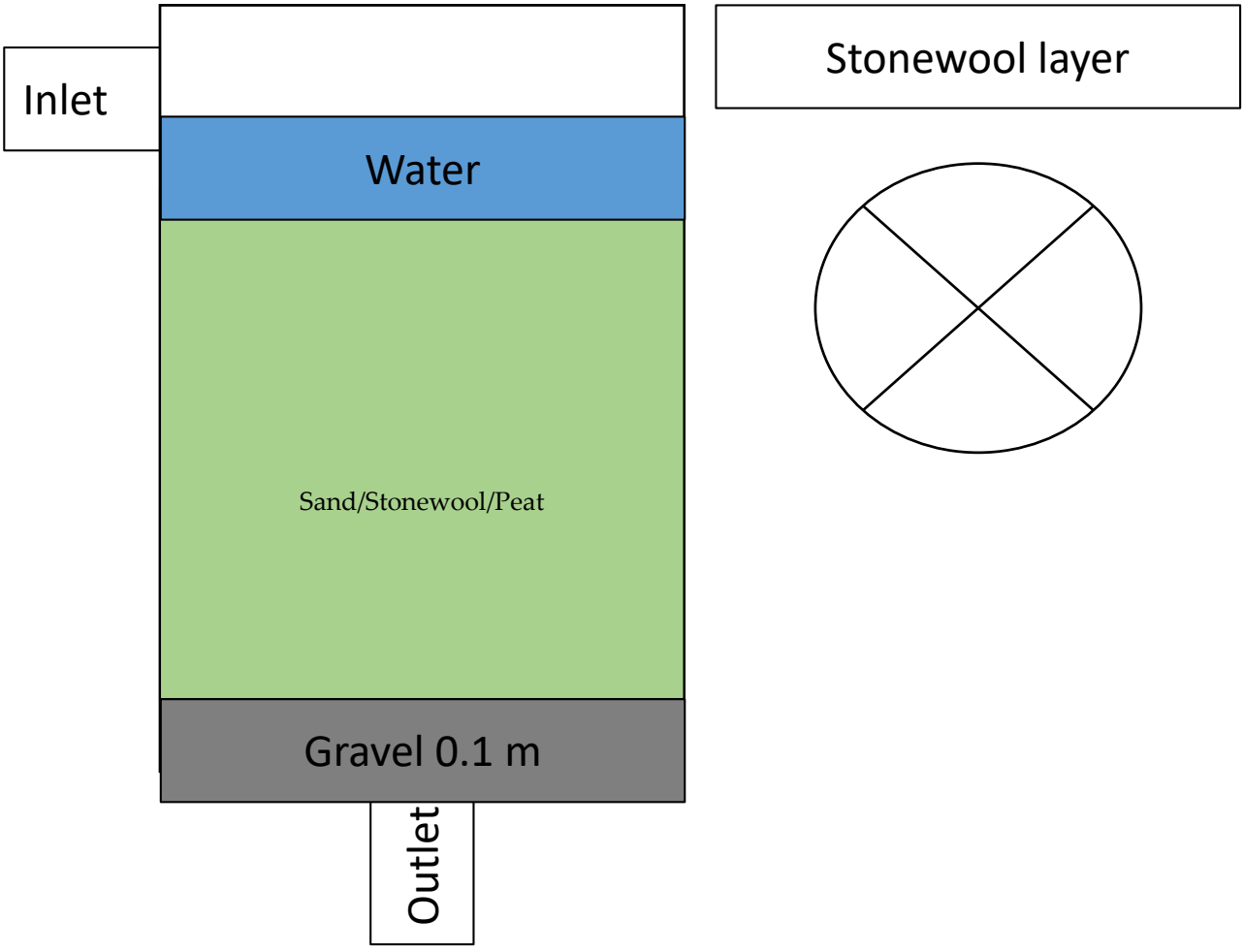


Figure S3. Sketch of the construction of the biofilters and the design of the stonewool layers.

