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Biofiltration systems for optimised stormwater management in urban areas

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Declaration

The candidate confirms that the work submitted is his/her/their own and that appropriate credit has been given where reference has been made to the work of others

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Abstract

Decrease in permeable areas due to urbanisation and increased frequency of extreme event due to climate change are putting more pressure on conventional drainage systems. This is leading to more frequent urban floods and water receptor deterioration. Sustainable drainage systems are green infrastructure that aim to achieve multiple benefits while managing stormwater runoff. Among these infrastructures, biofiltration systems are a promising retrofit option for site-constrained urban areas due to the vertical arrangement of treatment stages that leads to a relatively compact footprint. Existing knowledge about the influence of their design and configuration on hydrological, stormwater pollutant removal and long-term performance is limited and this has been identified as a barrier to their widespread uptake. Laboratory test were used to study the influence that high hydraulic conductivity amended biofilters have on removal performance and plant fitness.

Media were tested in laboratory and selected based on their physical-chemical and hydraulic characteristics to build a biofilter designed to treat dissolved pollutants. Non-vegetated test with control biofilters and configuration amended with Zeolite, GAC, and a mix of both, were dosed with the equivalent of an average annual runoff volume of Leeds (650 L) with synthetic stormwater simulating typical pollutants concentration of urban runoff areas. Results for this test informed the design that underwent a second phase were mesocosms in greenhouse were dosed with semi-synthetic runoff and monitored for 6 months for nutrients, heavy metals, and hydraulic conductivity. Biofilters were planted with two plant species characterised by different root system, *Carex flacca* and *Deschampsia Cespitosa*. At the end of the experiment biofilters were disassembled to investigate the fate of pollutants in media and vegetation. Results suggests that high hydraulic conductivity amended biofilters increase the removal performance of dissolved pollutants without compromising plant fitness possibly reducing the footprint of this system.

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Acronyms

ADWP	Average Dry Weather Period
AmCa	Amended column with *Carex Flacca*
AmDe	Amended column with *Deschampsia Cespitosa*
AmNP	Amended column non vegetated
CIRIA	Construction Industry Research and Information Association
CoCa	Control column with *Carex Flacca*
CoDe	Control column with *Deschampsia Cespitosa*
CoNP	Control column non vegetated
CSO	Combined Sewer Overflow
DC	Dissolved carbon
DIC	Dissolved inorganic carbon
DOC	Dissolved organic carbon
Eh	Activity of electrons
GAC	Granular Activated Carbon
IUPAC	International Union of Pure and Applied Chemistry
NPPF	National Planning Policy Framework
PAH	Polycycle aromatic hydrocarbons
PO4-P	Phosphate
SAB	SuDS Approving Body
SuDS	Sustainable Drainage Systems
SVP	filter layer with sand, vermiculite, and perlite
SVPT	filter layer with sand, vermiculite, perlite, and topsoil

TDN	Total dissolved nitrogen
TDS	Total dissolved solids
TN	Total nitrogen
TP	Total phosphorus
TS	Total Solids
TSS	Total suspended solids
XRF	X-Ray fluorescence analysis

Symbols

K_w	Hydraulic conductivity
q_e	Adsorption capacity at equilibrium

Chapter 1 Introduction

1.1 Background and problems

Managing surface runoff is an increasing challenge in most urban areas. Urbanisation reduces permeable surfaces, with consequent increase of runoff volume, putting more pressure on conventional and ageing drainage systems. This situation is exacerbated by climate change, which is causing a drastic rise in the probability of extreme weather and climate events around the globe (Miller and Hutchins, 2017). As a result, these two factors have increased the risk of pluvial flooding in urban environment and pollution of water bodies.

Urbanisation is increasing further and population living in cities is expected to increase to above 90% in most countries (EEA, 2017). Urban floods became a more relevant problem not only for the disruption of services, but also as economic and life-threatening menace since most of business and people live in cities (Pitt, 2008). Despite the Water Framework Directive’s objective to achieve good water quality status by 2015, 60% of water bodies still fail to achieve this standard due also to diffuse pollution (Priestley, 2015; Mourelatou et al., 2017). Pollutants deposited on impervious surfaces during dry periods are washed off and can reach water bodies affecting the ecosystem (Eriksson et al., 2007; Schimmelmann et al., 2016).

Substandard conventional drainage systems and the increased frequency of extreme rainfall events are the main causes of more frequent surface flooding and combined sewer overflows (Dolowitz et al., 2018). The management of urban stormwater has thus significantly changed in the past shifting towards an approach were multiple objectives drive the infrastructure design (Fletcher et al., 2015). Sustainable Drainages Systems (SuDS) “are designed to maximise the opportunities and benefits we can secure from surface water management” (Woods-Ballard et al., 2015). This technology is designed to support cities during severe rainfall, restore the water cycle to pre-development condition, support biodiversity, provide amenity and reduce diffuse pollution at source. One example of this technology are biofilters: these are vegetated areas that collect stormwater runoff allowing temporary ponding before infiltrating through a sand filter. Due to their flexible design and vertical arrangement of treatment stages they have the potential to be easily retrofitted in urban space delivering multiple benefits (Jose et al., 2015).

In the literature the pollutant removal performance of these systems for pollutants is generally higher than 90%, but dissolved pollutants represent a major challenge and often the data relative to dissolved heavy metals are not available (Davis et al., 2003; Blecken et al., 2009a; Søberg et al., 2014; Monrabal-Martinez et al., 2017). Biofilter design guidelines suggest 100-200 mm/h hydraulic conductivity in order to guarantee plant survival, water retention and pollutants control (Payne et al., 2015; Woods-Ballard et al., 2015). Under a climate change scenario where rain events are more intense, lower values of hydraulic conductivity could increase the risk of overflow, thus decreasing the overall treatment efficiency. The biofilter to drainage area ratio is also an important design criteria. Undersized biofilter are characterised by lower treatment performance due to greater overflow and more rapid clogging as a result of higher particulate matter mass management (Le Coustumer et al., 2012; Kandra, Deletić, et al., 2014). This decreases the possibility to retrofit biofilter in confined spaces. Hyperaccumulator plants are often used in phytoremediation, yet these plants have hardly been used in biofilters (Cristaldi et al., 2017; Muerdter et al., 2018). Sand is the most used media for biofiltration systems. The use of media amendments to improve the performances is limited, with no information about possible side effect on performance and plants (Grebel et al., 2013). Conflicting requirements for preventing flooding as well as protecting the natural environment form diffuse pollution, can lead to difficult decision in system design. This together with uncertainties in modelling pollutant removal processes is preventing a wide spread of this technology in the UK (Ashley et al., 2015).

This thesis addresses the uncertainty introduced by media amendments and hypertollerant plants to enhance pollutant treatment providing laboratory based data on the hydraulic processes and chemical treatment of dissolved pollutants.

1.2 Aim

The aim of this study is to investigate the influence of engineered media and plant species on pollutant removal performance of biofilter system within UK climatic conditions. This research uses analytic techniques and long term laboratory experiments of biofilter columns characterised by different configuration with and without engineered media and different plant species dosed with synthetic and semi-synthetic stormwater runoff.

1.3 Objectives

To achieve this aim, the objectives of the research are:

- To characterise the variability of physical, chemical and hydraulic property of soil media to be implemented in a biofilter.
- To determine the influence of soils amendments and antecedent dry weather period on the adsorption of dissolved pollutants in synthetic stormwater runoff of non-vegetated biofilters.
- To evaluate the effects that amendments and simulated UK water regime have on the pollutant removal performance of vegetated biofilter dosed with semi-synthetic stormwater runoff.
- To determine the type of impact that amendments have on the vegetation of biofilters by monitoring the fitness and development of shoots and roots.
- To assess the influence that high hydraulic conductivity has on vegetation fitness and biofilter treatment performance over time.
- To identify the vertical profile of pollutants in biofilters' media and the bioaccumulation in vegetation to address maintenance requirements.
- To evaluate the implication of research findings on biofilter design and maintenance.

1.4 Thesis outline

Chapter 1: Introduction summarises current context and describes current knowledge gaps and research needs regarding biofiltration systems. It also introduces aim and specific research objectives for this study.

Chapter 2: Literature review introduces background on climate change effect on urban environments, enforced laws in the UK, current water management, SuDS and biofilter, water quality remediation. The chapter also investigates the current knowledge gaps and further research needs connected with the topic in this thesis.

Chapter 3: Material and methods presents the methodology and instruments adopted in this research. The chapter states the area of study that informed laboratory experiments, the designs used and the detailed methods implemented to assess the removal performances of the investigated mesocosms.

Chapter 4: Biofilter media characterisation shows the results for physical-chemical and hydraulic characteristics of medias used in the research. It is also looking into the motivation connected with their use. The focus of Chapter 4 is to identify the possible effects that single media have on the biofilter's design.

Chapter 5: Phase I: non vegetated column test presents the results and discussion for the experiment using columns with no vegetation. The aim is to determine the treatment efficiency for dissolved phosphorus, copper and zinc, in order to narrow down the design to be used for the planted columns. Possible flaws in the laboratory setup were considered to improve accuracy.

Chapter 6: Phase II: vegetated column test detail the outcomes of the improved setup that was monitored for 6 months for a wider range of pollutants in order to highlight differences in performance among biofilters characterised by absence/presence of amendments and plants.

Chapter 7: Fate of pollutant in biofiltration system analyses pollutants concentration in plants and media via ICP-MS and the results of the image analysis on roots and shoots. The level of contamination is used to highlight problems in the design and suggest management procedures.

Chapter 8: Discussion brings together the results of the experiments.

Chapter 9: Conclusions, limitations and future research provides a summary of key findings and contribution of this research. The chapter also discusses limitation and further research opportunities.

Chapter 2 Literature review

2.1 Chapter overview

The chapter reports a comprehensive review of recent literature on biofiltration systems. Here is introduced Sustainable Drainage Systems and their multidisciplinary approach to manage stormwater runoff. A review of treatment performances and factors affecting biofilters treatment and water retention are here reviewed. The chapter concludes with knowledge gaps, aim, and objective of this thesis.

2.2 Urbanisation

Climate change is a worldwide increase of temperature due to anthropogenic CO_2 emission that is affecting linearly global mean precipitations. This lead to annual frequencies of events with peak discharge of 100-years return period to rise significantly in most countries in Europe (Collins et al., 2013; Alfieri et al., 2015). Cities face specific risks due to a fast development that reduce drastically permeable areas limiting ecosystem services and preventing rainfall to drain into the ground (Nirupama and Simonovic, 2007; Jovanovic et al., 2016; Martos et al., 2016). The majority of sewer systems have been designed more than 100 years ago and do not have the capacity to manage the increased amounts of water generate by the impermeable surface and the increased population. Therefore, when surface water volume exceeds the drainage capacity pluvial floods occur. This can lead to the destruction of properties and public infrastructure, loss of business and water contamination (Semadeni-Davies et al., 2008).

2.3 Water management

Conventional sewer systems consist in both combined sewer systems (CSS), and separate sewers. In the first, domestic and rain water run through the same pipes towards treatment plants, make it a cheaper option due to the lower resources needed to build it (Figure 2-1). When a storm event exceeds the designed capacity a combined sewer overflow (CSO) drains into receiving bodies pollutants derived by industrial, domestic, and urban activity such as motor oil, PAH, heavy metals, nutrients, pesticides, pathogen, and other pollutants (Butler and Davies, 2011).

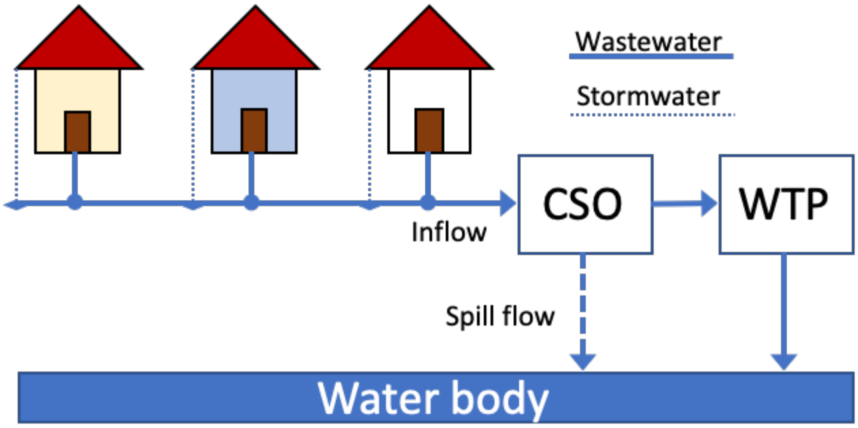


Figure 2-1 Schematic plan of a combined sewer system

In the second system (Figure 2-2), pipes that carry stormwater are separated by the ones that manage wastewater, thus rain water can be conveniently discharged into a body receptor while waste reach water treatment plants. The disadvantages involve slightly higher cost of excavation and pipes, as well as the impossibility to separate completely stormwater and wastewater. In fact, stormwater runoff has been shown to collect and transport contaminants originated by cars such as oil, heavy metals and solids directly in stream (Butler and Davies, 2011).

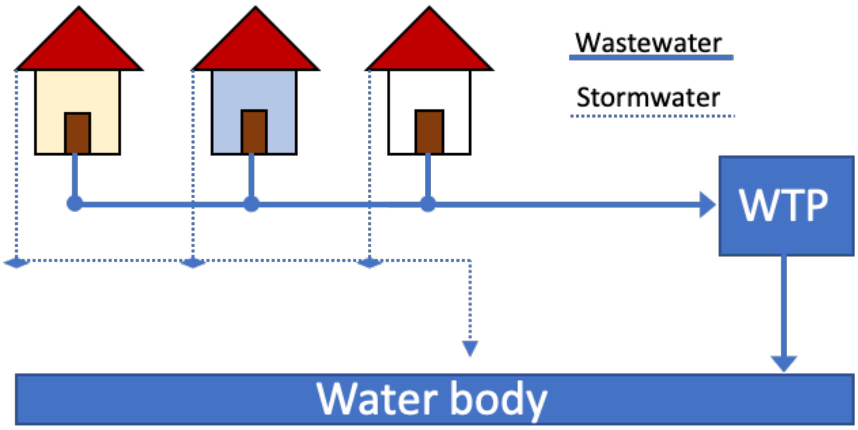


Figure 2-2 Schematic plan of a separate sewer system

In many studies, urbanisation and its runoff have been highlighted primary cause of stream water quality deterioration (Hatt et al., 2004). Small rain events of few millimetres are not enough to cause a hydraulic stress to the systems. However, high impervious catchments and frequent events can weaken water communities delivering altered water (e.g. poor oxygenated, low pH, high pollutants concentration) reducing biodiversity (Hatt et al., 2004; Walsh et al., 2006; Gołdyn et al., 2018). Macroinvertebrates, extensively studied organisms in water ecosystem, show a reduction in pollutant sensitive species (i.e. Ephemeroptera, Trichopteran and Plecoptera) and rise in tolerant taxa (i.e. Chironomidae) when exposed to urban stormwater runoff (Pratt et al., 1981; Walsh et al., 2006; Gresens et al., 2007).

Concentration in urban storm-water runoff typically exceed those of treated wastewater (LeFevre et al., 2015), and can contain a variety of harmful pollutants such as heavy metals, organic compounds, nutrients, and particulate matter that depends on the land use of the catchment (Charlesworth and Lees, 1999; Huber et al., 2016; Tedoldi et al., 2016).

2.4 Stormwater runoff constituents

Pollutants concentration depend on fixed site-specific factors like: land use, traffic area, operational characteristics; and climatic factors (Huber et al., 2016). Many dataset have been compiled highlighting the challenge to characterise stormwater runoff (Stotz and Krauth, 1994; Pitt et al., 1995; Sansalone and Buchberger, 1997; Mitchell, 2005; Flint and Davis, 2007; Lundy et al., 2012; Huber et al., 2016). A comprehensive matrix of urban can be found in Table 2-1 and it shows the variety of pollutants concentration across different sources.

Table 2-1 Concentration of pollutants from different urban areas

Urban and residential

		Cu (ug/L)			Zn (ug/L)			Pb (ug/L)				
Site	Site	Mean	min	max	Mean	min	max	Mean	min	max	More info	Source
Pedestrian and cycle way, yard		23			585			107			Total	Göbel et al. (2007)
Residential roads	European data	11.5	6	17	118.5	87	150	73	6	140	Dissolved	Lundy et al. (2012)
Suburban roads	European data	65	10	120	960	20	1900	225	10	440	Dissolved	Lundy et al. (2012)
Ultra-urban	Mount Rainer, Md.	110			1180			220			Dissolved	Flint et al. (2007)
Urban	Millcreek, Ohio	94.8	13	279	4054.4	209	14786	16	13	21	Dissolved	Sansalone and Buchberger (1997)
Urban	Millcreek, Ohio	135	43	325	4274	459	15244	64.4	31	97	Total	Sansalone and Buchberger (1997)

		TSS				
Site	Site	Mean	min	max		
Pedestrian and cycle way, yard	Northern European	7.4			Total	Göbel et al. (2007)
Urban roads	European data	2705.5	11	5400	Dissolved	Lundy et al. (2012)
Residential roads high density	European data	811.5	55	1568	Dissolved	Lundy et al. (2012)
Residential roads low density	European data	155	10	300	Dissolved	Lundy et al. (2012)

Parking lot

		Cu (ug/L)			Zn (ug/L)			Pb (ug/L)				
Site	Site	Mean	min	max	Mean	min	max	Mean	min	max		
Car parks and commercial areas	European data	103	1	205	350.5	1	700	5.5	1	10	Dissolved	Lundy et al. (2012)
Carpark	Lund, Sweden										Dissolved	Deletic and Makisimovic (1998)
Parking areas	Birmingham, Alabama	11.00	1.10	61.00	86.00	6.00	560.00	2.10	1.20	5.20	Dissolved	Pitt et al. 1995
Parking lot	Review/global	11.8	2.7	35	77.2	12	317	4.3	1	15.9	Dissolved	Huber et al. (2016)
Storage areas	Birmingham, Alabama	250.00	1.00	1520.00	22.00	3.00	100.00	2.60	1.60	5.70	Dissolved	Pitt et al. 1995
Vehicle service areas	Birmingham, Alabama	8.40	1.10	24.00	73.00	11.00	230.00	2.40	1.40	3.40	Dissolved	Pitt et al. 1995
Parking lot	Review/global	40.7	5	220	201	39	620	23.1	2.5	66	Total	Huber et al. (2016)
Car park		80			400			137			Total	Göbel et al. (2007)

		TSS				
Site	Site	Mean	min	max		
Car parks and commercial areas	European data	138.9	7.8	270	Total	Lundy et al. (2012)
Carpark	Lund, Sweden		5	417	Total	Deletic and Makisim
Parking areas	Birmingham, Alabama	110.00	9.00	750.00	Total	Pitt et al. 1995
Storage areas	Birmingham, Alabama	100.00	5.00	450.00	Total	Pitt et al. 1995
Vehicle service areas	Birmingham, Alabama	24.00	17.00	38.00	Total	Pitt et al. 1995

	Site	Site	Cu (ug/L) Mean	min	max	Zn (ug/L) Mean	min	max	Pb (ug/L) Mean	min	max		
Highway	Highway low density	Review/global	23.3	5.7	64	76.9	5	191	1.3	0.01	3.1	Dissolved	Huber et al. (2016)
	Highway high density, non urban	Review/global	34.6	4	100	204	8.6	577	12.8	12.8	12.8	Dissolved	Huber et al. (2016)
	Highway high density, urban	Review/global	35.5	4.1	151	217	11	2118	3	0.8	7.4	Dissolved	Huber et al. (2016)
	Highway	Weins, Germany	49			441			137			Dissolved	Stotz and Krauth (1994)
	Highway	Weins, Germany	88			737			58			Dissolved	Stotz and Krauth (1994)
	Highway low density	Review/global	60.7	13.3	140	306	32.3	1760	64.4	2.5	230	Total	Huber et al. (2016)
	Highway high density, non urban	Review/global	84.4	23	430	385	52.5	2210	31.7	4.4	90	Total	Huber et al. (2016)
	Highway high density, urban	Review/global	63.5	13	274	338	21	2234	33.1	1.4	220	Total	Huber et al. (2016)
	Service road		86			400			137			Total	Göbel et al. (2007)
	Motorway		65			345			224			Total	Göbel et al. (2007)

	Site	Site	TSS Mean	min	max		
Highway	Highway	Weins, Germany	64.00			Dissolved	Stotz and Krauth (1994)
	Highway	Weins, Germany	49.00			Dissolved	Stotz and Krauth (1994)
	Service road		150			Total	Göbel et al. (2007)
	Motorway		153			Total	Göbel et al. (2007)

2.4.1 Heavy metals

Metal species such as Cadmium, Chromium, Copper, Nickel, Lead, Platinum and Zinc are fundamentally persistent and can induce acute toxicity and carcinogenicity though not fully understood mechanisms (Tchounwou et al., 2012). Their bioavailability depends on the environmental redox and pH condition that influence the phase the metal is in: dissolved, colloid, or particles, the latter being the most predominant. The occurrence of heavy metals is site-specific and mainly due to car operation (i.e. breaking pads, tyre wear) and the increased use of private transport over the years became a major source of contamination (Huber et al., 2016; Hwang et al., 2016).

2.4.2 PAH

Cars are also responsible for polycycle aromatic hydrocarbons (PAHs): carcinogenic organic compound with two or more fused benzene rings produced during incomplete combustion of fossil fuel, organic matter and wood (Edwards, 2010). Road surface wear is major contributor of this pollutants since coal-tar-based asphalt coating agents contain high concentration of PAH (Van Metre and Mahler, 2010), making difficult to regulate emissions since it is contained in petroleum products (Hwang et al., 2018).

2.4.3 Nutrients

Vegetation is abundantly present in some city, but if not managed properly it can transform in a source of nutrients. Nitrogen and phosphorus occur from the mechanical and chemical decomposition of organic matter (e.g. leaves), atmospheric deposition due to weathering, and from anthropogenic sources (e.g. fertiliser) (Brett et al., 2005; Cisar et al., 2012; Schimmelmann et al., 2016). The excess of nutrients in rivers and lakes is responsible for eutrophication, an enrichment of phosphorus and nitrogen in water that lead to algae bloom, high respiration rates and subsequent depletion of oxygen in water harming organisms living in it (Correll, 1998; Cisar et al., 2012).

2.4.4 Dissolved Carbon

Dissolved carbon consists of inorganic and organic carbon. The first, DIC, is present in all natural waters, and it is composed of dissolved CO_2, HCO_3^-, and CO_3^{2-}. It is involved in the acid-base reactions in water and soil, and it represent a major buffer controlling pH in water (Zehnder, 1982). The second, is derived by decomposition of organic materials like plant residues (Kolka et al., 2008). DOC comprise of humic substances (e.g. carbohydrates, peptides, amino acids) and its decomposition can cause oxygen deficiency in water, unpleasant smells and host microbial community (Sounthararajah et al., 2015). It causes colour and odour in water, representing a challenge for water treatment plants because precursor of trihalomethane formation (cancerogenic pollutant), and can play an important role in transport of heavy metals in water (Katsoyiannis and Samara, 2007).

2.4.5 Solids

The transportation of most pollutants occurs through the strong affinity to solids (e.g. sediment, microplastics) (Deletić, 1998; Hunt et al., 2008; Hwang et al., 2018). The finer fraction of suspended solids, particle with diameter smaller than 150 μm comprising of soil, atmospheric deposition, vegetation, and others, represent the most abundant and polluted mass deposited during dry periods due to its high specific surface and cation exchange capacity (Revitt et al., 2014). These particles get washed off more easily during rain events (German and Svensson, 2002; M. Kayhanian et al., 2012) creating a phenomenon known as “first flush”, where 30% of runoff volume move more than 90% of the mass. This acts as mobile substrate influencing significantly the transport of pollutants from impermeable surfaces to water receptors (Deletić, 1998; Bach et al., 2010). Atmospheric and environmental condition like temperature and the presence of salts affects the availability of pollutants, with metals increasing up to 10 and 44 folds the concentration of suspended and dissolved solids (Monrabal-Martinez et al., 2018). Part of suspended sediment mass is represented by microplastics, found in 72% of European drinking water samples (Environment Agency, 2018). These particles result from the disintegration of plastic debris caused by mechanic abrasion (e.g.

tyres) and UV fragmentation. These particles and fibers derived from petroleum are typically sized below 5mm, although the scientific community is still debating the lower limits between micro and nanoplastics (Lassen, 2015; Magnusson et al., 2016; Blair et al., 2017; Jan Kole et al., 2017; Scudo et al., 2017).

2.5 Water regulation

Attempt to insure better water quality and quantity control has been enforced by many countries with different regulations: in USA water pollution has been addressed through the 1948 “Federal Water Pollution Control”, amended in 1974 and commonly known as Clean Water Act (CWA) (US EPA, 2010). In the United Kingdom (UK), the reorganisation of water, sewage and river management industry was reinforced through the Water Act 1973, where ten Regional water authority were in charge of water treatment, sewage, land drainage, river pollution and conservation. The duty related with river, drainage and pollution management were later passed to the National Rivers Authority (NRA) (Water Act 1989) and finally to the Environment Agency (EA) with the Environment Act 1995. Most of the recent British legislation relative to the environment protection was promoted by the European Union (EU). The water framework directive (2000/60/EC) (European Union, 2000) created a single system across Europe, setting a deadline to 2015 to achieve good chemical and ecological water status. However, a recent report from European Environment Agency and a briefing paper from the House of Commons showed that 60% of all the water body across Europe fail to meet the aimed “good ecological status”, with 38% of reported surface waterbodies under significant pressure caused by diffuse pollution (Priestley, 2015; Agency, 2018). In 2006, after many floods events across Europe caused 52 billion euro in economic damages and loss of lives, the European Commission proposed a Directive requiring the Member States to reduce and manage the risk that floods pose to human health, that came into force in 2007 with the Directive 2007/60/EC (European Union, 2007). The same year UK has been hit by a series of intensive rain (414mm), setting a record in a data series started in 1766. Gullies and drains were unable to coop with the excess water causing urban floods affecting thousands of people and damages estimated in 4bilion pounds (Environment Agency, 2007). The Secretary of State for the Environment, Flood and Rural Affair appointed Sir Michael Pitt, chair of South West Strategic Authority, to investigate independently the impacts of floods that have affected UK. The report suggested that floods occurred from several sources: river (fluvial) flooding, surface water (pluvial) flooding; both due by high volume and intensity of rainfall, generated by the unusual combination of the Polar Front Jet Stream, high North Atlantic sea surface temperature and low capacity to absorb and transport water on the territory. Sir Michael Pitt conclude the review giving strong advice on emergency response, recovery phase, and recommendation to improve UK’s ability to tackle emergencies (Pitt, 2008). From this work the UK government shaped the Flood and Water Management Act 2010, aiming at reducing flood risk associated with extreme, more frequent, weather.

Conventional sewer systems showed to be inadequate both as flood defence (Figure 2-3) and to maintain high water quality. Management of water in a changing climate condition is crucial to avoid people distress and negative impact on countries economy (Olds et al., 2018). The Directive 2000/60/CE suggested sustainable land use practice to manage flood risk, concept endorsed as well in the Pitt Review that identifies in Sustainable Drainage Systems (SuDS) a technique to reduce water discharge from developed sites, restore water resources, slow down water and passively treat runoff before getting into watercourses (Pitt, 2008). The use of SuDS is furthermore recommended by the Department for Environment, Food, and Rural Affair (DEFRA) (DEFRA, 2012) to tackle diffuse pollution from urban runoff and are one of the topic at the centre of the 25 year plan to improve the environment set by the British government in 2018 (HM Government, 2018). SuDS are regulated by Schedule 3 of the Flood and Water Management Act 2010, however, this came into force only in Wales on the 7th of January 2019. Under this regulation, SuDS need to be approved by the SuDS Approving Body (SAB) before construction begin. These areas need also to comply with standards that covers hydraulic management, water quality, amenity deliver and enhance biodiversity. In England the Government on the 19th of February

2019 amended the National Planning Policy Framework (Government's planning policies for England) (NPPF) requiring SuDS to be delivered only for major developments (10 dwellings or non-residential developments) (Gov.uk, 2019). There is no formal adoption authority since schedule 3 was not enacted, but the drainage schemes need to be approved by the Local Planning authority in consultation with the Lead Local Flood Authority.

Figure 2-3 Conventional drainage clogged with sediments and leaves. Poor management of conventional system can cause severe floods.

2.6 Sustainable Drainage Systems (SuDS)

SuDS is only one of the few acronym used to identify the sustainable approach to water management (Fletcher et al., 2015).

The objective of SuDS is to re-establish pre-development condition at source using a holistic approach. These systems are designed to maximise benefits and opportunities not only delivering water quality and quantity control, but also improving people quality of life in urban spaces and increasing biodiversity. Conventional drainage approaches consider stormwater as a problem to be removed as quickly as possible with a repressive disciplinary mechanism rather than a resource (Jones and Macdonald, 2007; Jose et al., 2015; Ashley et al., 2015). In 2007 the Construction Industry Research and Information Association (CIRIA) provided the first UK guideline that address the design, construction and maintenance of these systems that include: green roofs, filter strips, swale, ponds, wetlands, and biofilters (Woods-Ballard et al., 2007). The design criteria for these systems should comply with “the four pillars of SuDS design” (Figure 2-4): constrain peak runoff to greenfield rates (i.e. maximum 2 L/s/ha) for events that might impact the morphology, ecology or capacity of body receptors, to control peak runoff of events with 100-year return period, intercept, treat, and prevent short-term acute and long-term chronic pollution at source (Woods-Ballard et al., 2015). The presence of plants ensure more green spaces in cities improving biodiversity, carbon capture, and evapotranspiration that mitigate “urban heat island effects” (Pochee and Johnston, 2017).

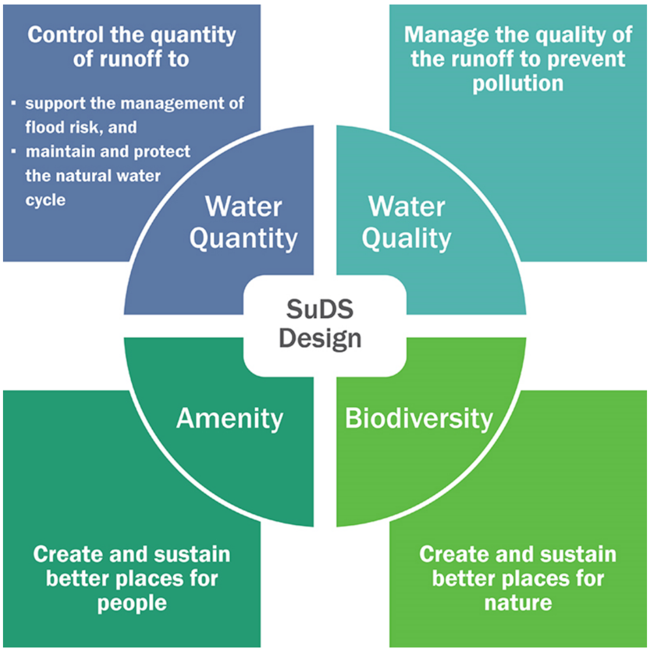


Figure 2-4 The four pillars of SuDS design (Woods-Ballard et al., 2015)

2.7 Biofilters

Among green infrastructures, biofiltration systems are a promising approach to control urban runoff in cities due to their vertical arrangement and relative small footprint. A biofilter is a planted shallow landscape feature with an underdrain system able to filter and slow down rain runoff in groundwater or conveyed it in rivers using pipes. Its flexible design makes it easy to retrofit in urban environment and optimise to a variety of climatic condition (Payne et al., 2015; Woods-Ballard et al., 2015), however some features are common in all designs:

- Hydraulic control: These consist in an inflow zone that controls the inflow rate; an overflow that permit high flows to bypass the biofilter; a ponding zone that control the volume of water treated.
- Vegetation: plants are not only crucial to ensure biodiversity and amenity, but also to maintain the hydraulic conductivity of the system, promote microbial community needed for bioremediation, and reduce the outflow volume through evapotranspiration.
- Filter media: its purpose is to remove pollutants, support plants and microorganism, reduce peak flows, and detain runoff. The filter media is generally a vertical combination of loamy sand, where the treatment occurs, a transition layer that prevents the filter media wash off, and a drainage layer that collects the treated water. A biofilter can either drain water with a perforated pipe or, if the water quality allows it, infiltrate directly into the ground.

The underlaying pipe in its basic design is straight, but recent designs tend to include a raised outlet to form a submerged zone that enhance nutrients, metal removal and as reservoir of water for dry periods (Zinger et al., 2013; Payne, Fletcher, Cook, et al., 2014).

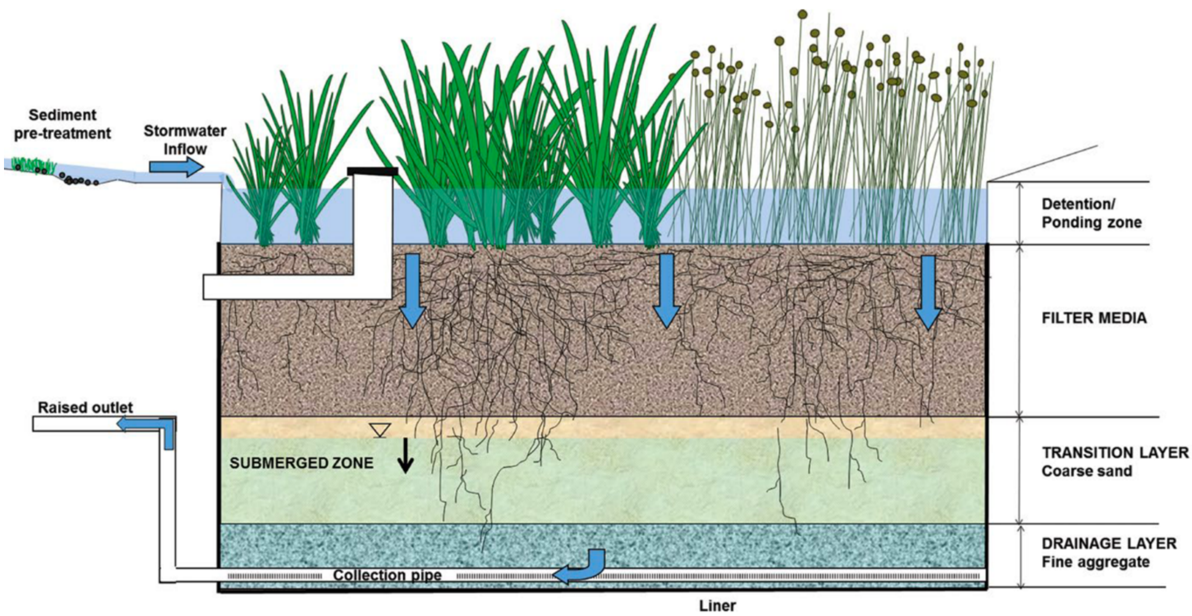


Figure 2-5 Schematic configuration recommended by Payne et al., 2015

2.7.1 Treatment performances and design

As water flows in the biofilter it is subjected to a wide range of processes: its velocity decrease and settle particles. The water then percolates through the media where physical filtration traps sediments and dissolved pollutants get adsorbed by the surface of the media. Plants and the microbial community promoted by the rhizosphere take up nutrients and, thanks to chemical transformation, contaminants get immobilised or degraded.

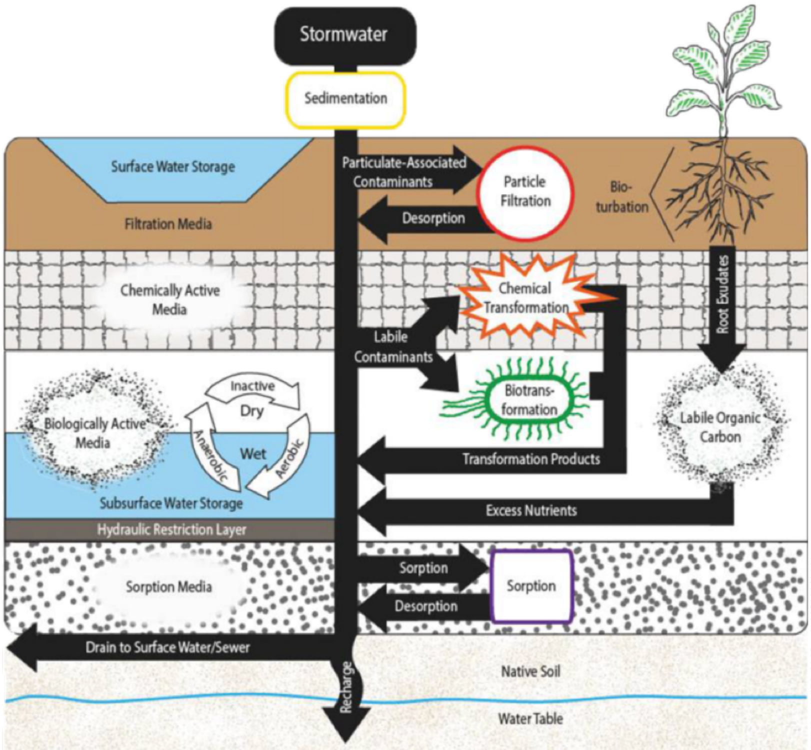


Figure 2-6 Treatment processes in biofilters (Grebel et al., 2013)

2.7.1.1 Suspended solids

The removal performance of total suspended solids in laboratory studies is greater than 90% (Blecken, Viklander, et al., 2007; Bratieres et al., 2008; Le Coustumer et al., 2012; Glaister et al., 2014; Liu and Davis, 2014), although in a recent research from Flanagan et al. in a full scale biofilter treating water from a highway in France TSS concentration in some cases were as high as road runoff, especially in winter, possibly due to erosion of fine particles from the media or the inefficient filtration process (Flanagan et al., 2019). This result has been found earlier also by (Hunt et al., 2008) in USA, where a biofilter draining runoff from a parking lot removed 60% of the inlet mass, specifying that filter media might have been drained by the under pipes. The use of winter tyres, that have up to 100 times more particles <10μm than summer tyres, the dry condition that promotes cracking in the filter, and the application of de-icing salt causing deflocculation have also been suggested as possible explanation for the phenomenon (Winston et al., 2016; Flanagan et al., 2019). Plant species influence the removal, with thicker root architecture responsible for a lower filtration efficiency due to water channelling and preferential paths (Fletcher et al., 2007; Le Coustumer et al., 2008). Due to the novelty of the field, there is not yet information related with the capacity of SuDS, and specifically biofilter, to remove microplastics.

2.7.1.2 Heavy metals

Suspended solids correlate with heavy metals concentration since these bond on the surface of particles transported by water (Hatt et al., 2006). (Gunawardana et al., 2011) found a correlation with high specific surface area and total organic carbon content in finer particles (i.e. <75μm), that represent 70% of solids, containing up to 60% of the total mass. Therefore, filtration play a major role in the removal of this contaminant from stormwater (Payne et al., 2015).

Heavy metal removal is generally positive, meaning that the concentration at the outlet is lower than at the inlet (Davis et al., 2006a; Hatt, Fletcher, et al., 2007b; Blecken et al., 2009b; Grebel et al., 2013; Paus et al., 2014; LeFevre et al., 2015). A study by (Davis et al., 2003) monitored laboratory mesocosms dosed with synthetic stormwater runoff for zinc, copper, and lead showing a reduction of the heavy metals of 95% compared with the influent. The same results have been achieved also on field, however, in one of the two facilities studied the treatment of this pollutant was lower than expected. The hypothesis led to the conclusion that difference in media, age, vegetation density, and depth are influencing the retention capacity, suggesting that metal removal is design dependent. Finally, the study highlighted that the accumulation of contaminant in the upper layer would not be an issue within short period, but require maintenance after 20-year lifetime (Davis et al., 2003). Blecken et al found similar results in 15 columns grown in climatic chambers planted with *Carex rostrata* under three different temperatures (3.2°C, 8.6°C, 18.6 °C) for the same three heavy metals. The columns were designed to maintain a sufficient hydraulic conductivity during the coldest months of the year increasing the diameter of the media used for the filter media. In fact, moisture freezing in the biofilter could decrease the pours size, thus increasing the chance of failure of the biofilter. Despite the limited content in clay and silt, which has high affinity with metals, the concentration of total heavy metals in the effluent were 95% lower than the inlet. The removal performances were higher at low temperature, suggesting that mechanical removal works even at near freezing point. However, the increased temperature showed a lower removal performance for copper, particularly in dissolved state. This metal forms a complex with dissolved organic carbon (DOC), and the increased biological activity under warmer temperature led to a leachate of this pollutant. The research highlight also that biofilm might increase the treatment as well as plants, however, the mass of pollutants in the media resulted higher than in the plant (Blecken et al., 2011). Leachate of dissolved copper and lead was later found also by (Søberg et al., 2014) in a similar design. The removal of metals occurs not only through filtration of particles, but also through adsorption with inorganic/organic colloids such as clays, organic matter (i.e. humic acids), metal oxides, hydroxides, metal carbonates and phosphates. The adsorption process is regulated by redox, contact time, metal speciation, and pH, with higher pH creating condition for the lowest solubility. This include a stronger mechanism less reversible, (specific adsorption) and a weaker outer-sphere complexes (non-specific adsorption). The first binds to organic matter, the second involve electrostatic phenomenon were cations from water and media surface exchange (Bradl, 2004). The inclusion of a saturation zone, as experimented by (Zinger et al., 2007), could prevent the leachate of metals. This led Blecken et al to test the inclusion of a saturation zone of 450mm with added cellulose carbon at the bottom of biofilters' design. This area positively enhanced the removal of copper by forming Cu-Organic matter complexes (Blecken et al., 2009a). The saturated condition of the biofilter decrease the level of oxygen, thus limiting the mobilisation of this metal. Long dry weather condition and the absence of this area correlated with lower removal due to oxidizing condition and preferential water path (Blecken et al., 2009b). These results were confirmed also by a later study, (Søberg et al., 2017), where it was highlighted that even in winter condition, when salt is spread on roads to prevent water freezing, increasing the mobility of heavy metals, the performance improved compared with a design with non-saturated zone. However, dissolved copper and lead still occasionally leached from the biofilters even for un-salted water (Søberg et al., 2017).

Although the media play a bigger role in metal removal, plants affects the treatment of this class of pollutants, with a general uptake between 5-10% (Blecken et al., 2009a). Plants with thicker roots (i.e. *Malaleuca ercifolia*) results in a lower performance for iron, aluminium, and chrome, possibly due to preferential flow paths, whereas no correlation was found with copper, zinc, and lead. The difference in performance among plants tend to wear thin with the accumulation of sediment that counter the roots effect (Feng et al., 2012). A common consequence of high concentration of metals in the ground is the physiological production by plants of reactive oxygen species (ROS), that interfere with transport protein harming the organism. Common mechanisms allow plants to avoid deterioration of their functionalities binding metals with organic exudate (i.e. phytostabilisation, phytofiltration), detoxification with amino acids in roots or metal-binding peptides, sequestration in vacuoles, or the production of antioxidants. Hypertollerant species are thus defined as plants that can exclude or resist high concentration of metal, while hyperaccumulators are capable to translocate the contaminant in the leaves without sustaining damages (Padmavathiamma and Li, 2007; Rascio and Navari-Izzo, 2011; Antoniadis et al., 2017). Phytoremediation is a common technique for remediating contaminated soil (Padmavathiamma and Li, 2007; Wuana and Okieimen, 2011; Cui et al., 2016; Cristaldi et al., 2017), however, hyperaccumulator species have never been used in biofilters (Muerdter et al.,

2018) possibly due to the difficulties to find a species adapted to SuDS condition (e.g. frequent flooding).

2.7.1.3 Nutrients

Nitrogen removal performance display great variability among studies (Strong and Paul F. Hudak, 2003; Hatt, Deletić, et al., 2007; Blecken, Zinger, et al., 2007; Osaka et al., 2008; Passeport et al., 2009; Blecken et al., 2010; Palmer et al., 2013; Payne et al., 2018) showing signs of leaching, particularly from biofilters containing high concentration of organic matter and its subsequent oxidation (Barrett et al., 2013), to 90% removal, for poor nutrient content loamy sand biofilters (Lucas and Greenway, 2008).

Key processes for nitrogen removal in biofilters are schematically represented in Figure 2-7 and comprise of:

- NH_4-fixation to soil particles during dry periods;
- mineralisation, which is the transformation of organic nitrogen to plant assimilable ammonium;
- N-assimilation by plant in the form of NH_4^+ or NO_3^-, the latter highly mobile;
- nitrification process of oxidation from NH_4^+ to nitrate in aerobic condition. It increases with temperatures;
- denitrification, the reduction from NO_3^- to N_2 in anaerobic condition (Collins et al., 2010; Nieder et al., 2011; Payne, Fletcher, Cook, et al., 2014).

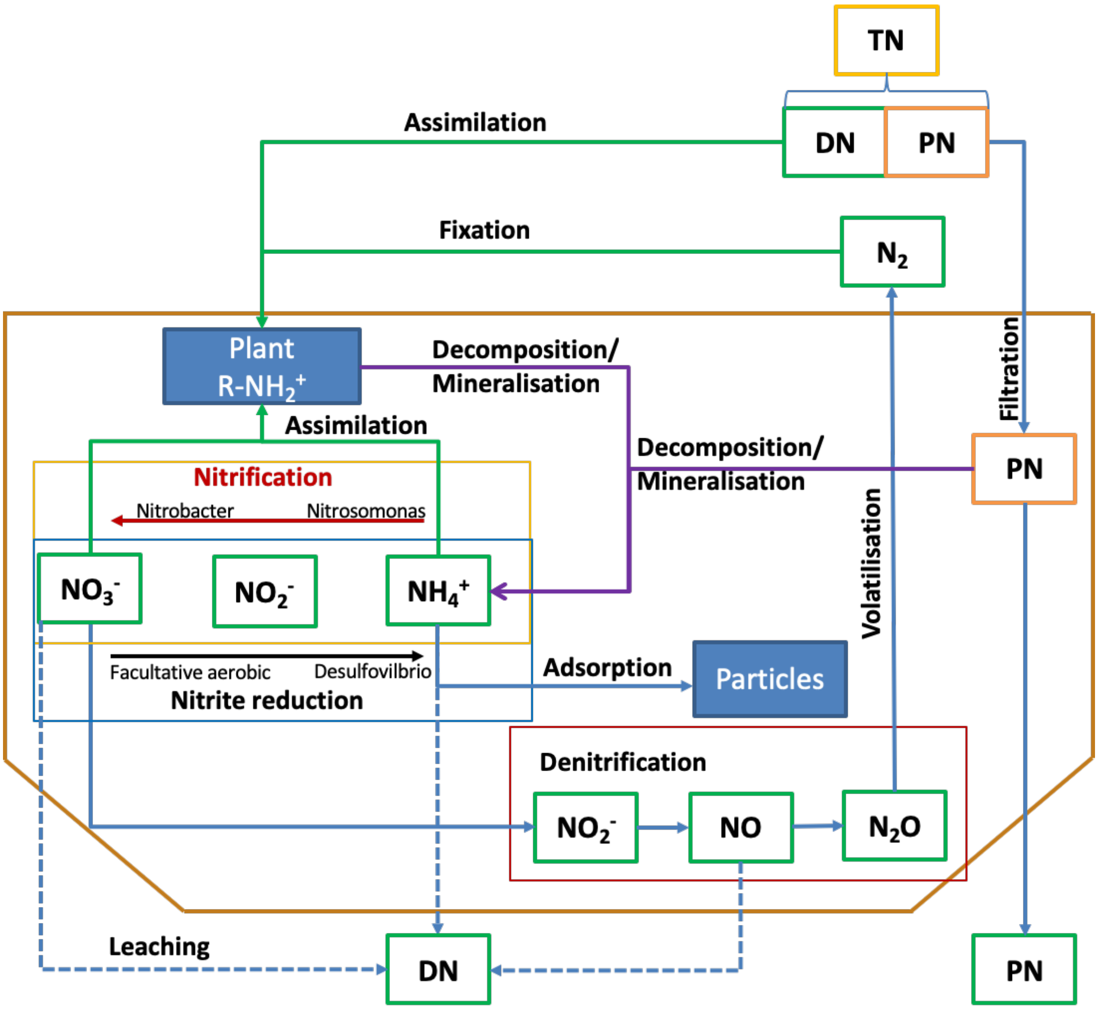


Figure 2-7 Schematic representation of fate of nitrogen in a biofilter. In dark yellow the boundaries of the biofilter. TN= total nitrogen; PN= particulate nitrogen; DN= dissolved nitrogen.

(Payne et al., 2014) concluded that nitrogen removal is driven by denitrification and biological assimilation with the first process contributing for only 3% of NO_3^- treatment compared with 89% of the latter despite the inclusion of a saturation zone to promote denitrification in the study as suggested by (Zinger et al., 2013). In fact, Zinger et al., found that retrofitting a biofilter with an anaerobic area and a carbon source, thus creating the anoxic condition necessary for denitrification, improved the treatment of nitrogen. Result similar to (Morse et al., 2018) that suggested a competition for this element between plants and microorganisms: top zones of the biofilter dominated by plant assimilation while bottom saturated areas characterised by denitrification processes.

In a study by Read et al from 2008, 20 different plant species native from Australia, as well as non-planted control columns, were dosed with synthetic stormwater to assess the difference in treatment performance for TSS, heavy metals, and nutrients. While no difference was found among non-planted columns and plant species for heavy metal and suspended solids treatment, planting did improve nitrogen and phosphorus control. However, the concentration in the effluent were still higher than in the inlet. The authors suggested that high evapotranspiration led aerobic condition that penalised denitrification, and dissolved nitrogen leached from organic material implemented in the design. The removal of phosphorus is also compromised by the choice of media, with an average 31% total phosphorus more in the effluent (Read et al., 2008).

Leaching of nutrient was found also in three field-scale biofilters installed in car parks at Monash University (Australia). Phosphorus leachate was associated with high organic content in the media, but the researcher suggested that the form of phosphorus, rather than the absolute amount, is the responsible and minimising P content in the filter media could reduce leachate (Hatt et al., 2009; Mullane et al., 2015). Phosphorus removal from stormwater runoff is driven by: adsorption to iron and aluminium oxides, precipitation of calcium compounds, plant uptake ($H_2PO_4^-$), and filtration (Hemwall, 1957; Blecken et al., 2010; Berretta and Sansalone, 2011). A schematic representation of phosphorus removal processes is in Figure 2-8.

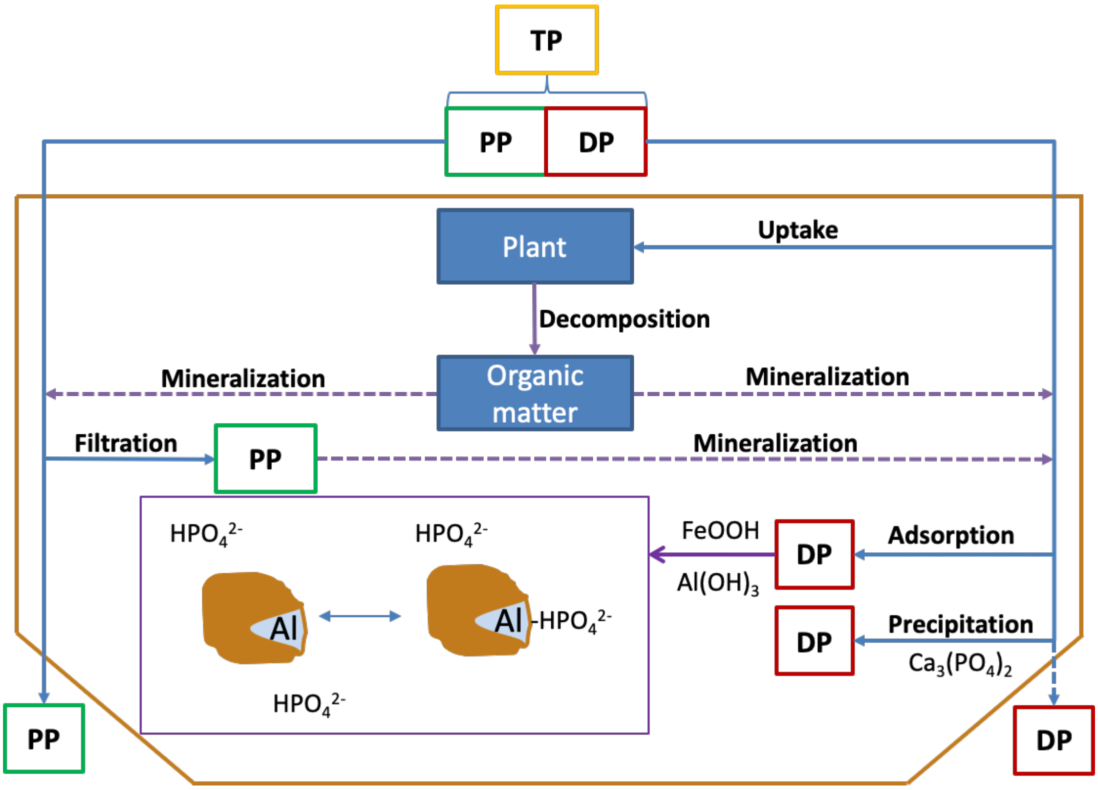


Figure 2-8 Schematic representation of fate of phosphorus in a biofilter (from (Liu and Davis, 2014)). TP= total phosphorus; PP= particulate phosphorus; DP= dissolved phosphorus.

(Lucas and Greenway, 2008) found adsorption and precipitation being the main drivers of phosphorus removal with plant uptakes accounting for only a small fraction. Oxygen from root oxidised iron in the media to ferric form boosting the adsorption of phosphorus. Leaching of phosphorus is a common problem experienced by many authors and it is associated mostly with the nature of the media and the breakdown of organic matter into phosphate (Davis et al., 2006b; Palmer et al., 2013; Zinger et al., 2013). Nonetheless, Barret et al found contrasting results, with substantial differences in treatment for different species (Barrett et al., 2013). A saturation zone could improve the removal through the precipitation of calcium hydroxyapatite and longer residence time, provided that this area contain limestone, also in non-planted configuration (Barrett et al., 2013; Palmer et al., 2013).

Amendments have been integrated in the design in an attempt to increase removal performance of biofilter especially for phosphorus removal. (Adhikari et al., 2016) tested various adsorbent materials finding alum and lime sludges, by products of water treatment process, to be the most effective for phosphorus. In fact, (Liu and Davis, 2014) used water treatment residual in their configuration achieving great results for total phosphorus retention due to the replacement of hydroxyl groups (OH^-) in the media with phosphorus. (Erickson et al., 2012; Weiss et al., 2016; Erickson et al., 2017) tested a biofilter configuration using iron enhanced sand (i.e. iron shaving) achieving removal performance higher than 90% for the duration of the test, compared to a control biofilter which performances peaked at 50% and soon turning into a source of pollution. The aerobic conditions in the media promoted the oxidation of iron to rust and once the phosphorus attached to it, its bioavailability is limited (Erickson et al., 2007). Similarly, (Glaister et al., 2014; Glaister et al., 2017) used an iron rich sand typical from Australia (Skye sand) reporting increased phosphorus treatment and no negative effects on plants.

Zeolite and activated carbon have potential to increase phosphorus adsorption capacity in water treatment due to the abundant micropore, high adsorption capacity for phosphorus, total organic carbon, heavy metals and polycycle aromatic hydrocarbons (Wang et al., 2010; Hale et al., 2012; Grace et al., 2015; Pawluk and Fronczyk, 2015). (Erickson et al., 2016) emphasised the quality of granular activated carbon to treat nitrogen. Biochar amended biofilter (Nabiul Afrooz and Boehm, 2017) reported low phosphorus and organic carbon removal, although the media was autoclaved, therefore no biological community could contribute to the treatment.

2.7.1.4 Role of plants

The role of plants in biofilters is not limited to enhance biodiversity and amenity, but also to increase evapotranspiration to reduce heat island effect and runoff, recover hydraulic conductivity, induce microbial growth (i.e. rhizosphere), increase oxygen level facilitating aerobic condition and uptake pollutants like metals and nutrients (Walker et al., 2003; LeFevre et al., 2013; Woods-Ballard et al., 2015; Payne et al., 2015).

In the study by Read et al., 2010, 20 different plant species where studied to assess the contribution of various trait (e.g. root length, leaf area, biomass) in the removal of contaminant from stormwater runoff in biofilters. Root traits were the most strongly correlated with nitrogen and phosphorus removal, while plants were found not important for the removal of heavy metals, with non-planted columns being more efficient in the adsorption. The author suggested that despite media playing a dominant role in metal sequestration, plants still play an important role in extending the lifespan of a biofilter (Read et al., 2010).

Table 2-2 List of plant species used in biofilters' experiments

Species	Author	Species	Author
Dryand.(Dilleniaceae	Read et al., 2010	Iris pseudacorus	Leroy et al., 2016
Kunzea ericoides	Read et al., 2010	Juncus amabilis	Read et al., 2010
Pomaderris paniculosa	Read et al., 2010	Juncus conglomeratus	Søberg et al., 2017/2014
Acacia suaveolens	Read et al., 2010	Juncus effusus	Leroy et al., 2016
Agrostis stolonifera	Charlesworth et al., 2016	Juncus flavidus	Read et al., 2010
Artemisia argyi	Cristaldi et al., 2017	Juncus kraussii	Szota et al., 2015
Avicennia marina	Cristaldi et al., 2017	Juncus refuste	Robert Brays associates
Banksia marginata	Read et al., 2010	Juncus usitatus	Szota et al., 2015
Brassica juncea	Cristaldi et al., 2017	Kandelia candel	Cristaldi et al., 2017
Buchloe dactyloides	Barrett et al., 2013	Leucophyta brownii	Le Coustumer et al., 2011, Read et al., 2010
Callistephus chinensis	Cristaldi et al., 2017	Limonium bicolor	Cristaldi et al., 2017
Carex appressa	Lefevre et al., 2015, Le Coustumer et al., 2011, Read et al., 2010, Blecken et al., 2009 , Szota et al., 2015	Lolium perenne	Leroy et al., 2016
Carex bichenoviana	Szota et al., 2015	Lomandra longifolia Labill	Read et al., 2010
Carex flacca	Palmer et al., 2013	M. sativa	Cristaldi et al., 2017
Carex microptera	Rycewicz-Borecki et al., 2016	Malaleuca ercifolia	Lefevre et al., 2015, Le Coustumer et al., 2011, Read et al., 2010
Carex panacea	Søberg et al., 2017/2014	Melilotus suaveolens	Cristaldi et al., 2017
carex praegracilis	Rycewicz-Borecki et al., 2016	Meticago sativa	Cristaldi et al., 2017
Carex rostrata	Robert Brays associates	Microlaena stipoides	Read et al., 2010, Le Coustumer et al., 2011
Correa alba Andrews	Read et al., 2010	muhlenbergia lindheimeri	Barrett et al., 2013
Dechampsia	Robert Brays associates	Myoporum parvifolium	Read et al., 2010
Dianella revoluta	Le Coustumer et al., 2011	Phalaris arundinaceae	Leroy et al., 2016, Søberg et al., 2014
Dianella revoluta	Read et al., 2010	Phragmites australis	Rycewicz-Borecki et al., 2016
Dodonaea viscosa	Read et al., 2010	Poa labillardierei	Read et al., 2010
Echinacea purpurea	Cristaldi et al., 2017	Popolus spp	Cristaldi et al., 2017
Festuca arundinacea	Leroy et al., 2016, Cristaldi et al., 2017	Populus spp	Cristaldi et al., 2017
festuca rubra	Leroy et al., 2016	Pultenaea daphnoides	Read et al., 2010
Ficinia nodosa	Szota et al., 2015, Read et al., 2010	Salix spp	Cristaldi et al., 2017
Gahnia filum	Szota et al., 2015	Salix viminalis	Lefevre et al., 2015
Galium palustre	Robert Brays associates	Salsola collina	Cristaldi et al., 2017
Goodenia ovata Sm.	Read et al., 2010	Scirpus acutus	Rycewicz-Borecki et al., 2016
Helianthus annuus	Lefevre et al., 2015, Cristaldi et al., 2017	Thalaspi caerulescens	Cristaldi et al., 2017, Lefevre et al., 2015
Hibbertia scandens	Read et al., 2010	Typha latifolia	Rycewicz-Borecki et al., 2016

2.7.1.5 Hydraulic characteristics

Field test in in Maryland (U.S.A) where water from car parks was drained, phosphorus removal resulted higher than 90% also for dissolved form, results partially to attribute to the choice of media that was poor in P. The topography of the green area did, however, affect the removal and hydraulic conductivity. The accumulation of sediment is generally higher at the entrance of a biofilter, due to the deposition of sediment. Nonetheless, the furthest area of the biofilter had not only the highest phosphorus and sediment concentration, but also the lower hydraulic conductivity: 463mm/h ±100mm/h compared with the further area: 291±60mm/h. This hinted that a depression was accumulating polluted sediment that influenced the flow of water through the media (Muerdter et al., 2016). As suggested by (Read et al., 2010), although do not impact significantly metal removal, plants are useful to maintain biofilter lifespan. In fact (Le Coustumer et al., 2012) in a large-scale column study found that sediment accumulation on top of a biofilter occlude pours, decreasing the overall hydraulic conductivity, therefore rising the risk of overflow. This phenomenon is known as “clogging”. This is caused not only by sediment accumulation and compaction (Sileshi et al., 2012), but also through growth of biofilm within the biofilter (Kandra et al., 2014; Kandra et al., 2015). In field-scale biofilters installed in car parks at Monash University (Australia), the systems showed 80% peak runoff flow attenuation and 33% reduced runoff through evapotranspiration (Read et al., 2010). As found for column experiment in controlled condition, plants were maintaining hydraulic conductivity through roots growth countering compaction and clogging (Lewis et al., 2008; Le Coustumer et al., 2012). (Scholz and Kazemi Yazdi, 2009) (Edinburgh – UK) found 50% of water evaporated, 35% infiltrated and only 15% discharged in a receiving body, highlighting the capacity of these system to control runoff quantity. (Sörensen and Emilsson, 2019) showed that an area in Augustenborg (Sweden) retrofitted with SuDS was significantly less affected by floods than neighbouring areas. (Recanatesi et al., 2017), using GIS data and bidimensional hydraulic models, determined that the retrofitting of sustainable systems could remove the hydraulic risk in 90% of the cases and in the 10% remining at least reduce the flooded areas. To operate a control over flow quantity, and the survival of plants, biofilters' guidelines suggest to design the filter hydraulic conductivity between 100 and 300 mm/h (Woods-Ballard et al., 2015; Payne et al., 2015), however this limits the retrofitting opportunity since small system (below 2% of its catchment) risk clog due to overload of sediment (Le Coustumer et al., 2012).

2.8 Chapter summary

Current water management relying on CSS is not effective in managing urban stormwater runoff and dealing with extreme events induced by climate change. Harvesting systems, like biofilters, that collects, infiltrate, evaporate, and clean water before reaching aquatic ecosystems have been proven effective in urbanized catchments (Walsh et al., 2012; Lundy et al., 2013; Rivers et al., 2018). However, despite the overall reliability of these system and UK Government's effort to introduce them as practice with the Flood and Water Management Act 2010, the technology is not taking off mainly due to lack of clear legal ownership, maintenance, and the continuous performance guarantee (Ashley et al., 2015; Melville-Shreeve et al., 2017; HCLG, 2018; Illman et al., 2019).

Literature review suggests that media choice for biofilter is crucial for treatment and make the difference between a sink or source of pollutants. Dissolve contaminants, like nitrogen, phosphorus, copper and zinc are still difficult to remove, and often the distinction between particle and dissolved form is unclear (LeFevre et al., 2015; Lim et al., 2015; Maniquiz-Redillas and Kim, 2016; Jiang et al., 2017). DOC play an important role in the leachate of pollutants, yet there is no major indication of this pollutant treatment by biofilters in literature. Amendments are rarely used in biofilters, without a clear indication of the effects on plants and reporting only few pollutants. Zeolite and Granular Activated Carbon are commonly used in water treatment systems and rarely used in combination in biofilter systems. No hyperaccumulator or hypertollerant plants have been used in biofilter, as highlighted also by (Muerdter et al., 2018).

To address these deficiencies, this study aim is to provide laboratory-based data on the effects of high hydraulic conductivity, amendments commonly used in water treatment, and hypertollerant plants in biofilter have on removal performance of urban stormwater runoff. Mesocosms will be designed according to (Woods-Ballard et al., 2015; Payne et al., 2015) and a mix of synthetic and semi-synthetic runoff will be used to test the biofilters.

Chapter 3 Methodology

3.1 Chapter overview

This chapter includes an overview of the methods and protocols used for each test and experiment presented in this thesis to answer the research questions in Chapter 1.

3.2 Area of study

Urban runoff is site specific due to fixed and site-specific factor that influence the composition like, for instance, land use, operational, topography, maintenance, vehicles and traffic volume. Car parks, due to the peculiar driving style and pollutant load (i.e. low speed and engine regime, repeated breaking and turning) represent a major treatment challenge (Revitt et al., 2014; Huber et al., 2016). Other studies relied on car parks insuring the reproducibility of this study (Davis et al., 2003; Géhéniau et al., 2015; Hong et al., 2017), thus the decision of simulate stormwater quality typical of these environments.

Eriksson et al., reported a list (Table 3-1) of priority pollutants based on the Water Framework Directive and has been thus used to select the parameters to monitor during the study (Eriksson et al., 2007). Due to resource constraint it was not possible to analyse PAH, Herbicides, Miscellaneous, BOD, COD and platinum. Iron, aluminium and barium were added in the list of monitored parameters as possible contaminant present in stormwater associated with tyres and brake erosion (McKenzie et al., 2009).

Table 3-1 List of selected stormwater priority pollutants (Eriksson et al., 2007)

Type	CAS number	Abbreviation	Name
Basic parameters	-	BOD	Biochemical oxygen demand
	-	COD	Chemical oxygen demand
	-	SS	Suspended solids
	-	N	Nitrogen
	-	P	Phosphorus
	-	pH	pH
Metals	7440-66-6	Zn	Zinc
	7440-43-9	Cd	Cadmium
	11104-59-9	Cr(VI)	Chromium
	7440-50-8	Cu	Copper
	7440-02-0	Ni	Nickel
	7439-92-1	Pb	Lead
	7440-06-4	Pt	Platinum
PAH	50-32-8	BaP	Benzo[a]pyrene
	91-20-3		Naphthalene
	129-00-00		Pyrene
Herbicides	5915-41-3		Terbutylazine
	40487-42-1		Pendimethalin
	13684-63-4		Phenmedipham
	1071-83-6		Glyphosate
Miscellaneous	25154-52-3	NPEO	Nonylphenol ethoxylates
	87-86-5	PCP	Pentachlorophenol
	117-81-7	DEHP	Di(2-ethylhexyl)phthalate
	7012-37-5	PCB 28	2,4,4'-Trichlorobiphenyl
	1634-04-4	MTBE	Methyl *tert*-butylether

A table by (Revitt et al., 2014) reports the typical concentration of the priority pollutants found in car parks in the UK and are used as target for the synthetic runoff used during the non-vegetated biofilter experiment and semi-synthetic runoff used instead during the vegetated biofilter experiment (Table 3-2).

Table 3-2 Ranges of pollutant concentration in runoff from urban areas with similar traffic use to car parks (table from (Revitt et al., 2014))

Pollutant type	Source	Event mean concentrations
Total suspended solids (mg L^{-1})	Car parks and commercial areas	7.8–270
	Residential	
	High density	55–1568
	Low density	10–300
	Urban roads	11–5400
	Roadside gully chambers	15–1840
Metals (μg L^{-1})	Car parks and commercial areas	Cd: < 1; Zn: <1–700; Pb: <1–10; Cu: <1–205; Ni: 2–493
	Residential roads	Cd: 0–5; Cu: 6–17; Zn: 87–150; Pb: 6–140
	Suburban roads	Pb: 10–440; Zn: 20–1900; Cu: 10–120
	Gully liquors	Pb: 100–850
Hydrocarbons (μg L^{-1})	Car parks and commercial areas	Total HC: 3.3–2000; Total PAH: 0.35–3000
	Residential	
	High density	Total HC: 0.67–25.0
	Low density	Total HC: 0.89–4.5
	Urban roads	Total HC: 2.8–31;
Nutrients (mg L^{-1})	Car parks and commercial areas	Total N: 0.41–2.54; NH_4–N: 0.2–4.6; TP: 0.04–0.53; orthoPO_4: 0.001–0.03
	Motorways and roads	TN:<4
	Residential	TN:<0–6; NH_4–N: 0.18–3.8; TP:0–1.16
	Gully Liquors	TN: 0.7–1.39

For the parameter not included in Revit et al., 2014 list other sources have been used as specified in Table 3-3. The production of synthetic and semi-synthetic stormwater runoff is described in paragraph 3.3.1..

Table 3-3 List of pollutants' sources, target concentration and reference paper used for the synthetic and semi-synthetic stormwater runoff. Semi-synthetic stormwater comprised only of Phosphorus, Copper and Zinc.

Parameter	Source	Target concentration	Reference paper
TSS	Gully pot	150 mg/L	Le Coustumer et al., 2008
TP	Tap water	0.53 mg/L	Revitt et al., 2014
PO4-P	Tap water	0.03 mg/L	Revitt et al., 2014
TN	Tap water	2.54 mg/L	Revitt et al., 2014
NH4-N	Tap water	0.2 mg/L	Revitt et al., 2014
NOx	Tap water	0.81 mg/L	Mitchell 2005
Aluminium	$Al_2(SO_4)_3$	3210 μg/L	Pitt et al., 1995
Barium	$BaCl_2$	9.6 μg/L	Berretta & Sansalone 2011
Cadmium	$CdCl_2 * 5H_2O$	1 μg/L	Revitt et al., 2014
Chromium	$K_2Cr_2O_7$	13 μg/L	Huber et al., 2016
Copper	$CuSO_4 * 5H_2O$	205 μg/L	Revitt et al., 2014
Iron	$FeCl_3 * 6H_2O$	4135 μg/L	Sansalone & Burchberger 1997
Lead	$Pb(NO_3)_2$	10 μg/L	Revitt et al., 2014
Nickel	$NiCl_2 * 6H_2O$	493 μg/L	Revitt et al., 2014
Zinc	$ZnSO_4 * 7H_2O$	700 μg/L	Revitt et al., 2014

Due to the possibility of retrofitting a biofilter for field experiments later in the project, 24 location in the city of Leeds have been surveyed. These have been characterised for their catchment, size, use (e.g. employee, supermarket), area of retrofitting, and ease of installation. Only one management company was interested in the project, Landsecurity (now Landsec) owner of some of the biggest shopping centre across UK, however, due to refurbishment of parking lot first, and the lack of drainage's blueprint later, the possibilities of retrofitting a biofilter in the White Rose Shopping Centre of Leeds were limited. Later in 2017 has been agreed with the Sustainability Service of the University of Leeds to retrofit a biofilter on campus after a first phase of design development (i.e. this research project).

3.3 Leeds rainfall regime

The mesocosms were dosed with a quantity of runoff typical for the city of Leeds, location of the laboratories of this study. The city is located in West

Yorkshire and characterised by Köppen-Geiger climate classification system as Cfb: warm temperature, fully humid, and warm summer.

The Environment Agency provided the 15 minutes resolution database relative to rain (0.2mm/15min) between 1998 and 2017 of Headingley, near Leeds University. The database has been classified into 2628 rainfall events, where individual events were separated by continuous average dry period of 6h as adopted by other research studying SuDS (Stovin et al., 2012). 96% of the events fall below the 1-year return period threshold (Figure 3-1). The largest event started the 15/06/2007, the year of one of the worst flood event in UK (Pitt, 2008), and had 95.8mm rainfall over 53 h, with a return period of circa 1 in 29.65 years.

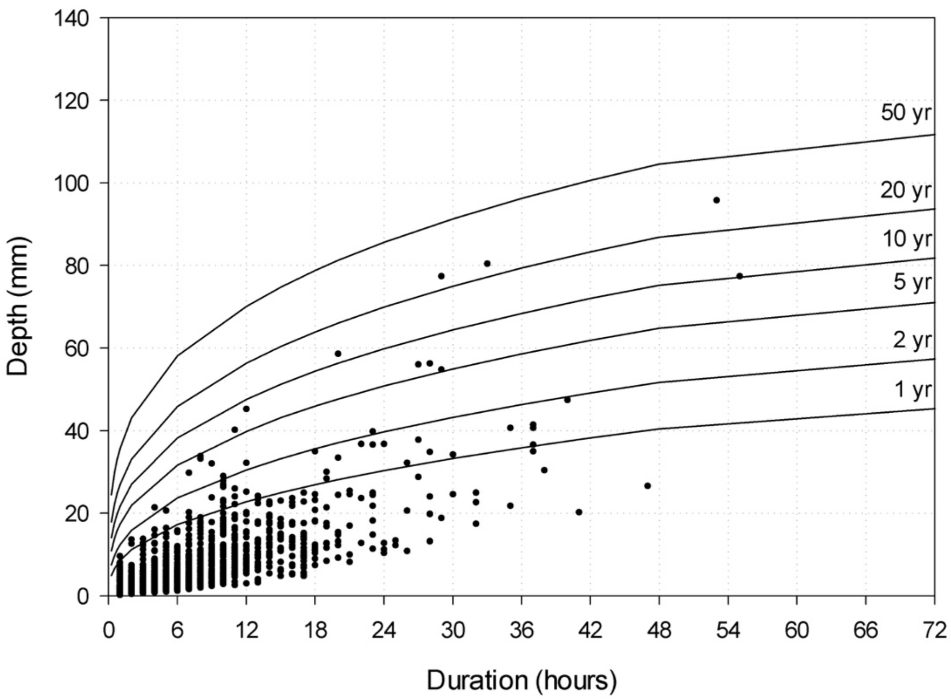


Figure 3-1 Rainfall characteristics for the 22-year data series compared with FEH return period estimated for Headingley.

The total rainfall per year, number of events, longest event duration, highest and average intensity, longest and average dry weather period were extracted from the database and have been reported in Table 3-4. Average rain depth for this area is circa 758.2 mm per year and this has been used to calculate the volume of runoff to apply in the first phase of the study as described in paragraph 3.5.3.1.

Table 3-4 Rainfall characteristic of Leeds - Headingley (UK)

Year	Rainfall per year (mm)	Number of events per year	Longest event duration (h)	Average event duration (h)	Highest intensity (mm/h)	Average intensity (mm/h)	Longest DWP (h)	Average DWP (h)
1996	558.0	160	52	5	3.6	0.58	747	46
1997	531.6	159	23	5	8.0	0.70	591	54
1998	764.0	182	32	5	2.7	0.63	722	42
1999	683.2	184	43	5	2.9	0.59	575	42
2000	1022.8	215	38	5	4.3	0.64	467	34
2001	651.2	187	44	5	2.2	0.62	303	43
2002	950.0	190	45	5	6.4	0.74	533	39
2003	531.8	145	29	5	6.8	0.64	1078	55
2004	766.4	230	33	4	4.1	0.56	202	34
2005	668.0	196	28	5	5.4	0.60	339	40
2006	836.6	205	28	5	4.6	0.70	293	37
2007	875.8	173	53	6	4.4	0.67	497	44
2008	927.4	208	28	5	4.3	0.61	303	39
2009	702.2	193	28	5	6.3	0.66	316	41
2010	617.2	180	26	5	4.2	0.61	340	43
2011	615.4	180	46	5	2.2	0.57	343	46
2012	1075.6	215	55	6	9.6	0.72	366	35
2013	670.2	192	41	5	4.2	0.60	442	42
2014	837.2	216	40	5	4.6	0.62	310	34
2015	831.8	201	29	5	7.8	0.72	305	38
2016	818.4	210	30	5	3.2	0.59	406	37
2017	744.6	209	40	5	3.3	0.57	312	41
Average	**758.2**	**192**	**37**	**5**	**4.8**	**0.63**	**445**	**41**

The total rainfall for spring, summer and autumn for every year has been calculated and average depth, dry weather period, intensity and duration have been calculated (Table 3-5) in order to simulate more accurately the volume of runoff and the dry period to use during the second phase of the study as described in paragraph 3.5.3.2.

Table 3-5 Depth (mm) and average dry weather period (ADWP) (h) extracted from the database for every year. The average for every season has been calculated and used in the experiment.

	Spring					Summer				
Year	Depth (mm)	ADWP (h)	Number of events	Average intensity (mm/h)	Average duration (h)	Depth (mm)	ADWP (h)	Number of events	Average intensity (mm/h)	Average duration (h)
1996	133.8	46	39	0.6	5	145.4	63	34	0.9	5
1997	89.6	66	30	0.8	4	141.0	74	34	1.0	4
1998	270.4	48	45	0.8	6	110.8	39	47	0.5	4
1999	179.2	45	45	0.7	5	91.8	53	36	0.6	4
2000	254.8	43	43	0.6	7	210.8	44	48	0.7	4
2001	175.8	44	44	0.6	5	107.2	58	41	0.7	4
2002	141.4	45	41	0.8	4	305.2	57	33	1.0	6
2003	128.0	63	36	0.7	5	176.2	64	34	0.9	4
2004	145.8	47	42	0.6	5	321.2	33	64	0.7	5
2005	191.6	41	48	0.6	5	160.2	66	32	1.0	5
2006	271.2	35	53	0.9	6	221.2	49	43	1.0	4
2007	232.4	65	31	0.7	6	268.8	47	42	0.8	6
2008	163.6	51	41	0.6	5	361.8	34	54	0.9	6
2009	130.0	55	40	0.6	4	199.4	41	50	0.8	4
2010	144.6	48	40	0.6	5	187.0	46	46	0.8	4
2011	84.6	80	28	0.6	4	159.2	39	52	0.6	4
2012	290.0	42	42	0.8	8	246.8	34	59	0.9	5
2013	103.2	63	37	0.5	5	194.8	48	40	0.9	5
2014	218.0	33	54	0.6	5	162.2	48	43	0.8	4
2015	166.0	52	42	0.6	5	184.4	51	42	1.1	4
2016	193.6	47	48	0.6	6	168.0	46	47	0.7	5
2017	137.2	72	33	0.5	7	291.6	35	67	0.8	5
Average	**174.8**	**51**	**41**	**0.7**	**5**	**200.7**	**48**	**45**	**0.8**	**5**

	Autumn				
Year	Depth (mm)	ADWP (h)	Number of events	Average intensity (mm/h)	Average duration (h)
1996	210.2	44	52	0.5	6
1997	178.0	39	52	0.6	5
1998	206.0	40	48	0.6	5
1999	212.2	53	41	0.6	7
2000	440.4	23	72	0.7	6
2001	207.8	38	50	0.8	4
2002	245.6	39	54	0.6	6
2003	122.2	46	42	0.5	5
2004	137.0	32	59	0.5	4
2005	201.0	35	55	0.6	5
2006	221.0	30	63	0.6	5
2007	153.0	40	45	0.6	4
2008	156.2	41	61	0.4	5
2009	272.4	30	58	0.7	5
2010	184.8	33	54	0.5	5
2011	181.6	37	58	0.6	5
2012	332.6	28	64	0.6	6
2013	205.0	30	66	0.6	4
2014	242.8	31	59	0.6	5
2015	317.6	26	67	0.7	5
2016	167.6	37	52	0.5	4
2017	160.4	39	50	0.5	5
Average	**216.2**	**36**	**56**	**0.6**	**5**

3.3.1 Synthetic and semi-synthetic stormwater

(Barrett et al., 2013) is the only author found to use actual stormwater for column experiments. This was collected on a residential street in Austin (Texas), and stored in a cold room (4°C) for 3 days before dosing the systems for only one experiment. Although the quality of the synthetic and actual stormwater differed, the researchers reported consistency between results obtained dosing the columns with the two typologies of water. Due to the difficulties to obtain and store huge quantity of stormwater runoff for the entire length of the experiments, it has been decided to produce synthetic and semi-synthetic stormwater runoff, practice followed by most of the authors that investigate biofilters' performance in laboratory. The difference between synthetic and semi-synthetic stormwater is the presence in the latter of sediments collected by actual water management systems (i.e. gully pot) (Søberg et al., 2017). Synthetic stormwater was used in non-vegetated biofilter experiments to assess the capacity of the media to adsorb dissolved pollutants. Semi-synthetic stormwater was used during vegetated biofilter experiment to assess the impact that sediments have on hydraulic conductivity, as well as assess the capacity of the biofilter to remove solid associated pollutants. Target concentration for synthetic and semi synthetic stormwater is reported in Table 3-3.

For this project, sediments were collected from gully pots distributed around car parks of the University of Leeds campus. These were then wet sieved down to 300μm, since more than 90% of urban dust mass in car parks is below this limit (Revitt et al., 2014), and oven dried at 60°C for 4 days to reduce the amount of water in the sediment and avoid the volatilisation of organic matter. The gully pot liquor was finally stored in several 125ml container and frozen until use. The solutions were freshly prepared before every dosing event mixing tap water, a known amount of metal salts, and finally, when needed, gully pot liquor. The solution was constantly mixed to ensure uniformity and homogeneous concentration of sediments and dissolved pollutants. During the vegetated column test a peristaltic pump was ensuring the constant mix of water. However, sediments quickly built up in the pipes clogging the pump, therefore, the constant mixing was afterward ensured using a long rod.

3.4 Media selection and configuration

A typical biofilter consist of layers of sand and gravel amended, when necessary, with topsoil and a carbon source (if saturation zone is included) (Payne et al., 2015).

Sand represents the most abundant media of the filtration system. CIRIA and Monash University guideline set particular targets for sand, that should comprise of particle size classes from 0.05 to 3.4mm. The content in clay and silt should be less than 3% to avoid leach of fine particles and ensure adequate hydraulic conductivity (typically between 100 and 300 mm/h). The minimum and maximum value (in mm) of the media used during this study are reported in Table 3-6. Sand has been sourced by David Ball specialist aggregate and Garside sand in form of 25kg bags from fraction A (1.18mm - 2.36mm) down to fraction D (150 μm – 300 μm). At the base of a biofilter, gravel (Specialist aggregate, 2.0mm – 8.0mm) is used as drainage layer to ensure high hydraulic conductivity and to bridge the overlying filter media and the drainage pipe.

Despite the possible leachate from organic matter, Topsoil is still necessary to help establish plants during the first months of operation of a biofilter. During its lifespan green infrastructures intercepts nutrient rich runoff being so the only source of nutrient available for plants (Payne et al., 2015). The inclusion of Perlite and Vermiculite, two horticulture amendments, can increase the filter porosity, water retention and, due to their high cation exchange capacity, rise the removal of pollutants such as nitrogen, phosphorus and heavy metals (Fletcher et al., 2007; Bratieres et al., 2008; Le Coustumer et al., 2012). These amendments have been sourced online and topsoil with no content in peat has been chosen for sustainability purposes. Woodchip is the carbon source used in the saturation zone due to the common availability compared to sawdust, pinewood, peat, leaf compost, and newspaper used in other studies despite the latter demonstrating increased nitrogen removal (Kim et al., 2003; Søberg et al., 2017).

Based on literature review, Zeolite (ZeoClin) and Granular Activated Carbon (PHO 12x30 AW) have been tested to assess the contribution that these amendments have on biofilters' performance and the effects on plants. These are commonly used in water treatment (Chaudhary et al., 2003; Kim et al., 2009), but rarely used in combination with biofilters. These media have been purchased from RS Minerals LTD and EUROCARB. Aluminium slag and biochar were considered for the design due to the rich aluminium oxide concentration of the first and the adsorption quality of the second. Nonetheless, these two amendments have been excluded due to the impossibility to ensure the same material for entire the length of the project. In fact, contacted providers could not ensure consistency of physical and chemical property of the product.

Table 3-6 Particle size distribution (in mm) of the media used to build the biofilters during this study

Media	Min (mm)	Max (mm)
Gravel big	5	8
Gravel medium	3	5
Gravel small	2	3
Sand fraction A	1.18	2.36
Sand fraction B	0.6	1.18
Sand fraxtion C	0.3	0.6
Sand fraction D	0.15	0.3
Top soil	0.045	5
Woodchip	2.36	5
Vermiculite	0.15	5
Perlite	0.15	5
Zeolite	0.7	1.6
GAC	0.59	1.68

3.5 Methods

3.5.1 Statistics

Results were analysed using SPSS software and plotted using SigmaPlot (v.13). Due to the not normal distribution of the data, this was analysed with a

Kruskal-Wallis test with Bonferroni's adjustment (for multi pairwise), and Mann-Whitney + Dunn post hoc test. Spearman test was performed to assess correlation between variables. Concentration and removal performances are plotted as box plots that describe median, upper and lower quartiles, minimum, maximum values and outliers (dots).

3.5.2 Biofilter media characterisation

The media have been tested for: particle size distribution, bulk density, elemental composition, chemical composition, adsorption capacity, water holding capacity, and hydraulic conductivity. The aim was to assess physical-chemical and hydraulic property to select media and characterise amendments that will be included in the design of a biofilter. The media characteristics results are presented in Chapter 4.

3.5.2.1 Physical characteristics: PSD, bulk density, oxides

The particle size distribution of media have been tested in accordance with ASTM F1632-03(2010). Media were oven dried for 48h at 60°C to avoid organic matter loss and then sieved with an appropriate stack of sieves and agitated on an automatic shaker table. The sieved material was afterward transferred on a weighing container and the percentage by mass of material retained on each test sieve and the cumulative percentage passing each of the sieve was calculated.

Bulk density of media have been tested in accordance with BS 1377-2:1990. A cylinder of known mass was filled with oven dried material (60°C for 48h) and its volume calculated. The mass of the specimen was then calculated by difference and the bulk density calculated as

$$\rho = \frac{m}{V} \times 10^{-6}\, Mg/m^3$$

Where m is the specimen mass (g) and V is the volume of the specimen (m^3).

The composition of oxides for the media investigated has been assessed through X-ray fluorescence analysis (XRF) using a ZSX Primus II (Rigaku). Samples were prepared according to the manufacturer: oven dried for 48h at 60°C and grinded with a disc mill (RS200) for 40 seconds and, for woodchip only, with a CryoMill (RETSCH – cryo cycles 3). Samples were then sieved down to 100μm and pressed into pellets (15 tons press bell). The machine was then set up according to the manufacturer and to avoid sample loss operated under helium gas in the sample chamber instead of vacuum (Takahashi, 2015). The semi-quantitative results are expressed in mass (%) of oxides.

3.5.2.2 Chemical characteristics: adsorption (q_e)

Adsorption capacity of the media have been carried following (Paus et al., 2014): 230ml of synthetic stormwater runoff and 1 gram of media were shaken on an orbital table at 100rpm for 24h. Water samples were filtered then analysed for PO4-P using a pocket colorimeter HACH DR890 using ascorbic acid method (PhosVer 3 - program 79), and analysed for dissolved Cu, and Zn with ICP-MS. Results were expressed in terms of adsorption capacity at equilibrium:

$$q_e = \frac{(C_0 - C_{24})V}{W}$$

where q_e is the adsorption capacity at equilibrium (mg/g), C_0 the initial solution concentration, C_{24} the concentration of solution after 24h, V is the volume of solution (in litre), and W is the dry mass of adsorbent used (g) (Sansalone et al., 2013).

3.5.2.3 Hydraulic characteristics

Water holding capacity was assessed saturating a known amount of filter media for 24h with tap water and let gravity drain the excess water for 2h before weighing the media (FLL, 2008). These tests were conducted only for the filter media in order to compare the moisture content in the planted column monitored with moisture sensors.

Constant head test was performed (ASTM International, 2000) to assess the hydraulic conductivity of the media and the filter. A known quantity of dry media was poured in a permeameter connected to two manometers and a constant head filter tank. The media was maintained in saturated condition for at least 1h before the start of the test. The inlet valve was then open from the inlet tank and once stable condition were met (no drift in the manometers), a sample of water was collected while recording the time of collection, temperature and head height.

The hydraulic conductivity was then calculated as

$$K = \frac{QL}{AtH}$$

Where K is the hydraulic conductivity, Q the quantity of water discharged, L distance between manometers, A cross sectional area of specimen, t total time of discharge, H difference in head on manometers.

Value for hydraulic conductivity were corrected for temperature.

3.5.3 Column test

To assess the effect that Zeolite and GAC have on removal performances and plant health two different tests have been organised: using only soil, using soil and plants.

Due to limitation in resources, the first experiment was necessary to narrow down and eliminate possible flaws in designs used in the second stage of this study (i.e. Phase II).

3.5.3.1 Non-vegetated column test

A column experiment was run to assess the removal performance for dissolved pollutants of filter columns amended with Zeolite, GAC, and a mixture of the two. The results for this test are in Chapter 5.

12 PVC columns (150mm i.d., 1300mm high) were sandblasted to prevent preferential flow on the inner wall (Blecken et al., 2007). The drainage pipe was raised to establish a saturation zone of 400mm.

The tested configurations were characterised from top to bottom (Figure 3-2):

- Protection layer: 100mm of 5.0-8.0mm coarse gravel
- Top filter layer: 100mm mix by volume of 10% perlite, 10% vermiculite, 20% topsoil, and 60% 0.6-1.18mm sand.
- Bottom filter layer: 200mm mix by volume of 10% perlite, 10% vermiculite, and 80% 0.6-1.18mm sand.

- Amendment layer: 100mm consisting of 0.59-1.68mm GAC or 0.7-1.6mm Zeolite. In the configuration with both the amendments, the layer was equally divided in two, one for each amendment. In the control this layer was absent and had the same mix as Bottom filter layer.
- Transition layer: 100mm of 0.15-0.30 mm sand.
- Saturation zone: three layers of 100mm depth (for a total of 300mm) with different granulometry (0.3-0.6mm, 0.6-1.18mm, 1.18-2.36mm) that bridge to the drainage layer. 5% by volume of woodchip was added as carbon source.
- Drainage layer: 30mm of 2.0-3.0mm fine gravel, 30mm of 3.0-5.0mm medium gravel, 40mm 5.0-8.0mm coarse gravel on top of the perforated drainage pipe (20mm i.d.).

The media were light hand-compacted according to construction practice (Le Coustumer et al., 2012).

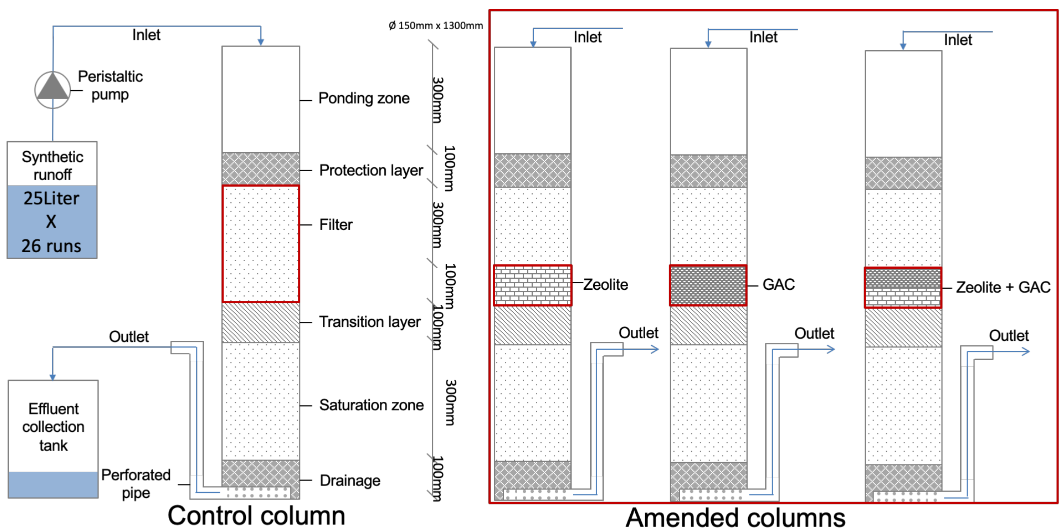


Figure 3-2 Experimental setup for the column test with no-vegetation

Biofilters were sized 2% of its catchment and were dosed with the runoff generated in a year by an hypothetical car park of area 0.88m^2. Based on paragraph 3.3 in the area of Headingley – Leeds rain averagely 758.2mm/year. The runoff applied to the biofilter was calculated using the rational equation

$$Q = c \times i \times A$$

where Q is the peak discharge, *c* is the rational equation runoff coefficient (here assumed as worst case scenario equal to 1), *i* the rainfall intensity and *A* the drainage. Based on this data the quantity of runoff generated in a year from an area of $0.88m^2$ is circa 650 litres. Therefore, the setup was dosed with 25 litre of synthetic stormwater runoff (prepared according to paragraph 3.3.1) simulating 26 event for a total of 650 litres using a peristaltic pump. The peristaltic pump flow was diverted into several pipes using manifolds to feed every column with 100ml/min of synthetic stormwater runoff so that every column was receiving exactly 25 litres of water in circa 4h. Due to possible fluctuation every pipe flow and outlet was checked every hour to make sure every biofilter was receiving the right amount of water.

3.5.3.1.1 Sample collection

The 25-litre runoff was all collected to calculate the event mean concentration (EMC) and analysed for pH, temperature, conductivity, and dissolved oxygen with a HACH HQ40d (PHC101, CDC401, LBOD101). The water was splashing in the collection tank, therefore for this experiment was used as indication for presence/absence of respiration processes.

Two 0.5 L composite samples were collected from the outlet collection tank of every biofilter and two 15ml samples filtered and analysed for PO4-P, using a HACH DR890 pocket colorimeter (ascorbic acid method – program 79). Two 15ml filtered samples were acidified with 150μl of HCl processed with an ICP-MS for dissolved Cu and dissolved Zn. Results were expressed in terms of concentration and removal performance. This was determined using:

$$RP = \frac{M_{inflow} - M_{outflow}}{M_{Inflow}} \times 100$$

where RP is the removal performance of the analyte (in %), M_{inflow} the inflow mass of the analyte, and $M_{outflow}$ the outflow mass (Fuerhacker et al., 2011).

3.5.3.2 Vegetated column test

After the experiment described in 3.5.3.1, the design of the biofilter has been modified to avoid possible hydraulic failure and address phosphate removal.

In this experiment, plants have been included to assess the effects that amendments have on the removal performance and on plant fitness.

Due to the inclusion of plants in the design, columns were designed differently from the previous experiment. 20 columns 197mm i.d. were built in Perspex in order to monitor roots development and the walls were sanded to avoid preferential path. A 100% lightproof mylar sheet 110μm (lighthouse Silver DIAMOND) has been tailored around the columns in order to prevent the interaction between roots and sun, and avoid the growth of algae like in previous studies (Subramaniam et al., 2014). The reflective material was secured with Velcro straps and the sheet removed once a month to take picture of the media and to monitor roots. The drainage pipe was raised to establish a saturation zone of 400mm. For sustainability purposes and for resource limitation, 4 PVC columns used in the previous experiment were used for designs that did not include plants.

Plant species choice was based on literature review and excluding species that were not considered autochthonous: *Carex flacca*, *Deschampsia cespitosa* (Figure 3-3). The family Carex has been extensively studied in many laboratory experiments (Bratieres et al., 2008; Zinger et al., 2013; Søberg et al., 2014), while Deschampsia has been used in phytoremediation studies (Kucharski et al., 2005; Antoniadis et al., 2017). Both plants are considered sturdy, resilient to frequent wetting and establish quick in sandy soils.