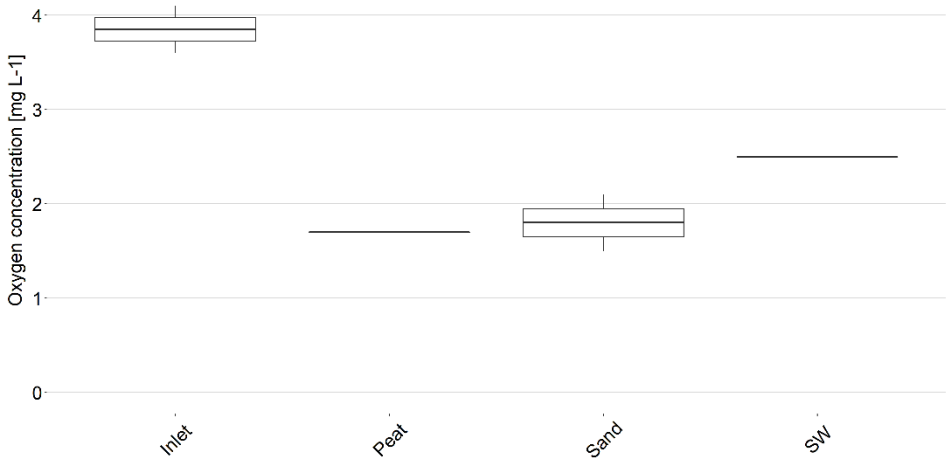


Figure S4. Oxygen concentrations from the three biofilters outlet and at the inlet (SW = stonewool).

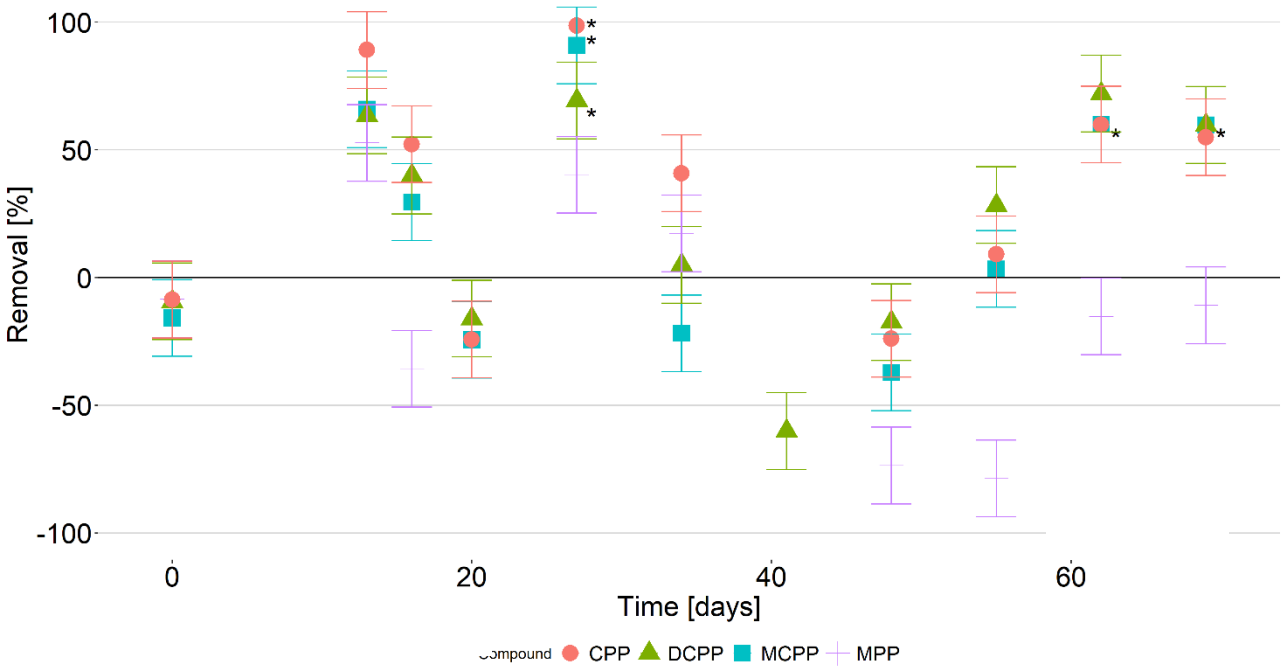


Figure S5. Peat amended sand: Removal rate (%) of CPP (●), DCPP (▲), MCPP (■), and MPP (+) during the experimental period in the 1% peat amended biofilter. 4 data points (>−100%) were removed from the graph. Error bars were set to ±15%, and asterisks (*) shows where outlet values were below LOQ.