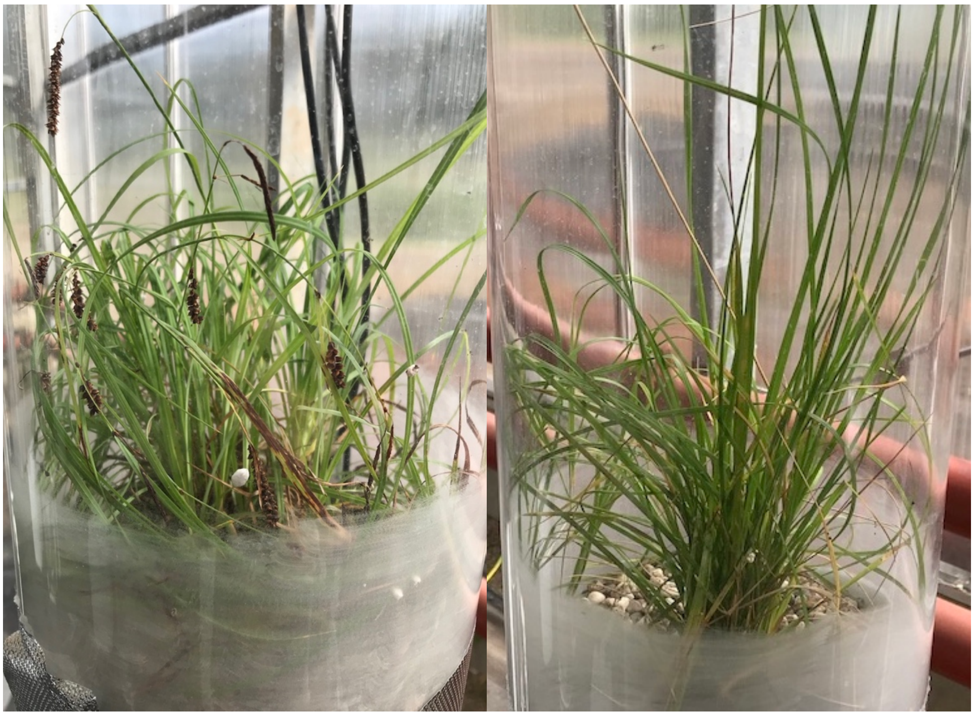


Figure 3-3 Side view of *Carex flacca* (left), and *Deschampsia cespitosa* (right).

The tested configurations were characterised from top to bottom (Figure 3-4):

- Protection layer: 30mm of 5.0-8.0mm coarse gravel. This layer is thinner to allow plants to grow in.
- Top filter layer: 100mm mix by volume of 10% perlite, 10% vermiculite, 20% topsoil, and 60% 0.6-1.18mm sand.
- Bottom filter layer: 200mm mix by volume of 10% perlite, 10% vermiculite, and 80% 0.6-1.18mm sand.
- Amendment layer: 100mm consisting of 0.59-1.68mm GAC or 0.7-1.6mm Zeolite. The layer was equally divided in two, one for each amendment. In the control this layer was absent and had the same mix as Bottom filter layer.
- Transition layer: 100mm of 0.6-1.18 mm sand.
- Saturation zone: two layers consisting of 200mm of 0.6-1.18mm sand and 100mm 1.18-2.36mm sand that bridge to the drainage layer. 5% by volume of woodchip was added as carbon source.
- Drainage layer: 40mm of 2.0-3.0mm fine gravel, and 65mm of 5.0-8.0mm coarse gravel on top of the perforated drainage pipe (20mm i.d.).

The media were light hand-compacted according to construction practice (Le Coustumer et al., 2012).

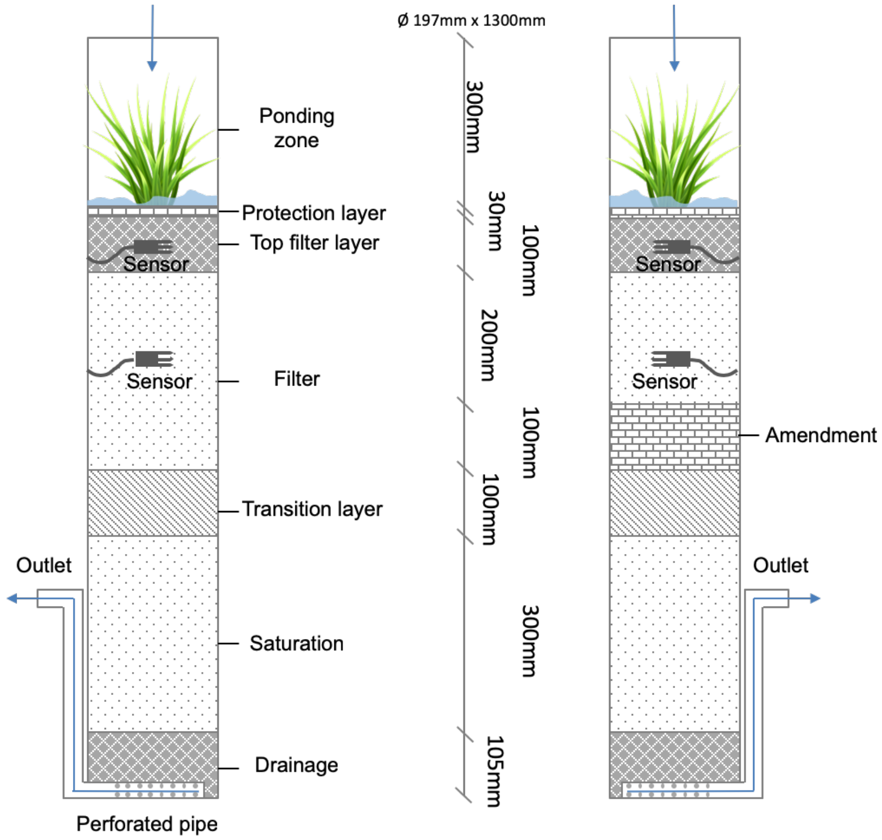


Figure 3-4 Vegetated columns used for the experiment in greenhouse. The raised pipe has a tap that allows to prevent outflow from columns if needed.

In total 24 biofilters, including replicates, were tested:

- 5 perspex columns were designed according to (Woods-Ballard et al., 2015) vegetated with *Carex flacca*. This design was named after the acronym “CoCa” (Control Carex).
- 5 perspex columns were designed according to (Woods-Ballard et al., 2015) vegetated with *Deschampsia cespitosa*. This design was named after the acronym “CoDe” (Control Deschampsia).
- 2 columns were designed according to (Woods-Ballard et al., 2015) and no vegetation was included. This design was named after the acronym “CoNP” (Control NoPlant).

- 5 perspex columns were designed according to (Woods-Ballard et al., 2015), an added layer of amendments and vegetated with *Carex flacca*. This design was named after the acronym “AmCa” (Amended Carex).
- 5 perspex columns were designed according to (Woods-Ballard et al., 2015), an added layer of amendments and vegetated with *Deschampsia cespitosa*. This design was named after the acronym “AmDe” (Amended Deschampsia).
- 2 columns were designed according to (Woods-Ballard et al., 2015), an added layer of amendments and no vegetation was included. This design was named after the acronym “AmNP” (Amended NoPlant).

Due to the requirement of lights by plants and to achieve condition close to reality the setup was installed in a greenhouse (Bardon grange – Headingley). Sensors were installed to monitor temperature, relative humidity and solar radiation (Appendix 3). For this experiment, the setup was watered with volumes of runoff matching seasons (i.e. spring, summer and autumn) of a biofilter 4% of its catchment to make sure to not cause premature clogging in the biofilter as suggested by (Le Coustumer et al., 2008).

Based on paragraph 3.3 in the area of Headingley – Leeds rain averagely 758.2mm/year and the average rain for spring, summer and autumn is on average 174.8, 200.7 and 216.2 mm/season respectively.

The runoff applied to the biofilter was calculated using the rational equation

$$Q = c \times i \times A$$

where Q is the peak discharge, *c* is the rational equation runoff coefficient (here assumed as worst case scenario equal to 1), *i* the rainfall intensity and *A* the drainage. Based on this data the quantity of runoff generated during spring, summer and autumn was circa 133, 153 and 165 litres respectively for vegetated biofilters, while for non-vegetated biofilters, due to the lower area of the non-vegetated biofilter columns, it was 77, 88 and 95 litres respectively. Columns were watered every 48h according to ADWP characteristic of Leeds. An attempt was made to water plants according to seasons ADWP (i.e. 51h spring, 48.5h summer, 36.0 autumn), however, due to health and safety regulation it was not possible to water plants during the weekend or after 3pm. Therefore, biofilters were watered every two days, three times a week.

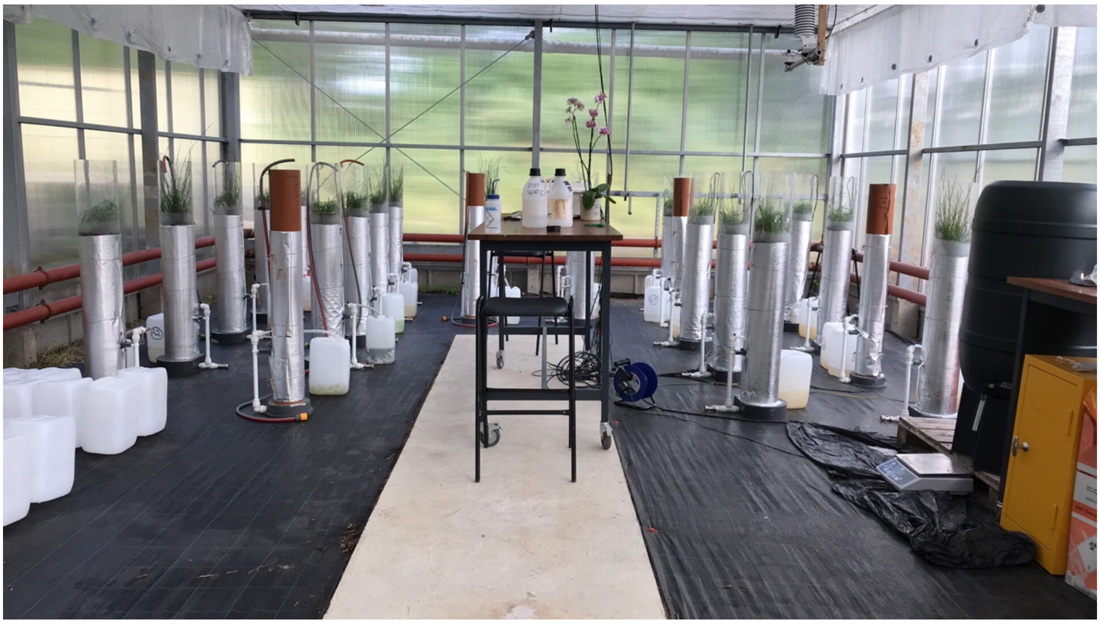


Figure 3-5 Panoramic view of the neo-built biofiltration facility. On the left, columns have accessory pipes for hydraulic conductivity assessment. On the right, columns installed with sensors. Water was prepared in a 250 litre water butt. Samples were collected every two weeks swapping outlet tanks with clean ones (bottom left)

Columns including plants were randomly located to ensure that the position was not affecting the results, and dosed with 3699ml of semi-synthetic stormwater runoff during spring, 4248ml during summer, and 4575ml during autumn. Since non-vegetated columns' internal diameter was lower (150mm vs 197mm), these were watered with 2145ml, 2463ml and 2653ml respectively. The experiment lasted 6 months and the routine was organised in 4 weeks:

- Week 1: watering Monday, Wednesday, and Friday.
- Week 2: watering Monday, and Friday. Sample collection on Wednesday.
- Week 3: watering Monday, Wednesday, and Friday. Plant observation on Friday.

- Week 4: watering Monday. Sample collection on Wednesday. Hydraulic conductivity experiment on Friday.

Water was weighted (1ml = 1g) and then poured in the column using a watering can with a shower head to prevent media displacement.

The outlet runoff was collected to calculate the EMC and analysed for pH, temperature, conductivity, and dissolved oxygen with a HACH HQ40d (PHC101, CDC401, LBOD101). This time, a food-grade silicon pipe was added at the end of the raised pipes and lay down at the bottom of the collection tank, so that water splashing was minimised, and a correct reading of DO could be taken. Composite samples were then filtered and analysed for pollutants in Table 3-7.

Table 3-7 Parameters assessed during phase II test

	TS + TSS + TDS + PSD
	TP + PO4-P
	TN + TDN + NO_x + NH_4-N
	DC + DOC + DIC
	THM - DHM: Al, Cr, Fe, Ni, Cu, Zn, Cd, Ba, Pb
	DO
	pH
	Conductivity
	Moisture content
	Stomatal conductance
	Hydraulic conductivity
	Temperature
	Relative humidity
	Solar radiation

3.5.3.2.1 Nutrients

Nutrients were collected within 6 hours from the dosing and analysed within 12horus from the collection with an autoanalyzer (Skalar san ++) for total and dissolved species: the first were digested with an alkaline persulphate solution, the second were filtered and analysed directly. Due to an error in protocol, the first 2 months were not analysed for dissolved nutrients. Part of the filtered sample (3ml) was used to assess dissolved carbon using an Analytik Jena Multi N/C 2100. The data were then reported for concentration and removal performance.

3.5.3.2.2 Heavy metals

Heavy metals were collected with two separate 125ml containers: one sample was filtered in a 15ml centrifuge tube and acidified with 150μl of HCl; the second was acidified with 500μl of HCl, and then digested with a mix of HNO_3 (70%)+HCl (40%) at 95°C for 2.5h, finally filtered (polyvinylidene) following EPA standards (US EPA 200.2). The samples were then analysed with an ICP-MS. The data were then reported for concentration and removal performance.

3.5.3.2.3 Solids

1 litre of outlet was used to analyse samples for TS and TSS according to Standard Methods 2540 using a 5-digits scale (Sartorius, ±0.0001g accuracy). Part of the water was examined with a COULTER LS230 laser diffraction for PSD of inlet and outlet water. Although some microplastics were found by visual inspection of inlet samples as shown in Figure 3-6, this was not analysed due to resource limitation. The data were then reported for concentration and removal performance.

Figure 3-6 Filter showing the presence of microplastic, possibly glitters (circled), in inlet sediments.

3.5.3.2.4 Hydraulic conductivity

Hydraulic conductivity was assessed on 6 columns out of 24, one for each design. It has been decided to minimise the effect that tap water could have had on water quality due to wash out of pollutants and on microorganisms due to the altered microclimatic in the biofilter. The water quality was still assessed on these columns as well and no substantial difference was found with the replicate. The hydraulic conductivity test has not been extended to other columns due to limitation. To measure K_w and to ensure saturated condition the columns' saturation zone was emptied and water was flowing from the bottom tap for 30 minutes. After this period of time the tap at the bottom of columns was shut and biofilter left with water ponding (at least 10cm above the surface) for 60 minutes. The columns' tap was then opened, and a flow of water maintained for 30 minutes more while overflowing from the top of the column. Finally, a sample of water from the raised bottom pipe was collected, while cheeking time with a stopwatch, and weighted. The last operation was repeated two more times to make sure the outflow was stable. In similar experiments that assessed hydraulic conductivity, the flow was maintained for 24h (Le Coustumer et al., 2009). However due to health and safety, as well as sustainability reasons, it has been adopted a shorter time of 4/5h (depending on the time needed to collect a sample), as in other studies (Riley et al., 2018). Results were expressed in mm/h using Darcy's law:

$$Q = -KA\frac{\Delta H}{L}$$

where Q is the flow in cm^3/s, K is the hydraulic conductivity in cm/s, H is the hydraulic head, L the bed length in cm, and A the area of the bed in cm^2.

3.5.3.2.5 Sensors

Moisture content of the columns was monitored every 5 minutes using a moisture sensor 5-TM from Decagon buried at 8cm and 25cm depth (Figure 3-7). This sensor has been chosen over other for its accuracy (2% after calibration), the inclusion of a temperature sensor, and the possibility to fit into a narrow column without interference with the surrounding Perspex. The aim was to monitor the moisture content in the top part of the filter, where plants established, and in the middle of the bottom filter. It was not possible to insert a sensor in the amendment layer due to complication in the calibration process. In fact, the calibration consisted in creating a sensor specific calibration curve, that correlate dielectric permittivity reading of the sensor and water content assessed experimentally. The sensor read a cylindrical volume of soil of 5cm diameter and 10cm height (from the internal rod) making impossible to install it between two different layers. Data were corrected for temperature since dielectric permittivity is temperature dependent. The sensors were connected to a Campbell Scientific datalogger CR1000X.

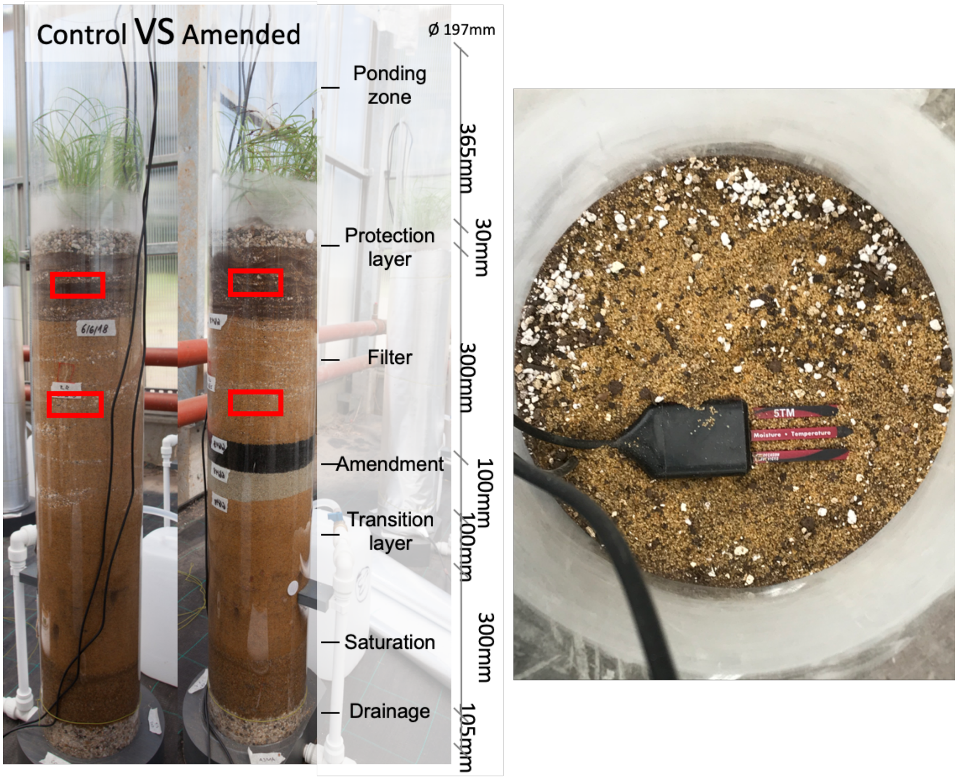


Figure 3-7 Installation of moisture sensors (red rectangles). This has been installed slightly decentred since the field of dielectric permittivity generate from the internal rod (top one marked with “5TM”).

Leaf gas exchange was measured between 9am and 3pm on three different plants of the same species and same design (Szota et al., 2015). A leaf porometer SC-1 by Decagon Device was used to measure the stomatal conductance by holding 3 or more blades of grass together for a correct reading as recommended by the operational instruction of the manufacturer. Every 4 weeks, qualitative data relative to plant health (i.e. longest shoot, diseases, deepest root, presence/absence flowers) were noted down as well. Thanks to the transparency of the columns, it was possible to have an insight of the lateral root growth.

A pyranometer (CS300), and temperature-relative humidity probe (CS215) were used to monitor the environmental condition in the greenhouse. Despite windows being open, temperatures were above the average compared with the outside despite the greenhouse being north-oriented.

3.5.4 Fate of pollutant in biofiltration system

At the end of the 6-month period, 3 columns for each design including plants have been disassembled to assess the concentration of pollutants at 6 depth, in shoots and in roots. Columns that were tested for hydraulic conductivity, and those including sensors, were not disassembled because used for further studies (not in this project).

The columns were turned upside down and sampled at the surface (protective layer), at 8.0cm (Top filter layer), 23.0cm (filter media), 35.5cm (GAC layer), 40.5cm (Zeolite layer), and 68cm (saturation zone) from the surface. These were dried at 60°C for 48h and processed as described in paragraph 3.5.4.1 - Total metal and nutrient concentration.

Plants were extracted completely from the soil, making sure not to break any root in the soil, and washed to extract all the media from the roots as shown in Figure 3-8. The longest root and shoot length, as well as 95% bulk) for each plant was manually measured with a measuring tape, and a picture was taken (see Appendix 4).The plants were then divided into shoots, roots, and stems. The roots were cut in small segments of 2-4 cm and placed in a bucket with water, then approximately 10 grams wet weight were sampled. The rest of the roots were oven dried at 60°C for 48h, weighted and shredded for further analysis of heavy metals and nutrient as described in the following paragraph.

3.5.4.1 Chemical characteristics: heavy metals and nutrients

Total metal and nutrient concentration in the media were determined after acid digestion (H_2O_2 + H_2SO_4 + HCl analytic grade) with Li_2SO_4 addition for higher digestion temperature and Se catalyst in the oxidation of organic material using an aluminium block digester (Carter and Gregorich 2007). SRM 1573a Tomato leaves and RTC-CRM033 Loamy sand 10 reference materials were included in the digestion to monitor the digestion recovery efficiency. Al, Cr, Fe, Ni, Cu, Zn, Cd, Ba, and Pb were then analysed by ICP-MS (Thermo Fisher iCAPQc), while TN and TP by autoanalyzer (Skalar San ++).

3.5.4.2 Image analysis

To assess the root surface, the wet sample was spread out on a transparent acrylic tray and scanned with an EPSON Perfection V700 with backlight at 800dpi to obtain crisp images of roots. The image was processed using ImageJ: firstly, the picture was transformed in 16 bit, a scale was set to associate pixel to cm, then using the function “threshold” a mask that overlies the roots was created, finally, the impurity (grain of sand or amendment) were removed. The root surface was then measured counting the black pixels obtaining the surface area in cm^2 (Tajima and Kato, 2011). Roots where then dried in the oven at 60°C for 48h and weighted to calculate the surface area per gram (Glaister et al., 2017).

20 leaves for each plant were collected, attached to adhesive paper, and scanned with an EPSON 11000XL at 800dpi to obtain a digital image and calculate surface area per gram, in the same way as for the roots, and length per gram using ObjectJ, an ImageJ plugin to calculate distances. The un-scanned shoots were oven dried at 60°C for 48h, weighted and shredded for further analysis of heavy metals and nutrient as described in paragraph 3.5.4.1 - Total metal and nutrient concentration (Glaister et al., 2017).

Figure 3-8 A plant (Deschampsia) is getting washed on top of 3 filters. Roots that get eventually washed away can thus be retrieved

3.6 Chapter conclusion

This chapter described methodologies used during each experiment of this project that include standard methods and practice for biofiltration studies. It also reports media and plants species used in this study. The results for the test described are in chapter 4, chapter 5, chapter 6, and chapter 7.

Chapter 4 Biofilter media characterisation

4.1 Chapter overview

This chapter presents the results of particle size distribution, bulk density, and chemical analysis for 15 media. X-ray fluorescence technique examined the presence of oxides considered important for a biofilter. Constant head test highlighted differences in the hydraulic conductivity. The differences in removal performance for selected pollutants is discussed in relation with the oxide composition analysed. Finally, implication for the biofilters' design that will undergo laboratory test are outlined.

4.2 Physical properties

4.2.1 Particle size distribution

Biofilters are subjected to a high inflow of suspended solids that influence water quality and increase the risk of clogging the first layer of the system. Clogging is defined as the reduction of permeability and consequent decrease in infiltration rate (Bouwer, 2002), and particle sizes is closely related with this parameter.

Particle size distribution chart for the media assessed is in Figure 4-1. The guidelines from CIRIA and Monash university (Woods-Ballard et al., 2015; Payne et al., 2015) suggest to use media with particles finer than 2.0 mm and bigger than 0.063. Sand, the most abundant media in the biofilter, GAC and Zeolite meet this requirement. Perlite, vermiculite, woodchip, TopSoil and gravel will be used: as amendments to increase drainage and soil porosity, retain moisture, as source of carbon for bacteria or nutrient for initial plant establishment and protecting the biofilter from erosion, explaining the divergence in PSD from the guidelines.

It is important to notice how topsoil's particles smaller than 0.065mm exceed 10%. The migration and redistribution of the finer fraction could increase the probability of failure in biofilter. Test on field undertaken at Monash University by (Hatt et al., 2014) demonstrated that the addition of a "clog resistant" layer above the filter can reduce the formation of a thin impervious layer of sediment that cause hydraulic failure. This layer is characterised by high particle diameter (i.e. 0.5-2 mm), however it is not considered heavy enough to sustain wind erosion. A layer of coarse gravel (5-8 mm) has been used instead to ensure erosion control, protecting the filter from clogging and ensuring an easy access to maintenance.

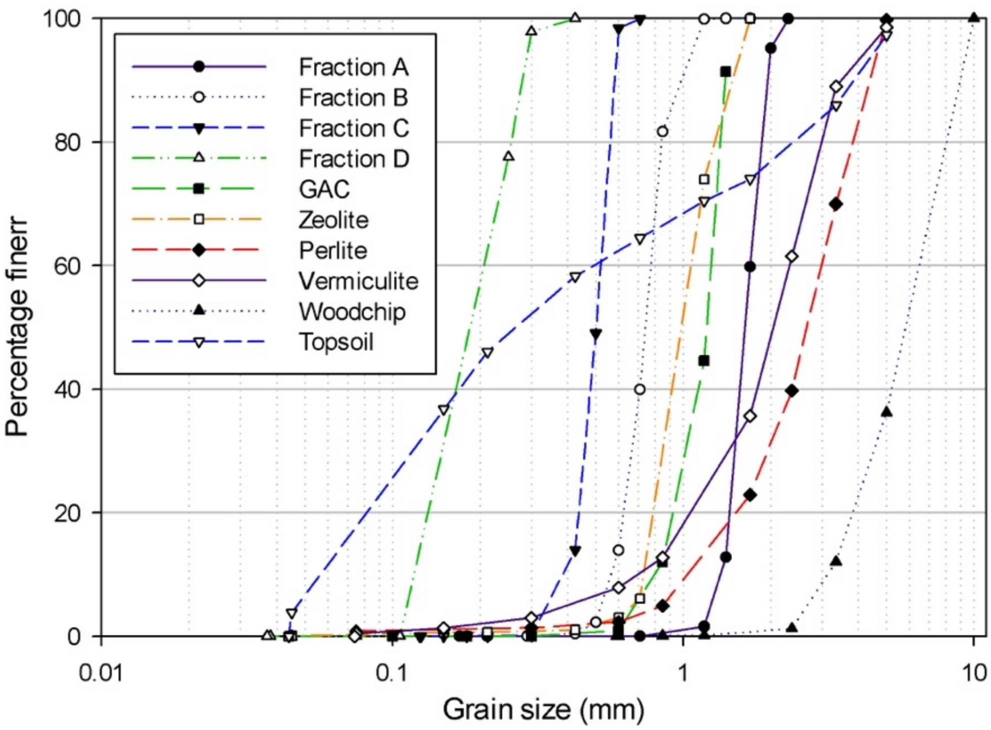


Figure 4-1 PSD of the media under assessment

4.2.2 Bulk density

The growth-limiting bulk density (GLBD) is defined as the soil density where root penetration and elongation is prevented (Daddow and Warrington, 1983). This value is texture dependent, is higher for coarser media and for sandy loam and pure sand is of 1.59 and 1.74 g/cm^3 respectively.

The bulk density has been assessed in accordance with BS EN 1097-6:2013, and the values are presented in (Table 4-1). It can be noted that the media used to design the biofilter are below these values, suggesting that roots will not be prevented to grow.

Media like vermiculite, perlite, GAC, and Zeolite have a high specific surface (BET method). This could be an advantage for biofilm growth, as well as adsorption site pollutants. No specific test has been conducted, however the provider of GAC and Zeolite has shared this information: 1500 m^2/g and 46 m^2/g respectively.

Table 4-1 Physical characteristics for media under assessment

Media	PSD (min-MAX) (mm)		ρ (g/cm^3)	*Void ratio*	BET (m^2/g)	K_w (mm/h)
Gravel Big	5.00	8.00	1.47	44.89	-	-
Gravel Medium	3.00	5.00	1.47	46.13	-	-
Gravel Small	2.00	3.00	1.44	44.34	-	-
Fraction A - Yellow	1.18	2.36	1.57	39.97	-	-
Fraction B- White	0.60	1.18	1.57	41.23	25	9890.85
Fraction B - Yellow	0.60	1.18	1.64	37.35	-	-
Fraction C - White	0.30	0.60	1.55	42.74	-	4454.89
Fraction D - White	0.15	0.30	1.52	42.86	-	1652.68
Top soil	0.05	5.00	0.74	73.54	-	204.92
Woodchip	2.36	5.00	0.29	86.77	-	-
Vermiculite	0.15	5.00	0.11	n.a.	-	-
Perlite	0.15	5.00	0.11	94.51	-	-
Zeolite	0.70	1.60	0.79	71.00	40-46	1657.75
GAC	0.59	1.68	0.47	78.26	1200	6936.66
Basalt	3.00	8.00	n.a.	n.a.	-	-
Top filter	-	-	1.53	-	-	241.44
Bottom filter	-	-	1.59	-	-	2890.53

4.3 Chemical properties

4.3.1 XRF

The higher presence of aluminium and iron oxide has been suggested to enhance the removal performance of phosphate (Glaister et al., 2014).

X-ray fluorescence analysis (XRF) (ZSX Primus II) was conducted to determine the elemental composition (i.e. oxides) of the media under assessment by measuring the secondary radiation emission after a sample is exposed to X-ray. Samples were oven dried for 48h at 60°C prior to grinding, sieved down to 100μm, and then pressed (15 tons) to create pellets.

The percentage of SiO_2, Fe_2O_3, and Al_2O_3 are in Table 4-2. It should be noted that the values for Fraction B - Yellow are close to the one specified by the provider: SiO_2 98%, Fe_2O_3 1.3%, Al_2O_2 0.3%. Difference were expected due to the possible differences in the methodology (i.e. grinding time, machine), and the homogeneity of the media.

White sand (i.e. Fraction B-C-D) has generally a low content of iron compared to yellow sand (Fraction A and Yellow B). Comparing the XRF values of previous studies, yellow sand fraction B has a lower percentage of iron and aluminium than Skye sand (Glaister et al., 2014). The coarser sand used in the biofilter (Fraction A) has a much higher presence of iron and aluminium compared with Skye sand: 8.4 and 1.0 respectively. However, since this sand is located in a saturated zone in anaerobic condition, it is expected that will not increase the adsorption capacity of phosphate since the adsorption mechanism involving iron oxyhydroxide requires aerobic condition. Zeolite, GAC, Perlite, Vermiculite, and Basalt have a great volume of Fe_2O_3, and Al_2O_3, based on these data the removal performance of phosphate seems to be assured by many media.

Table 4-2 XRF analysis results for selected oxides. [a](Glaister et al., 2014)

Media	SiO_2 (%)	Fe_2O_3 (%)	Al_2O_3 (%)
Gravel Big	95.6	0.7	1.7
Gravel Medium	95.0	1.0	1.8
Gravel Small	93.6	1.0	2.6
Fraction A - Yellow	89.0	8.4	1.0
Fraction B- White	97.6	0.8	0.1
Fraction B - Yellow	97.5	1.1	0.3
Fraction C - White	97.7	0.7	0.2
Fraction D - White	98.3	0.5	0.1
Top soil	67.1	6.5	11.1
Woodchip	5.4	4.7	1.6
Vermiculite	42.3	13.5	10.3
Perlite	75.6	1.3	12.9
Zeolite	73.5	2.2	12.8
GAC	16.5	10.2	3.6
Basalt	46.8	13.5	16.3
Top filter	-	-	-
Bottom filter	-	-	-
Skye sand[a]	94	1.8	2.2
Loamy sand[a]	99	0.21	0.58

4.3.2 Adsorption capacity at equilibrium q_e

Dissolved pollutants are the most bioavailable fraction in urban runoff (Kayhanian et al., 2012) and have been used as performance indicator for the tested media. As suggested by (Huber et al., 2016) copper, zinc and cadmium are mostly in dissolved state and have been used in a batch test as proxy to assess the adsorption capacity at equilibrium (qe) for heavy metals. Phosphate has been used as proxy for nutrient adsorption capacity since the major mechanism of phosphorus retention in biofilter is adsorption and precipitation (Liu and Davis, 2014). At this stage nitrogen analysis has been excluded since removal mechanisms are more biological dependent (Payne et al., 2014). For this test 1 gram of media in 230 ml of synthetic stormwater, three replica per media, was shaken at 240 rpm on an orbital table for 24h (Paus et al., 2014).

Value of q_e are listed in Table 4-3 and removal performances in Figure 4-2. As expected, Top Soil and woodchip leach phosphate, resulting in a negative adsorption capacity value. Vermiculite, GAC and Zeolite are the media with the highest adsorption capacity, 0.085 mg/g, 0.055 mg/g, 0.043 mg/g respectively, probably due to the content in aluminium and iron oxide, and the high specific surface. The contribution of oxides seems to be relevant also for sand, with yellow sand having twice the capacity of white sand (0.023 mg/g, 0.011 mg/g), but not for basalt, that registered the lowest q_e among the tested media.

Table 4-3 q_e values for media investigated

	PO4-P (mg/g)	Cu (ug/g)	Zn (ug/g)	Cd (ug/g)
Fraction B	0.011 ±0.009	6.91 ±2.312	4.24 ±2.251	0.007 ±0.002
Yellow B	0.023 ±0.006	7.204 ±3.966	1.838 ±3.968	0.012 ±0.003
Gravel big	0.023 ±0.001	5.699 ±1.854	0.701 ±2.065	0.008 ±0.002
Basalt	0.005 ±0.003	7.376 ±3.167	3.114 ±4.1	0.014 ±0
Top Soil	-0.18 ±0.03	42.732 ±2.302	70.812 ±2.127	0.751 ±0.434
Perlite	0.029 ±0.033	25.245 ±2.244	32.043 ±9.9	0.23 ±0.133
Vermiculite	0.085 ±0.016	43.948 ±1.936	73.919 ±1.751	0.793 ±0.453
GAC	0.055 ±0.029	39.765 ±3.79	60.404 ±5.787	0.428 ±0.495
Zeolite	0.043 ±0.009	31.007 ±4.271	51.936 ±6.94	0.097 ±0.048
Wood	-0.07 ±0.016	7.256 ±1.72	26.382 ±2.656	0.406 ±0.526

The heavy metal adsorption capacity followed the same trend, with sand, basalt and gravel having the lowest values, while Zeolite, GAC, vermiculite and perlite having the highest q_e. Vermiculite and perlite have been chosen not only to improve drainage and moisture content in the column (Lewis et al., 2008), but also because previous researchers proved their capacity of absorbing heavy metals (Feng et al., 2012). As suggested by many authors (Bradl, 2004; Blecken et al., 2009b), soil organic matter is an important influencing factor in heavy metal adsorption, thus justifying the adsorption capacity of TopSoil. GAC and Zeolite do not present this inconvenient, suggesting the idea that these two media might be able to increase the lifespan of the biofilter for heavy metal adsorption, without compromising phosphate removal.

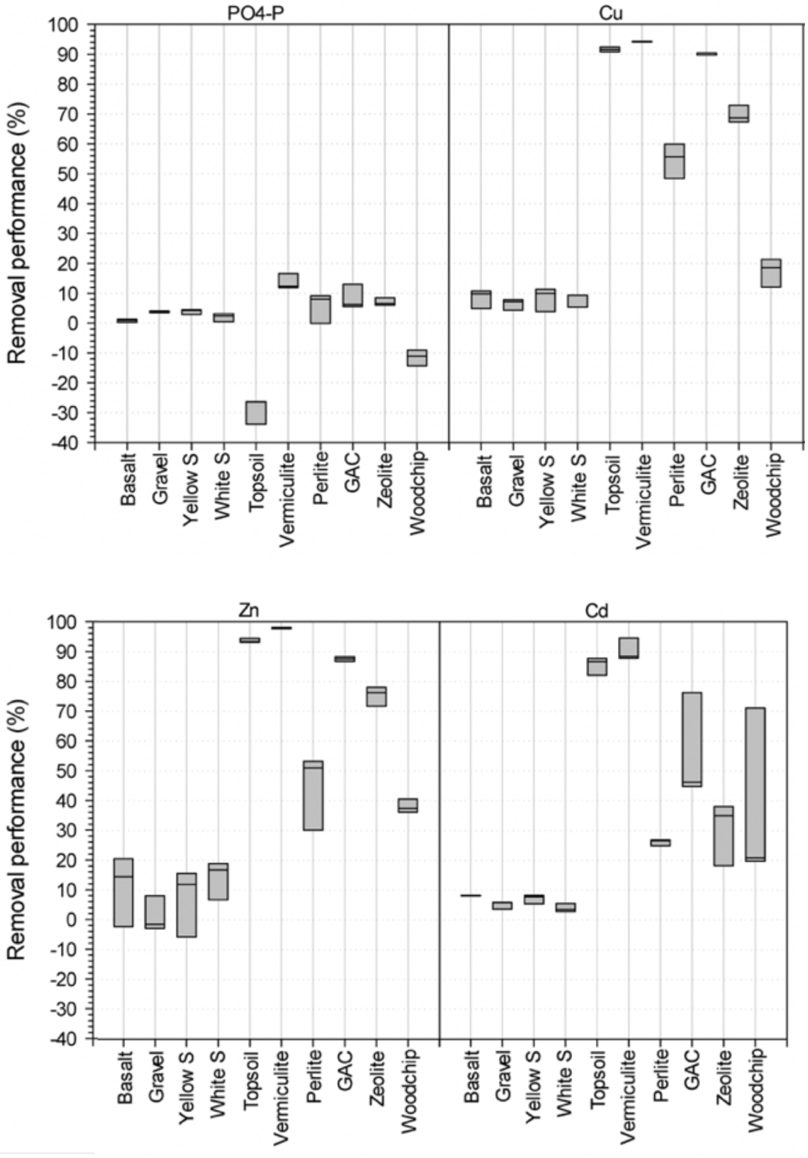


Figure 4-2 Removal performance for PO4-P, Cu, Zn, Cd

After phase I test, when low to negative performance have been noted, a batch test using yellow sand and basalt has been performed. These two media have been analysed based on the results of (Glaister et al., 2014), where sand with high content of iron and aluminium oxides increased removal performance of phosphate. White sand removal performance was 1.85%, while yellow sand was doubly so (3.74%). Despite basalt's high presence of these two oxides (Table 4-2), the removal performance was low (0.81%), thus has been decided not to introduce it in the design and use gravel instead.

From this data it can be concluded that Zeolite and GAC have the potential to increase the adsorption capacity of dissolved pollutants, thus increasing the lifespan of a biofilter.

4.4 Hydraulic properties

4.4.1 Water holding capacity

Maximum water holding capacity, the amount of water held by a specific soil for plant use, for top and bottom filter layer was assessed using (FLL, 2008). This value will later be compared against the water content registered by the sensor installed in the biofilter top layer (SVPT) and bottom layer (SVP).

The medias were dried, placed in a 148mm i.d. cylinder with a perforated bottom, and weighed before being immersed for 24 hours. Finally, the cylinder was left to drip for 2 hours and weighted again.

The test showed that water holding capacity for the two media is similar, SVPT= 21.49% and SVP= 18.89%. The 2.6% increase in water content in SVPT can be due to the presence of organic matter in Top Soil that retain more moisture than sand (Hudson, 1994).

4.4.2 Hydraulic conductivity

Hydraulic conductivity represents the ability of water to pass through a media. The two main biofilter guidelines used in this study, (Payne et al., 2015) and (Woods-Ballard et al., 2015), suggest that K_w should fall between 100 mm/h and 300 mm/h in order to ensure an adequate flow-quality control and to avoid excessive stress to plants. In order to avoid overflow due to a low ratio biofilter-to-catchment size a higher hydraulic conductivity has been selected.

To test the hydraulic performance of selected media a constant head test method (ASTM D2434 - 68(2000)) has been performed as described in paragraph 3.5.2.3. Due to the impossibility to establish a hydraulic head, the media with the highest PSD (i.e. gravel, Fraction A) were not assessed.

Sand Fraction B (9890 mm/h) has the highest hydraulic conductivity, followed by fraction C (4454 mm/h), and finally fraction D (1652 mm/h). Among the amendments Zeolite (1657 mm/h) has a similar hydraulic conductivity as Fraction D, while GAC is much higher (6936 mm/h).

Based on this data, sand fraction B has been used as the main component of the filter media to ensure a high infiltration rate. 20% top soil, 10% vermiculite and 10% perlite have been added to sand to simulate the top part of the biofilter (SVPT), no top soil was added to test a representative layer of the bottom filter (SVP). As expected, the organic matter contained in top soil, as well as vermiculite, increased the water retention capacity, decreasing K_w of one order of magnitude: 241 mm/h for SVPT and 2890 mm/h for SVP.

Applying Darcy's law successively for each layer, the equivalent vertical hydraulic conductivity K_v (Table 4-4) for the designed columns have been calculated as

$$K_v = \frac{b}{\sum_{i=1}^{n} \frac{b_i}{K_i}}$$

Where b is the length of the biofilter layer, b_i the thickness of a layer, K_i the specific hydraulic conductivity. The equivalent hydraulic conductivity is used as indication since gravel and Fraction A hydraulic conductivity values were not available.

Columns' design for experiment in chapter 5 included Fraction C and D, with an estimated hydraulic conductivity of 1341 mm/h. The inclusion of an amendment layer improved the conductivity only for GAC, while the designs containing Zeolite generally have a lower K_w.

Based on the conclusion of the experiment described in chapter 5, the design of the biofilter has been changed to increase the hydraulic conductivity and to avoid possible failure point due to the presence of really fine material (i.e. Fraction C and D) in the middle of the column.

Table 4-4 Hydraulic conductivity values for media and designs

Media test		Column test	
Media	mm/h	Design	mm/h
Fraction B	9890	Control	1341
Fraction C	4454	Z+GAC	1334
Fraction D	1652	GAC	1388
GAC	6936	Zeolite	1285
Zeolite	1657	Plant test	
Top filter	241	Control	1433
Bottom filter	2891	Amended	1425

4.5 Discussion

4.5.1 Differences between media

The chosen amendments seem to increase phosphate and heavy metal adsorption, thus extending the life span of a biofilter. Vermiculite and perlite, despite having a really high q_e, will probably have a limited impact on the removal performance since their presence in the biofilter is low (10% by volume). Organic matter has high heavy metal adsorption; however, it leaches nutrients representing a possible source of phosphate that affects negatively the removal performances. The estimated hydraulic conductivity is higher in biofilters including GAC, however the presence of Zeolite decreases the water flow. Although sand has a low q_e, differences between yellow and white sand is evident, with the former having twice the adsorption capacity of the latter.

4.5.2 Implication for design

As suggested by (Blecken, Zinger, et al., 2007), the upper part of the biofilter will include only 20% of top soil by volume to avoid leaching of nutrients. Woodchip is an important carbon source for denitrifying bacterial that might populate the anaerobic zone of the biofilter (Glaister et al., 2014), while perlite and vermiculite are indispensable to increase the porosity of the soil, retain moisture and slightly increase the cation exchange capacity of the biofilter.

Based on the data provided in this chapter, the four designs that underwent phase I test included white sand Fraction A-B-C-D, gravel, and, when required, Zeolite, GAC, and a combination of the two. The aim was to identify flows in the designs, improve them, and prepare for the second experimental phase where the effect of amendments on plant growth, performance, and hydraulic conductivity was studied.

4.6 Chapter summary

In this chapter data relative to the physical, chemical and hydraulic property of selected media is reported. Based on the data and the availability of media, the experiment described in chapter 5 tested a combination of Fraction A-B-C-D without vegetation in order to assess the capacity of the filter media and amendments to treat dissolved pollutants in synthetic stormwater runoff.

Chapter 5 Phase I: non vegetated column test

5.1 Chapter overview

This chapter outlines the results for the column study. Analysis of phosphate and heavy metals are here presented and discussed. The implications are used to select the design for phase II. Part of this work has been published in (Berretta et al., 2018).

5.2 Results

The evolution of removal performance for phosphate and dissolved heavy metals was examined during two distinctive experiments. Dissolved oxygen, temperature, conductivity, pH and hours between two dosing events were monitored to assess the influence that these variables have on the treatment. In the first experiment four column were tested in couples: control vs Z+GAC, and Z vs GAC. 25 litres of synthetic stormwater were poured in each column using a peristaltic pump. A representative sample for the inlet and outlet was collected and analysed for PO_4-P, dissolved Cu and Zn. In the second experiment eight columns, two replicates per design, were tested in parallel using the same synthetic stormwater runoff. 25 litre of water per column were dosed using a peristaltic pump. The flow was set to 100ml/min for 4h and checked every hour for every column. Samples were analysed not only for the previous pollutants, but also for Al, Fe, Ni, Cd, Ba, and Pb. Due to the different dosing period, the data for the two experiments will be commented separately. In Table 5-1 the composition of the synthetic stormwater runoff used for the two experiments.

Table 5-1 Synthetic stormwater composition for the two experiments. Target concentrations for inlet water are based on Table 3-3

	Target	1st experiment	2nd experiment
pH	-	7.1 ±0.2	7.3 ±0.2
conductivity	-	326.1 ±55.6	378 ±45.1
DO	-	9.3 ±0.5	9.6 ±0.4
PO4-P (mg/L)	0.03	0.83 ±0.07	0.97 ±0.03
Cu (ug/L)	205	258.71 ±52.35	197.99 ±35.58
Zn (ug/L)	700	339.99 ±41.58	460.71 ±33.84
Al (ug/L)	-	-	22.5 ±24.89
Fe (ug/L)	-	-	9.18 ±7
Ni (ug/L)	-	-	1.65 ±0.55
Cd (ug/L)	1	-	0.86 ±0.04
Ba (ug/L)	-	-	73.46 ±10.91
Pb (ug/L)	-	-	0.07 ±0.11

5.2.1 Probe analysis data

Samples of inlet and outlet water were analysed for pH, and dissolved oxygen using a HQ11D portable probe from Hach. A summary of the data for the two experiment can be found in Table 5-2.

Samples were not shaken previous DO assessment; however, water was splashing when filling the outlet tank increasing the oxygen concentration making the reading unreliable. Despite the reoxygenation, outlet values were significantly lower than the inlet (9.3 mg/L) for both the experiment ($p<.001$), suggesting that bacterial activity is depleting the oxygen in the column through respiration.

During the two experiments, pH outlet for Control, Zeolite, and Z+GAC design was non statistically significant different from the inlet. Only GAC has registered an increase in pH (7.9 ± 0.6) possibly due to the nature of the media. A similar high pH has been noticed also during the first half of the second experiment, but with further application of synthetic water the pH has settled around 7.

5.2.2 Phosphate

For the first experiment the removal performance of phosphate was on average 23.52% (±22.77), 19.54% (±12.47), 6.04% (±11.10), 20.51% (±19.34) for Control, Zeolite, GAC, Z+GAC (Figure 5-1). In Table 5-2 the concentration for phosphate for the two experiments.

Table 5-2 Average concentrations of dissolved pollutants and probe analysis values for the two experiments. Number of samples=26

	1st experiment				2nd experiment			
	Control	Zeolite	GAC	Z+GAC	Control	Zeolite	GAC	Z+GAC
pH	7.1 ±0.2	7.2 ±0.2	7.9 ±0.6	7.1 ±0.1	7.1 ±0.1	7.1 ±0.2	7.1 ±0.4	7.1 ±0.3
conductivity	277.9 ±107.7	333.1 ±29.9	315.8 ±19.2	291.3 ±104.8	383.6 ±48.2	390.8 ±52.2	382.5 ±47.1	389.2 ±48
DO	8.1 ±0.8	8.5 ±0.7	6.6 ±0.8	7.8 ±1	7.3 ±1.1	7.4 ±1	7.3 ±0.9	6.8 ±1
PO4-P (mg/L)	0.68 ±0.16	0.65 ±0.15	0.77 ±0.18	0.67±0.13	0.74 ±0.17	0.71 ±0.18	0.78 ±0.16	0.73 ±0.17
Cu (ug/L)	20.43 ±3.4	10.03 ±1.6	7.95 ±0.85	17.93 ±3.63	6.01 ±8.22	5.53 ±6.25	5.4 ±14.32	3.23 ±2.03
Zn (ug/L)	19.52 ±16.28	7.42 ±3.24	10.22 ±10.63	11.76 ±6.06	9.25 ±6.73	5.77 ±2.81	11.99 ±8.43	10.6 ±6.45
Al (ug/L)	-	-	-	-	53.37 ±50.2	54.13 ±56.35	43.48 ±43.79	51.95 ±64.1
Fe (ug/L)	-	-	-	-	72.64 ±196.46	57.24 ±134.19	84.69 ±244.67	66.91 ±173.67
Ni (ug/L)	-	-	-	-	1.52 ±1.47	1.64 ±2.97	1.3 ±1.59	1.75 ±2.85
Cd (ug/L)	-	-	-	-	0.03 ±0.07	0.02 ±0	0.02 ±0	0.02 ±0
Ba (ug/L)	-	-	-	-	52.65 ±16.86	11.27 ±7.59	51.52 ±14.23	11.38 ±5.86
Pb (ug/L)	-	-	-	-	0.09 ±0.19	0.08 ±0.11	0.08 ±0.11	0.07 ±0.11

A Kruskal-Wallis H test was run to assess if there was a difference in removal performance among the four designs. The distribution of removal performances values was not similar, and there was a statistically significant difference among groups ($p < .001$). A post hoc test, pairwise comparison using Dunn's procedure with a Bonferroni correction for multiple comparison, revealed statistically significant differences between GAC and Control ($p=.002$), Z ($p<.001$), and Z+GAC ($p=.007$), but not among other designs. A hypothesis is that the higher pH of activated carbon is lowering the adsorption process in the column amended by GAC due to a reduction in exchangeable aluminium with an increase of pH (Danilo and Burnham, 1974). However, a Spearman bivariate correlation did not find statistical evidence ($r_s(26) = -.359$ $p=0.71$).

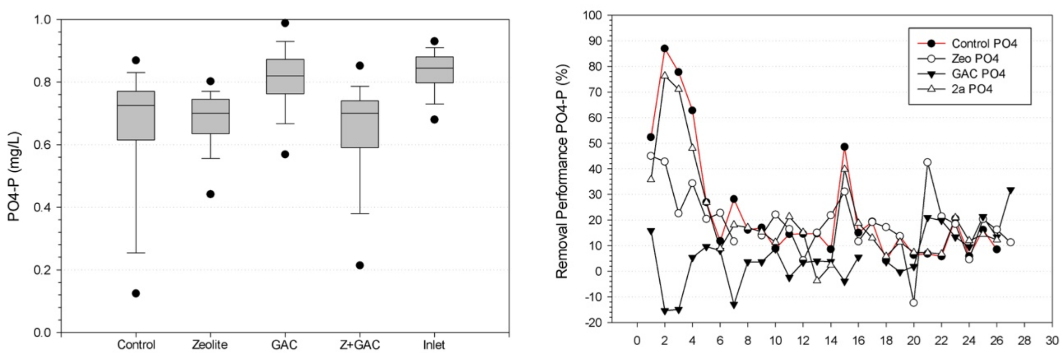


Figure 5-1 Phosphate concentration and removal performance for the first experiment. On the abscissa, the test number.

The second experiment show a similar trend for phosphate (Figure 5-2) with average removal performance for the 4 design: 23.39% (±18.05) 26.63% (±19.33), 18.82% (±17.95), 24.27% (±18.84) for Control, Zeolite, GAC, Z+GAC respectively.

A Kruskal-Wallis test shows statistical differences among design ($p=.006$). Columns including zeolite perform slightly better than the control, while the single-amended column GAC rank the lowest (Zeolite>Z+GAC>Control>GAC). Despite Zeolite ranking higher than Z+GAC, in the second half of the experiment the latter performed better than the former, while GAC's average remained lower than Control. The adsorption of phosphate experienced by similar studies underline a removal higher than 90% for sand based filters (Hatt, Deletić, et al., 2007; Glaister et al., 2014; Liu and Davis, 2014). It should be noticed that in these studies the concentration of dissolve phosphorus is averagely half than what is used in this test (i.e. averagely 0.35 mg/L). The low performance could be attributed to leachate of phosphate from topsoil and woodchip, a concern expressed in chapter 4, low adsorption capacity of white sand, absence of plants, and high inlet concentration.

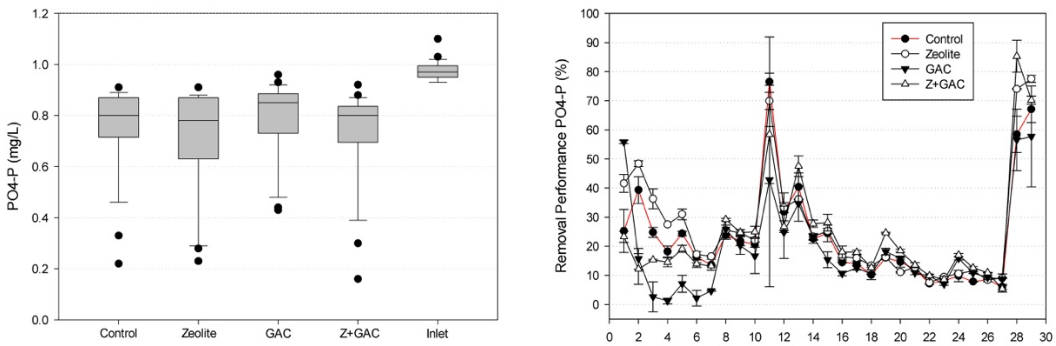


Figure 5-2 Phosphate concentration and removal performance for the second experiment. On the abscissa, the test number.

Another reason could be the lack of dry period between two events. In fact, a moderate positive correlation between removal and antecedent dry period among all designs has been found for both tests (Figure 5-3): ($r_s(102)=0.467$ $p<0.001$ for the first experiment and $r_s(224)=-0.692$ $p<0.001$ for the second. The increase in performance could be due to ferric oxyhydroxide formation during dry period as suggested by (Hatt et al., 2007).

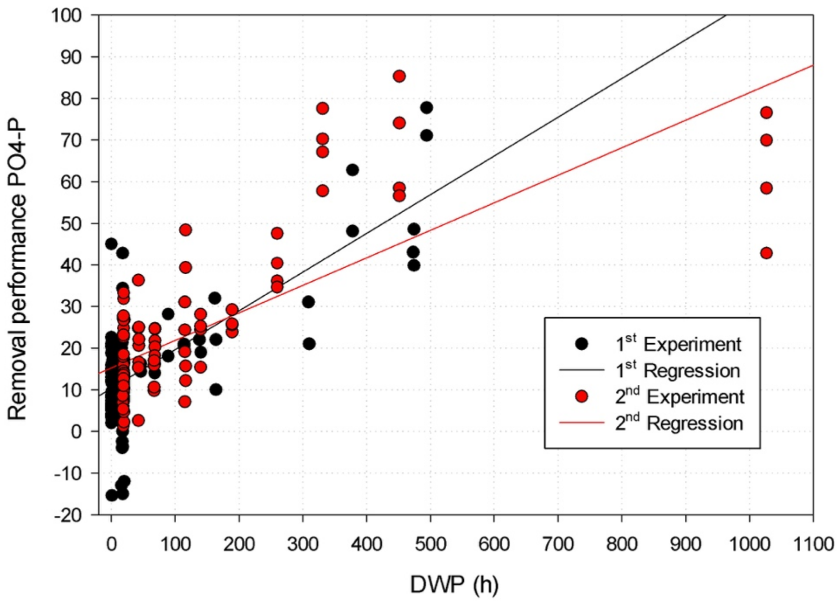


Figure 5-3 Correlation between phosphate removal performance (%) and DWP in hours.

5.2.3 Heavy metals

The inlet and outlet water quality were compared, where possible, with UK water standards. These generally address total concentration of a pollutant rather than distinguish between phases, although the dissolved part is the more mobile and chemical reactive (Andradottir and Vollertsen, 2014; Maniquiz-Redillas and Kim, 2016). Legislation often miss to set limits for inland water protection for all heavy metals. In these cases, this thesis will refer to drinking water limits to compare the water quality of the outlet when possible.

For both experiments, dissolved copper and zinc removal was on average higher than 90%, result in line with other studies (Davis et al., 2006a; Hatt, Deletić, et al., 2007; Blecken et al., 2009b), but much higher than (Søberg et al., 2014) where leaching of dissolved copper occurred. Concentration for the two experiments can be found in Table 5-2. It can be noted how the concentration outlet in the first two experiment for single amendment columns was 5 and 2 μg/L for Zeolite and GAC respectively, while for control and Z+GAC was averagely 14 μg/L highe. Statistically significant differences for the two heavy metals removal performance was observed in the first experiment, with amended design treating on average more Cu and Zn than control (p<.001).

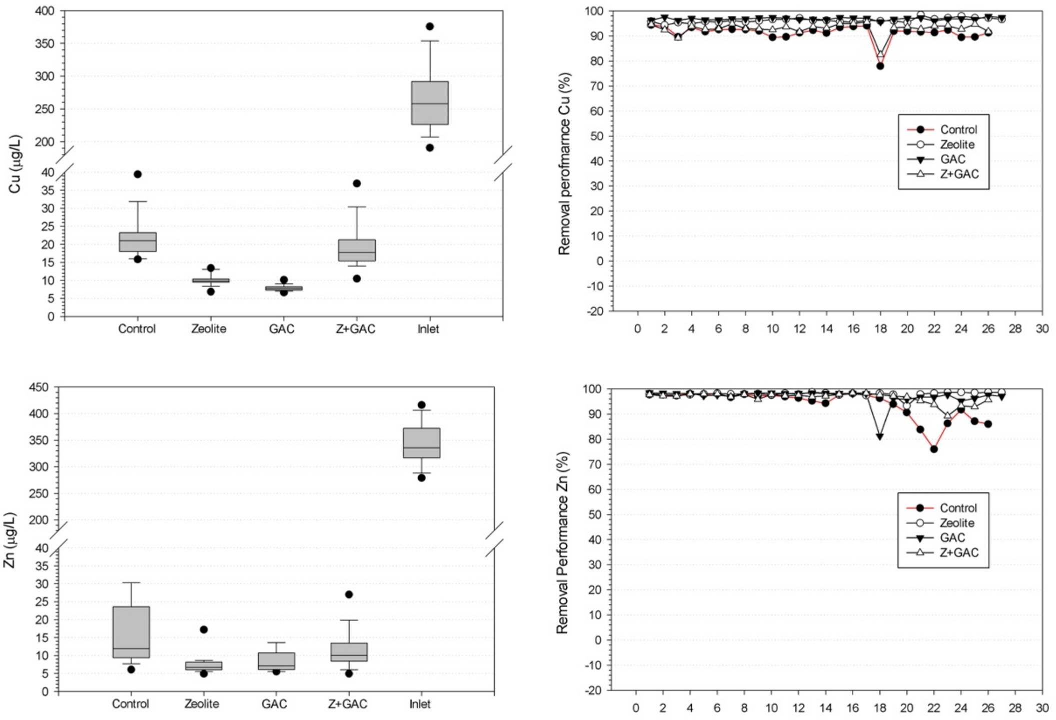
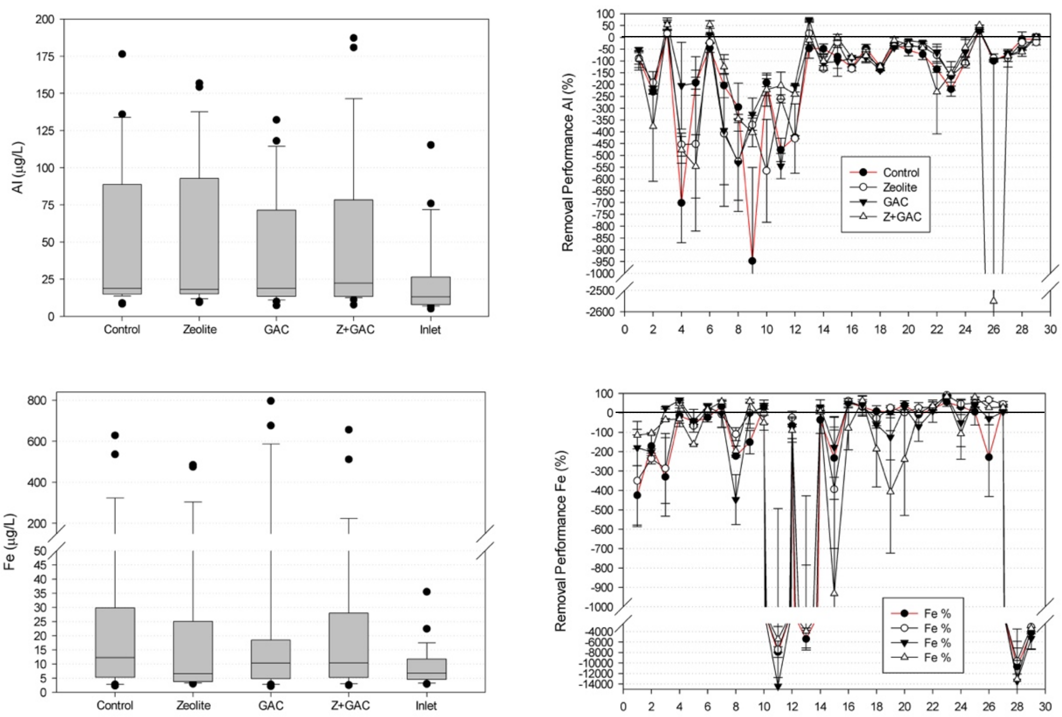


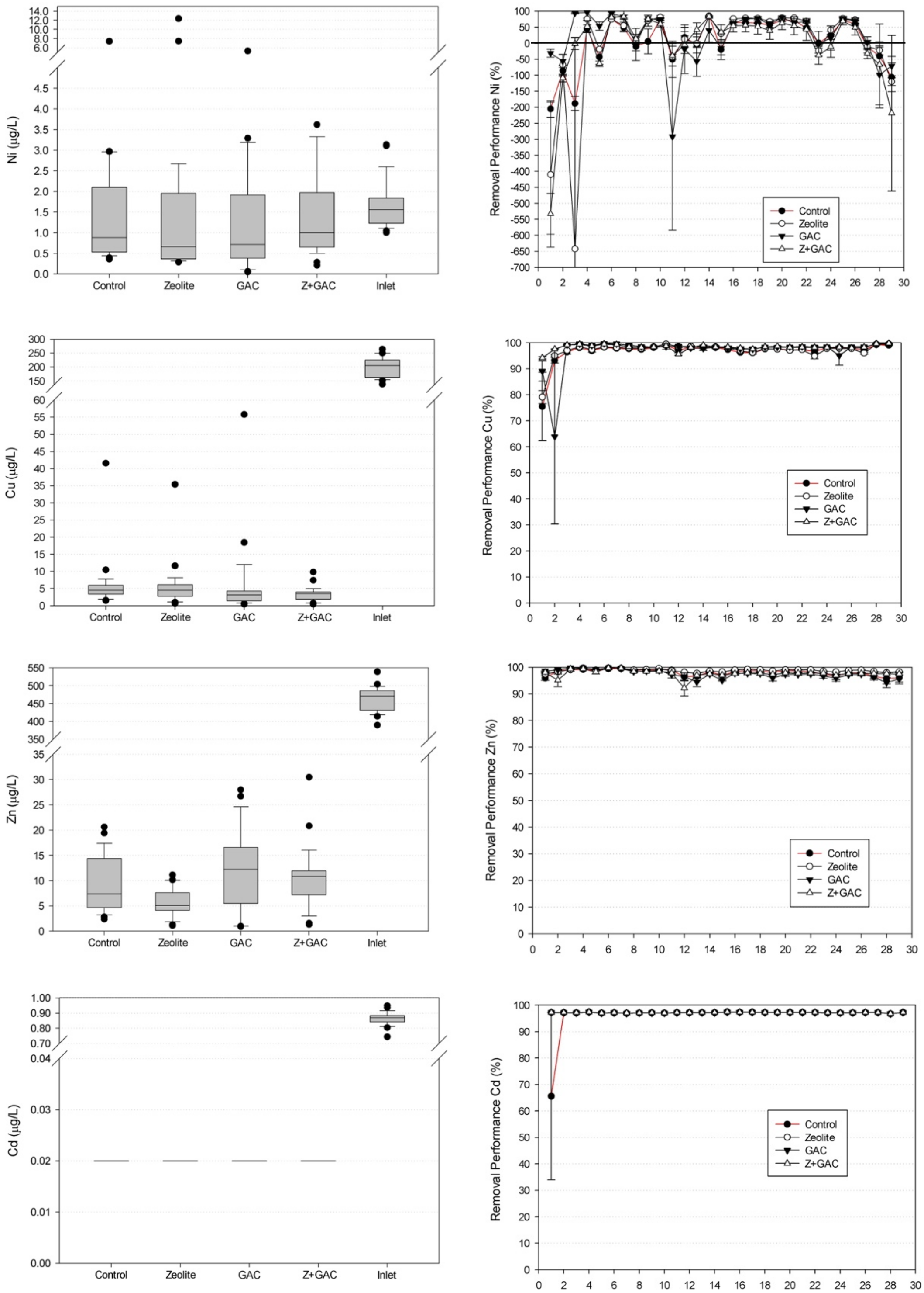
Figure 5-4 Concentration and removal performance for Copper and Zinc for the first experiment. On the abscissa, the test number.

The new experiment setup allowed to test up to 8 columns in parallel. Synthetic stormwater was prepared in the same way to be able to compare the data with the previous experiment, therefore only copper and zinc have been added in the synthetic stormwater solution, however, more dissolved heavy metals (i.e. Fe, Al, Ni, Cd, Ba, Pb) have been assessed to find possible relations for the low phosphate adsorption.

This experiment confirmed the high treatment capacity of the biofilter to remove dissolved copper and zinc, with outlet concentration averagely below 20µg/L for Zn. Copper most strict limit is 5µg/L, and although averagely the columns comply with this value, there were cases with outlet concentration slightly higher. The second limit (22µg/L) is met apart from the first 2 runs probably due to the wash out of small particles from the biofilter. Column filled with Zeolite have the highest Zn removal performance (mean rank Z>Control>Z+GAC>GAC), while GAC is more efficient in Cu treatment (mean rank GAC>Z+GAC>Z>Control). No limit for dissolved Zinc is set by UK legislation, so it is not possible to assess whether the outlet water met the requirement for this dissolved metal.

A non-parametric Kruskal-Wallis test showed no difference in removal performance for the newly assessed metals, but there is statistical difference between inlet and outlet concentration with a net removal only for cadmium, and barium. In fact, design amended with Zeolite have a statistically higher removal performance ($p<.001$) than GAC and Control for barium (Figure 5-5), but not for cadmium, which treatment is not affected by the design ($p=.994$). Although nickel and lead were not added in the inlet water, these two pollutants were present in the tap water in small concentration. These were averagely low: 1.65μg/L for nickel and 0.07μg/L for lead, well below the standard for surface water for abstraction for drinking water purposes: 20μg/L and 50μg/L respectively. The nickel removal for the four design was not statistically different and averagely 6.30%, -5.25%, 21.02%, -3.85% for Control, Zeolite, GAC, and Z+GAC respectively. Lead treatment was negative for all designs, with Z+GAC having slightly higher performances (-8.25%). Despite the leaching, the concentrations at the outlet were below the limits.





Ni (µg/L)
Control
Zeolite
GAC
Z+GAC
Inlet
Removal Performance Ni (%)
Cu (µg/L)
Removal Performance Cu (%)
Zn (µg/L)
Removal Performance Zn (%)
Cd (µg/L)
Removal Performance Cd (%)

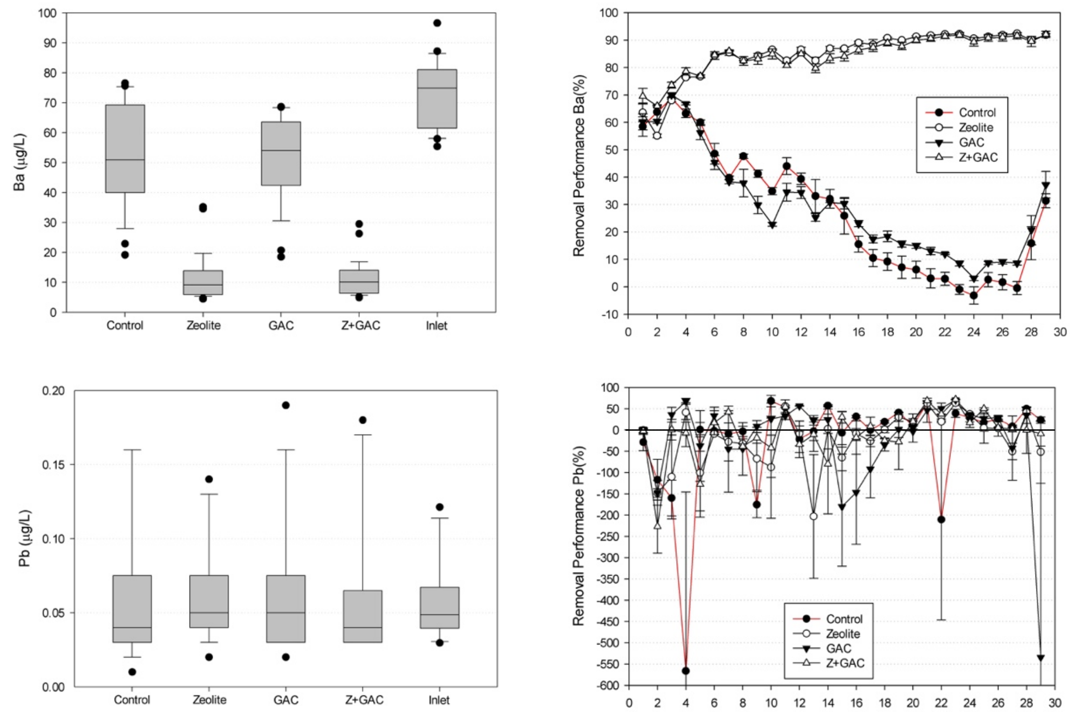


Figure 5-5 Heavy metals concentration and performance for the second experiment. On the abscissa, the test events.

Iron outlet concentration increased specifically during events: 11, 13, 15, 19, 28, and 29. A Spearman test showed correlation between iron concentration in outlet and DWP (rs(224)=.527 p<.001). A quick comparison with Figure 5-2 shows that during these events the removal performance of PO_4-P increased, suggesting that the oxidising environment in the unsaturated part of the biofilter increases the concentration of FeOOH, but, at the same time, the reducing acidic condition of the saturation zone mobilise this metal in form of Fe^{2+} as suggested by the Eh-pH diagram in Figure 5-6. The presence of sand Fraction A in this area could have worsen the leaching of iron since the content in Fe_2O_3 it is higher than in white sand (see chapter 4). The iron concentration at the outlet were averagely below the limits for direct abstraction to potable supply: 300μg/L.

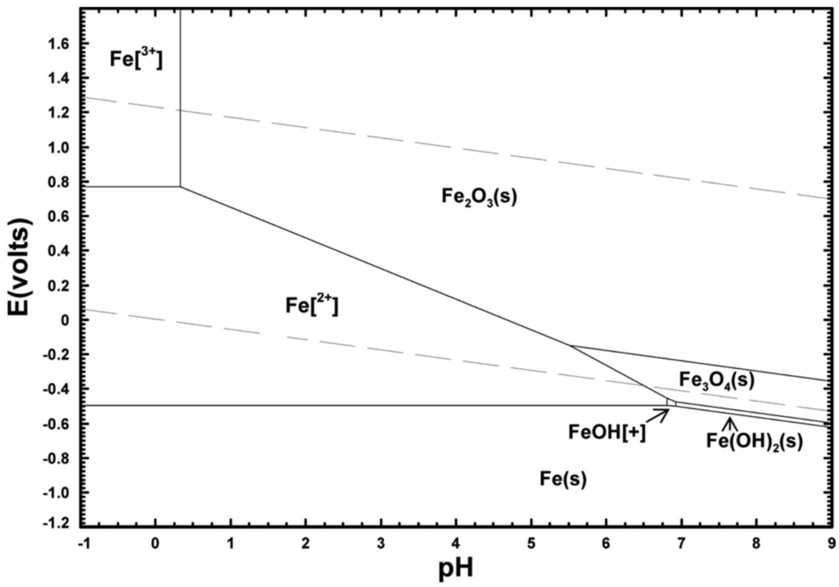


Figure 5-6 Pourbaix field diagram for iron in water *(Eisele and Gabby, 2014)*. Between the two dashed line, the water stability field at 298.15K

Similarly, aluminium depends mainly on low pH to form Al^{3+} as also suggested by (Danilo and Burnham, 1974), therefore the acidic environment of the saturation zone could have affected the leaching of this metal.

In other studies (Blecken et al., 2009b) it has been noticed how after long dry spells the concentration of copper, lead and zinc tend to increase in the outlet. Longer dry period creates cracks and preferential paths in the biofilters with the consequent migration of particles in the outlet that increases the export. Decaying biofilms could have reduced the sorption capacity and caused a flush of organic matter-metal complex. As suggested by the authors, a saturation zone at the bottom of the column reduced significantly the risk of leachate, however, as it has been noted during this experiment, reducing condition and low pH promoted by bacterial activity in the saturation zone could increase the risk of iron and aluminium leachate.

5.2.4 Hydraulic conductivity

During run 12, 23 and 27 columns were flooded using inlet water in order to assess the hydraulic conductivity in saturated condition using Darcy's law:

$$Q = -KA\frac{\Delta H}{L}$$

where Q is the flow in cm^3/s, K is the hydraulic conductivity in cm/s, H is the hydraulic head, L the bed length in cm, and A the area of the bed in cm^2. K_w values are generally higher than 1500mm/h, as previously estimated in chapter 4, and design including GAC have a faster flow than Zeolite Figure 5-7.

As expected, the column did not experience clogging due to the exclusion of suspended solids from the synthetic stormwater responsible for the formation of a clogged layer on top of the biofilter that reduce water infiltration rate.

The variability experienced in this experiment could be attributed to the migration of small media particles in the column that modified water path in the column. The natural heterogeneity of sand and amendments' PSD, and the uncertainty of the method used to assess the hydraulic conductivity could also explain the variation within the designs. In a study of 2012, Le Costumer et al. found that the coefficient of variation across control columns dosed with just tap water was around 50%. In their study, the hydraulic conductivity was measured after maintaining a hydraulic head constant for 24h (Le Coustumer et al., 2012). Due to laboratory constraint it was not possible to maintain such long hydraulic head, probably influencing the saturation level of the column and thus the readings.

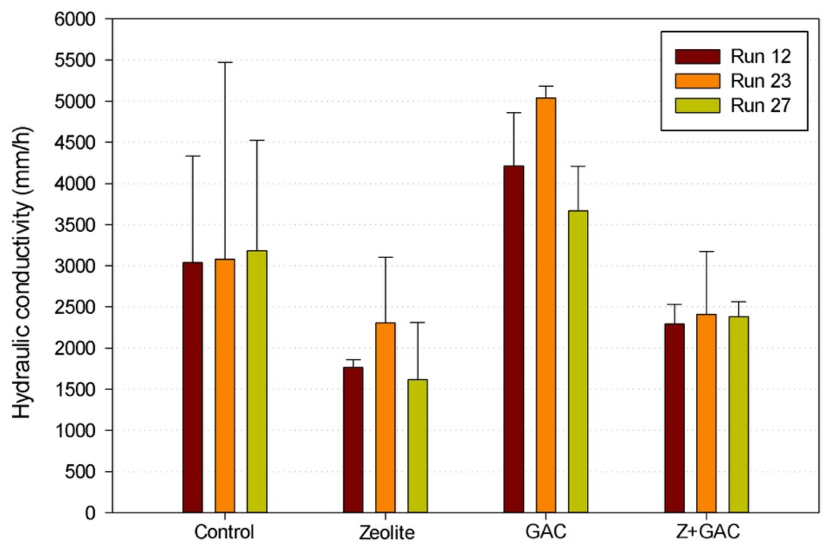


Figure 5-7 Hydraulic conductivity measured across the four design for run 12, 23, and 27

5.3 Discussion

5.3.1 Implication for design

Granular activated carbon is affecting the pH of outlet water, possibly influencing negatively the adsorption capacity of the design. This effect reduced with time, particularly in the second half of the second experiment. After a dry period, low PO4-P concentration at the outlet has been noticed reinforcing the hypothesis that aerobic condition in the unsaturated area of the biofilter promote the formation of ferric oxyhydroxide increasing the removal performance of phosphate.

The experiment suggested that the lack of plant and short antecedent dry periods are two weak points for the adsorption of phosphate. GAC have an effect on pH and this influence negatively the removal performance of phosphate. However, this phenomenon is less evident in Z+GAC possibly due to the minor volume of granular activated carbon used, 5cm vs 10cm, or because Zeolite offers a buffer zone.

The heavy metal adsorption exceeded 90% in all designs, with Zeolite column performing better for dissolved Zn and Ba, and GAC more efficient for dissolved Cu treatment. Despite that, biofilters sometimes fail to insure the most restrictive standard for copper of 5μg/L, but the outlet concentrations are generally lower than 22μg/L, the second highest limit. Cadmium have a positive removal with outlet concentration below the detection limit of the ICP-MS. Iron and aluminium leached from the biofilter probably due to the anaerobic acidic condition of the saturated zone that promote reducing condition. Nickel and lead concentration do not differ between inlet and outlet, suggesting that the biofilter does not have the capacity to adsorb this heavy metal at low concentration.

The hydraulic conductivity for the four design was higher than 1500mm/h. Despite the lack of suspend solids in the synthetic stormwater, the hydraulic conductivity varied during the experiments suggesting that the smaller fraction of media used to build the biofilter rearranged in the column creating preferential paths. In previous studies, 24h head was maintained constant to ensure saturation and a constant K_w; however, it was not possible for this experiment to maintain a head for such long time possibly affecting the readings. Generally, clogging occurs in the first 10cm of the columns, making the maintenance easier substituting only the first few layers. In this tested designs included the finer sand, fraction D, in the transition layer representing a bottleneck for migrating particles. This could increase the chance of failure in a deep area of the filter. As a consequence, the maintenance could potentially be more complicated.

Based on these results the column design has been amended in an attempt to increase the adsorption of phosphate and avoid potential hydraulic failure in the middle of the biofilter.

As highlighted in chapter 4, yellow sand has a higher phosphate removal performance, hence will be used instead of white sand. In addition, to prevent the accumulation of sediment in the middle of the column limiting the water flow in the design the fraction of sand will be changed. The inclusion of plants, a seasonal water regime with an ADWP and a controlled environment have been introduced in an attempt to control more variables.

Based on these two experiments, the amendments that will be tested in the next phase will be Z+GAC, called from now on “amended”, being a compromise between copper and zinc removal and having a higher phosphate treatment.

5.4 Chapter summary

In order to find a design to test in a full controlled environment and efficiently manage resources, a preliminary experiment on four design has been carried on.

The first phase addressed the experimental design flaws, the second phase included more replicas and investigate further the adsorption of phosphate, and heavy metals in dissolved state.

The experiments highlighted a low removal performance for phosphate (<30%) and high treatment performance for dissolved Cu and Zn (>90%) for all designs.

The observed values of phosphate, iron, and aluminium retention have a moderate affinity with antecedent dry period, highlighting how multiple subsequent events reduce the adsorption capacity of a filter media for the nutrient and long dry spell increase the leachate of certain heavy metals. Furthermore, pH seems to affect the retention capacity of phosphate. GAC removal performance was consistently lower than any other design, possibly due to the nature of the amendment, which pH is, for this product, around 8. In contrast with this observation the removal performance for dissolved heavy metals was not affected by pH.

Dry weather period and the re-arrangement of particles could potentially influence treatment and clog the column due to the finer fraction in the middle of the column, increasing maintenance costs.

All the above findings helped to improve the filter design that will accommodate plants in the next experimental phase. Yellow sand, the exclusion of finer sand fraction, a shallower gravel layer and a seasonal dry weather period will be included in order to address the limitation of the design and testing more accurately the setup.

The following chapters presents the results and discussion of the experiments including vegetation. The results presented here will be brought together with a synthesis and discussion which will be presented in Chapter 9.

Chapter 6 Phase II: vegetated column test

6.1 Chapter overview

This chapter presents the results of the monitoring campaign of comparative experiment between amended design and control. 24 mesocosms have been built and monitored for a 6 months period. Chemical and physical characterises are reported before discussing implications that media and plants have on the biofilter's design.

6.2 Results

6.2.1 Monitoring programme

The comparative experiment monitored priority pollutants, hydraulic and environmental variables of 24 columns (6 design: 5 replicas each for vegetated biofilter and 2 replicas for non-vegetated biofilters) for 6 months from June to November 2018. A total of 288 samples have been collected. As described in paragraph 3.5.3.2 columns were dosed with semi-synthetic stormwater every 48h (Figure 6-1) according to Leeds AWDP and sample collected every two weeks. Semi-synthetic stormwater inlet composition and target concentration are in(Table 6-1). Once a month hydraulic conductivity test and stomatal conductance were assessed. Moisture content of six columns, one for each design, solar radiation, relative humidity and temperature were continuously monitored using sensors (appendix 3).

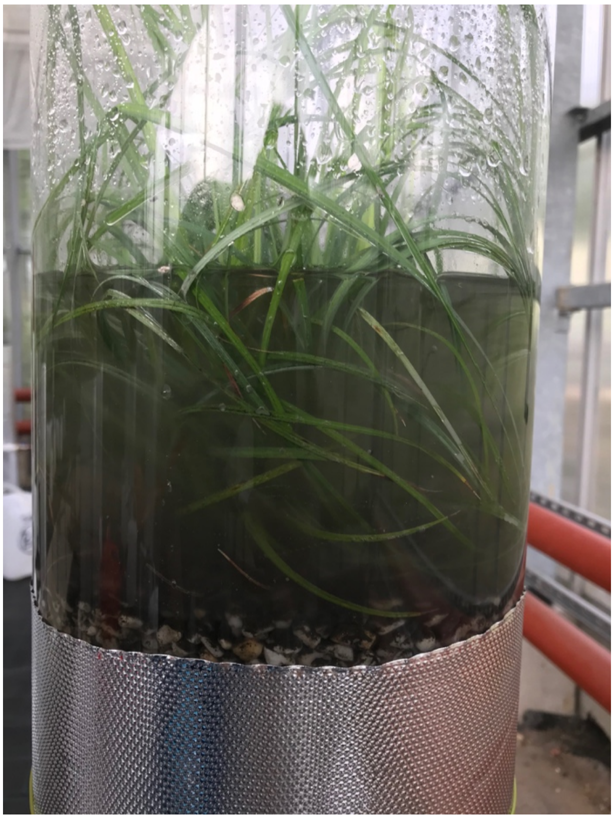


Figure 6-1 During a dosing event water was flooding the ponding area. The colour reflects the content of particulate matter of the semi-synthetic stormwater runoff

Table 6-1 Inlet and target concentrations for the semi-synthetic stormwater runoff used for the vegetated column experiment

	Analyte	Unit	Inlet concentraion	Target concentration
Nutrients	TP	mg/L	1.52 ±0.44	0.53 mg/L
	PO4-P	mg/L	0.87 ±0.22	0.03 mg/L
	TN	mg/L	2.16 ±0.55	2.54 mg/L
	TDN	mg/L	1.58 ±0.42	
	NH4-N	mg/L	0.05 ±0.02	0.2 mg/L
	NO_x	mg/L	1.24 ±0.33	0.81 mg/L
Total heavy metals	Al	μg/L	3047.1 ±3714.2	3210 μg/L
	Cr	μg/L	58.8 ±89.0	13 μg/L
	Fe	μg/L	5431.4 ±6852.0	4135 μg/L
	Ni	μg/L	55.1 ±14.8	493 μg/L
	Cu	μg/L	144.3 ±73.1	205 μg/L
	Zn	μg/L	300.7 ±265.8	700 μg/L
	Cd	μg/L	1.4 ±1.2	1 μg/L
	Ba	μg/L	135.8 ±109.8	9.6 μg/L
	Pb	μg/L	41.1 ±57.9	10 μg/L
Dissolved heavy metals	Al	μg/L	9.1 ±2.3	
	Cr	μg/L	0.7 ±0.2	
	Fe	μg/L	3.7 ±2.7	
	Ni	μg/L	55.6 ±64.2	
	Cu	μg/L	6.2 ±2.5	
	Zn	μg/L	32.5 ±10.1	
	Cd	μg/L	0.1 ±0.08	
	Ba	μg/L	58.5 ±12.0	
	Pb	μg/L	0.1 ±0.06	
	TSS	mg/L	188.08 ±249.76	150 mg/L
	TDS	mg/L	518.58 ±477.47	
	DOC	mg/L	1.9 ±1.28	
	DIC	mg/L	17.17 ±3.62	
	pH		6.58 ±0.29	
	DO	mg/L	10.85 ±1.52	
	Conductivity	μS/cm	402 ±52	
	temperature	℃	16.3 ±4.2	

6.3 Removal performance

6.3.1 Nutrients

6.3.1.1 Total Phosphorus and phosphate

A Kruskal-Wallis U test indicated net removal of TP and PO4-P from semi synthetic stormwater runoff ($p<.001$). The inlet TP and PO4-P concentration ranged approximately from 0.961 to 5.208 mg/L and 0.737 to 1.030 mg/L respectively, and the effluent were consistently between 0.002 to 1.858 mg/L and 0.003 and 0.277. Event number 2 has an unusual concentration for TP and PO4-P due to a failure in the peristaltic pump pipe clogged with fine sediment and consequent irregular distribution of solids. After this event the use of a stirring rod has been used to avoid failures.

The removal performance of phosphorus and phosphate was averagely higher than 90% for both design and plants (Table 6-2). Comparing the removal performance of non-vegetated designs for this and the experiment reported in Chapter 5 it is evident the positive effect that yellow sand, ADWP, and plants made on the adsorption of phosphate. The high K_w could also be responsible for the improved removal performance since sediment oxygen status increase faster in low content moisture, thus increasing the concentration of iron hydroxide responsible for fast adsorption process of phosphorus. A non-parametric Kruskal-Wallis U test showed no statistical difference among designs, however, in Figure 6-2 it can be noted a trend in TP and PO4-P removal performance decreasing from October (point 7 Figure 6-2).

Table 6-2: Average removal performance with standard deviation for phosphorus across 6 months experiment based on 60 samples per design for vegetated biofilters and 24 samples per design for non-vegetated biofilter. CoCa= Control Carex; CoDe= Control Deschampsia; CoNP= Control No-plants; AmCa= Amended Carex; AmDe= Amended Deschampsia; AmNP= Amended No-Plants.

	Average concentration (mg/L)		Average removal performance (%)	
	TP	PO4-P	TP	PO4-P
CoCa	0.062 ±0.062	0.043 ±0.043	95.54% ±3.93	95.26% ±6.38
CoDe	0.057 ±0.06	0.042 ±0.062	95.86% ±4.33	95.32% ±6.99
CoNP	0.084 ±0.095	0.069 ±0.09	94.07% ±5.79	92.82% ±8.87
AmCa	0.091 ±0.238	0.028 ±0.042	92.8% ±21.03	96.85% ±4.59
AmDe	0.056 ±0.054	0.034 ±0.017	96.01% ±3.5	96.3% ±5.13
AmNP	0.054 ±0.893	0.017 ±0.082	96.19% ±3.47	98.12% ±2.19
Inlet	1.525 ±0.439	0.878 ±0.226	-	-

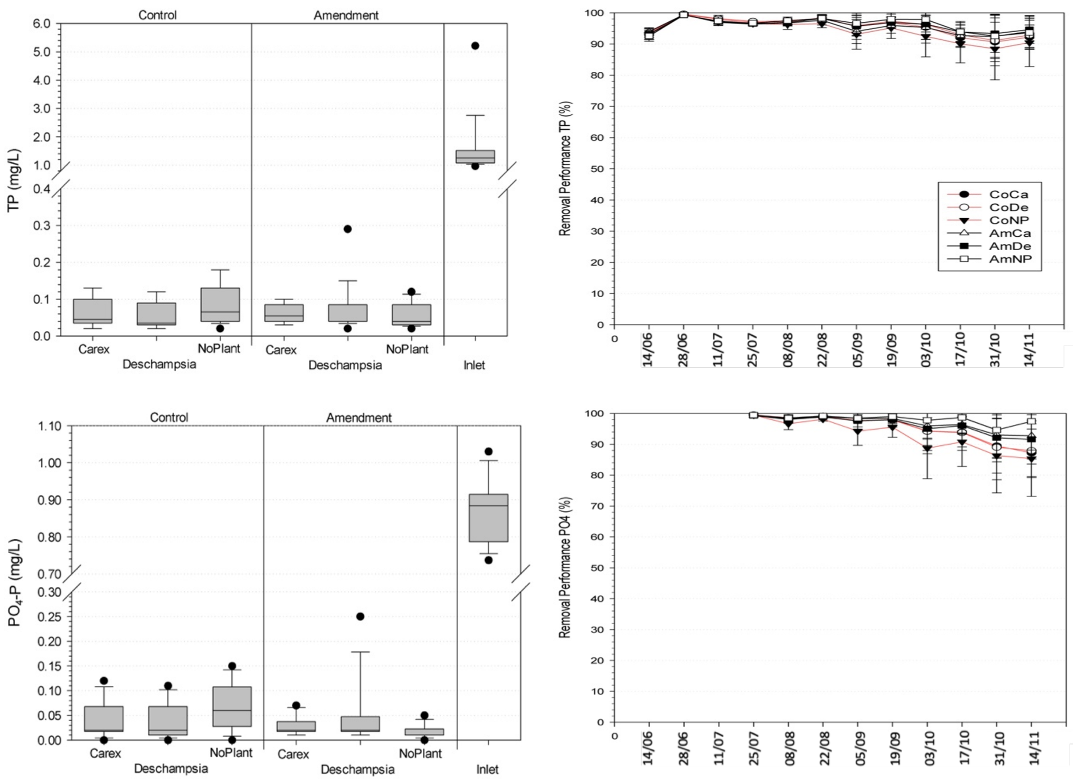


Figure 6-2 Concentration and removal performance of total phosphorus and phosphate. On the abscissa, the test events.

As shown in Figure 6-3, there was statistically significant difference between summer (from 28/06 to 19/09) and autumn (from 03/10 to 14/11) removal performance for TP ($p<.001$) and for PO4-P ($p<.001$), with amended columns having a higher PO4-P removal performance in autumn than control ($p=.005$). This could either be attributed to a negative trend in performance, due to a slow saturation of the free adsorption site of the media, or to a seasonal effect.

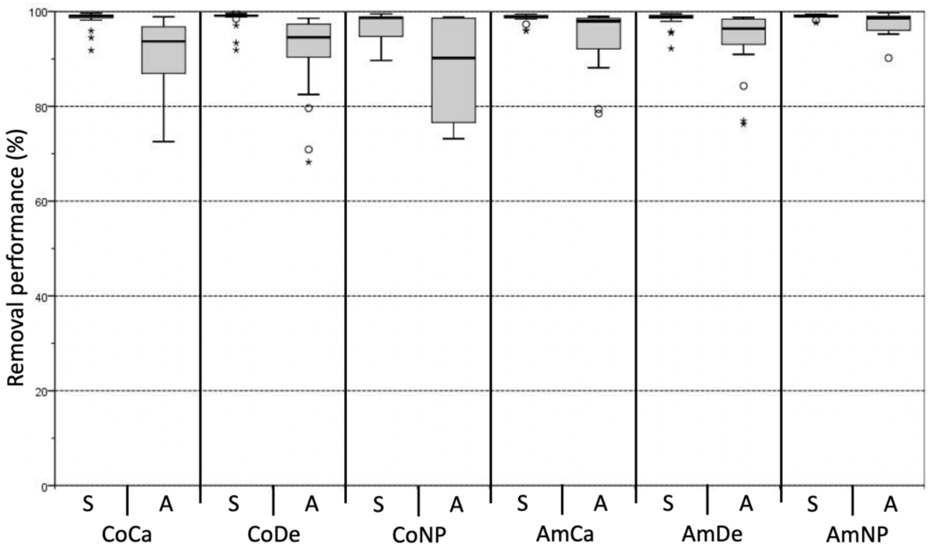


Figure 6-3 Seasonal differences among designs removal performance of PO4-P. Number of samples for summer = 35 for vegetated design, 14 for non-vegetated design. Number of samples for autumn = 20 for vegetated design, 8 for non-vegetated design.

Reactions for P adsorption are categorized into fast (i.e. adsorption) and slow (i.e. precipitation, fixation), and are dependent by environmental factor such as temperature, moisture, retention time, water and media characteristics. The lower temperature, together with lower solar radiation, and higher relative humidity (Figure 11-7, Figure 11-8, Figure 11-9) that characterise autumn might have affected the evapotranspiration rate and consequently the soil moisture, that increase during this season. A Kruskal-Wallis test showed a statistically significant difference between summer and autumn moisture, with averagely higher moisture in the colder season. A high soil moisture could reduce the oxygen level preventing the formation of iron oxyhydroxide, one of the compounds responsible for fast adsorption.

(Mustafa et al., 2004) claimed that ion exchange sorption of phosphate on iron oxyhydroxide increased with temperatures. The sensors installed in the greenhouse registered a negative trend of temperature from 20.4 C° (±4.14) in Summer to 11.5 C° (±2.4) in Autumn, possibly explaining the flex in performances. In contrast, (Blecken, Viklander, et al., 2007) argued that dissolved phosphorus outflow concentrations in biofilter with no saturation zone was not only non-temperature dependent, but that the removal performance was slightly higher under colder temperature, probably due to the limited biological activity that could cause some leaching. The discrepancy in results could be due to the different design (i.e. no saturation zone), as well as the lower inlet PO4-P concentration used in Blecken's test (i.e. 0.031 ±0.017 mg/L).

Limitation in plant growth due to the colder season could have led to a lower plant uptake rate. However, the flex in performance has involved non-vegetated columns as well, suggesting that plants uptake is marginally responsible for the treatment. In fact, there is no statistical difference among control and amended columns both with and without vegetation, suggesting that yellow sand has a greater impact on the adsorption than the plant uptake. Nonetheless, plants are responsible for P uptake after this has being retained restoring the capacity of the filter media. It is important to note that plants have not fully occupied the columns and this could have contributed to the limited differences.

Slower time-dependent process where the reaction between soil and phosphate continue for a long time, but at a decreasing rate (Barrow, 1978), could explain the higher removal performance of phosphate in AmNP. The hydraulic conductivity of this design decreased dramatically during the last months increasing the contact time between the soil and the polluted water giving enough time to P to find reactive site and get adsorbed. However, this hypothesis does not explain CoNP which has a similar K_w and did not show the same pattern. One possible conclusion is that the presence of amendments promoted the removal performances of phosphorus.