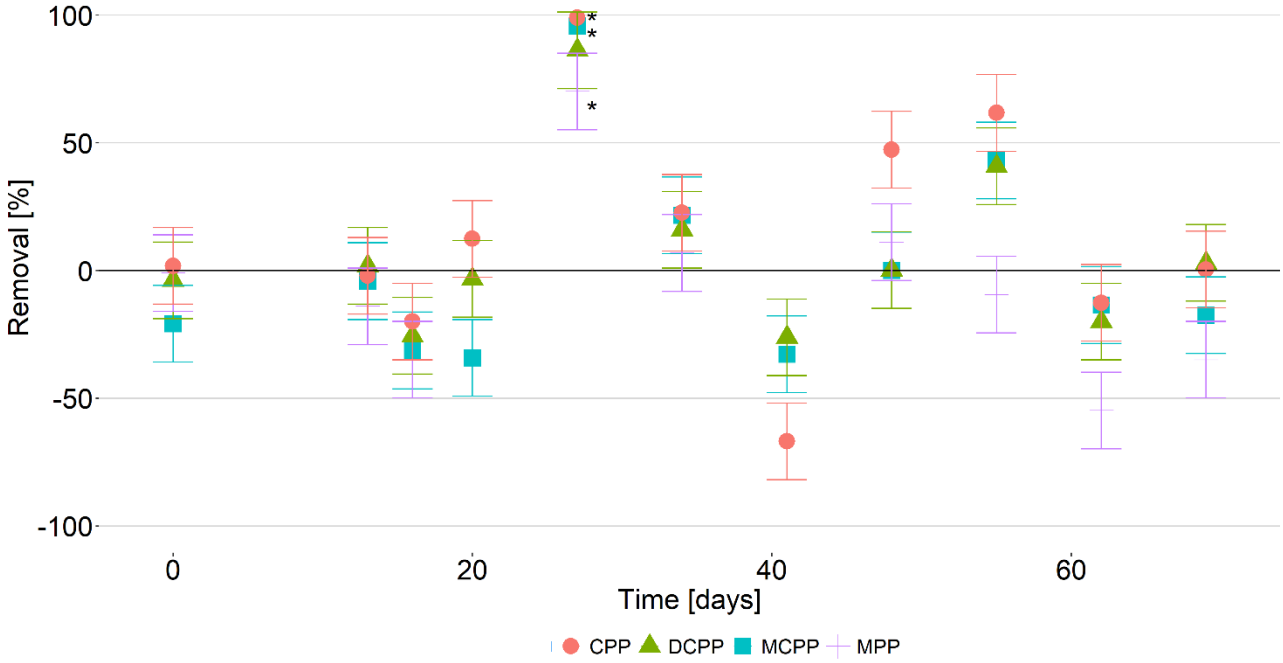


Figure S6. Stonewool: Removal (%) of CPP (●), DCPP (▲), MCPP (■), and MPP (+) during the experimental period. 2 data points (<−100%) were removed from the graph. Error bars were set to ±15%, and asterisks (*) shows where outlet values were below LOQ.