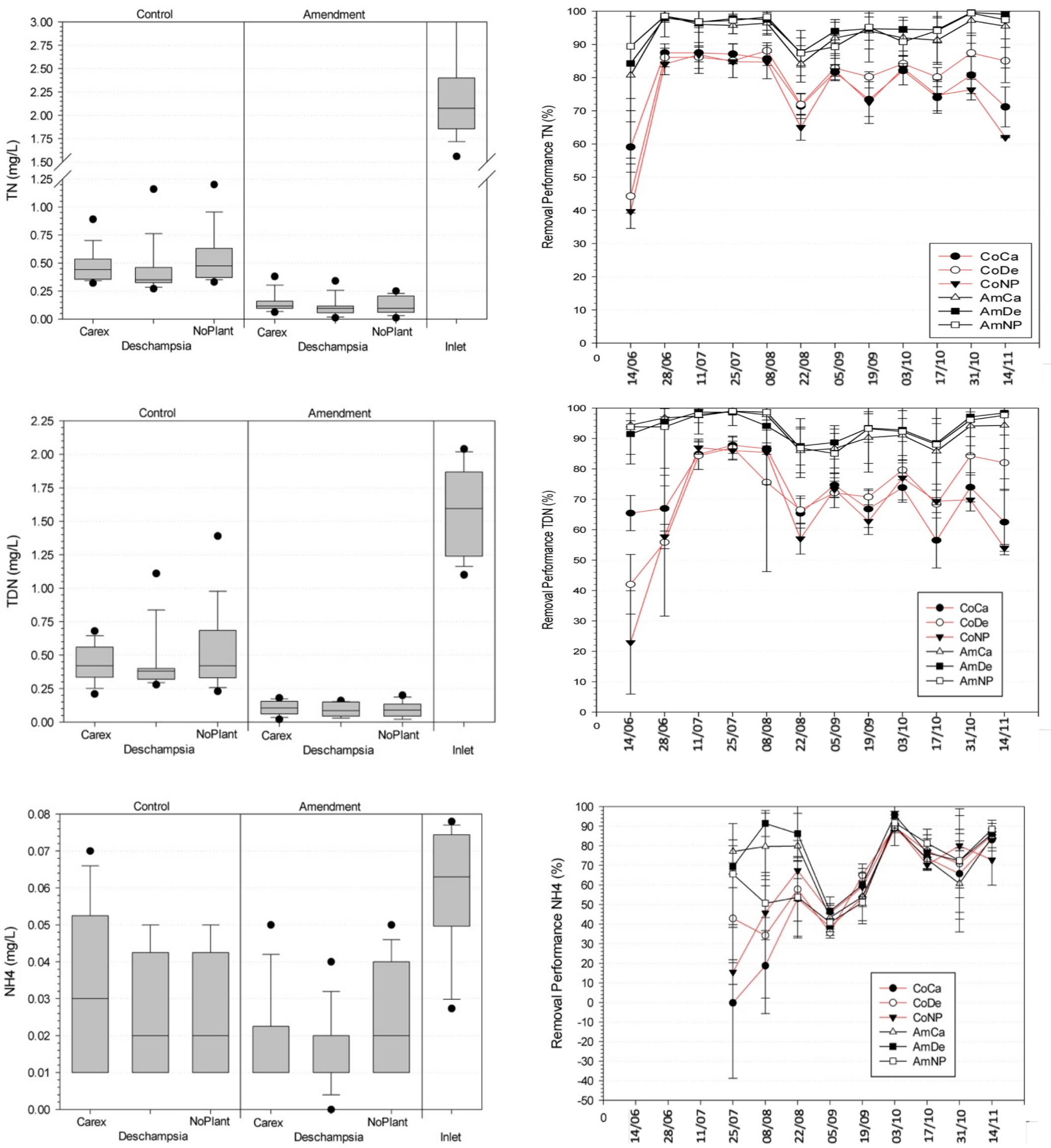
The K_w negative trend was due to sediment accumulation over time on the first few cm of the columns, phenomena known as “clogging”. This caked layer accumulates particulate phosphorus that may potentially partition back to the aqueous phase due to microbiological processing that alter the biofilter (Berretta and Sansalone, 2012), causing phosphorus export. Lastly, the decline in adsorption capacity could indicate that the fast-reversible true sorption sites have reached capacity and there is an adsorption equilibrium mechanism between the regeneration of sorption and the inlet phosphorus added. The competition of ion for active site could results in the release of some pollutants, but being the specific surface of GAC (1500 m^2/g) and Zeolite (45 m^2/g), much higher than sand’s (25 m^2/g), thus having more active sites, it seems likely to conclude that the amendments can delay this effect.

In conclusion, according to data amendments are marginally increasing the removal performance of TP. A decrease in performance has been observed during autumn, probably due to a change in environmental condition, exhaustion of adsorption capacity, lower biological uptake, and repartition. No difference in uptake has been observed among plants at this stage, suggesting that media is mostly responsible for PO4-P retention.

In the second phase of this experiment the columns have been disassembled and a representative core sample for each layer collected and analysed for nutrient and heavy metal concentration. This data is presented in Chapter 7 and will inform the hypothesis about a correlation between amendments and higher PO4-P removal.

6.3.1.2 Total Nitrogen and dissolved forms

A summary of mean concentration for inlet and outlet, and removal performance for the 6 designs is presented in Figure 6-4 while influent and effluent concentration are reported with mean and standard deviation in Table 6-3. Removal performance are generally high, probably due to high denitrification rates promoted by the saturation zone. As it will be specified later in paragraph 6.3.5, DO was exceptionally low at the outlet, sign that microbial respiration is depleting oxygen in the column, specifically in the saturation zone designed for denitrification. A Kruskal-Wallis U test indicated net removal for the four analysed form of N from semi synthetic stormwater runoff (p<.001). As shown in Table 6-4, A Mann-Whitney test U showed a statistically significant difference between control and amended columns (p<.001) with amended columns performing constantly better than control columns. This is a clear sign that GAC and Zeolite are helping with the removal of this pollutant. The result is in line with the findings of (Erickson et al., 2016) that suggest how GAC could capture more nitrate than sand, justifying ion exchange as driving force of treatment.



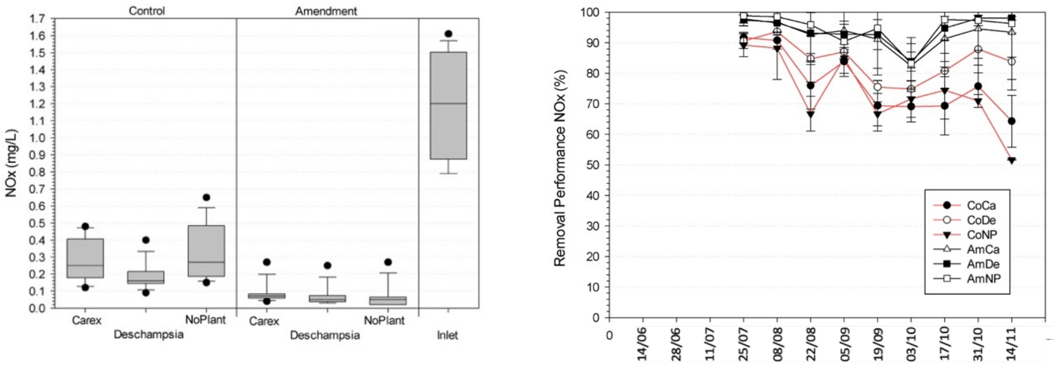


Figure 6-4: Nitrogen concentration and removal performance.

Table 6-3 Concentration in mg/l for TN, TDN, NH_4-N and NOx across 6 months experiment based on 60 samples per design for vegetated biofilters and 24 samples per design for non-vegetated biofilter.

	TN	TDN	NH4-N	NO_x
CoCa	0.474 ±0.474	0.444 ±0.444	0.03 ±0.03	0.281 ±0.281
CoDe	0.444 ±0.256	0.446 ±0.304	0.024 ±0.02	0.189 ±0.108
CoNP	0.551 ±0.261	0.534 ±0.337	0.023 ±0.017	0.323 ±0.187
AmCa	0.146 ±0.188	0.105 ±0.106	0.017 ±0.014	0.09 ±0.11
AmDe	0.109 ±0.115	0.093 ±0.096	0.014 ±0.022	0.071 ±0.068
AmNP	0.115 ±0.647	0.096 ±0.335	0.022 ±0.02	0.068 ±0.321
Inlet	2.165 ±0.55	1.587 ±0.421	0.055 ±0.021	1.236 ±0.326

As for phosphorus, there is no statistical difference among plant species and no-planted columns, highlighting that the contribution of plants is marginal in the treatment of nitrogen forms. In contrast, for column with no amendments there is statistically significant difference for TN (p=.050) and NOx (p=.001) with CoDe treating more NOx than CoCa and CoNP. The root architecture of Deschampsia comprise of small roots that displaced less media than Carex. This way the diffusion of oxygen through the biofilter could be limited, increasing the anaerobic pockets in the biofilter, thus the denitrification. The presence of roots and their exudates promotes the growth of microorganism in the rhizosphere, absent in non-vegetated columns.

Table 6-4 Removal performance for the nitrogen forms analysed based on 60 samples per design for vegetated biofilters and 24 samples per design for non-vegetated biofilter.

	TN	TDN	NH4-N	NO_x
CoCa	78.46% ±9.72	72.11% ±11.38	52.82% ±34.26	76.67% ±11.46
CoDe	80.13% ±12.51	72.39% ±17.53	62.11% ±25.09	84.3% ±8.13
CoNP	74.65% ±13.42	66.88% ±18.53	60.78% ±23.18	73.83% ±12.93
AmCa	92.8% ±9.91	92.78% ±7.71	71.39% ±18.43	92.63% ±8.58
AmDe	94.86% ±6.63	93.73% ±5.94	76.02% ±17.33	94.18% ±5.69
AmNP	94.5% ±4.14	93.51% ±4.88	66.21% ±18.6	94.75% ±4.99

As opposed to phosphorus treatment, nitrogen performances do not drop towards the end of the experiment, nonetheless, a difference between season exist. Since the experiment started the 30th of May, only one data is available for Spring, making difficult to formulate a hypothesis. Despite this limitation, it can be concluded that the average removal, particularly for control column (TN 49.69% ±11.86, TDN 48.61% ±19.49), was lower in the first month of operation than the subsequent months. The responsibility for the low TN retention can be attributed to dissolved nitrogen as it can be seen in Figure 6-4. The low or negative event concentration in recently built biofilters has been experienced also by (Flanagan et al., 2018). In their paper it has been hypothesized that emission from the biofilter's medium is most likely the source of leached nutrient. Unlikely control column, column with amendments did not experience such a low removal performance (TN 83.65% ±19.67, TDN 93.08% ±4.93), contributing to the hypothesis that GAC/Zeolite layer is beneficial for dissolved pollutants retention, confirming (Erickson et al., 2016) results.

Generally summer months have a higher removal performance than autumn ($p=0.001$) as reported by the mean removal performances value in Table 6-5, probably due to an improved denitrification rate promoted by increased temperatures, thus microbial denitrification, and biological uptake. In fact, a peak in nitrogen process might be promoted by temperatures between 30-35° C (Payne, Fletcher, Cook, et al., 2014). Despite performances being constantly higher than 80% for both design during summer, a flex has been noted the 22nd of August (point 6 TN chart Figure 6-4) where the average TN removal for control and amended columns passed from 86.53% and 97.79% respectively, to 70.04% and 86.11% respectively, possibly due to an unusually low inlet concentration (point 6 Figure 6-5) of TN that induced desorption.

Table 6-5 Average removal performance for TN, TDN, NH_4-N, and NOx for control and amended design for different seasons. C= control; A= amended. Number of samples for spring = 20 for vegetated design, 4 for non-vegetated design. Number of samples for summer = 35 for vegetated design, 14 for non-vegetated design. Number of samples for autumn = 20 for vegetated design, 8 for non-vegetated design.

	TN	TDN	NH4-N	NO_x
C spring	49.69 ±11.86	48.61 ±19.49		
C summer	82.07 ±7.27	74.35 ±14.62	41.05 ±27.34	83.45 ±9.96
C autumn	79.51 ±7.85	71.8 ±11.43	79.23 ±14.57	74.28 ±11.08
A spring	83.65 ±19.67	93.08 ±4.93		
A summer	94.55 ±5.12	93.57 ±6.54	66.04 ±19.19	94.68 ±6.08
A autumn	95.46 ±5.13	92.87 ±7.22	80.48 ±13.9	92.31 ±7.94

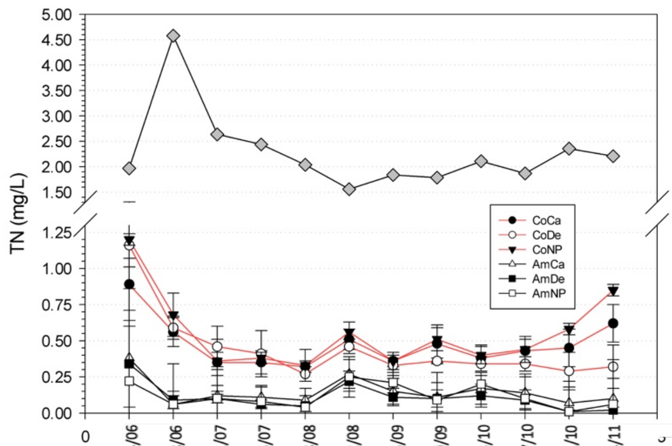


Figure 6-5 concentration of TN at the inlet and outlet. On the abscissa, the sample collection number. In grey, the inlet concentration.

Autumn is characterised by lower air and soil temperature, lower solar radiation, and high relative humidity (see paragraph 6.4) than summer months. In such climatic condition it is expected that microbial and plants contribution decrease marginally below 10° C, and below 5° C to drop drastically (Payne, Fletcher, Cook, et al., 2014). During this season there is a statistically significant difference for control columns from summer to autumn for removal performance of TN, TDN, NH_4-N and NOx, as suggested by the mean value in Table 6-5.

The higher removal of NOx and lower treatment of NH_4-N during summer suggests that the rate of mineralisation was higher than nitrification in those months. The high temperature of summer promotes the mineralization of ammonia to nitrate mediate by *nitrosomonas* and *nitrobacter* through nitrification. This process might be suppressed by heterotrophic bacteria if carbon is readily available (like in the saturation zone), competing with autotrophic nitrifying bacteria for ammonium and oxygen. Removal performance for NH_4-N are higher in autumn for all designs. This could be due to the colder temperature that limited the decomposition processes mineralizing nitrogen into ammonia through ammonification. The removal of ammonia can be driven by adsorption as a cation, chelation and substitution reactions. A lower K_w could have improved the biofilter removal due to a longer contact time between the influent and the media.

In conclusion, there is statistically significant difference between control and amended columns, with the second removing more nitrogen and being more stable than the first. No difference between plants in amended columns have been observed, showing that the inclusion of a saturation zone is important to prevent leachate and that amendments are capable of controlling this nutrient. Control Deschampsia remove more NOx than control Carex and no-plant control, suggesting that the finer root system prevent oxygen diffusion that might limit denitrification. Climatic condition seems to play a role in nitrogen removal, with lower removal of NH_4-N in summer compared with autumn.

In Chapter 7 the columns have been disassembled and a representative core sample for each layer collected and analysed for TN and will inform the hypothesis about a correlation between amendments and higher nitrogen removal.

6.3.2 Heavy metals

The results for total and dissolved heavy metals concentration and removal performance for the six design is presented in Table 6-6.

A non-parametric test shows statistical difference for dissolved heavy metals between amendment and control, with the former having a higher removal performance than the latter for Al, Ni, Cu, Zn, Cd, Ba, and PB, except Cr, and Fe where removal was higher for control columns. It is difficult to infer a trend in designs since the removal performance of specific heavy metal change according to plant and media composition. For clarity, the results will be divided in total heavy metal and dissolved heavy metal.

The inlet and outlet water quality were compared with UK water standards. These generally address total concentration of a pollutant rather than distinguish between phases, although the dissolved part is the more mobile and chemical reactive (Andradottir and Vollertsen, 2014; Maniquiz-Redillas and Kim, 2016). Legislation also miss to set limits for inland water protection for all heavy metals. In these cases, this thesis will refer to drinking water limits to compare the water quality of the outlet when possible.

Table 6-6 Average concentration in μg/L (±standard deviation) for total and dissolved heavy metals for the six design and inlet

		CoCa	CoDe	CoNP	AmCa	AmDe	AmNP	Inlet
Total	Al	11.291 ±11.291	6.734 ±13.721	7.065 ±15.345	12.64 ±28.204	10.029 ±27.934	0.711 ±0.308	3047.118 ±3714.255
	Cr	1.002 ±1.002	1.34 ±1.532	1.563 ±2.139	1.158 ±1.239	1.219 ±1.187	1.433 ±1.385	58.799 ±89.014
	Fe	306.71 ±306.71	227.599 ±176.193	152.253 ±124.079	743.931 ±470.391	419.367 ±514.906	931.577 ±610.9	5431.439 ±6852.04
	Ni	3.664 ±3.664	4.415 ±3.315	4.654 ±1.546	3.602 ±2.336	2.396 ±2.561	4.429 ±1.436	55.069 ±14.844
	Cu	10.162 ±10.162	19.033 ±53.678	15.737 ±7.186	5.568 ±2.186	7.787 ±3.845	10.584 ±6.252	144.319 ±73.072
	Zn	37.797 ±37.797	46.635 ±18.726	123.086 ±42.004	40.847 ±19.098	37.379 ±23.636	130.733 ±52.614	300.712 ±265.851
	Cd	0.03 ±0.03	0.036 ±0.012	0.045 ±0.015	0.023 ±0.018	0.027 ±0.014	0.047 ±0.019	1.424 ±1.246
	Ba	55.039 ±55.039	55.136 ±8.791	62.477 ±10.066	24.767 ±7.618	24.52 ±8.069	35.078 ±12.953	135.832 ±109.778
	Pb	0.201 ±0.201	0.222 ±0.12	0.137 ±0.093	0.162 ±0.144	0.16 ±0.114	0.096 ±0.078	41.139 ±57.883
Dissolved	Al	2.465 ±2.465	3.046 ±3.969	2.344 ±1.921	1.58 ±1.169	1.697 ±1.604	13.778 ±43.365	9.105 ±2.356
	Cr	0.062 ±0.062	0.056 ±0	0.056 ±0	0.056 ±0	0.056 ±0	0.056 ±0	0.723 ±0.19
	Fe	18.443 ±18.443	5.424 ±4.554	4.313 ±3.132	253.564 ±343.99	77.849 ±200.267	34.244 ±50.559	3.767 ±2.744
	Ni	3.907 ±3.907	4.234 ±3.194	4.658 ±1.445	3.874 ±2.585	2.441 ±2.655	4.046 ±1.265	55.585 ±64.191
	Cu	6.212 ±6.212	8.686 ±5.027	12.672 ±7.349	1.648 ±1.937	4.281 ±4.393	3.374 ±4.844	6.19 ±2.518
	Zn	32.328 ±32.328	37.691 ±14.748	111.201 ±40.668	24.958 ±20.565	30.615 ±21.87	109.581 ±50.133	32.527 ±10.129
	Cd	0.021 ±0.021	0.025 ±0.016	0.034 ±0.014	0.008 ±0.012	0.017 ±0.017	0.022 ±0.021	0.139 ±0.081
	Ba	57.691 ±57.691	58.479 ±8.241	66.586 ±9.724	27.81 ±8.268	27.719 ±8.479	37.248 ±12.758	58.484 ±11.994
	Pb	0.112 ±0.112	0.122 ±0.064	0.091 ±0.051	0.082 ±0.056	0.095 ±0.065	0.079 ±0.057	0.113 ±0.061

There is statistical difference between control and amended columns for all the heavy metals apart from aluminium, Chrome, and Zinc. Amended design tend to have a higher removal performance for all heavy metals, but, as noted in the previous chapter, not for Fe. The removal of total heavy metal depends not only on adsorption but mainly on filtration. The particle filtration in biofilters tend to be really high (>90%) correlating with the removal of this pollutant.

Dissolved heavy metal treatment rely on chemisorption (covalent or coordination bonds, hydroxyl groups are responsible for this), precipitation (due to change in redox and pH condition), and biotransformation, rather than filtration, and these behaviours are controlled by a variety of factors such as pH, redox potential, media, complexing agents like humic acids and so on. Due to the nature of the Perspex column and limitation in resources, it was not possible to install redox potential and pH sensor across the columns, so it is not possible to give indication about the distribution of heavy metal species as a function of pH.

6.3.2.1 Aluminium

Removal performance for total aluminium is on average really high (99%) (Figure 6-6). A Kruskal-Wallis test show statistical difference between designs: non-planted columns have a higher removal performance than planted columns. No difference between columns with and without amendments, although Deschampsia perform slightly better than Carex (mean rank AmNP>CoNP>AmDe>CoDe>AmCa>CoCa). The average inlet concentration exceeded 3000μg/L, while outlet concentrations were much lower with an average 8μg/L, much lower than the 200μg/L recommended for drinking water purposes (water quality regulations 2000).

Dissolved Aluminium removal performance was higher in non-planted design followed by amended design and finally by control (AmNP>CoNP>AmDe>AmCa>CoCa>CoDe).

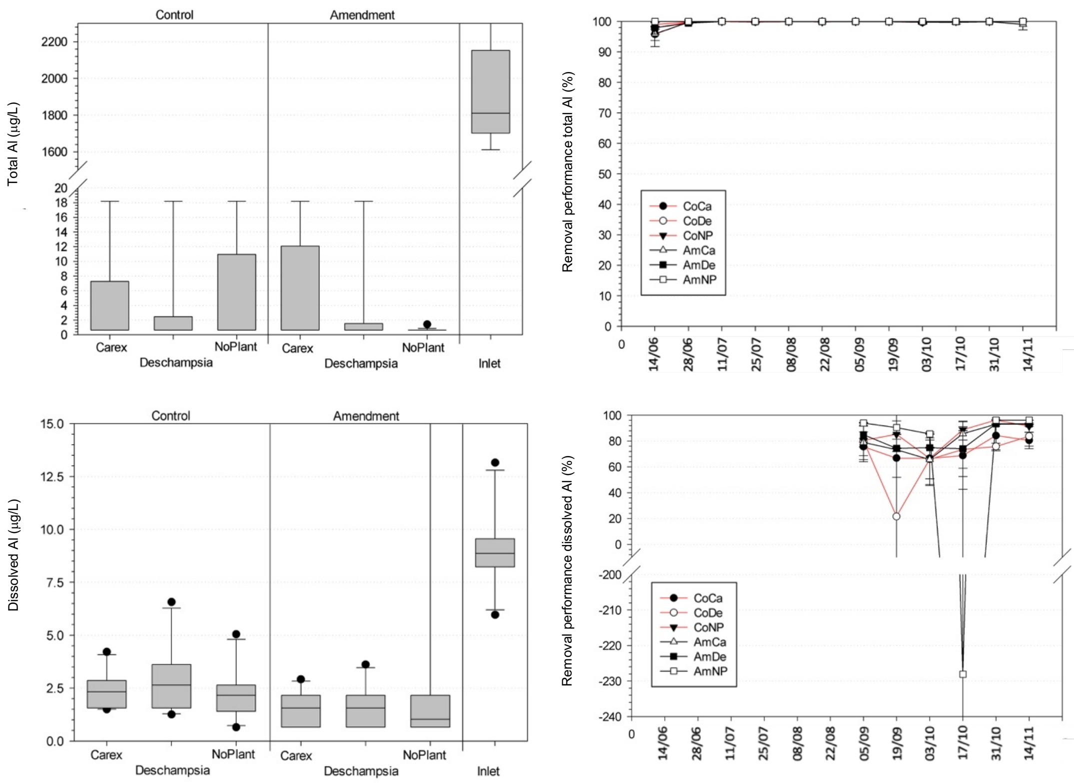


Figure 6-6 Concentration for aluminium (on the left) and removal performance (on the right) based on 60 samples per design for vegetated biofilters and 24 samples per design for non-vegetated biofilter.

6.3.2.2 Chromium

No statistical difference was found for chromium treatment (Figure 6-7). However, the removal of non-planted columns results higher than the planted designs (Mean rank: AmNP>CoNP>CoCa>AmDe>AmCa>CoDe). Inlet concentration for this pollutant exceeded both standards for potable supply and protection of sensitive freshwater aquatic life: 50μg/L and 5μg/L respectively. Outlet concentrations were well below the limits with an average of 1.28μg/L (Council Directive 74/464/EEC replaced by Water Framework Directive 200/60/EC).

Dissolved chromium removal performances are higher than 90% for all the design, and there is statistically significant difference among no-planted and planted columns, with the former removing more dissolved chromium than the latter (CoNP>AmNP>AmDe>CoCa>CoDe>AmCa). There is no difference between control and amended column, suggesting that the removal performance in this case is not enhanced by the presence of GAC and Zeolite. However, plant seems to have a negative effect on the adsorption possibly due to the change induced by roots exudates.

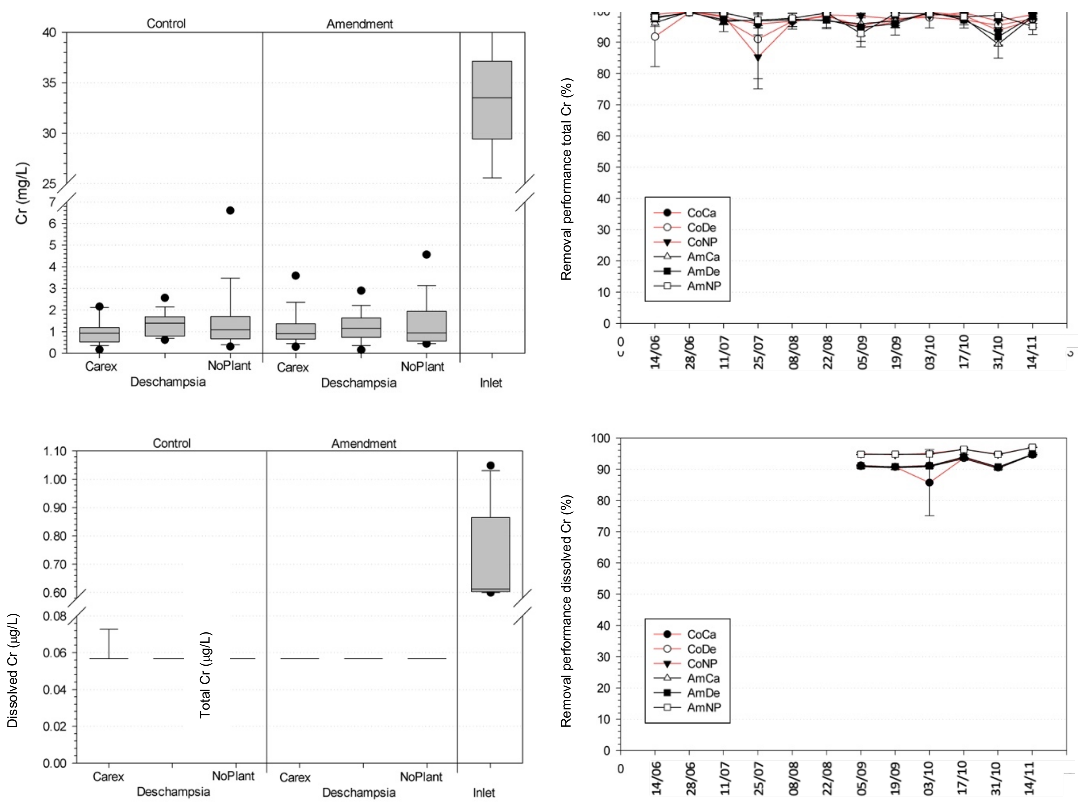


Figure 6-7 Concentration for chromium (on the left) and removal performance (on the right) based on 60 samples per design for vegetated biofilters and 24 samples per design for non-vegetated biofilter. The gap for dissolved pollu

6.3.2.3 Iron

As for the dissolved part, the removal of iron is different between designs with amended column having a lower treatment than the control (Figure 6-8). This might be due to the high concentration of iron present in GAC and Zeolite. Small particles, as well as dissolved iron, might migrate through the biofilter. Among the designs, it seems that Deschampsia affect less the removal performance of iron, probably due to its small and thin root system that prevent channelling the water as Carex root system do. Mean rank CoNP>CoDe>CoCa>AmDe>AmNP>AmCa. A possible explanation for the lower removal performance is the migration of fine particles from GAC and Zeolite. The two amendments have a smaller diameter than the sand and a higher iron oxide concentration. The slightly lower suspended solids retention, on average less than 1 mg/L, could be responsible for the higher concentration of iron in the inlet.

Dissolved iron removal performances are generally higher for designs without amendments, suggesting that GAC and Zeolite are responsible for leaching the heavy metal: CoNP>AmNP>CoDe>CoCa>AmDe>>AmCa. Concentration outlet range between 2.36 to 1329.54 μg/L, 0.7 to 1195.87 μg/L, 0.70 to 158.75 μg/L for AmCa, AmDe, and AmNP respectively. There are statistical differences between designs with plants leaching more iron than non-planted columns as can be noted from Table 6-6, indicating that the interaction between roots and media is probably freeing complexed iron. This is more evident in AmCa: many plants' roots in this design reached the amendment and in certain case the development of roots in this layer was higher. A hypothesis is that roots freed iron bonded in GAC and Zeolite changing the pH with roots exudates. Chapter 7 will report the concentration of iron for single media and, therefore, an indication on the fate of this pollutant. Despite the lower removal performance, dissolved concentration at the inlet and outlet were lower than the limit for protection of sensitive freshwater aquatic life (1000μg/L), as well as the concentration for direct abstraction to potable supply (300μg/L). Only AmCa concentration sometimes exceed this limit, probably due to the mobilisation of iron operated by roots exudate.

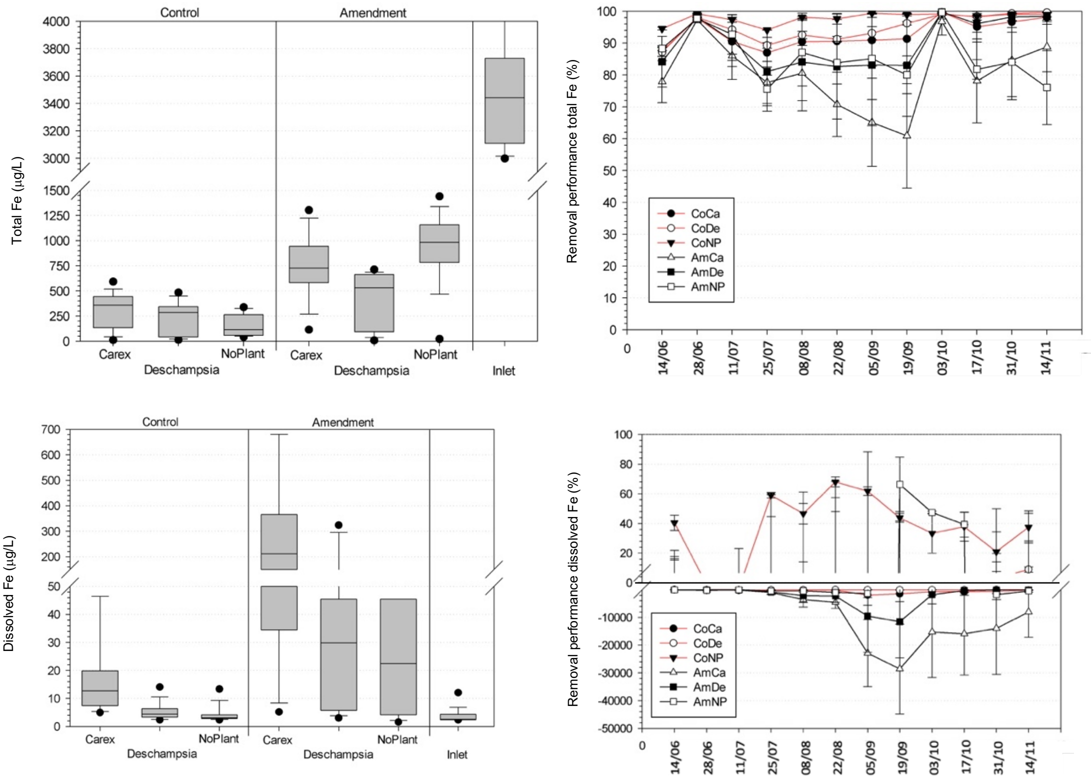


Figure 6-8 Concentration for iron (on the left) and removal performance (on the right) based on 60 samples per design for vegetated biofilters and 24 samples per design for non-vegetated biofilter.

6.3.2.4 Nickel

Removal of Nickel, mean rank AmDe>AmNP>CoNP>CoCa>AmCa>CoDe, is higher than 90% for all the designs with AmDe statistically significant more efficient than all the other designs (Figure 6-9). Concentration at the inlet exceed the 50µg/L limit for direct abstraction of potable water, and protection of aquatic life. Biofiltration systems are efficiently reducing the total amount with an average of 3.86µg/L.

Dissolve nickel performance are always positive and a non-parametric test shows statistical difference among designs, with a mean rank order following the order AmDe>AmNP>CoNP>CoCA>AmCa>CoDe. There is no statistical difference between CoNP and AmNP suggesting that the contribution of amendment is minimal. However, there is difference between designs with and without amendment, especially between CoDe and AmDe, with the latter having higher treatment performances. The data seems to show no difference between amended and control but a statistical difference between the two Deschampsia.

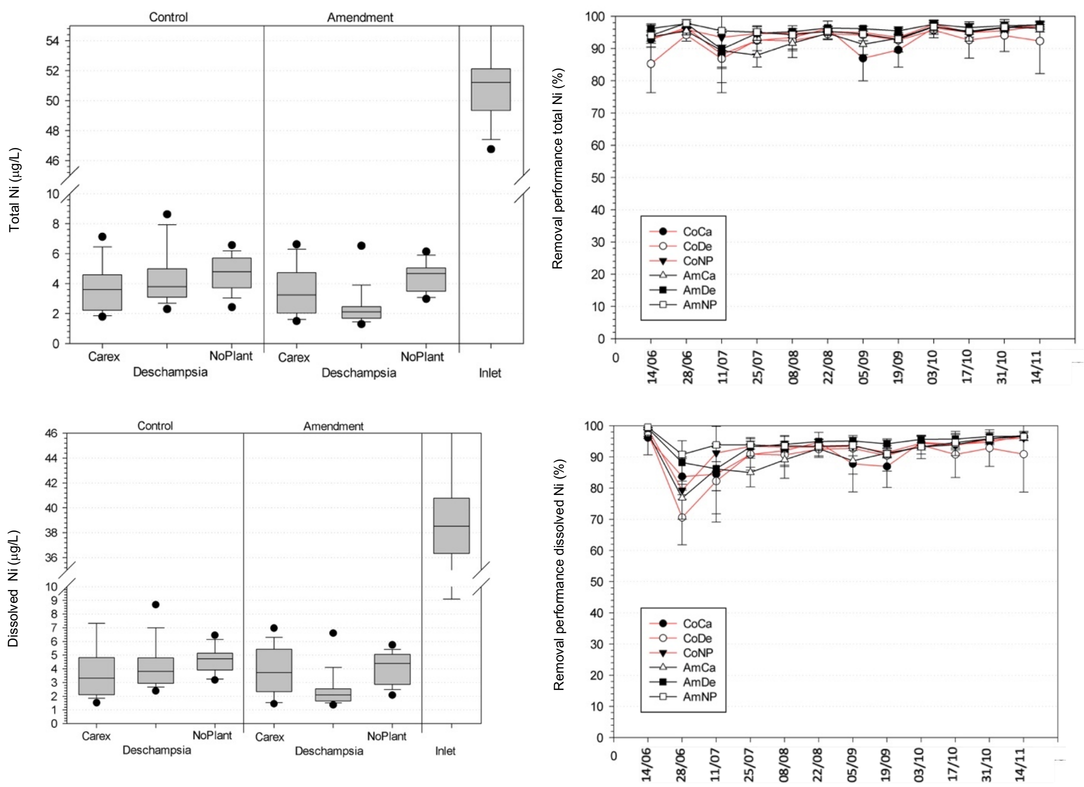


Figure 6-9 Concentration for nickel (on the left) and removal performance (on the right) based on 60 samples per design for vegetated biofilters and 24 samples per design for non-vegetated biofilter.

6.3.2.5 Copper

There is statistically significant difference between the removal performance of dissolved copper of control and amended columns with the latter having a higher removal (mean rank AmNP>AmCa>AmDe>>CoCa>CoNP>CoDe) (Figure 6-10). It is evident that the amendment layer is beneficial for the treatment of dissolved copper. The plant choice seems to influence the removal of dissolved copper, with Deschampsia having a lower removal in both designs. Cu is efficiently removed binding it to organic matter as reported by (Blecken et al., 2009a), where columns fitting a submerged zone with carbon source increased removal by 12%. Despite the similar design, the control column in this study leached dissolved Cu, and the outflow concentration increased during autumn when moisture is averagely higher and temperatures low, thus, theoretically, preventing the possible oxidation of sediments and limiting the amount of DOC produced by biological activity. In fact, (Blecken et al., 2011) noticed a negative trend of dissolved Cu correlating with higher temperature due to a possible increase in biological activities that lead a flushing of DOM. Copper exist in solution in a form complexed with soluble organic (Bradl, 2004), and organic bonding in the form of humic materials is an effective mechanism of Cu removal. The more developed root system of Carex might have increased the presence of humic acids, thus bonding more dissolved copper. As shown in paragraph 6.3.4, amended columns are efficient in DOC removal, consequently bonding the complexed copper to GAC more efficiently than control columns. This hypothesis is supported by a Spearman's rank-order correlation showing a weak positive relationship between dissolved copper and DOC concentration (r_s=+0.375), similar result found also by (Flanagan et al., 2019). Dissolved copper concentration limits for protection of inland freshwaters is water hardness dependent. For water hardness below 10mg/L of $CaCO_3$, dissolved copper limit is 5μg/L, for hardness higher than 100mg the limit is 112μg/L. The lower concentration of 5μg/L is met mostly by amended columns. The only combination that controlled dissolved Cu more efficiently indluced Carex. All the biofilter were meeting the second limit of 22μg/L for water hardness below 50mg/L $CaCO_3$.

As for the dissolved part, the removal performance of amended column for total copper is higher than control. However, the differences in removal performance among designs are small suggesting that copper is present more in bounded form. Since no plant is present there is no displacement of sand, thus less chance for particles to migrate from the columns. As previously noted, the dissolved copper efficiency is higher in amendments, meaning that the total removal is affected by this parameter. Mean rank AmCa>AmNP>AmDe>CoNP>CoCa>CoDe.

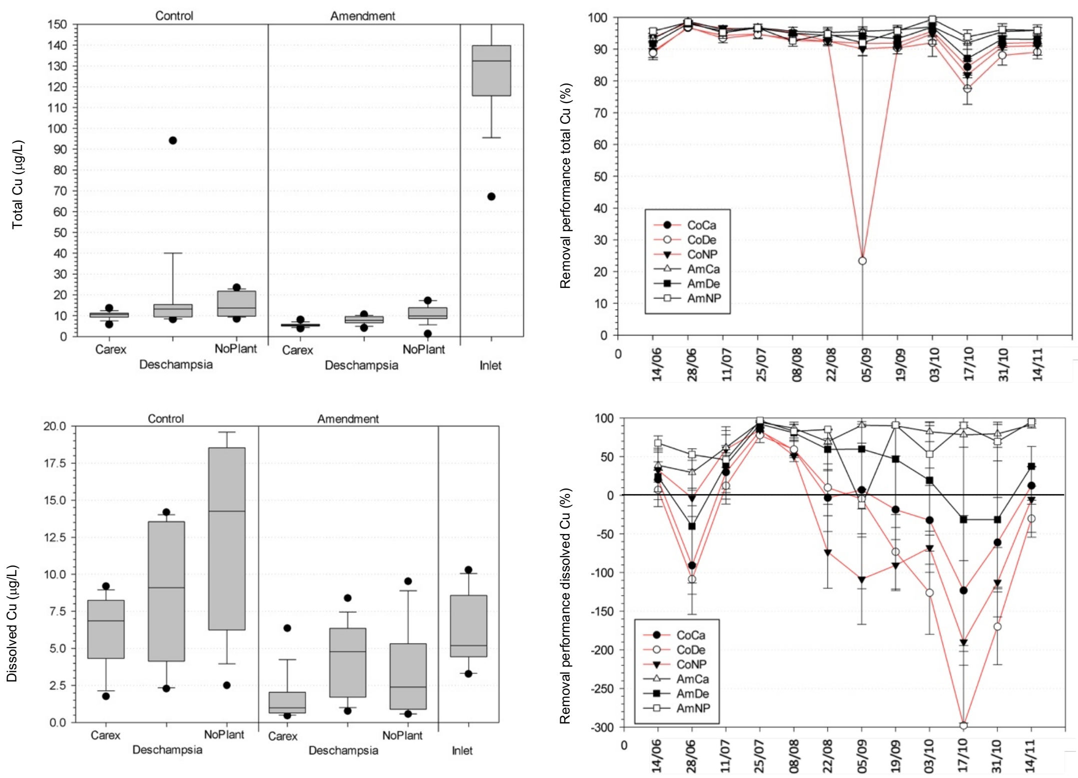


Figure 6-10 Concentration for copper (on the left) and removal performance (on the right) based on 60 samples per design for vegetated biofilters and 24 samples per design for non-vegetated biofilter.

6.3.2.6 Zinc

Designs with no-plants tend to have a lower Zinc removal performance than planted columns suggesting that the presence of plants is positively impacting this heavy metal. AmDe>CoCa>AmCa>CoDe>CoNP>AmNP (Figure 6-11). Total zinc concentration limits for protection of inland freshwaters is water hardness dependent. For water hardness below 10mg/L of $CaCO_3$, total zinc limit is 30µg/L. This limit was exceeded by most of the columns, with non-planted designs leaching this pollutant. All the biofilter were meeting the second limit of 200µg/L for water hardness below 50mg/L $CaCO_3$.

Removal performance for dissolved Zinc is lower than expected based on the experiment in chapter 5. The difference might be due to the change of sand, from white to yellow, or the use of a more complex semi-synthetic stormwater runoff where dissolved Zn has a lower concentration: 32.52µg/L instead of

460μg/L. Small addition of Zn re-dissolving from the solids filtered by the columns could be the responsible for the negative performance, as well as leaching from component of the biofilter itself. Although humic acids play a role in its adsorption (Flanagan et al., 2019), zinc has also the lowest sorption affinity based on a test carried by (Cortés Páez et al., 2014). There is a statistically significant difference in removal for the six design ($p<.001$), particularly in non-planted columns, where treatment is the lowest with -101.49% and -83.16% for CoNP and AmNP respectively, highlighting the positive effect that plants have on the removal, although it is generally assumed that only a small part of metals are then uptake into plants (Davis et al., 2001; Blecken et al., 2011). The mean rank order of treatment analysed with a Kruskal-Wallis test is AmCa>>AmDe>CoCa>CoDe>>AmNP>CoNP, thus amended columns perform better than control.

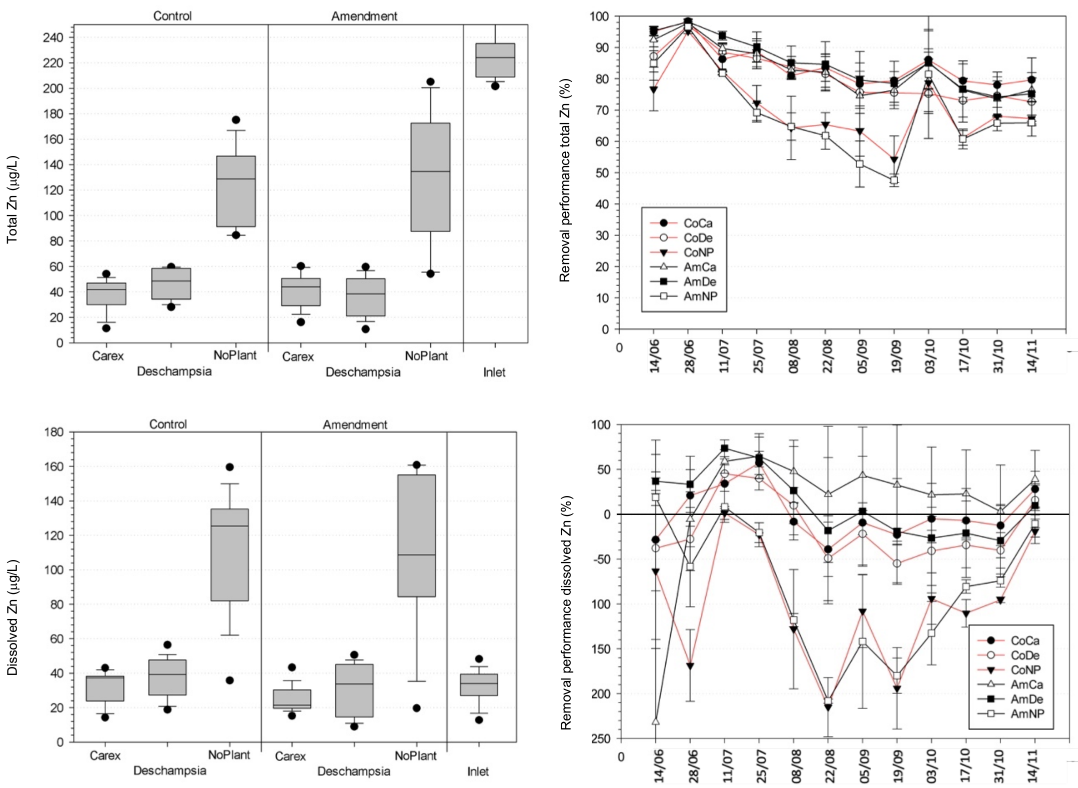


Figure 6-11 Concentration for zinc (on the left) and removal performance (on the right) based on 60 samples per design for vegetated biofilters and 24 samples per design for non-vegetated biofilter.

6.3.2.7 Cadmium

Cd removal for this pollutant was higher than 95% for all design (Figure 6-12). Despite that, difference in removal were statistically different for AmCa, having a higher removal than CoCa and CoDe. Mean rank AmCa>CoNP>AmDe>AmNP>CoCa>CoDe. Cadmium was often below the detection limit of the ICP-MS, thus achieving the limit of 5μg/L set for protection of aquatic life. It should be noticed that this limit was met also by the inlet water, possibly due to the low addition of this heavy metal in the semi-synthetic stormwater.

For what concern dissolved cadmium removal the mean rank order is AmCa>AmNP>AmDe>CoCa>CoNP>CoDe. Amendments are statistically significantly different from control removing more Cd than the control, probably due to the high cation exchange capacity of GAC and Zeolite. AmCa and AmNP have been found to perform better than AmDe. The limits for dissolved cadmium for protection of aquatic life is set to 2.5μg/L, threshold amply met by all the design with an average outlet concentration of 0.02μg/L.

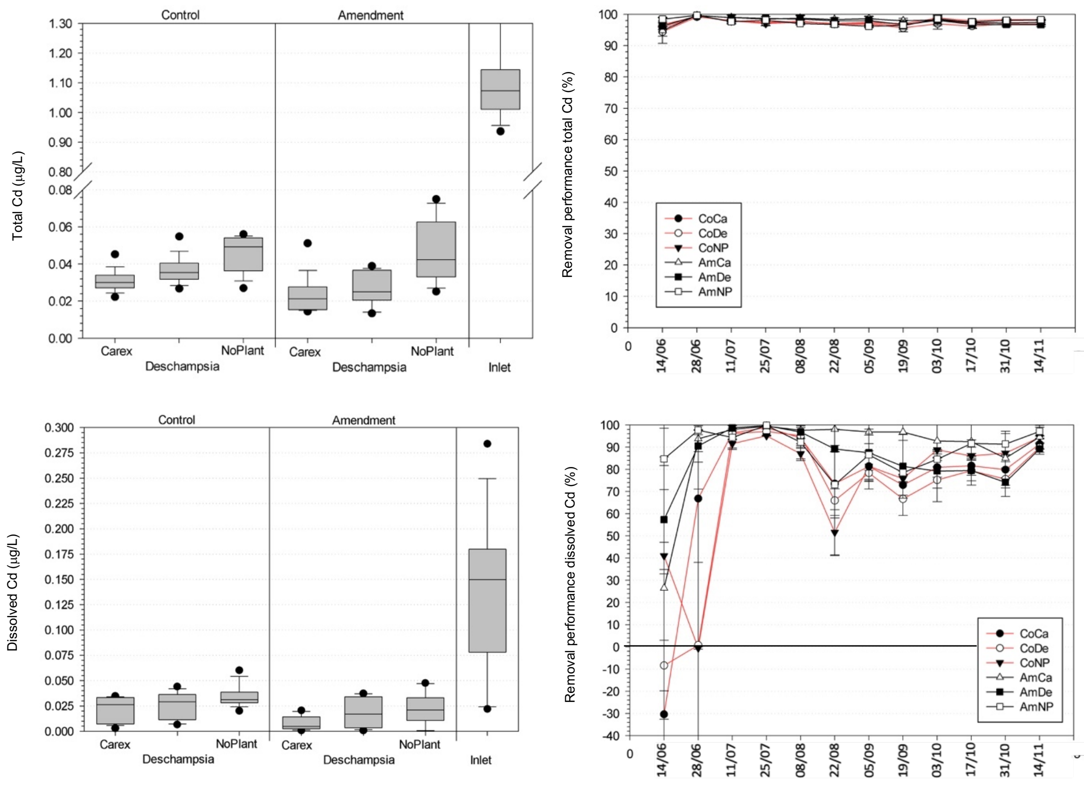
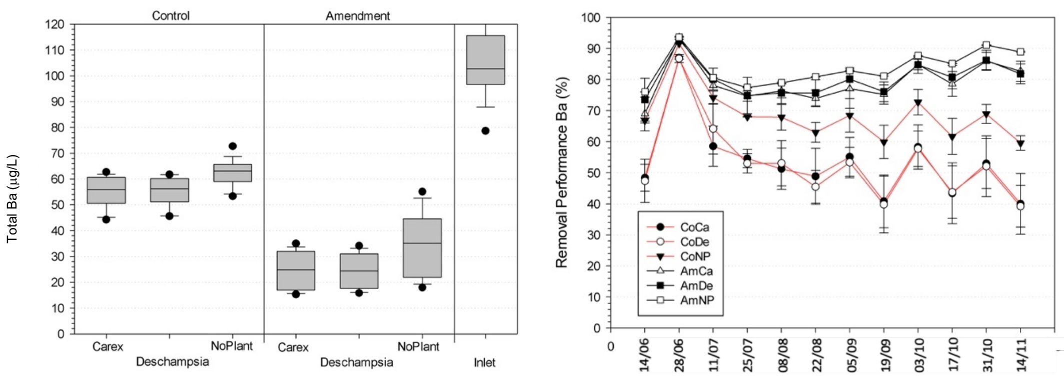


Figure 6-12 Concentration for cadmium (on the left) and removal performance (on the right) based on 60 samples per design for vegetated biofilters and 24 samples per design for non-vegetated biofilter.

6.3.2.8 Barium

There is difference between planted and no planted design for removal of Barium with no planted design having generally higher removal performances than planted columns (Figure 6-13). Design with amendments have a higher removal performance than control confirming the results of experiment in chapter 5. The mean rank is AmNP>AmDe>AmCa>CoNP>>CoCa>CoDe.

As per dissolved barium, the removal performance of amended column is generally higher than control. This is in virtue of the higher dissolved Barium removal capacity. There is statistical evidence that amendments are removing more barium than control columns and no difference among column with amendments. AmNP>AmDe>AmCa>CoNP>CoCa>CoDe. The legislation in this case does not distinguish between total and dissolved Barium. The limits for this metal is set to 100μg/L for water needing simple physical treatment and disinfection for transformation in drinking water and 1000μg/L for water needing normal treatment before drinking purposes. Outlet water met, for both total and dissolved concentration, these limits.



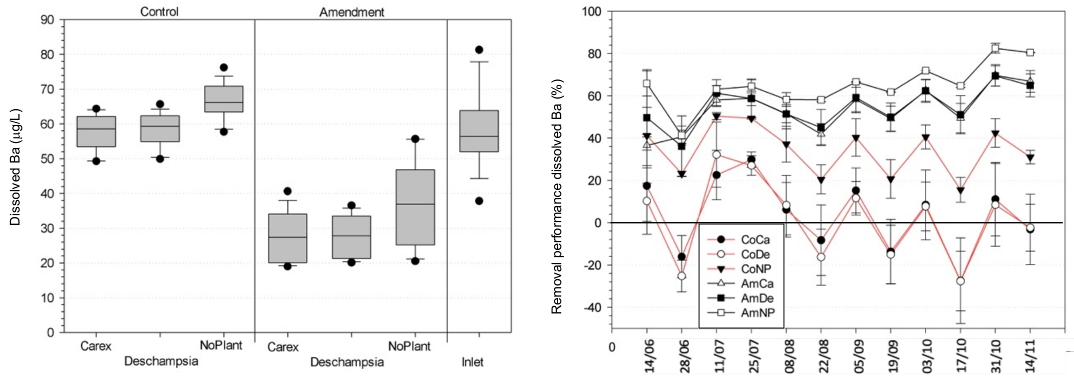


Figure 6-13 Concentration for barium (on the left) and removal performance (on the right) based on 60 samples per design for vegetated biofilters and 24 samples per design for non-vegetated biofilter.

6.3.2.9 Lead

Removal performance for Lead are different for all the columns with no-plants designs performing better than planted columns (Figure 6-14). However, amended plants perform better than plants without amendments, and Carex performs slightly better than Deschampsia. Mean rank AmNP>CoNP>AmCa>AmDe>CoCa>CoDe. Total lead concentration limits for protection of freshwater aquatic life is 4µg/L for hardness below 50 mg/L $CaCO_3$, and 20µg/L for harder water (>250 mg/L $CaCO_3$). Inlet water consistently exceeded this limit (41.14µg/L) and biofilters discharged water which concentration was averagely 0.16µg/L.

There is difference in removal performance of dissolve lead, specifically, non-planted column performs better than planted columns. This might be due to the preferential flow paths created by plants with their root, and the binding of this metal to fluvic acids (Bradl, 2004). Control columns have a lower treatment than amended columns probably due to the adsorption capacity of GAC and Zeolite. Mean rank order for dissolved lead is AmNP>CoNP>AmCa>AmDe>CoCa>CoDe.

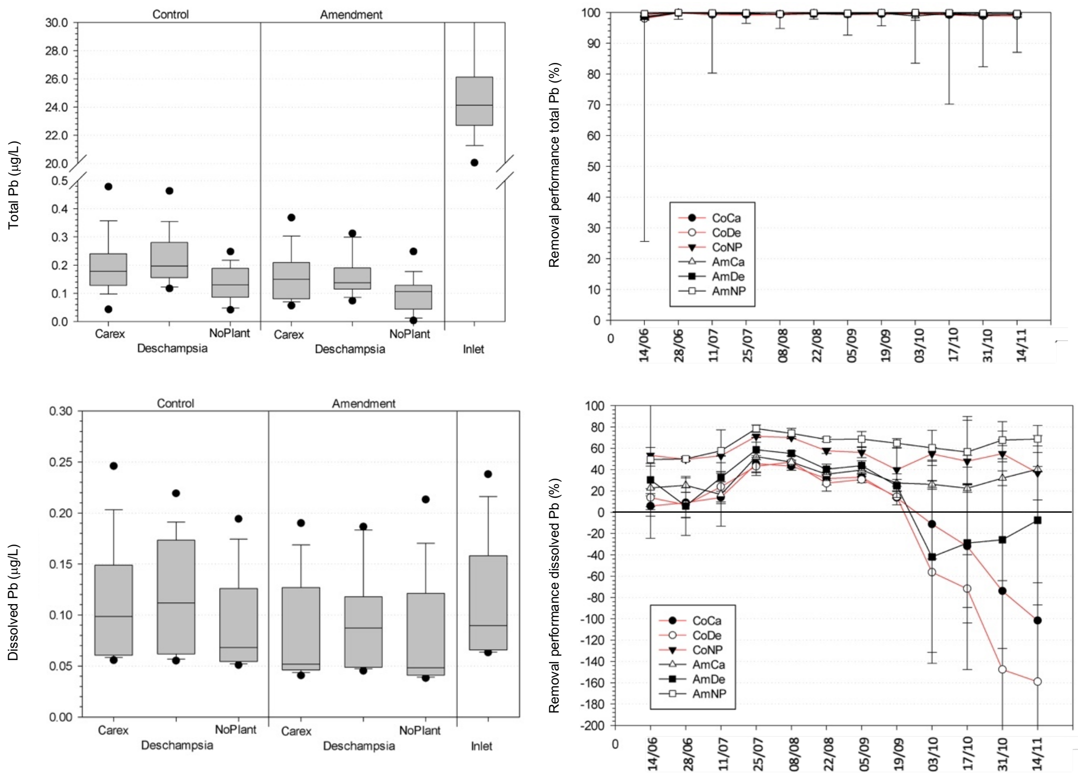


Figure 6-14 Concentration for lead (on the left) and removal performance (on the right) based on 60 samples per design for vegetated biofilters and 24 samples per design for non-vegetated biofilter.

Removal of total heavy metal is higher than 90% for all designs. Copper and Barium are more efficiently treated by amended designs, promoting the hypothesis that GAC and Zeolite high specific surface and cation exchange capacity is making the difference. As suggested by previous studies (Davis et al., 2001; Blecken et al., 2011) plants increase removal efficiency. The capacity of biofilter to stop particles through filtration is mostly responsible for the high removal of particulate bond heavy metals. Nonetheless, the choice of amendments is mostly responsible for dissolved heavy metals treatment rather than plants species. The development of plants through the biofilter, and the interaction of roots humic acid with the media, could determine displacement of particles and desorption that could affect the performances. Concentration at the outlet for total heavy metals were below UK standard limits for freshwater protection and often even lower than the concentration for human consumption. Only total Zinc was found leaching from the biofilters especially from non-planted columns.

Difference in design have been found for selected heavy metals. Limitation prevented for collection of redox condition and oxygen level in the column. Tested biofilters were found effective in the removal of most of the dissolved heavy metals. Statistic difference between control and amended suggest the positive role of GAC and Zeolite on removal performance, especially for Cu, Zn, and Ba. However, leaching of Iron has been noted for amended columns. Non-planted column performed generally higher, probably due to a longer contact time between media and water due to the reduced hydraulic conductivity. However, the inclusion of plants is still beneficial, as shown for dissolved Zinc. The concentration of dissolved heavy metals at the outlet met the limits set by UK legislation most of the time. Amendments efficiently controlled dissolved copper concentration better than control, maintaining the outlet below the strictest limit of 5μg/L. Dissolved iron concentration was often higher for AmCa possibly due to the media displacement operated by roots and humic acid dissolution change in Eh.

6.3.3 Total and dissolved solids

Filtration capacity of the biofilter is on average higher than 98% among all the design (Table 6-7). A Mann-Whitney U test was run to determine if the removal performance between control and amended column was different. Median treatment was statistically significantly higher in control biofilters (99.34%) than in amended biofilters (98.96%) suggesting that amendments' finer fraction could pass through the transition layer and end up in the outlet, although the difference is averagely less than 1 mg/L.

Table 6-7 Removal performance for TSS and TDS (± standard deviation)

	mg/L		Removal performance %	
	TSS	TDS	TSS	TDS
CoCa	1.28 ±1.28	328.67 ±328.67	99.15 ±0.57	20.86 ±30.95
CoDe	1.17 ±1.13	327.06 ±79.41	99.2 ±0.87	21.7 ±30.61
CoNP	0.87 ±0.75	344.31 ±105.39	99.4 ±0.56	16.32 ±34.5
AmCa	2.45 ±3.97	338.65 ±89.57	98.15 ±3.21	16.81 ±32.33
AmDe	1.37 ±1.16	323.1 ±72.55	99.11 ±0.74	23.96 ±26.27
AmNP	2.11 ±1.31	325.34 ±76.2	98.39 ±1.17	23.8 ±25.39
Inlet	188.08 ±249.76	518.58 ±477.47	-	-

As shown in Figure 6-15, and confirmed by a Kruskal-Wallis test, there is a statistically significative difference among AmCa and the other design, but not with AmNP.

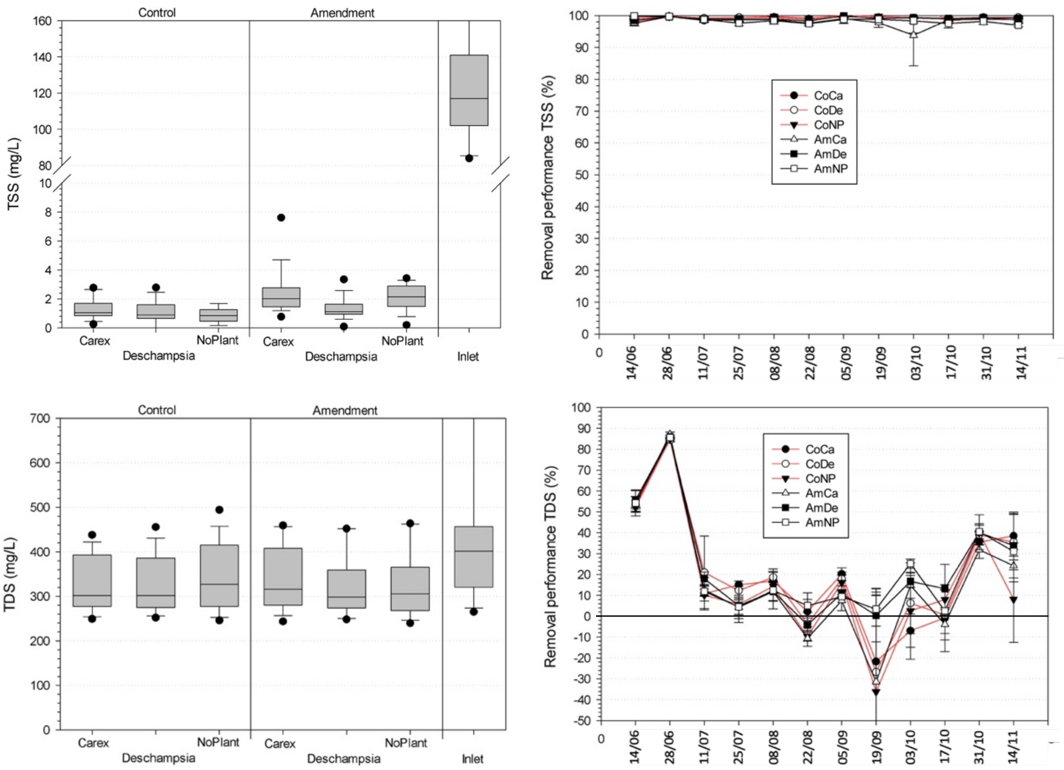


Figure 6-15 Concentration for total suspended and dissolved solids (on the left) and removal performance (on the right). based on 60 samples per design for vegetated biofilters and 24 samples per design for non-vegetated biofilter.

Despite the difference between control and amendments, the removal gap in performance is extremely small and with the accumulation of sediment in the biofilter and the migration of smaller particles from GAC and Zeolite, the differences will further diminish. The higher fraction of sand used in the biofilter, as well as the higher K_w, is not compromising the filtration capacity that remains well above 98%.

The removal of TDS is not different among design and did not have a removal as consistent and high as TSS since it does not rely on filtration, but adsorption and ionic exchange. The removal is low but positive during the spring and first months of summer, but it is negative, meaning a production of TDS from the column, in the hottest month of summer (end of august, September). This could be due to an increased mineralisation and decomposition process that form colloids, and humic acids.

Samples were also analysed with a COULTER LS230 laser diffraction to assess the PSD of inlet and outlet Figure 6-16. Inlet particle size range between 0.05μm and 213.80μm, while outlet for control biofilter range between 0.04μm and 4.24μm, and for amended biofilters between 0.04μm and 43.65μm. It should be noted that AmNP particles range was similar to control (0.04μm and 3.86μm) suggesting that plant roots displaced GAC and Zeolite, and finer particles migrated from the column. d90 for the six designs was not dissimilar, ranging from 2.47μm and 3.16μm, while for the inlet was 82.79μm. 50% of the particles (d50) where finer than 1.45μm for amended column and circa half that size (0.68μm) for control biofilters, while particles between 0.04 and 0.24 represent d10.

These results suggest that biofilters efficiently removed particles above 3μm, while amendments increase the solids in the outlet water due to media displacement mediated by plant roots.

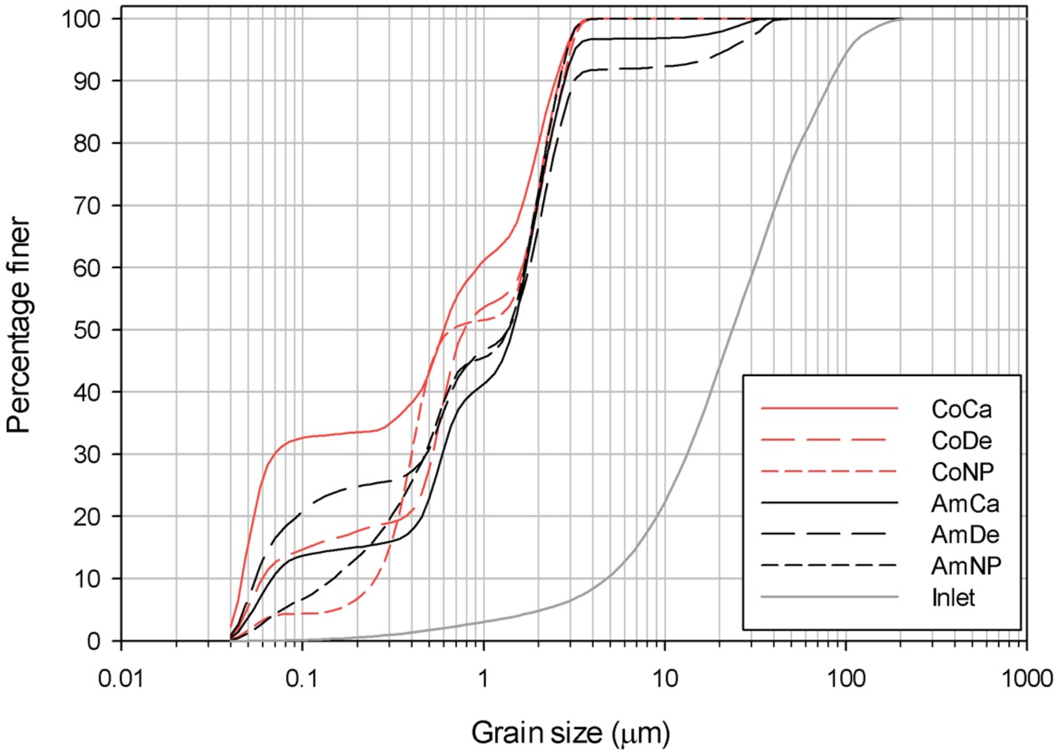


Figure 6-16 Particle size distribution for the six design and the inlet.

6.3.4 Dissolved Carbon

Average removal performance for DOC, DIC, and DC are in Table 6-8 and Figure 6-17. A non-parametric test Kruskal-Wallis-u with Dunnett's pairwise and Bonferroni's adjustment highlight that there is statistical significative difference among designs. Specifically, there is a significant difference between design with and without plants, with the former having a lower removal efficiency than the latter.

Table 6-8 Concentration and removal performance for DOC and DIC (± standard deviation)

	Removal performance (%)		Concentration (mg/L)	
	DOC	DIC	DOC	DIC
CoCa	-47.83 ±130.42	-22.6 ±29.19	2.66 ±2.4	21.35 ±3.07
CoDe	-29.53 ±88.44	-26.94 ±32.47	2.44 ±2.19	21.98 ±3.18
CoNP	7.85 ±65.16	28.3 ±18.45	2.81 ±2.39	21.04 ±3.43
AmCa	-7.75 ±113.12	-51.35 ±34.04	1.94 ±1.96	26.02 ±4.1
AmDe	25.88 ±67.91	-51.47 ±31.56	1.6 ±2.1	27.06 ±4.22
AmNP	50.48 ±53.47	12.26 ±20.82	1.7 ±2.3	26.77 ±5.27
Inlet	-	-	1.9 ±1.28	17.17 ±3.62

A Mann Whitney U test shows that removal performance of DOC is higher in design incorporating amendments (mean rank = 168.51) than control (mean rank = 120.49) ($p < .001$). The same test has been repeated for DIC and DC, and it has been found that the median of Control for DIC (-15.69%), and for DC (-14.93%) is higher than the one in the amended design (DIC= -43.44%, DC= -32.77%).

Organic matter produced by plants decompose through bacterial respiration resulting in CO_2 that enhance dissolved inorganic carbon concentration and organic molecules thus increasing dissolved organic carbon concentration.

One of the possible explanations why amended columns perform well for DOC, but poorly for DIC is connected to this phenomenon. Amendments promote bacterial activity since their high specific surface area can host a more extensive biofilm, thus increasing the decomposition of DOC. The increase in decomposition and bacterial respiration inevitably increases CO_2 concentration in water. The absence of plants and rhizosphere induced by roots inhibit both bacterial growth and the development of DOC in no-planted biofilters. With less DOC available the respiration is also limited, explaining why concentration of DIC outlet for no-planted biofilter is lower than planted designs.

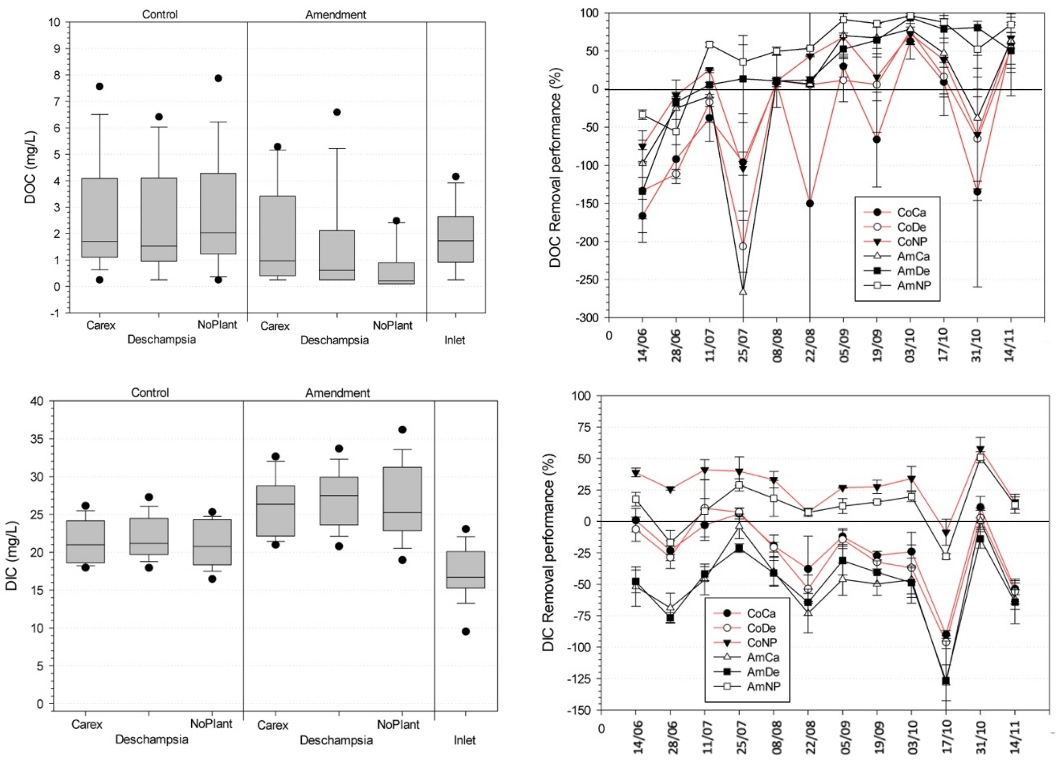


Figure 6-17 Concentration for dissolved organic and inorganic carbon (on the left) and removal performance (on the right). On the abscissa, the sample collection events.

6.3.5 Probe analysis data

During the experiment in greenhouse parameters such as conductivity, pH, dissolve oxygen, and temperature have been noted. Average value for these parameters can be found in Figure 6-19.

6.3.5.1 Conductivity

Conductivity depends on the concentration of ions, and it expresses the capacity of water to conduct electricity.

Generally, water conductivity increased passing through the biofilters and this difference is higher in amended designs. The higher conductivity in the outlet could be explained by the abundancy of ion in the water, especially in the saturation zone, and the wash out of minerals. Amendment might exchange ions with water increasing the conductivity.

6.3.5.2 Temperature

The water temperature at the inlet is constant through the experiment around 10°C and shows a step rise passing through the biofilter. This change is due to the temperature of the media. Moisture sensors showed an increase in soil temperature that reach a peak during mid-day (see Appendix 3). The internal temperature of the columns is probably influencing the microbial activity, plant growth and adsorption rate of the biofilter. Unfortunately, it was not possible to control the climate in the greenhouse. The difference in temperature between inlet and outlet water decreases over time while approaching winter.

6.3.5.3 pH

A Kruskal-Wallis U test showed statistical difference between inlet and outlet for the control and amended columns ($p=.041$), nonetheless there is no difference between amended and control columns as observed during the experiment in chapter 6, probably due to the buffer effect that the rhizosphere, the saturation zone and the carbonic acid operate. The pH of outlet in all design had a negative trend from an average of 6.75 at the beginning of the experiment, to an average of 6.26. Planted designs have a lower pH than design with no plants, possibly due to an increase of microbiological activity in the rhizosphere, dead organic matter decomposition and in the saturation zone. The anaerobic respiration not only decrease pH due to acid formation (i.e. sulphuric), but respiration increase the CO_2 in water altering the carbonic acid equilibrium. Although a specific analysis has not been conducted, a strong smell has been noted coming from outlet water. Figure 6-18 shows the saturation zone one of the columns, in particular a dark spot around woodchip. The saturation zone promotes anaerobic condition for denitrification. In this environment, heterotrophic bacteria (e.g. *Desulphovibro*, *desulphuricans*, *desulfotomaculum*) use sulphate instead of oxygen to decompose organic matter in a process known as dissimilatory sulphate reduction. The black spots that can be seen are due to metal sulphides formed from the sulphide released by bacteria and the iron available in the environment.

Figure 6-18 A black spot, sign of sulphur reduction in saturation zone

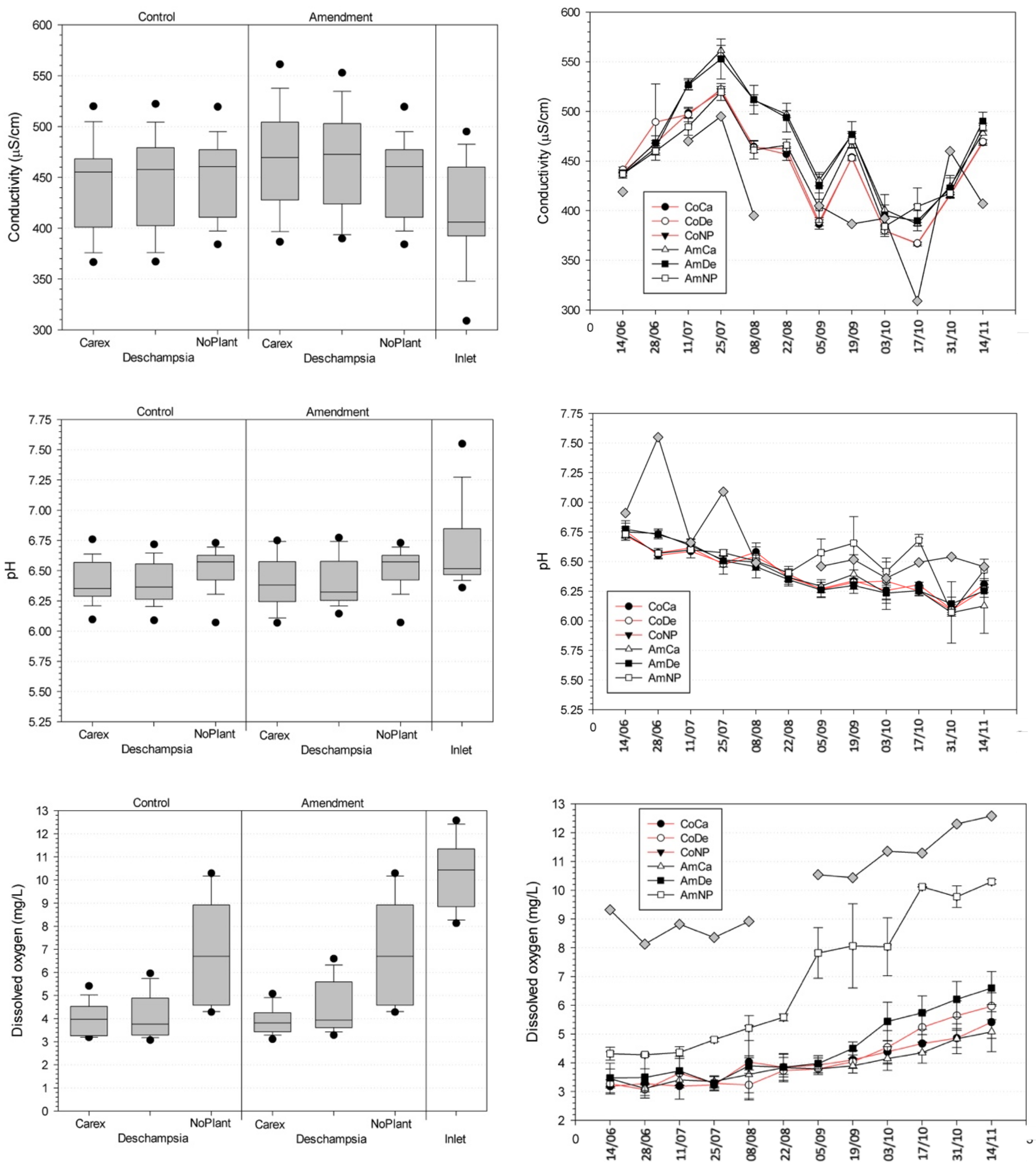
6.3.5.4 Dissolved oxygen

The dissolved oxygen difference between inlet and outlet is high in the design with plants. Average dissolved oxygen for the 6 designs are 4.0 mg/L, 4.11 mg/L, 6.88 mg/L, 3.90 mg/L, 4.51 mg/L, 7.53 mg/L, and 10.85mg/L for CoCa, CoDe, CoNP, AmCa, AmDe, AmNP, and Inlet respectively. No statistical difference between the no-plant designs, however this could be due to the sampling condition for these specific columns. No-plant columns had consistently lower K_w, therefore sampling collection was sometimes postponed 24h after the dosing. This means that outlet water had enough time to reach equilibrium with the surrounding environment.

The difference in oxygen between inlet and outlet is due to the bacterial respiration in the column and in the saturation zone. Lignin breakdown in water could cause oxygen depletion (Gubernatorova and Dolgonosov, 2010) if the necessary fungi are present. The low oxygen in the saturation zone was likely due to the respiration of microorganisms respiration in this area.

Oxygen levels in water increased during the experiment, maybe due to the decrease in temperature that determined two effects: firstly, an impact on the microbiological community fitness, thus decreasing the number of bacteria and the decomposition rates, secondly, the intrinsic property of water for which oxygen increase at lower temperature (Figure 11-7).

Low oxygen in outlet is a possible threat for receiving water. Hypoxia is responsible for low water quality and could potentially kill downstream organism, like macroinvertebrates and fishes, causing severe trophic cascades.



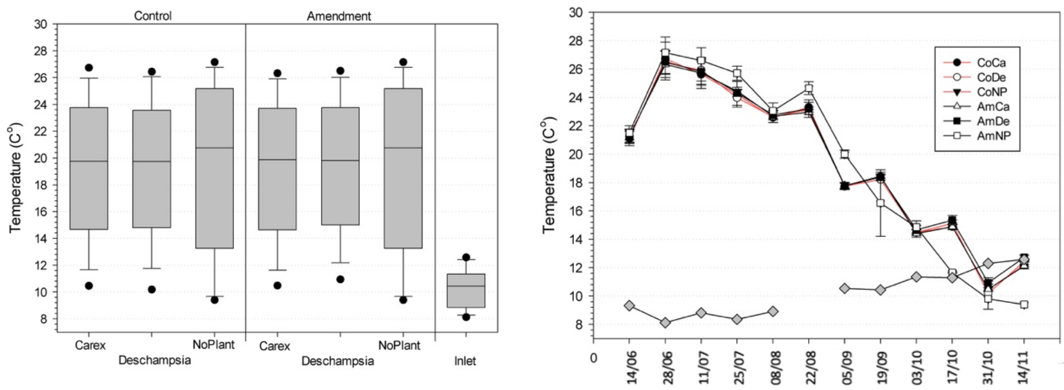


Figure 6-19 Conductivity, pH, Dissolved Oxygen and temperature for the different design and the inlet (black line, grey filling). On the abscissa, the sample collection events.

Additional water parameters have been collected during the 6 months experiment. Conductivity is slightly higher in amended column probably due to cation exchange of Zeolite and GAC. Outlet temperature correlate with the one registered by moisture sensor installed, and it is higher than inlet water. pH shows a negative trend probably associated with the anaerobic area created by the saturation zone at the bottom of the column that promotes not only denitrification, but also sulphate reduction, that can induce water acidification. Furthermore, the anaerobic zone contributes also to the low dissolved oxygen available in the outlet water due to the bacterial respiration. Hypoxia is a serious threat to water ecosystem and can cause trophic cascade.

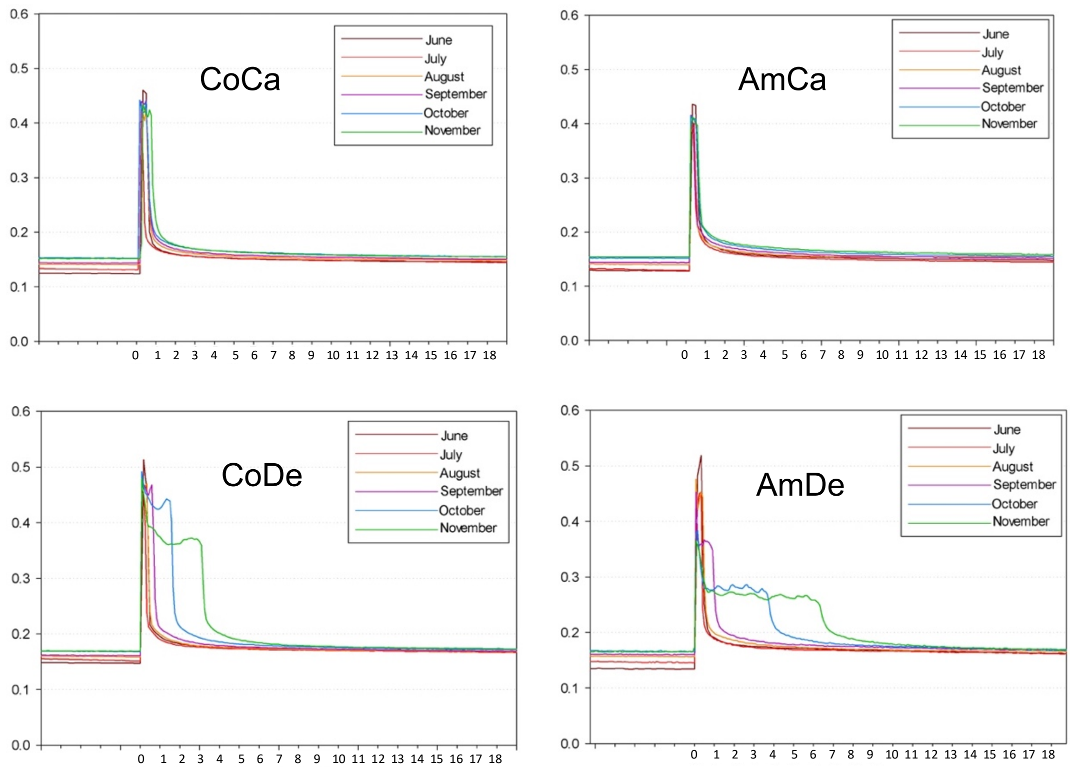
6.4 Hydraulic performance

6.4.1 Moisture content and stomatal conductance

Moisture content where installed in 6 of the 24 columns at the depth of 8cm and 25cm from the surface.

As shown from Figure 11-1 to Figure 11-6 (Appendix 2) , water content follows a vertical profile increasing with depth, probably due to the environmental condition that the two layer faces, with the surface of the biofilter being more exposed to evapotranspiration than the deeper one. This behaviour has been found in the past associated with greenroofs (Berretta et al., 2014).

The trend of water content presents always a spike when water is poured in the biofilter, followed by a reduction in moisture that drop faster in hotter days. During the day, when temperature and solar radiation are higher, the water content deeper in the column increase, probably due to the combination of evaporation, for non-planted column, and transpiration, for planted column. In Figure 6-20 are depicted the water content θ (cm^{3}of water/cm^3 of soil) values for the sensor at -25cm from the surface for the tested biofilters. Time 0 represent the instant in which semi-synthetic stormwater runoff is poured in the columns. On the abscissa the time (in hours) passed from time 0. During the last months of the experiment, moisture in soil was higher than in summer with no-planted column showing sign of failure and water struggle to drain. This can be seen especially in November where moisture content remains high for more than 24hours. It can be noted how moisture content in the biofilter increased during the experiment, with Deschampsia and non-vegetated design retaining water for longer than Carex design.



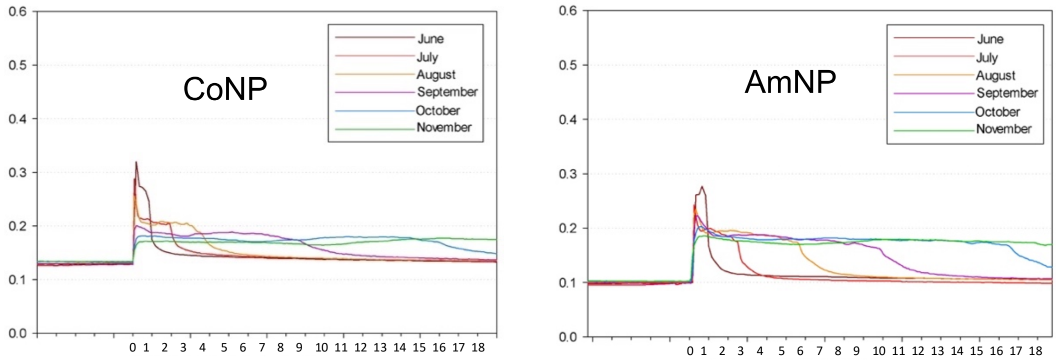


Figure 6-20 Water content from June to August for the six months experiment. On the ordinate the water content θ (cm^3 of water/cm^3 of soil); on the abscissa the hours from the start of a dosing event. CoCa= Control Carex; CoDe= Control Deschampsia; CoNP= Control No-plants; AmCa= Amended Carex; AmDe= Amended Deschampsia; AmNP= Amended No-Plants.

As suggested by other authors (Daly et al., 2012; Payne et al., 2018), evapotranspiration is a key component for the restoration of biofilter's retention capacity. The setup built for this experiment did not allow for an accurate measurement of evapotranspiration, however a good indicator of transpiration can be assessed with a leafporometer (SC-1 from Decagon) that measures the stomatal conductance of a plant leaf. Stomatal conductance measures the rate of gas exchange (i.e. water loss) and its value can determine differences among plants and whether the gas exchange was affected by the presence of amendments.

Transpiration is the evaporation of water from plants and depends on stomatal aperture that regulate the gas exchange of CO_2 and H_2O necessary for the photosynthesis. Three plants per design were randomly selected at the beginning of the study, and in the months of August, October and November three reading were taken from each of the chosen biofilters at least two days after a watering event.

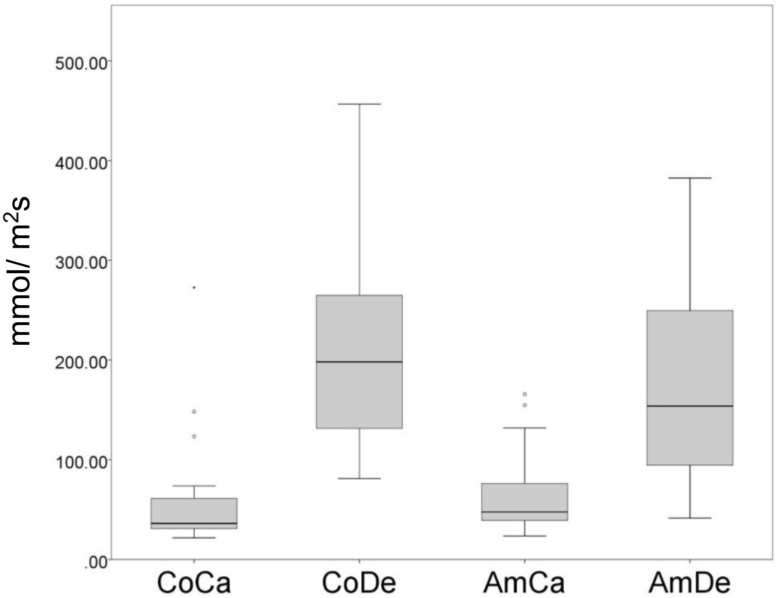


Figure 6-21 Stomatal conductance values for the vegetated biofilters. CoCa= Control Carex; CoDe= Control Deschampsia; AmCa= Amended Carex; AmDe= Amended Deschampsia.

As can be observed from Figure 6-21 a non-parametric Kruskal-Wallis test highlighted a statistically significant difference among designs ($p<.001$). Specifically, the difference is between the plant Carex and Deschampsia, with the first having a lower transpiration than the second, and amendments not affecting the gas exchange values.

Furthermore, in Figure 6-22, it can be seen that there are differences between AmDe and CoDe in October, but not in November. There is no substantial difference between AmCa and CoCa for the three monitored months.

An hypothesis is that the different environmental condition of the three months has affected the stomatal conductance.

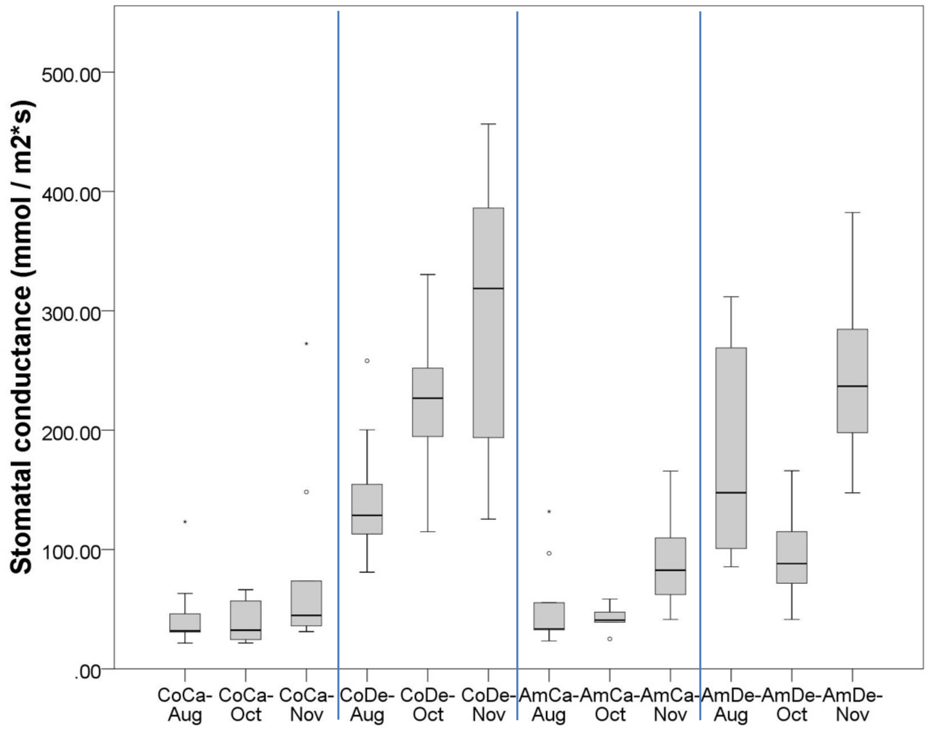


Figure 6-22 Change in stomatal conductance for the four design for the months of August, October, and November.

The opening and closing of stomatal, triggered by the presence of light to minimise water loss and maximise CO_2 assimilation, as well as the rate of transpiration, is affected by relative humidity, temperature and wind speed.

Water moves from high to low water potential and the water potential for air relates to relative humidity as

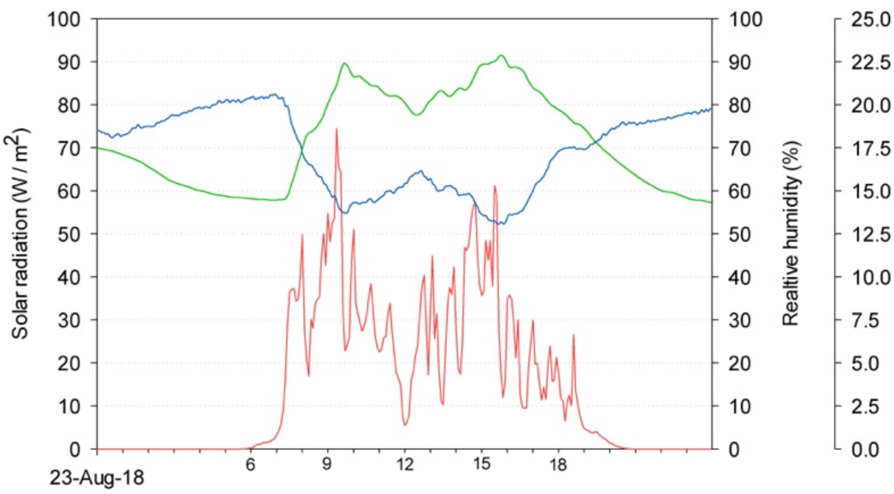
$$\psi_{air} = \frac{RT}{V_w^0} \times \ ln \ (\frac{RH}{100})$$

Where R is the ideal gas constant, T the temperatures, V^0_w is the molar volume of water, RH is relative humidity (Lambers et al., 2008). Therefore, the lower the RH and higher the temperatures, the higher the water potential. Air that contains less water vapor have extreme negative water potential.

With the increase of transpiration, the water vapor concentration around adjacent leaves increases as well, inducing a negative feedback, reducing the driving forces for transpiration. This thin zone of calm air adjacent to the leaf is called boundary layer, whose gas concentration, temperature and air flow is modified by the leaf. Its limit is defined as the point at which the properties of air are 99% of the values in ambient air. This layer increases the resistance for water vapor transfer and consequently CO_2-H_2O. Wind can dissipate this layer promoting gas exchange between the plant and the environment. Since the columns where protected in a greenhouse, the boundary layer in the column remained invariant possibly affecting plant health and evapotranspiration.

Soil moisture remained constant: 0.17% and 0.15% for Deschampsia and Carex on average. As described in paragraph 6.4.2, Carex tend to have a higher K_w than Deschampsia and this might have affected the water availability and moisture retention.

Solar radiation, relative humidity, and temperature for the three days in exam are in Figure 6-23.



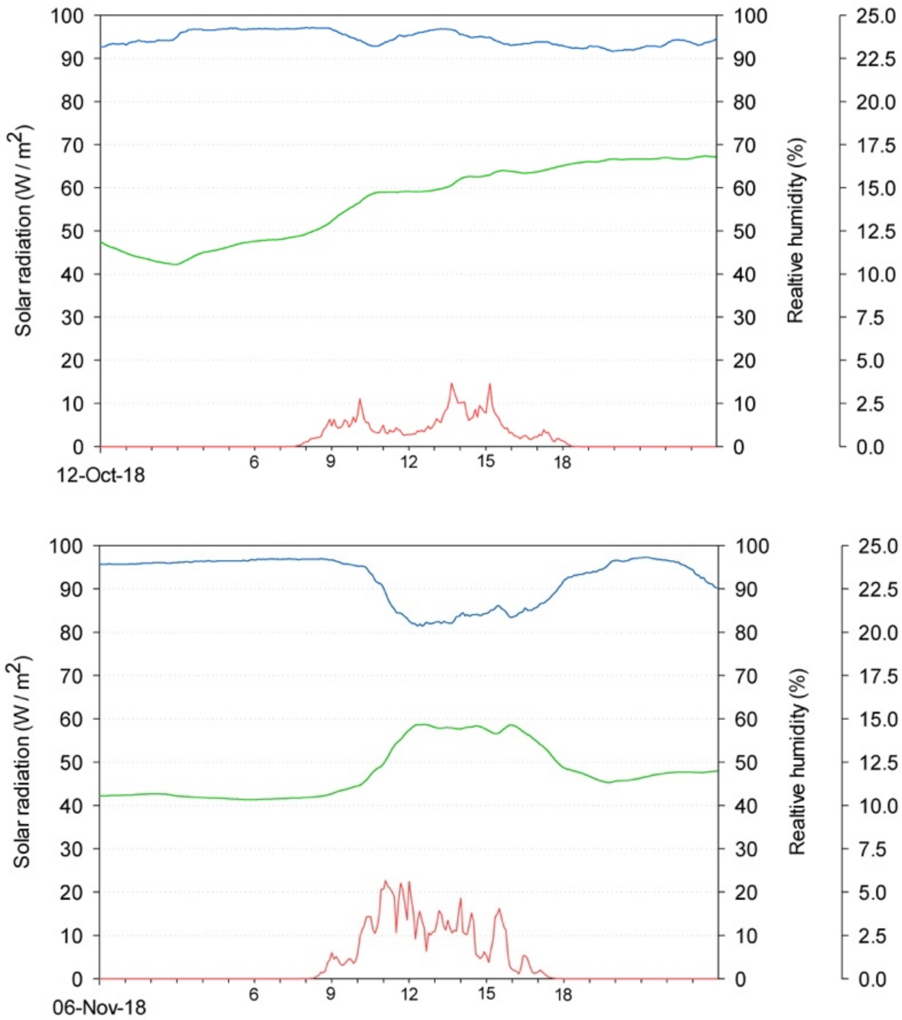


Figure 6-23 Relative humidity, temperature and solar radiation registered for the greenhouse during August, October, November. Blue for RH, Green for Temperature, red for solar radiation

Although, the solar radiation during August was significantly higher, the stomatal conductance was lower than in November, but not October when a storm shielded the greenhouse from the sun. Dry air and higher temperatures of August expect to increase transpiration due to a greater vapor pressure difference between the leaves and the environment. However, the perplex columns and the absence of wind might have affect plants' boundary layer, thus the relative humidity and the capacity of exchanging CO_2 and H_2O. This phenomenon might be noted, for instance, in Figure 6-24, where small droplets of condensation can be seen on the side of the column. If this is particularly true for Carex, which leaves rest entirely in the column cutting out air circulation, it might have affected less Deschampsia' leaves that in many cases outgrown the Perspex column and stand straight leaving more space for air to circulate, thus a different microclimate.