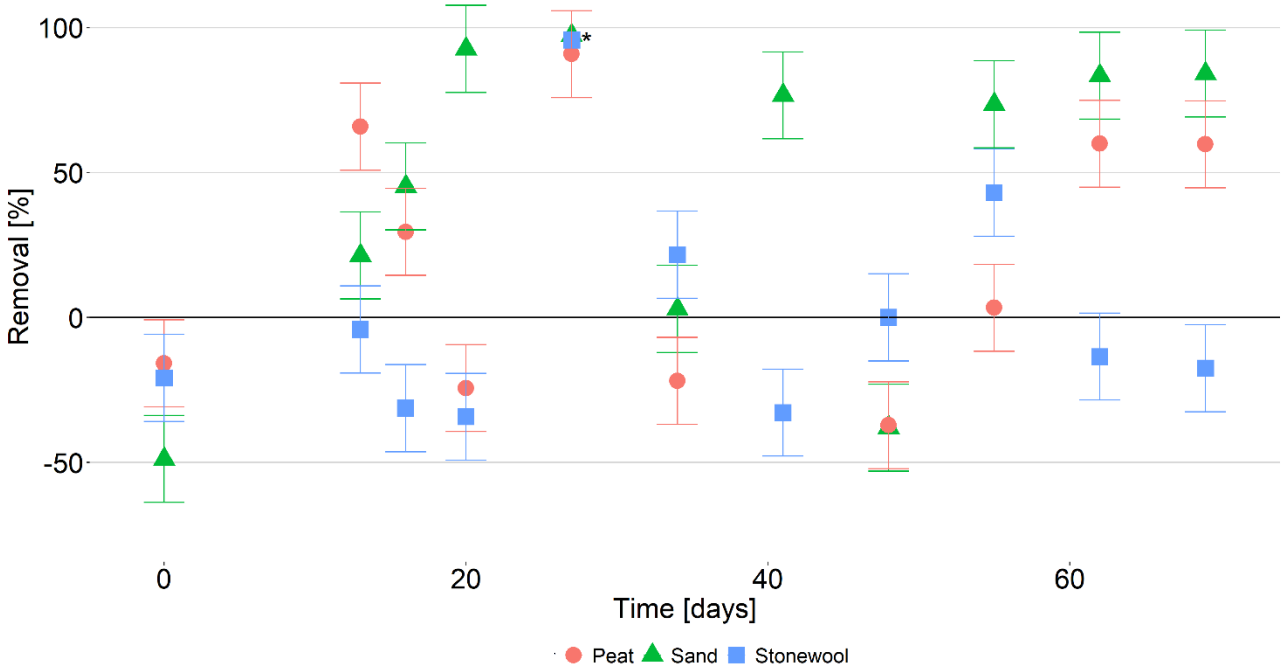


Figure S7. Removal (%) of MCPP from the three different biofilters during the experimental period; Peat (●), Sand (▲), and Stonewool (■). Error bars were set to ±15%, and asterisks (*) shows where outlet values were below LOD.

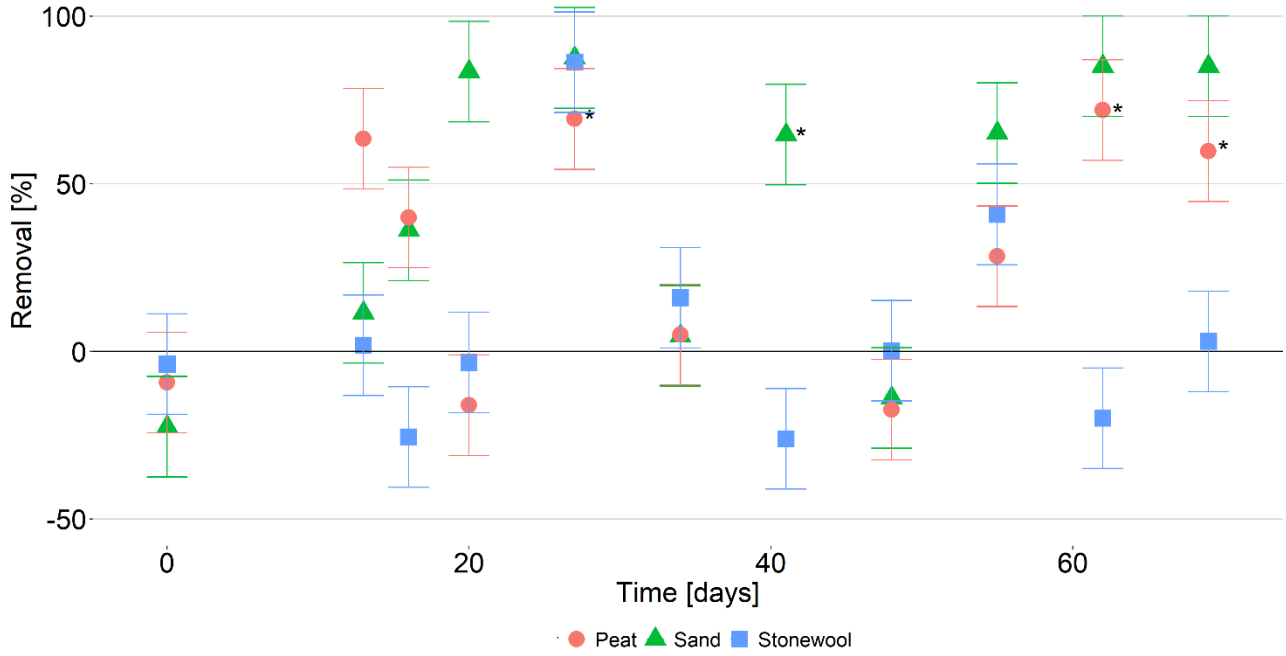


Figure S8. Removal (%) of DCPP from the three different biofilters during the experiment; Peat (●), Sand (▲), and Stonewool (■). Error bars were set to ±15 %, and asterisks (*) shows where outlet values were below LOD.