Evapotranspiration is certainly involved in loss of water thus in the regeneration of water retention capacity in biofilters. Deschampsia have statistically different stomatal conductance than Carex, and amendments are not influencing this value. No-planted column have lower moisture than planted columns, but the water content remains constant for more than 24h in November, showing sign of failure.

The presence of clouds significative affects RH, solar radiation, and temperature, affecting stomatal conductance, therefore the capacity of the biofilter to regenerate before a new rain event.

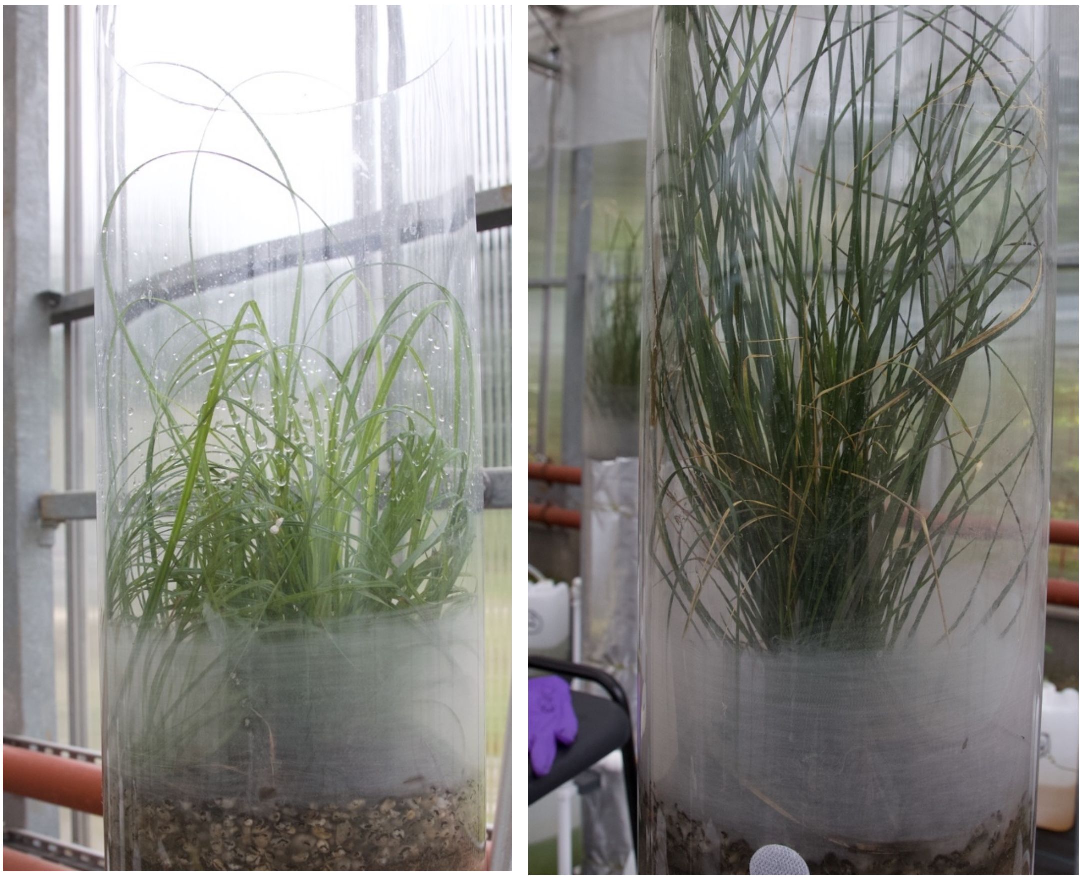


Figure 6-24 Droplets of moisture in Carex (left). Deschampsia (right) does not show moisture retention on the Perspex wall

6.4.2 Hydraulic conductivity

Hydraulic conductivity has been monitored once a month on the same six columns after a sampling event to avoid introduction of factor of stress that might influence the biological community of the biofilter, thus the removal performance.

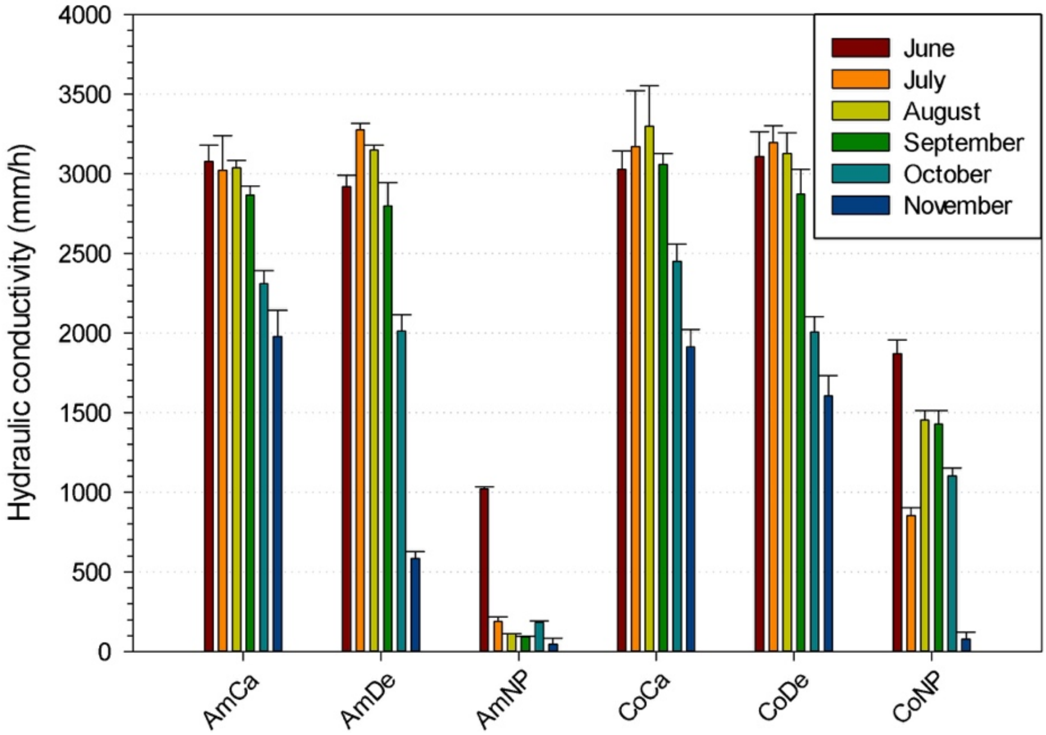


Figure 6-25 Hydraulic conductivity for the six designs. CoCa= Control Carex; CoDe= Control Deschampsia; CoNP= Control No-plants; AmCa= Amended Carex; AmDe= Amended Deschampsia; AmNP= Amended No-Plants.

The saturation zone of the column was drained, and a constant flux of inlet water was maintained for 30 minutes. The tap at the bottom of the column was then closed, and the column left for an additional hour flooded with tap water to ensure saturated condition. Finally, the 40 cm tap was opened, a head maintained constant for 30 minutes before water was collected for minimum one minute to calculate hydraulic conductivity. To ensure that the flow from the outlet was constant, a measure was taken every 20 minutes for three times

(Figure 6-26). For column which conductivity was low (i.e. CoNP, AmNP) the collection of water was longer than 60 seconds, reaching up to 17 minutes. The calculated values were then corrected for water density at 20°C as follow:

$$K_{20^\circ\mathrm{C}} = K_{measured}\frac{\eta_{measured}}{\eta_{20^\circ\mathrm{C}}}$$

Where $K_{20^\circ C}$ is the hydraulic conductivity at the temperature of 20°C, K measured is the hydraulic conductivity at the measured temperature, $\eta_{measured}$ is the density of water at the measured temperature, $\eta_{20^\circ C}$ the density of water at 20°C.

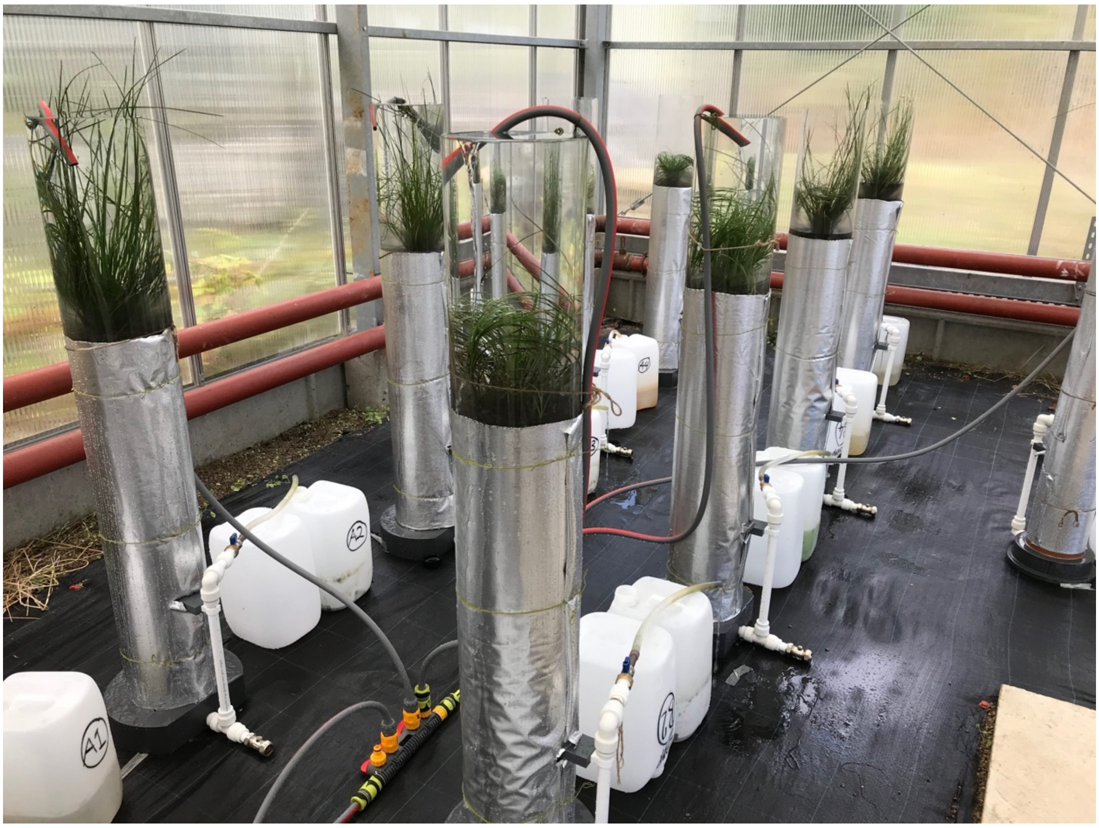


Figure 6-26 Hydraulic conductivity test: columns were connected in series using two 4-ways tap connector. Columns were flooded for 2.5 hours before the test.

There is statistical difference between design with and without plants (p<.001), due to the contribution of plants to create preferential path and macropores which water can enter (Le Coustumer et al., 2012), but overall no difference between Carex and Deschampsia (p=0.710). During the progression of the experiment and the consequent accumulation of sediments (Figure 6-27) and biological clogging (Bouwer, 2002; Kanmani et al., 2014) hydraulic conductivity declined as shown in Figure 6-25. This regression is more accentuated in column with no plants, CoNP and AmNP, that pass from 1868 mm/h and 1021 mm/h to 78 and 45 mm/h respectively.

Figure 6-27 A detail of column AmCa: the gravel turned black showing sign of blocking suspended solids. A small sprout can be seen in the middle of the picture affecting K_w

Planted columns are overall not significantly different (p=0.954), however for October the difference are significative (p=0.30), with Deschampsia having a lower K_w than Carex, and in the month of November (p=0.24) AmDe having the lowest hydraulic conductivity among planted designs. The difference observed in October might be connected to the different diameter and root development of the two plant species, with Carex having longer and thicker roots than Deschampsia (Figure 6-28). Another detail is that Carex is propagating through the media piercing the gravel protection layer. This make sure that the sediment accumulated on the top of the column is displaced over time, delaying the clog.

Figure 6-28 Detail of the first 10 cm for Carex (left) and Deschampsia (right)

Clog is defined by (Segismundo et al., 2017) as the reduction to 15-20% of the original Kw. Although this definition might be correct for their study, it is unjustified for high conductivity columns for which a reduction to 15-20% of the initial value would mean for instance, a final value of 460/615 mm/h, which is enough for water to infiltrate and above the suggested values of 200-300 mm/h (Payne et al., 2015; Woods-Ballard et al., 2015). The accumulation of sediment, as well as the biological clogging and possibly compaction, are all relevant to the decrease in hydraulic conductivity. Plant species play a role in increasing the resilience to these stress for longer period and roots development is vital to displace the filtered particles that will inevitably clog non-planted columns.

The change of hydraulic conductivity reflected the moisture content of biofilters as shown in Figure 6-20. The water content registered by the sensors increases during the experiment: from a shorter peak during June, to a wider peak in November. Non-vegetated biofilters retained water for longer by the end of the experiment compared with vegetated biofilters. There is difference between the two species, with Carex maintaining a lower water content than Deschampsia. The inclusion of moisture sensors in a biofilter can thus help identify when a system needs maintenance: if water content remains high for too long it means that the system is close to clogging and need to e managed as soon as possible.

6.5 Plant growth

6.5.1 Plant general status

All the plants survived until the end of the experiment and resist to a successive 1-month-long draught (winter) without wilting thanks to the inclusion of a saturation zone, the presence of vermiculite that increased the water retention, low temperature and low solar radiation. Once a month, columns were stripped of their reflective mylar cover to observe roots and shoots development, compression/expansion stresses, sediment accumulation, and take pictures. No sign of compression/expansion have been noted during the 6 months. The variable observed in plants were three: longest shoot, number of flowers, depth of the visible roots.

In the first few weeks from the start of the experiment it has been noted that some *Carex flacca*'s leaves developed yellow-red-black spots (Figure 6-30 - right), while on *Deschampsia cespitosa* a fine white powder. The two pathogens have been inducted by two distinctive fungal species: the first can cause Rust, the second Mildew (Staples, 2000; Micali et al., 2008; Gessler et al., 2011; Rampitsch et al., 2016). The spores of these fungal species could have been transported with the sediment collected in gully pots (Chong et al., 2013), and developed thanks to low air circulation and high moisture trapped in the Perspex column: the perfect environment for these pathogen to develop. To avoid interferences with water quality tests, it has been decided to not use any fungicide during the experiment. After 2 months mildew reduced and disappeared, probably due to the way Deschampsia's leaves rest (straight) compared with Carex (folded), resulting in a better aeration of the column.

6.5.2 Inflorescence, leaves, and root status

Inflorescences appeared during the warmest months for most of the plants. Carex grown in amended biofilters tend to have more flower and for longer period compared to Deschampsia and the ones planted in control columns (Figure 6-29).

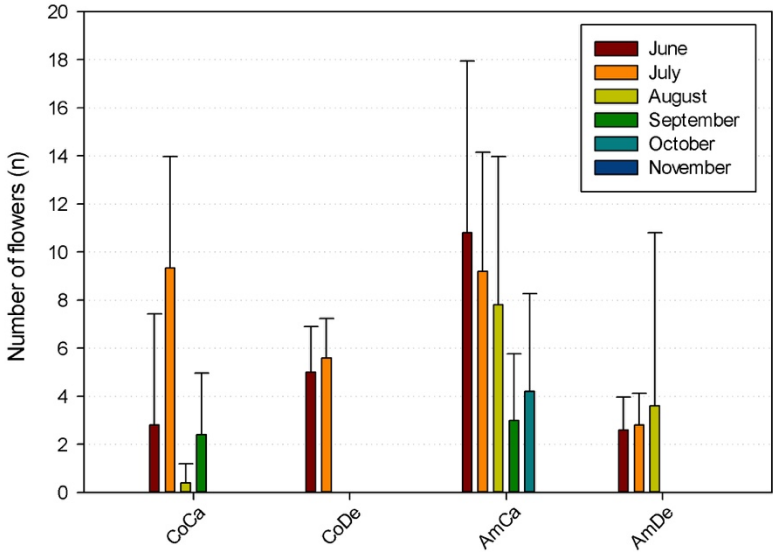


Figure 6-29 number of flowers for the two species and two designs. AmCa resulted the combination with more long-lasting flowers.

There was no difference in shoot length for the two species and the maximum length was reached in August (Table 6-9). *Carex* leaves showed signs of necrosis, especially on the tips, due to the contact with the ground. The leaves were covered by polluted sediment in a high moisture environment (Figure 6-30). Due to *Deschampsia's* resting position, no sign of necrosis was seen.

Table 6-9 Maximum shoot length registered for 6 months for the 6 design (CoCa=Control Carex; CoDe=Control Deschampsia; AmCa=Amendment Carex; AmDe= Amendment Deschampsia)

	CoCa	CoDe	AmCa	AmDe
June	Not available	Not available	Not available	Not available
July	35.8 ±9.5	63.2 ±19.2	42 ±6.6	59.6 ±22.7
August	51.6 ±2.5	54.8 ±6.6	53.0 ±6.0	51.6 ±10.4
September	53.0 ±4.0	57.8 ±7.8	56 ±4.8	55.4 ±12.1
October	55.2 ±3.3	51.6 ±4.4	55 ±6.2	59.2 ±14.8
November	53.8 ±5.4	53.4 ±5.4	54.8 ±7.3	54.8 ±13.3

Figure 6-30 Sign of necrosis on *Carex* flacca (left), and rust (right)

Despite the impossibility to see through the media, the transparent column allowed to observe lateral roots. Roots from *Deschampsia* were thinner than *Carex's*, approximately 0.5mm and 1mm respectively, thus impacting on the hydraulic conductivity as previously noted in paragraph 6.4.2. No data was available for June since plants were too small and no roots were visible on the side of the column (Table 6-10). All plants reached the depth of amendment layer (-33cm), thus interacting with GAC and Zeolite when possible. *Carex* grown in amended biofilters showed a longer lateral root compared to the other combination, suggesting that GAC and Zeolite are not harming the plant. In chapter 7, plants were extracted from the biofilter and measured. Pictures of the cleaned plants can be found in appendix 4.

Table 6-10 Root depth for the two species and two design. From observation of lateral roots, plants reached the depth of amendments in September. No data is available for June because roots were not visible.

	CoCa	CoDe	AmCa	AmDe
June	Not available	Not available	Not available	Not available
July	-21.0 ±2.0	-21.3 ±5.9	-32.3 ±17.1	-18.1 ±3.0
August	-28 ±6.4	-28.4 ±5.4	-33.2 ±2.6	-29 ±5.7
September	-37.4 ±5.9	-35 ±6.6	-45.8 ±1.9	-36.2 ±7.0
October	-37.6 ±7.1	-38 ±4.6	-45.8 ±1.9	-36.2 ±7.0
November	-38.6 ±6.3	-38.6 ±4.5	-46.0 ±2.0	-36.2 ±7.0

6.6 Discussion

6.6.1 Designs consequences on treatment performance

The use of a bigger fraction of sand (0.6-1.18mm) and higher hydraulic conductivity (K_w>3000mm/h) has not compromised the removal performance of nutrients, heavy metals, and TSS.

The removal of suspended solids is higher than 98% despite the higher PSD used for this test, however the removal of dissolved solids is less efficient, particularly in summer, probably due to the more intense microbial activity promoted by higher temperatures. Amendments were slightly less efficiently in the removal of solids from the stormwater; however, laser diffraction results suggest that Zeolite and GAC are a source of fine sediment that get displaced by plant roots, thus increasing the outlet concentration.

Amendments do have a positive effect on the removal performance of dissolved nutrients, TDN and PO4-P, as well as some heavy metals like dissolved Cu, Ni and Ba; however, amended design tend to leach some iron. The presence of GAC and Zeolite increases respiration rates from microorganisms, reducing the amount of DOC and the displacement of heavy metals.

Plants were not affected by the low water retention (even during the hottest period), the presence of pathogens and by amendments. In fact, plants seem to use amendments as resource of water and nutrients, possibly increasing the resistance to drought. Yellow sand is not compromising the growth of plants in accordance with previous researches (Glaister et al., 2017).

Although vegetated and non-vegetated biofilters do not differ in removal performances, plants are still vital to maintain hydraulic conductivity and avoid clogging. Non-planted columns perform significantly worse than planted columns, with Carex maintaining a higher infiltration rate than Deschampsia, and lower moisture content. The propagation of the plant, coupled with its ticker root system, displace the media, creating channels for water infiltration. In a full scale biofilter is then advisable to populate the area close to the inlet with sturdy plant which root system can help avoid clogging, reduce the flow, thus distributing more efficiently the suspended load.

6.6.2 Dry weather period implications on removal performance

The first experiment described in chapter 6 highlighted that short dry periods decrease dramatically the removal performance of the columns. With and ADWP of 48h the removal performance was stable and higher than 80% for all the pollutants. Iron was still leaching from the biofilter, a concern expressed in chapter 5. A possible solution for this problem is to use less iron oxide rich sands in the saturation zone to prevent the mobilisation of Fe^{2+} due to a lower E_h and low pH.

6.6.3 Evolution of moisture content, temperature and solar radiation

The season are characterised by unique condition of solar radiation, and temperature (Appendix 3) affecting the removal performance, due to bacterial and plant activity and the transpiration. The columns were not isolated from the environment, thus affecting the temperature of the soil. This might have had an impact on the biological community living in the biofilter, impacting the respiration or increasing performances.

6.6.4 Effect of temperature and solar radiation on transpiration

The stomatal conductance is influenced by temperature, relative humidity, and wind. Plants present different values for H_2O exchange, that can be attribute to the diverse species, or the growth condition. Perspex columns and the absence of wind is influencing the boundary layer, affecting plant health and possibly evapotranspiration.

6.6.5 Design and maintenance

The decision to reduce the size of gravel protection layer has ensured an easy installation of plants. As specified in the previous chapter, the use of gravel instead of sand as protection layer is to avoid wind dusting away the media. Although walking on the biofilter is not advisable since it could harm plants and roots, walking on gravel rather than sand might help access the biofilter for maintenance, avoid compaction distributing the weight of someone's body.

Dissolved oxygen was low at the outlet, possibly due to the bacterial respiration and the saturation zone added. In order to make sure to avoid hypoxia it is advisable to re-oxygenate outlet water before reaching a water body receptor.

6.7 Chapter summary

In this chapter, the data for nutrient, heavy metals, DOC, TSS, hydraulic conductivity, and stomatal conductance have been presented and discussed. Amendments increase removal performance of biofilters, without compromising in hydraulic conductivity or harming plants. In the following chapter it will be discussed the accumulation of pollutants in the media, and whether there is a difference in uptake of plants for an optimised biofilter's waste management.

Chapter 7 Fate of pollutant in biofiltration system

7.1 Chapter overview

Concentration of nutrients and heavy metals in plants and media are here reported and discussed. The implications are used to assess where pollutants accumulate, whether amendments impact plant fitness, and to provide recommendation for biofilter maintenance.

7.2 Plant characteristics

After the experiment described in Chapter 6, 12 vegetated biofilters not used in the hydraulic conductivity test and the ones not including sensors, three for each design including plants, were dismissed and soil samples were collected at six depth in order to assess the concentration of pollutants in the protection layer, in the filter media including topsoil, in the middle of the filter media and at the depth of amendments layer. Once plants were cleaned from the soil, a representative sample from roots and leaves was collected. These were sampled according to paragraph 3.5.4 These were analysed for nutrients, heavy metal and through computer image analysis for surface and length.

The aim was to assess whether amendments included in biofilters affected plants growth and where pollutants have accumulated.

Pictures of plants, leaves and roots can be found in Appendix 4 (from Figure 11-10 to Figure 11-12).

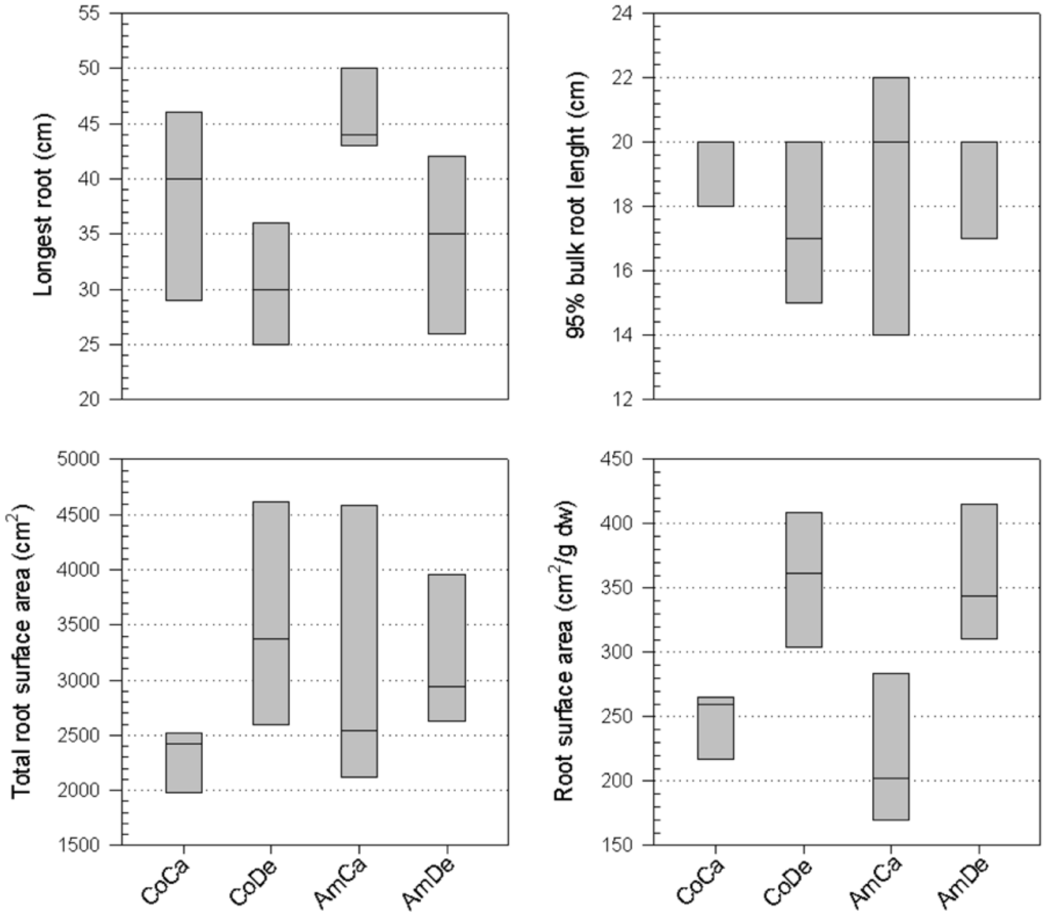


Figure 7-1 Root parameters: Longest root and bulk length measured using a measuring tape; surface area measured using ImageJ threshold analysis. On the abscissa, CoCa= Control Carex; CoDe= Control Deschampsia; AmCa= Amended Carex; AmDe= Amended Deschampsia.

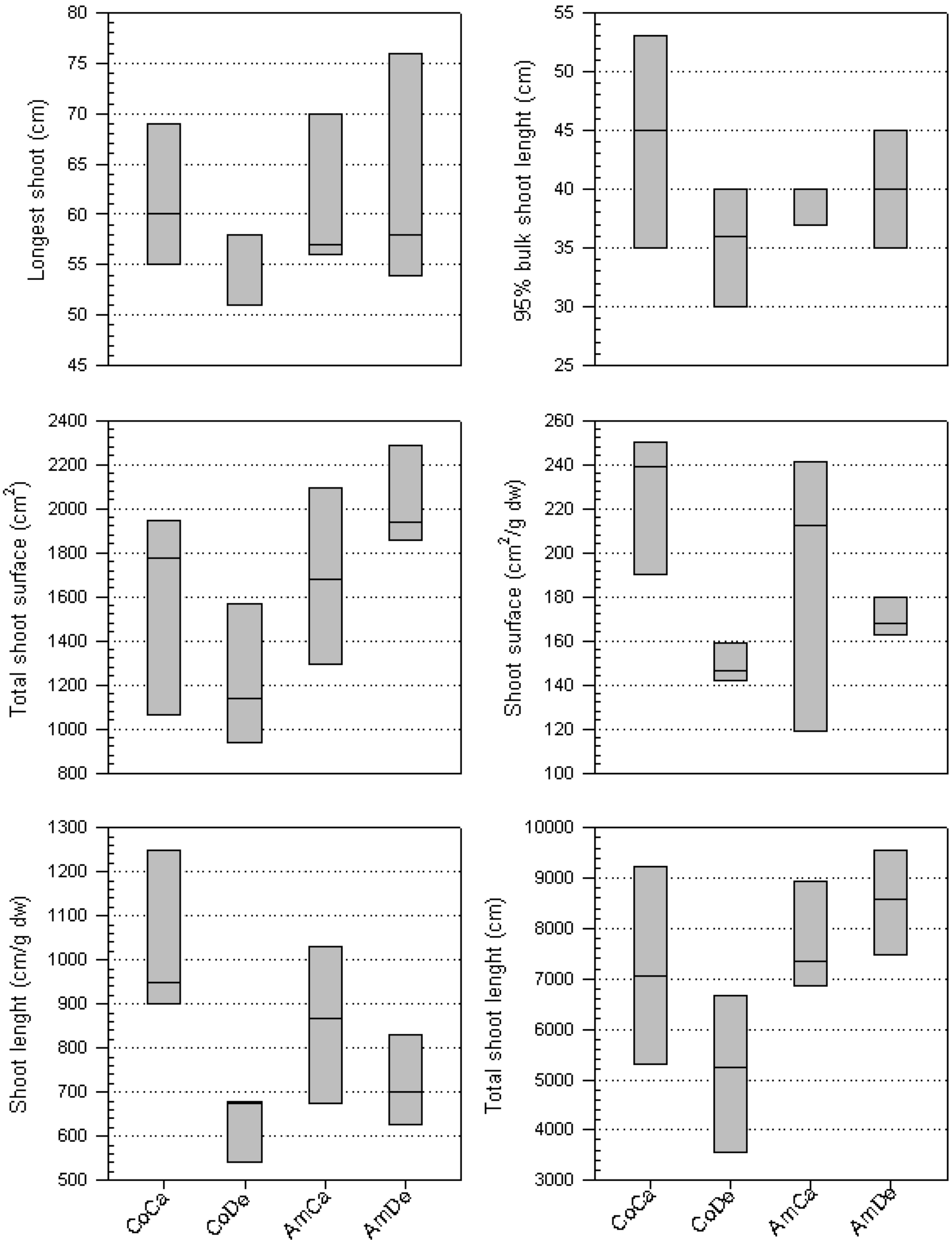


Figure 7-2 Shoot parameters: Longest shoot and bulk length measured using a measuring tape; Total length and shoot surface measured using ImageJ threshold analysis. On the abscissa, CoCa= Control Carex; CoDe= Control Deschampsia; AmCa= Amended Carex; AmDe= Amended Deschampsia.

A Kruskal-Wallis test was conducted to determine whether statistical difference existed in longest root, bulk root, root mass, root surface, among groups that differed in their design and plants. During the experiment all plants reached the amendment layer, thus interacting with it (Figure 7-3).

From the values reported in Table 7-1 it can be noted that in most of the plants, apart from AmDe, the biomass is higher belowground. There was no statistical difference in root biomass, however, shoot and plant mass in amended column was on average 5 grams higher than in control (p=0.026).

Table 7-1 Dry weight of roots, shoots and plants

	Root mass (g)	Shoot mass (g)	Plant mass (g)
CoCa	9.42 ±1.75	7.3 ±2.97	16.73 ±4.22
CoDe	9.85 ±2.31	8.07 ±1.63	17.92 ±3.76
AmCa	13.76 ±2.08	9.15 ±1.55	22.92 ±3.62
AmDe	9.22 ±3.26	11.95 ±1.65	21.17 ±3.07

Although no statistical differences were found for root parameters among designs, it has been noted that Carex grown in amended column had slightly longer roots than control, 45cm and 38cm respectively, thus explaining the higher biomass (Figure 7-1). Without considering the media plants were growing in, Carex roots were longer than Deschampsia's (p=0.041). Roots of Carex were much thicker than the second specie, thus affecting the hydraulic conductivity and performance of the column as observed in chapter 6. Unfortunately, it was not possible to analyse root images for dimeter and length due to limitation in software availability, nonetheless, it was possible to analyse the surface area.

Table 7-2 Average values for root parameters (± standard deviation)

	Longest root (cm)	Bulk root lengt (95%) (cm)	Root surface per gram (cm^2/g)	Root surface (cm^2)
CoCa	38.33 ±8.62	18.66 ±1.15	247.46 ±26.45	2309.24 ±285.78
CoDe	30.33 ±5.5	17.33 ±2.51	358.2 ±52.37	3529.31 ±1023.12
AmCa	45.66 ±3.78	18.66 ±4.16	218.3 ±58.86	3084.5 ±1319.48
AmDe	34.33 ±8.02	19 ±1.73	356.39 ±53.78	3178.68 ±693.04

The mean rank for total root surface area for all groups were similar, however, the specific root surface was statistically higher in Deschampsia, 358 cm^2/g

and 356 cm^2/g for CoDe and AmDe, than in Carex, 247 cm^2/g and 218 cm^2/g for CoCa and AmCa respectively (Table 7-2).

Figure 7-3 Deschampsia roots growing in granular activated carbon

Above ground, AmDe has the highest biomass (11.95g) followed by AmCa (9.15g), CoDe (8.07g) and finally CoCa (7.30g) (Table 7-3).

The presence of amendments in the design seems to not affect the growth of the plant, with no statistically significant difference for any of the parameter under investigation. Deschampsia grown in columns containing GAC and Zeolite showed longer shoots compared to the one planted in the control design, 62cm and 55 cm respectively, that reflects also in the bulk shoot length: 40cm and 35cm respectively Figure 7-2).

Table 7-3 Shoot parameters with (± standard deviation)

	Longest shoot (cm)	Bulk Shoot lenght (95%) (cm)	Number of shoots	Shoot lengh per gram (cm/g)	Shoot surface per gram (cm^2/g)
CoCa	61.33 ±7.09	44.33 ±9.01	190 ±49.48	1033.31 ±186.83	226.66 ±31.86
CoDe	55.66 ±4.04	35.33 ±5.03	215.66 ±59.8	630.65 ±78.44	149.28 ±8.75
AmCa	61 ±7.81	39 ±1.73	233 ±14.79	857.92 ±178.34	190.99 ±64.04
AmDe	62.66 ±11.71	40 ±5	293.66 ±32.57	719.81 ±103.96	170.14 ±8.92

	Total shoot length (cm)	Total shoot surface (cm^2)
CoCa	7198.32 ±1955.05	1596.52 ±466.21
CoDe	5161.35 ±1556.85	1215.09 ±319.61
AmCa	7716.38 ±1093.62	1689.77 ±400.43
AmDe	8532.28 ±1047.5	2026.88 ±229.29

Shoot surface is related with evapotranspiration: the bigger the surface, the higher the transpiration, although, as discussed in the previous chapter, this is not the only parameter that influence the transpiration. Carex had a higher shoot specific surface area compared with Deschampsia ($p<0.015$), however this difference is not reflected in total shoot surface, where AmDe had a higher value than the other species due to its averagely higher biomass.

In conclusion, the data support the idea that GAC and Zeolite do not harm the plant growth during the first 6 months of the growth cycle, with no statistical difference between plants grown in control and amended design. In fact, biomass is greater in the latter design, showing that it might be beneficial for the growth and survival of plants. The two species have differences in root specific surface, with Deschampsia having a larger surface than Carex ($p<0.002$).

7.3 Pollutants in plants

The concentration of heavy metals and nutrients in the plants is reported in Table 7-4. It can be noted that the concentration for copper, zinc, and cadmium for *Carex* are similar to the one reported by (Blecken et al., 2011): 57.8μg/g, 119.75μg/g, 0.5μg/g circa respectively.

Table 7-4 Average concentration (± standard deviation) for heavy metals and nutrient

	Al (mg/g)	Cr (µg/g)	Fe (mg/g)	Ni (µg/g)	Cu (µg/g)	Zn (µg/g)
CoCa	2.28 ±1.31	59.98 ±6.9	1.66 ±0.7	47.35 ±6.74	75.96 ±14.03	115.98 ±12.67
CoDe	2.76 ±0.79	134.89 ±108.1	2.85 ±1.38	107.14 ±57.56	100.1 ±9.15	234.9 ±32.12
AmCa	1.79 ±0.15	54.05 ±16.31	1.89 ±0.25	43.08 ±9.78	61.23 ±8.17	108.07 ±16.71
AmDe	3.91 ±2.33	135.23 ±61.86	2.42 ±0.6	108.47 ±32.04	115.57 ±11.6	234.49 ±14.79
	Cd (µg/g)	Ba (µg/g)	Pb (µg/g)	TN (mg/g)	TP (mg/g)	
CoCa	0.68 ±0.19	20.13 ±0.59	2.23 ±0.54	18.61 ±3.29	6.06 ±1.09	
CoDe	3.35 ±1.39	20.24 ±2.4	1.73 ±0.43	21.04 ±0.98	4.67 ±0.27	
AmCa	0.67 ±0.31	25.51 ±5.67	2.52 ±0.75	22.58 ±0.97	6.15 ±0.24	
AmDe	2.67 ±0.59	20.48 ±1.95	2.19 ±0.14	23.38 ±1.15	4.33 ±0.34	

There is statistical evidence that the concentration of nitrogen is higher in amended plants than in the species grown in the control design (p=.050), while phosphorus concentrations are higher in Carex species (p=.034), particularly AmCa that, thanks to its higher biomass, can accumulate more phosphorus (65.5 mg). In Figure 7-4, it can be noted how the mass of nitrogen is concentrated on average above ground in the shoots, rather than in the roots, while for phosphorus the mass above and below ground is approximately the same.

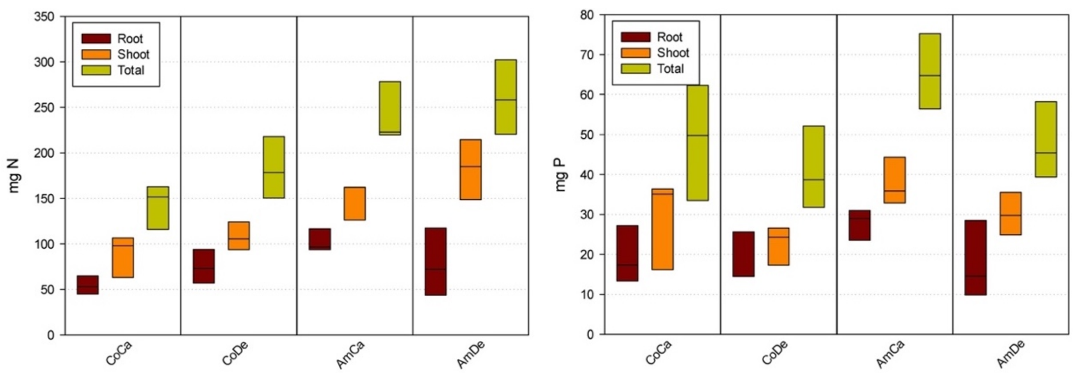
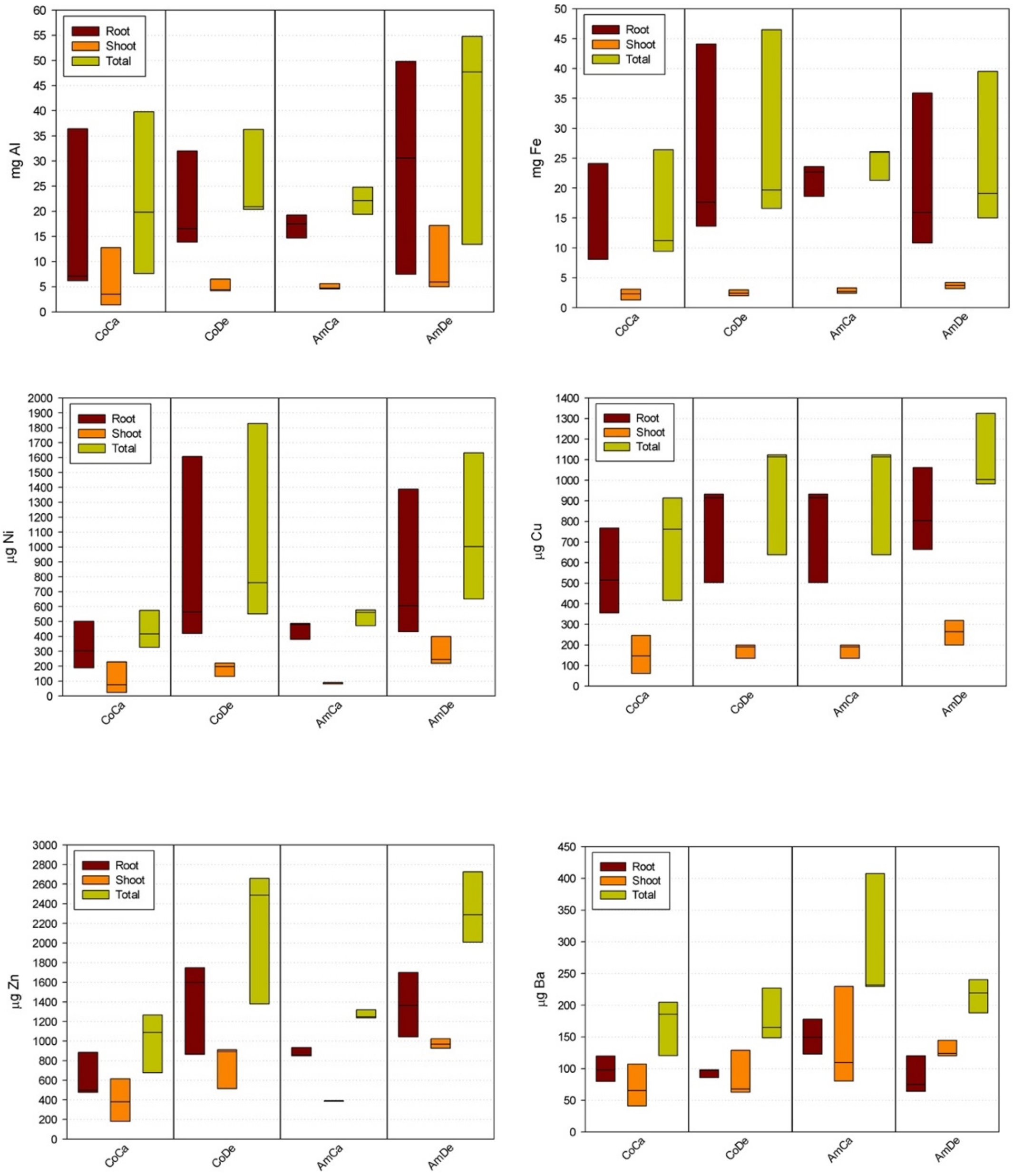


Figure 7-4 Mass of nitrogen in roots, leaves, and in the entire plant. Box plot based on three sample per design, and three replica per plant part.

On the opposite, the two plant species manifest profoundly different behaviours for what concern heavy metals as shown in Figure 7-5. In fact, Deschampsia concentration of Nickel, Copper, Zinc, and Cadmium is statistically higher than in Carex, and the mass of these metals is much higher in roots than in leaves: $p=.003$, $p=.012$, $p<.001$, $p=.002$ for these metals respectively. The difference might be due to the bioaccumulation capacity of Deschampsia (Kucharski et al., 2005), or the larger specific root surface that increase adsorption sites.



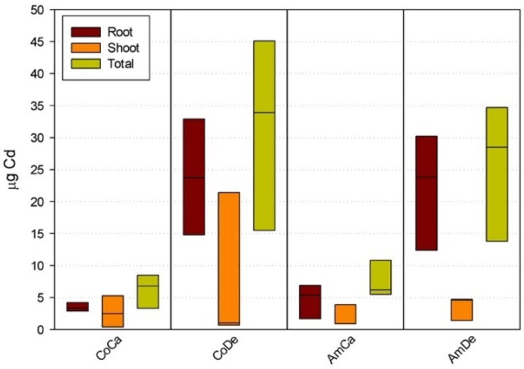


Figure 7-5 mass of heavy metals in roots, leaves, and in the entire plant. CoCa= Control Carex; CoDe= Control Deschampsia; CoNP= Control No-plants; AmCa= Amended Carex; AmDe= Amended Deschampsia; AmNP= Amended No-Plants.

7.4 Vertical pollutant profile

The concentrations of metal and nutrients from the media sampled at different depths after extraction procedure, as illustrated in paragraph 3.5.4.1, are illustrated in Figure 7-6 and Figure 7-7. The charts illustrate the concentration for the four designs at the end of the experiment compared with the medias' concentration used before starting the experiment. No statistical was found between the biofilter with the two different species, however, statistically significant differences were found at the depth of the amended layer (-35.5cm and -40.5cm).

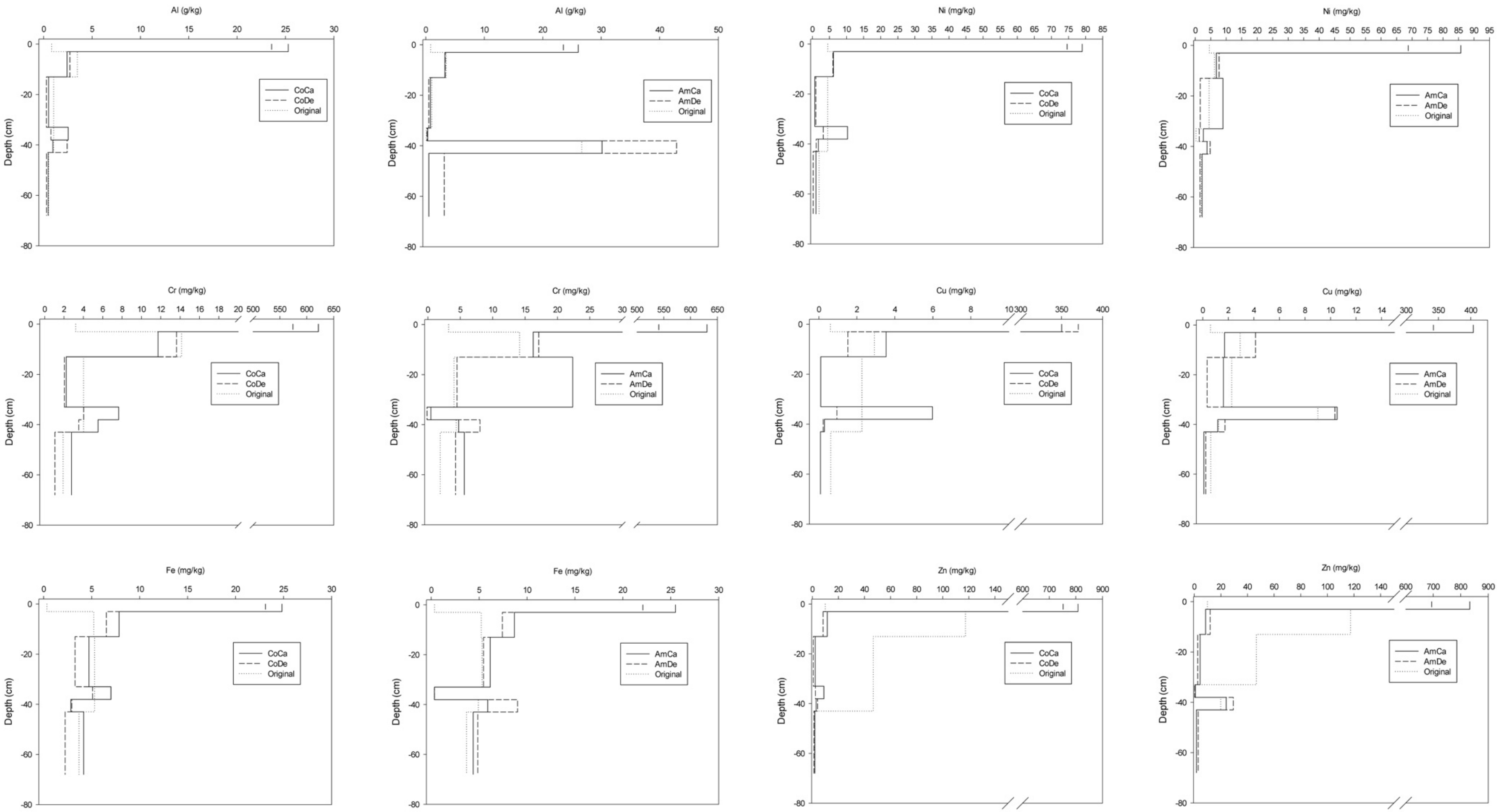


Figure 7-6 Vertical profile of heavy metals concentration for each sampled zone.

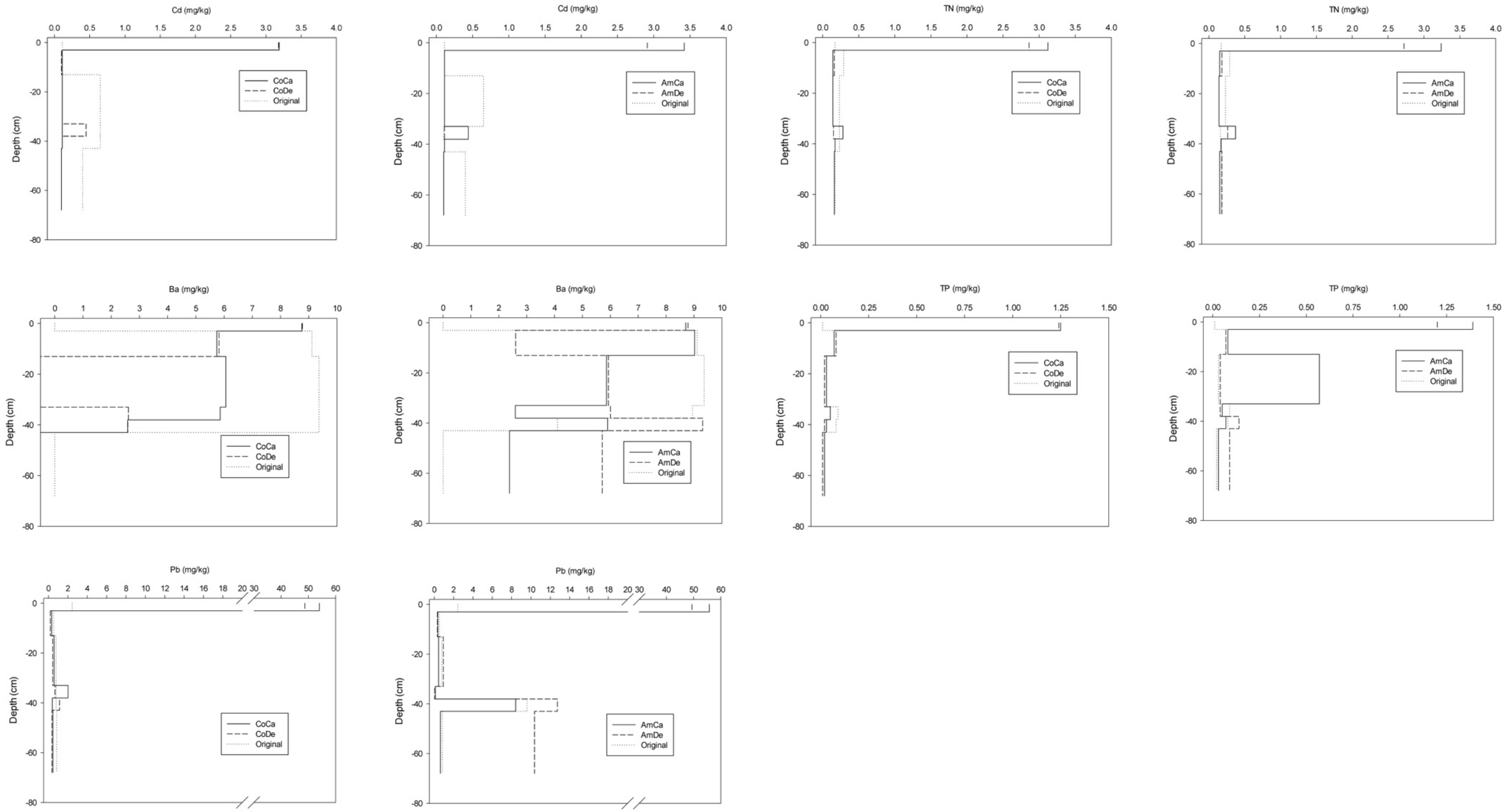


Figure 7-7 Vertical profile of heavy metals and nutrient concentration for each sampled zone.

The data shows that the concentration of heavy metals and nutrients is far higher in the first few centimetres. The lower PSD of the top filter layer is responsible for sediment filtration that accumulate eventually forming a “cake layer” that will, with time, clog the column (Grebel et al., 2013). As suggested in the previous chapter, the clogging effect might be delayed with the introduction of plants (paragraph 4.4.2).

There was no statistically significant difference for the concentration of heavy metals and nutrient for the top layer of the filter containing top soil (i.e. -8cm below ground), however, Zinc’s concentration in the biofilter has been found averagely lower than the unused media at -23cm from the surface: 2.45μg/kg the former and 46.6μg/kg the latter ($p=.044$) (Figure 7-6).

At the depth of 35.5cm below the surface the control design still have sand mixed with vermiculite and perlite (SVP), while amended columns have 5 cm of GAC. At -40cm below the surface, control columns have 5cm more of SVP, while amended columns have 5 cm of Zeolite.

SVP has a lower concentration of Zinc (5.56μg/kg) compared with the original concentration (46.6μg/kg) ($p=.046$), while GAC’s concentration of zinc is not statistically different from the original: 0.52μg/kg and 0.20μg/kg respectively. Copper concentration in activated carbon (10.42μg/kg) is higher than the one in sand (3.47μg/kg), however, this difference is due to the higher concentration of copper in the original media (GAC: 8.99μg/kg SVP: 2.26μg/kg) (Figure 7-6). The content in copper for the two filter media were not statistically different from the original.

Deeper in the column, at -40.5 cm, SVP showed again lower concentration of Zn (3.38μg/kg) compared with the unused media (0.20μg/kg) ($p=.013$), but not for Zeolite ($p=.096$) which concentration do not differ from the original, although after the experiment was slightly higher: 19.83μg/kg and 26.92μg/kg respectively. Copper concentration in SVP were lower than at the beginning of the experiment: 0.20μg/kg and 2.26μg/kg respectively ($p=.040$), while no statistical difference was found for Zeolite: 1.45μg/kg 1.24μg/kg respectively.

The saturation zone, at -68cm, had the same design both for control and amended column. The mix of sand and woodchips used in the saturation zone did not include vermiculite and perlite, affecting Zinc concentration that was lower compared with SVP mix: 1.69μg/kg and 46.6μg/kg respectively. This might suggest that perlite and vermiculite affect the presence of this metal in the column rather than the sand. The concentration of pollutants among designs and between the original unused media was not statistically significant for any metal.

The lower concentration of Zinc in the sand filter media after the experiment, probably due to the wash off from the stormwater, could justify the low to negative removal performances found during the experiment in chapter 6, and the minor presence of SVP in the amended columns could explain why this design experienced a lower leachate.

The Pourbaix chart for Zinc in Figure 7-8 shows that this metal is predominantly in its Zn^{+2} form for pH below 9 and positive potential, and this is in solid state for Eh below the water stability field. In the saturation zone, anoxic condition occurs, characterised by negative potential that could prevent the leachate of zinc.

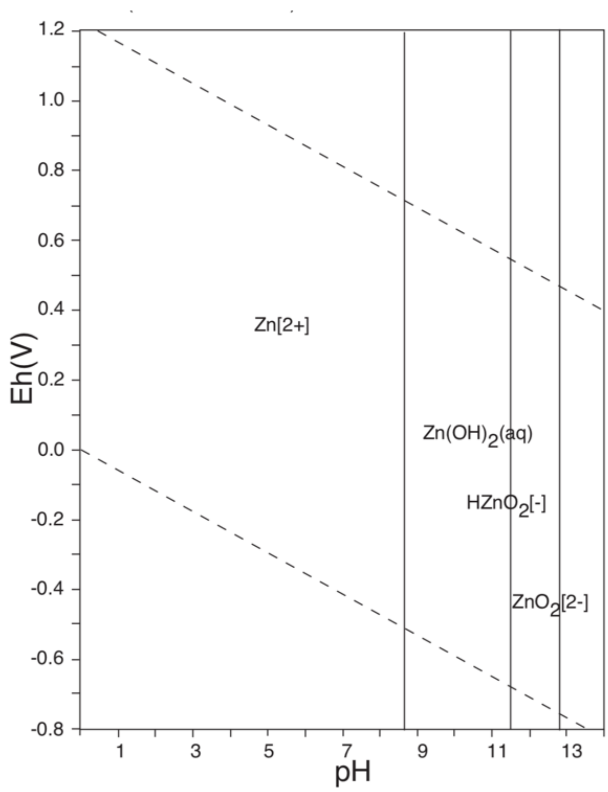


Figure 7-8 Pourbaix field diagram for zinc in water (Takeno, 2005). Between the two dashed line, the water stability field at 298.15K

7.5 Discussion

7.5.1 Implication for maintenance

Deschampsia, the hypertollerant plant chosen for this study, has proven to accumulate more Nickel, Copper, Zinc, and Cadmium than Carex, while the latter has a higher concentration of phosphorus.

The lower concentration of heavy metals in the aerial part of plants make easier and safer the harvesting of nutrient that is more concentrated above ground. The heavy metal rich roots, being buried underground, make less available pollutants that would otherwise be a potential threat to people and wildlife.

The concentration of nutrients and heavy metals in the six depths shown in Figure 7-6 and Figure 7-7 suggests that the gravel protection layer of the filter media is responsible for the highest removal due to the sediment filtration on top of the filter media as found in chapter 6 (Figure 6-15).

The implementation of a gravel layer on top of the biofilter could potentially help the maintenance of the biofilter due its high PSD: fine sediment infiltrate quicker through gravel and sand preventing the dust off operated by wind, limiting the contact with people and wildlife. The high weight of the gravel will also avoid the filter erosion in windy environment, as well as allowing operators to walk safely on the biofilter to operate maintenance.

No differences have been observed for pollutants between the media before and after the experiment, although a statistically significative difference has been noted with the concentration of zinc and copper, that changed by the end of the experiment. The depletion of Zn from the perlite and vermiculite due to weathering could explain the low to negative removal performance for the dissolved part observed during the experiment in Chapter 6. The lower presence of SVP in the amended column could explain the higher removal performance for this metal. Further research is needed in order to validate these results.

7.6 Chapter summary

In this chapter, the data relative to the analysis of plant physical, chemical characteristics, as well as the vertical concentration profile in the biofilter has been presented. The two species differ substantially for specific root surface, and root length, with Deschampsia having a bigger surface and higher metal concentration, and Carex deeper root system and higher concentration of nitrogen. It has been concluded that amendments are not affecting the growth of the two species, in fact, the biomass of plants grown in amendments and bulk roots are statistically higher than the control. Plants tend to accumulate nutrient in the aerial part, while heavy metals are more present in the roots: making easier the harvest of nutrient and less bioavailable the metals.

From the data available for pollutants’ vertical profile it seems that Zinc leached from the sand filter (SVP), explaining the poor removal performance for this pollutant obtained during the previous experiment, however, the presence of a saturation zone could prevent further flush of this metal. Further research is needed to validate these results.

Chapter 8 Discussion

8.1 Chapter overview

This chapter brings together and discuss the results of tests previously described.

8.2 Biofilter media characterisation

Based on the adsorption capacity experiment described in chapter 4, GAC and Zeolite have, on average, twice the adsorption capacity for both nutrient and heavy metals compared with sand and gravel. Vermiculite and perlite have been added in the design due to their ability to increase heavy metal adsorption in biofilters as reported by (Bratieres et al., 2008) and confirmed during this experiment: 43.95μg/g and 25.34 μg/g respectively for Copper (Table 4-2). However, due to the low presence of these two media, 10% by volume as suggested by Bratieres et al., 2008, will likely have a limited impact on the removal but an increase porosity and water holding capacity. TopSoil has the highest adsorption capacity for heavy metals among all the media tested due to the specific adsorption operate by organic matter. However, its adsorption capacity for phosphate is negative, has shown in Table 4-3, and could lower the removal performance. As a form of precaution to prevent leachate, as well as suggested by (Blecken, Zinger, et al., 2007), only 20% by volume have been mixed in the upper layer of the biofilter since the presence of TopSoil is necessary for the initial establishment of plants.

The adsorption capacity of phosphate by white sand has been found lower compared to yellow sand (11μg/g and 23μg/g respectively). White sand has been included in the filter media of non-vegetated biofilters tested in chapter 5 due to the media availability from the provider.

8.3 Phase I: non-vegetated column test

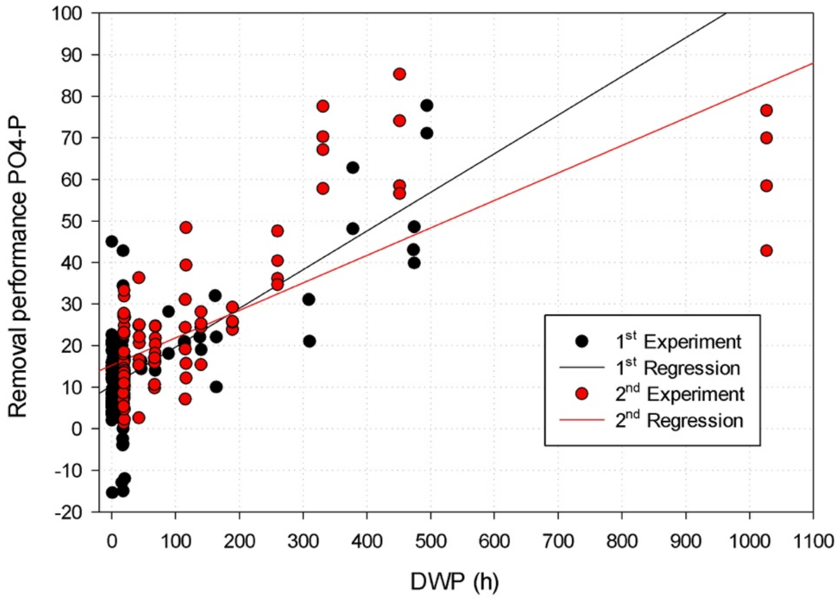
The experiment with non-vegetated biofilter and synthetic stormwater runoff showed a positive but low removal performance of phosphate by every design and an excellent removal performance for dissolved copper, zinc and cadmium (

Table 8-1). Biofilters including only GAC in their design were not as effective in phosphate removal as control and zeolite including biofilters. The non-vegetated column experiment has highlighting a moderate affinity with antecedent dry period and removal performance of PO4-P (Table 8-2).

Table 8-1 Removal performance and hydraulic conductivity for the non-vegetated biofilters and synthetic stormwater runoff (chapter 5). Lowest performing designs are coloured in red, second lowest in orange, second highest yellow and highest in green.

	First experiment				Second experiment			
	Control	Zeo	Gac	Z+GAC	Control	Zeo	Gac	Z+GAC
PO4 (%)	20 ±18 n=26	20 ±12 n=26	6 ±11 n=26	17 ±16 n=26	23 ±18 n=58	27 ±19 n=58	19 ±18 n=58	24 ±19 n=58
Al					-173 ±233 n=58	-168 ±206 n=58	-131 ±175 n=58	-223 ±662 n=58
Fe					-1029 ±3148 n=58	-804 ±2308 n=58	-1256 ±4576 n=58	-972 ±3124 n=58
Ni					6 ±78 n=58	-5 ±204 n=58	21 ±103 n=58	-4 ±133 n=58
Cu	91 ±3 n=26	96 ±1 n=26	97 ±0 n=26	93 ±3 n=26	97 ±5 n=58	97 ±4 n=58	97 ±9 n=58	98 ±1 n=58
Zn	94 ±6 n=26	98 ±1 n=26	97 ±3 n=26	96 ±2 n=26	98 ±1 n=58	99 ±1 n=58	97 ±2 n=58	98 ±2 n=58
Cd					96 ±8 n=58	97 ±0 n=58	97 ±0 n=58	97 ±0 n=58
Ba					28 ±23 n=58	85 ±9 n=58	29 ±19 n=58	85 ±7 n=58
Pb					-26 ±155 n=58	-21 ±81 n=58	-24 ±164 n=58	-8 ±71 n=58
Kw mm/h					3099 ±1752 n=6	1896 ±680 n=6	4307 ±750 n=6	2361 ±477 n=6

Table 8-2 Correlation between phosphate removal performance (%) and DWP in hours.



As many authors have suggested (Mustafa et al., 2004; Hatt, Fletcher, et al., 2007a) dry condition in the unsaturated filter media promotes the formation of ferric oxyhydroxide that bond dissolved phosphorus. The lack of vegetation in the setup have also negatively affected the removal performance of this nutrient since plants have been found to improve the nutrient retention in biofilters (LeFevre et al., 2015). Granular activated carbon is influencing pH of outlet water (7.9 versus 8.1 of control columns) and this might explain the lower phosphate adsorption for this design. Z+GAC design seems not be influenced by this phenomenon possibly due to the lower volume of granular activated carbon used, 5cm vs 10cm, or the buffer zone offered by Zeolite.

Removal performance of dissolved Zinc and Copper exceeded 90% for every design. Biofilters including amendments performed on average higher than the control column: Zeolite removed more Zn and Ba while GAC was more efficient in Cu removal. The adsorption of heavy metal is promoted by the presence of clays (like Vermiculite (Barshad and Kishk, 1969)), organic matter (TopSoil) and higher pH. Other heavy metal monitored during the second experiment described in chapter 5 (aluminium, iron, nickel, cadmium, barium and lead), but not added to the synthetic stormwater runoff, showed a different trend compared to zinc and copper. Cd present a high removal performance with outlet concentration lower than the detection limit of an ICP-MS for every design (0.02 μg/L). Iron and aluminium outlet concentration are generally higher than the inlet (22.5 μg/L) for the four design tested probably due to anaerobic acidic condition of the saturated zone that promoted reducing condition during long dry spell. Barium is well removed by design containing Zeolite (average 11.27 μg/L and 11.38 μg/L for Zeolite and Z+GAC respectively), while control and GAC only containing biofilters reduce in time their capacity to remove this dissolved metal from the runoff (52.65 μg/L and 51.52 μg/L respectively). Lead and nickel leach from the biofilters although the outlet concentrations do not statistically differ among design and inlet water.

Phosphate concentration in outlet water is lower than inlet runoff for control and designs that include Zeolite. Biofilters containing only GAC were leaching phosphate in some occasion, possibly determined by the increased value of pH. The data shows that biofilters can manage high concentration of heavy metals added to stormwater runoff, zinc and copper, for the entire duration of the experiment with no influence from ADWP or high hydraulic conductivity.

During this set of tests it has been found indispensable to take into consideration ADWP and the inclusion of vegetation in order to simulate more accurately biofilters for a more realistic removal performance evaluation.

The hydraulic conductivity estimated using the constant head test described in chapter 3 (1337mm/h on average) was lower than the hydraulic conductivity calculated during the experiment with non-vegetated biofilters (2577mm/h on average). K_w of biofilters did not change significantly across the experiment due to the absence of suspended solids in the synthetic stormwater runoff used. However, variability has been noticed probably caused by the saturation level of the columns and the migration of small particles. Fraction D has been removed from the design for the following experiment in greenhouse to prevent fine particles to clog the columns to a deep level that can result in an increase in maintenance cost.

8.4 Phase II: vegetated column test & fate of pollutants in biofiltration system

The use of vegetated biofilters including a bigger fraction of sand (0.6-1.18mm) and higher hydraulic conductivity (K_w>3000mm/h) has not compromised the removal performance of nutrients, heavy metals and TSS. The K_w of the six design tested (CoCa, CoDe, CoNP, AmCa, AmDe and AmNP in Table 8-3) is plant-specific: biofilters including Carex flacca maintained high value of hydraulic conductivity compared with those planted with Deschampsia cespitosa and non-vegetated. In fact, the accumulation of sediment over time by the latter significantly dropped the flow through the columns, from 1868mm/h to 78mm/h of CoNP and from 1021 mm/h to 45 mm/h of AmNP, showing sign of clogging.

Table 8-3 Hydraulic conductivity for the vegetated biofilters and semi-synthetic stormwater runoff (chapter 6). Lowest performing designs are coloured in red, second lowest in orange, second highest yellow and highest in green.

	CoCa	CoDe	CoNP	AmCa	AmDe	AmNP
Kw mm/h	2973 ±810 n=18	2840 ±970 n=18	1224 ±689 n=18	2882 ±784 n=18	2663 ±1206 n=18	314 ±430 n=18

Moisture retention in biofilters, monitored by sensors 5-TM, highlighted the risk of failure for non-vegetated biofilter which moisture increased over time (Table 8-4). Over time the lack of water retention capacity can results in poor removal performance due to an increase in overflows. The accumulation of sediments on the top layer of the biofilter is responsible for the decrease in infiltration capacity of biofilters. Kandra et al., 2015 suggests that biological films growing in the filter could also cause a decrease in flow speed (Kandra, Callaghan, et al., 2015), nonetheless, it was not possible with this experimental setup to test this hypothesis. Vegetated biofilters are less affected by these phenomena due to roots growth through the media that maintain the infiltration capacity. Especially Carex flacca which shoots growth from below ground displace sand, gravel and fine sediment creating infiltration path for the polluted runoff.

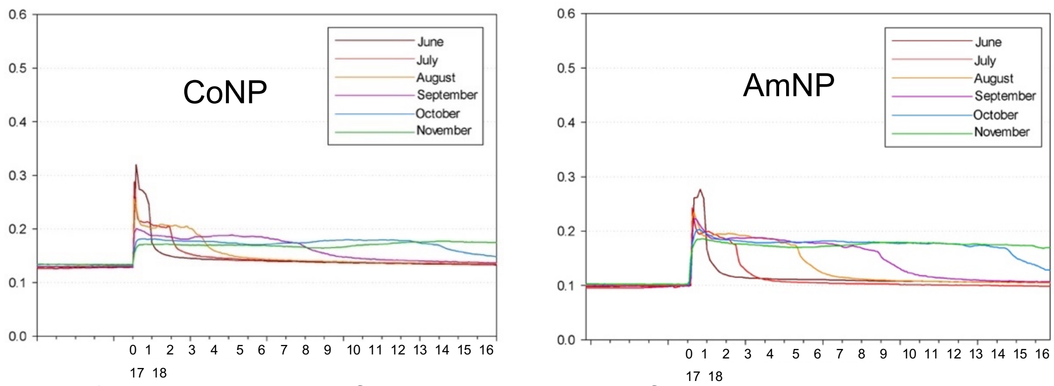


Table 8-4 Water content from June to August for the six months experiment for non-vegetated biofilters. On the ordinate the water content θ (cm^3 of water/cm^3 of soil); on the abscissa the hours from the start of a dosing event. CoNP= Control No-plants; AmNP= Amended No-Plants.

The use of a coarser sand (without fraction D and C) and vegetation in biofilters did not compromise the removal performance of suspended solids that was higher than 98% for every design, although amendments slightly impact the removal of solids (99.34% for control biofilters versus 98.96% of amended biofilters) (Table 8-5).

Table 8-5 Removal performance for suspended and dissolved solids for vegetated biofilters and semi-synthetic stormwater runoff (chapter 6). Lowest performing designs are coloured in red, second lowest in orange, second highest yellow and highest in green.

	CoCa	CoDe	CoNP	AmCa	AmDe	AmNP
TSS	99 ±1 n=60	100 ±3 n=60	99 ±1 n=24	98 ±3 n=60	99 ±1 n=60	98 ±1 n=24
TDS	21 ±31 n=60	22 ±31 n=60	16 ±35 n=24	17 ±32 n=60	24 ±26 n=60	24 ±25 n=24
DOC	-48 ±130 n=60	-30 ±88 n=60	8 ±65 n=24	-8 ±113 n=60	26 ±68 n=60	50 ±53 n=24
DIC	-23 ±29 n=60	-27 ±32 n=60	28 ±18 n=24	-51 ±34 n=60	-51 ±32 n=60	12 ±21 n=24

Pollutant accumulation test showed that most of the pollutants accumulate in the first few centimetres between gravel and filter layer due to filtration and decantation processes. Fine sediment infiltrate quicker through gravel preventing dust off operated by wind and limiting the contact with people and wildlife. The high weight of the gravel also avoids filter erosion in windy environment as well as allowing operators to walk safely on the biofilter to operate maintenance without incurring in filter media compaction.

Due to the high affinity between solids and pollutants the removal performance for total heavy metal was higher than 90% for all biofilters. Amended designs were found more efficient in the removal of copper and barium, control biofilters were more efficiently removing iron, while for the other heavy metals no significative differences were found among designs (Table 8-6).

Table 8-6 Removal performance of total heavy metals for vegetated biofilters and semi-synthetic stormwater runoff (chapter 6). Lowest performing designs are coloured in red, second lowest in orange, second highest yellow and highest in green.

		CoCa	CoDe	CoNP	AmCa	AmDe	AmNP
Total HM (%)	Al	100 ±2 n=60	100 ±1 n=60	100 ±0 n=24	99 ±1 n=60	100 ±1 n=60	100 ±0 n=24
	Cr	97 ±3 n=60	96 ±6 n=60	97 ±5 n=24	97 ±3 n=60	97 ±3 n=60	98 ±2 n=24
	Fe	93 ±7 n=60	95 ±4 n=60	98 ±2 n=24	80 ±15 n=60	90 ±13 n=60	86 ±11 n=24
	Ni	93 ±6 n=60	92 ±6 n=60	95 ±2 n=24	94 ±4 n=60	96 ±4 n=60	95 ±2 n=24
	Cu	92 ±4 n=60	85 ±44 n=60	93 ±5 n=24	96 ±2 n=60	94 ±4 n=60	96 ±3 n=24
	Zn	85 ±8 n=60	81 ±10 n=60	71 ±12 n=24	83 ±10 n=60	85 ±11 n=60	69 ±14 n=24
	Cd	97 ±1 n=60	97 ±2 n=60	98 ±1 n=24	98 ±2 n=60	98 ±1 n=60	98 ±1 n=24
	Ba	53 ±14 n=60	53 ±14 n=60	69 ±9 n=24	79 ±7 n=60	80 ±7 n=60	84 ±6 n=24
	Pb	99 ±1 n=60	99 ±1 n=60	100 ±0 n=24	99 ±1 n=60	99 ±0 n=60	100 ±0 n=24

Laser diffraction results (Figure 6-16) suggest that Zeolite and GAC, rich in iron oxides, were a source of fine sediment displaced by plant roots possibly explaining the higher concentration of this metal in the outlet and the small suspended solids treatment difference with control.

Dissolved heavy metals efficiency was higher in amended biofilters for aluminium, copper, zinc, cadmium, lead and barium. Dissolved zinc removal was lower to negative, especially for non-vegetated design, compared with previous biofilter tested with synthetic stormwater runoff possibly due to the different mix of pollutants in the runoff used (Table 8-7).

Table 8-7 Removal performance of dissolved heavy metals for vegetated biofilters and semi-synthetic stormwater runoff (chapter 6). Lowest performing designs are coloured in red, second lowest in orange, second highest yellow and highest in green

		CoCa	CoDe	CoNP	AmCa	AmDe	AmNP
Dissolved HM (%)	Al	74 ±17 n=30	67 ±47 n=30	85 ±13 n=12	82 ±14 n=30	82 ±13 n=30	39 ±184 n=12
	Cr	91 ±5 n=30	92 ±2 n=30	95 ±1 n=12	92 ±2 n=30	92 ±2 n=30	95 ±1 n=12
	Fe	-510 ±1581 n=60	-41 ±81 n=60	32 ±26 n=24	-9506 ±1398 n=60	-2371 ±6738 n=60	-453 ±929 n=24
	Ni	91 ±8 n=60	90 ±9 n=60	93 ±5 n=24	91 ±7 n=60	94 ±6 n=60	94 ±2 n=24
	Cu	-10 ±79 n=60	-54 ±111 n=60	-35 ±93 n=24	74 ±24 n=60	30 ±83 n=60	68 ±48 n=24
	Zn	1 ±47 n=60	-16 ±45 n=60	-101 ±79 n=24	10 ±119 n=60	11 ±58 n=60	-83 ±80 n=24
	Cd	74 ±58 n=60	68 ±41 n=60	73 ±28 n=24	89 ±27 n=60	85 ±16 n=60	89 ±11 n=24
	Ba	3 ±22 n=60	2 ±23 n=60	34 ±13 n=24	54 ±12 n=60	55 ±14 n=60	65 ±11 n=24
	Pb	-2 ±76 n=60	-19 ±84 n=60	54 ±14 n=24	32 ±16 n=60	16 ±67 n=60	64 ±9 n=24

Metal analysis at different biofilters' depth showed that vermiculite and perlite weathering might be responsible for the increase concentration in outlet water of this heavy metal. Amendments higher dissolved copper removal performances might be associated with the capacity of GAC to adsorb DOC through chemical adsorption (H-bonding and Van der Waals forces) and a high specific surface (Sounthararajah et al., 2015). Lower concentration of DOC in outlet water can be an advantage due to its affinity with heavy metals. In fact, organic matter in the form of humic materials is an effective mechanism for copper removal (Bradl, 2004). During summer months higher temperatures can promote microbial activity, mineralisation and decomposition processes of colloids and humic acids, resulting in the oxidation of DOC and a higher concentration of DIC due to respiratory activity. GAC and Zeolite thanks to a higher specific surface than sand and gravel (Table 4-1) promote a denser microbial community explaining the higher concentration of DIC and lower concentration of DOC (Table 8-5). A Spearman's rank-order test showed a weak positive relationship between dissolved copper and DOC concentration (r_s=+0.375) supporting the hypothesis that GAC is beneficial for the removal of dissolved copper in runoff. No differences in removal performances were found among designs for nickel and chrome, however control columns were more efficient for iron. As experienced with synthetic stormwater runoff used in experiment described in chapter 5, amended columns were leaching more dissolved iron than control (Figure 5-5). A hypothesis is that roots reached the amendments and freed iron bonded in GAC and Zeolite changing the pH with roots exudates. Yellow iron rich sand in the saturation zone might free Fe^{2+} due to anaerobic condition characterised by a lower E_h and low pH. The use of white sand poor in iron oxide in the saturation zone could prevent the mobilisation of iron that occurs also in control designs.

Although the presence of plants does not generally impact significantly the removal performance of heavy metals, the absence of vegetation is detrimental for biofilters longevity and multi ecosystem service delivery. In fact, plants growth is responsible for maintaining hydraulic conductivity, regenerating biofilters' water retention capacity through evapotranspiration, increase removal performance of heavy metals (i.e. Deschampsia for dissolved zinc) and regenerating the filter capacity to adsorb metals and nutrients.

The presence of plants, yellow sand and an average dry weather period between dosing events increased the average removal performance for dissolved phosphorus from an average 30% to 90%. According to the data (

Table 8-8) amendments are marginally increasing the removal performance of TP.

Table 8-8 Removal performance of nutrients for vegetated biofilters and semi-synthetic stormwater runoff (chapter 6). Lowest performing designs are coloured in red, second lowest in orange, second highest yellow and highest in green

		CoCa	CoDe	CoNP	AmCa	AmDe	AmNP
Nutrients	TN	78 ±10 n=60	80 ±13 n=60	75 ±14 n=24	93 ±10 n=60	95 ±7 n=60	95 ±4 n=24
	TDN	72 ±11 n=60	72 ±18 n=60	67 ±19 n=24	93 ±8 n=60	94 ±6 n=60	94 ±5 n=24
	NH4	53 ±35 n=45	62 ±25 n=45	61 ±24 n=18	71 ±19 n=45	76 ±18 n=45	66 ±19 n=18
	NOx	77 ±12 n=45	84 ±8 n=45	74 ±13 n=18	93 ±9 n=45	94 ±6 n=45	95 ±5 n=18
	TP	96 ±4 n=60	96 ±4 n=60	94 ±6 n=24	93 ±21 n=60	96 ±4 n=60	96 ±4 n=24
	PO4 (%)	95 ±6 n=45	95 ±7 n=45	93 ±9 n=18	97 ±5 n=45	96 ±5 n=45	98 ±2 n=18

A decrease in performance has been observed during autumn probably due to the decrease active adsorption sites, repartition, colder environmental condition that lead to lower biological uptake. NH_4-N removal seems also to be affected by colder temperatures, probably due to a lower rate of decomposition processes mineralizing nitrogen into ammonia through ammonification. Nitrogen removal performance is higher in amended columns due to adsorption, chelation and substitution of ammonia. *Deschampsia cespitosa* removed more NOx compared with *Carex appressa* suggesting that fine root system prevent oxygen diffusion that might limit denitrification. The different removal performances for NOx of non-vegetated biofilters, with control having an overall lower removal performance than amended columns (74% and 95% respectively), could be attributed to the presence of a richer microbial community hosted by media with a higher surface per gram and a higher adsorption capacity. Harvested plants showed higher concentration of nutrient aboveground while metals were accumulated in roots preventing the interaction with people and wildlife. Especially Deschampsia, the hypertollerant plant, accumulated more nickel, copper, zinc and cadmium compared with Carex that accumulated more nitrogen. Vegetation grown in amended biofilters were characterised by a higher biomass and bulk roots, suggesting that GAC and Zeolite have a positive impact on plants stimulating root growth (Table 8-9).

Table 8-9 Vegetation parameters collected after the end of the dosing period. Lowest performing designs are coloured in red, second lowest in orange, second highest yellow and highest in green

	CoCa	CoDe	CoNP	AmCa	AmDe	AmNP
Shoot surface cm^2	1597 ±466 n=3	1215 ±320 n=3		1690 ±400 n=3	2027 ±229 n=3	
Root surface cm^2	2309 ±286 n=3	3529 ±1023 n=3		3085 ±1319 n=3	3179 ±693 n=3	
Root mass (g)	9 ±2 n=3	10 ±2 n=3		14 ±2 n=3	9 ±3 n=3	
Shoot mass (g)	7 ±3 n=3	8 ±2 n=3		9 ±2 n=3	12 ±2 n=3	
Plant mass (g)	17 ±4 n=3	18 ±4 n=3		23 ±4 n=3	21 ±3 n=3	

The two species differ substantially for specific root surface, and root length, with Deschampsia having a bigger surface and higher metal concentration, and Carex deeper root system and higher concentration of nitrogen. It has been concluded that amendments are not affecting the growth of the two species, in fact, the biomass of plants grown in amendments and bulk roots are statistically higher than the control. Vegetation seems to use amendments as resource of water and nutrients, possibly increasing the resistance to drought. This is especially evident in a plant of Carex in Figure 8-1 where a mass of roots developed where GAC and Zeolite amendments were located.

Figure 8-1 Picture of Carex flacca taken after being harvested and washed. In the red box the agglomeration of roots that have developed through the amendments.

8.5 Chapter summary

The presence of vegetation has been found indispensable to insure constant hydraulic conductivity, regenerating biofilter's water holding capacity and regenerating pollutant control as highlighted by the vegetation/soil analysis.

Dissolved oxygen low outlet concentration due to microbial activity could cause hypoxia in receptive body. A splash area should be implemented to considerably re-oxygenate outlet water increasing water quality.

Non-planted columns perform significantly worse than planted columns, with Carex maintaining a higher infiltration rate than Deschampsia and lower moisture content. The propagation of the plant, coupled with its ticker root system, displace media creating channels for water infiltration. In a full scale biofilter is advisable to populate the area close to the inlet with sturdy bushy plants with a tick root system to prevent clogging and reduce the flow thus distributing more efficiently the suspended load.

Zeolite and GAC are increasing the removal performance of dissolved pollutants and would should be used in heavy metals polluted sites. The combination of plants prevents hydraulic conductivity to drop too fast and to accumulate heavy metals under the surface of the biofilter. The leachate of iron should be addressed either introducing a lower iron rich sand in the saturation zone or pre-washing the media before use in order to remove the smallest particles. To assess the removal performance of this design on other pollutants (i.e. PAH) and to address the evolution of performance over time future research should focus on monitoring a full scale biofilter managing stormwater runoff from a real car park.

Chapter 9 Conclusions

9.1 Chapter overview

This chapter collects the findings of the project and relates them to the objective and aims of this research. It also addresses limitations, suggestions and key findings are here reported. Finally, the chapter ends with recommendations and future research needs identified by this study.

9.2 Conclusions

The effects that media amendments, plant species and high hydraulic conductivity have on the removal performance of pollutants and plant growth have been assessed through two distinctive column experiments of stormwater biofilter

Preliminary physical-chemical and hydraulic property test on selected media aimed at characterising media to include in a biofilter design. Particle size distribution test indicated that the media chosen for the design of biofilters used in this study are not preventing the growth of plant roots. The presence of iron oxide analysed with XRF analysis has been shown to be important for phosphate removal. The higher volume of this oxide in amendments and yellow sand showed the potential that these media have to adsorb more phosphorus. An adsorption test highlighted the metal adsorption capacity of Zeolite and GAC compared with sand, potentially increasing the lifespan of a biofilter. Despite leaching phosphate, organic matter is important to sustain plants in their initial establishment. The smaller particle size distribution and water holding capacity of topsoil influence the hydraulic conductivity of the filter media, with higher values for lower organic content filters.

Experiments with non-vegetated columns and synthetic stormwater runoff aimed at selecting the biofilters design to test in greenhouse with vegetated columns. Non-vegetated columns showed poor phosphate removal performances that were correlating with short dry weather period between two events. The low content of clay and silica in the of white sand and a low ADWP affected negatively the presence of aluminium and iron oxides responsible for phosphate adsorption. Dissolved copper and zinc treatment were higher than 90%, but export was observed for low inlet concentration of iron from the saturation zone probably due to reducing acidic condition in the saturation zone. Although no sediments have been added to the inlet water, variability of the hydraulic conductivity was observed highlighting the possibility that fine particulate matter and biofilm were affecting the water path and saturated condition were not met. The results obtained in phase I informed the design that underwent the second phase of this study that included vegetation in the design.

During the second phase of this study, vegetated columns were dosed for 6 months using synthetic stormwater that included particle matter. Based on experiment in phase one, yellow sand was used to address the low removal performance of phosphate. Although removal of particulate bound metals was generally higher than 90% for all designs, leachate from the media was observed for dissolved Cu and Zn particularly for control and non-planted designs. Amended biofilters' treatment for TDN, PO4-P, Zn, Cu, and Ba were generally higher than control. Non-planted designs treated the least thereby confirming the positive influence of plants. While TDS removal was averagely low, TSS were well treated by all designs reaching treatment performances higher than 98%. Laser diffraction analysis showed how plants growth can displace the media increasing particulate matter in the outlet, particularly for amended vegetated design. The presence of Zeolite and GAC impacted the transformation of DOC, increasing DIC concentration in the water. A positive correlation between DOC and Cu was observed, explaining the higher removal of copper from the biofilter containing amendments. Low dissolved oxygen in outlet water was a sign that the saturation zone was in anaerobic condition, and this can have a negative effect on receiving water. Although plants were not playing a significant role in the treatment of pollutants, hydraulic conductivity and moisture content were influenced by root architecture of distinct species. *Carex flacca* was characterised by thicker, deeper, and faster root growth that helped maintaining high hydraulic conductivity and low water content in the column compared with *Deschampsia cespitosa*. The hydraulic conductivity of non-vegetated column dropped quickly due to the accumulation of sediment at the top of the column, resulting also in higher water content for longer time.

At the end of the 6 months experiments 12 biofilters were disassembled to investigate the fate of pollutants in the media and in the plants. Plants grown in amended biofilters had a higher biomass than control, suggesting that Zeolite and GAC are not only increasing the performance, but also promoting plant growth. Pollutants were accumulated in different part of the plants:

nutrients in leaves and heavy metals in roots. *Deschampsia cespitosa* manifest hypertollerant traits, accumulating more Ni, Cu, Zn, and Cd than *Carex flacca*. The vertical profile of heavy metals showed a higher concentration of heavy metals and nutrients in the protection layer due to the accumulation of sediment in this area. The concentration of pollutants tend to drop after the first layer. Lower Zn concentration in the sand after the experiment suggested export from this media, thus explaining the lower removal performance for this metal in the previous experiment.

9.3 Summary of findings

- Biofilter water quality is better than stormwater runoff, concluding that the retrofitting of this system is always beneficial.
- AWDP impacts phosphorus adsorption. Longer dry periods promote the formation of iron oxyhydroxide that efficiently adsorb phosphorus.
- Yellow sand has twice the phosphorus adsorption capacity of white sand, increasing significantly the removal performance of this nutrient
- Amendments have a higher removal performance for Zn, Cu, Cd, Ba, TDN, PO4-P.
- Although plants were not contributing as much as the media in the adsorption of pollutants, small roots from Deschampsia displace less media, increasing anaerobic pockets in the biofilter, leading to a more efficient denitrification in control columns.
- The higher temperature of summer promotes the mineralization of ammonia to nitrate increasing the removal of NOx.
- Removal performance for NH_4-N are higher in autumn. This could be due to the colder temperature that limited the decomposition processes mineralizing nitrogen into ammonia through ammonification
- Hydraulic conductivity changes over time due to the accumulation of sediment, however plants play a vital role in preserving it. *Carex flacca* is indicated for areas that have a high concentration of TSS, and should be planted in depressed areas that deposit more particulate matter.
- Non-vegetated columns have lower performances and clog over time faster as shown by moisture content sensors and K_w test.

- The chosen plants are particularly resistant to high hydraulic stress, moisture changes and diseases. Carex showed sign of necrosis due to the position and the narrow column that accommodate the plant, but survived to the 6-months test.
- The inclusion of moisture sensors in the biofilter can help identify maintenance needs of a green area. Especially when water content is too high for too long.
- Perlite and vermiculite show sign of zinc leachate, affecting the removal performance of vegetated column test.
- Amendments do not harm plants: species grown in Zeolite and GAC have a higher biomass than the one grown in control columns.
- *Deschampsia* accumulates more heavy metals in roots than *Carex.*
- *Carex* accumulates more nitrogen than *Deschampsia.* Since nutrient concentration is higher in aerial parts, the recovery of TN and TP can be easily achieved cutting shoots.
- Gravel protection layer trap sediments above the filter media, showing higher concentration of nutrients and heavy metals compared with deeper layers. Gravel protects the biofilter from erosion without preventing plants to germinate or to grow through. Maintenance of the biofilter is assisted since walking on gravel is easier.

9.4 Strength, limitations and future works

Limited studies have tested amendments to improve the treatment performance in biofilters (Erickson et al., 2012; Grebel et al., 2013; Glaister et al., 2014). However, most of these researches do not consider the impact that amendments have on vegetation. Guidelines advise against the use of high hydraulic conductivity to ensure plant survival and adequate treatment performances (Payne et al., 2015; Woods-Ballard et al., 2015). Nonetheless, the limited amount of space in cities requires biofilters with a smaller footprint that retain treatment capacity without overflowing. Plants used in phytoremediation could potentially enhance the removal performance of pollutants from water and soil, however these have hardly been implemented in biofilters (Muerdter et al., 2018). It is then necessary to investigate the effects that amendments, high hydraulic conductivity, and hypertollerant plants have on biofilters.

This project organised the first facility to investigate biofilters in Leeds University. The tests were undertaken in laboratory using mesocosms that reduced the complexity of a field scale experiment. However, these limits the environmental variables such as wind, presence of earth macroinvertebrates and other organisms and the complexity of runoff that might change over time (i.e. salt addition during winter). Future laboratory work should be undertaken in an environment chamber to control more accurately solar radiation, temperature, wind and relative humidity using automated watering system to simulate exactly real AWDP.

Plant species were investigated in separate columns limiting the observation of their interaction. Biofilters in full scale setup are often planted with 8-12 plants/m^2 (Payne et al., 2015). One of the two species involved in this study could dominate the other limiting the biodiversity and the performance of the biofilter. Future studies should focus on the interaction of the two and investigates more autochthone plant species for their contribution on removal performance.

The use of synthetic/semi-synthetic stormwater runoff and laboratory mesocosms is a consolidate practice. A field experiment could provide data on the interaction with organic and emerging pollutants, as well as more representative data on evapotranspiration. Although microplastics were found in the inlet (Figure 3-6), it was not possible to assess them due to resource limitation. Future research should include this emerging pollutant to assess the reliability of biofilters.

This work observed the seasonality effects on the removal of some pollutants, and a reduced hydraulic conductivity within the time for several of the designs. A longer experimental period could help determine whether winter and spring condition induce a different behaviour as well as the evolution of hydraulic conductivity, and it could assess the contribution of plants in a mature biofilter.

For some heavy metals, the removal performance change according to soil pH and Eh. The use of dissolved oxygen, pH, and redox potential sensors in a biofilter could help identify a correlation between soil moisture, and adsorption capacity, therefore predict the treatment of heavy metals and nutrients.

Using Perspex column enabled monitoring the evolution of roots but a more sophisticated approach, for instance X-Ray computed tomography, or improved image software (WhinRhizo) could be used to acquire data of water flow path, and have a better understanding of the interaction between plants and media.

Amendments have the potential to increase removal performance and lifespan of biofilters without side effects on vegetation or hydraulic conductivity. Increasing the thickness of the amendment layer, or reducing it, could bring different outcomes. It is suggested that future work on the subject should assess the minimal/maximum thickness of this layer.

The inclusion of open-source hardware (i.e. Arduino, Raspberry Pi) could be used to constantly monitor the biofilter status, remotely share data for maintenance, or empty the saturation zone to accommodate more water before a forecasted weather alert for a better flood control system.

9.5 Key findings

Biofilters are an efficient technology to intercept water at source lowering the risk of floods, controlling water quality before discharging in water bodies or to water treatment plants, and increase biodiversity.

It was the first time that biofilters with high hydraulic conductivity were amended with layers of Zeolite and GAC and tested with plants. Data collected during the project concluded that amendments can prolong the lifespan of a biofilter, enhancing treatment without harming plants. High hydraulic conductivity was not affecting removal performances or treating the survival of plants, thus opening the possibility to reduce the biofilter area to catchment ratio. Low dissolved oxygen is a potential threat to the ecosystem; therefore, a splash area should be installed to re-oxygenate the water before discharging in a water body. The presence of gravel as protection layer can help to access the biofilter for maintenance without disturbing the filter media and the high granulometry of gravel allows also an easy recover of particulate matter. The inclusion of sensors in the biofilter is suggested to constantly monitor the water content and intervene promptly removing the clogged layer when moisture content remains too high for too long. *Carex* and *Deschampsia* showed to be drought, flood, and pest resistant. Practitioner should include a mix of thick root and fine roots species to maintain hydraulic conductivity for longer. Hypertollerant species accumulate a higher concentration of heavy metals in their root rather than transporting on their leaves. This might regenerate the filter in the long term increasing the overall lifespan of the biofilter. Pollutants accumulate in the first few centimetres of the biofilter, confirming other studies that showed how scraping the top 10cm can restore the capacity of the biofilter for more than 30 years.

This study provide data that confirm the positive contribution that amendments have on biofilter performance and vegetation biomass of plants. The high hydraulic conductivity is not compromising vegetation health and removal performance allowing for a more compact footprint of the system.

Chapter 10 References

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Chapter 11 Appendix

11.1 Appendix 1

Table 11-1 Concentration of pollutants from urban areas

Urban and residential

		Cu (ug/L)			Zn (ug/L)			Pb (ug/L)				
Site	Site	Mean	min	max	Mean	min	max	Mean	min	max	More info	Source
Pedestrian and cycle way, yard		23			585			107			Total	Göbel et al. (2007)
Residential roads	European data	11.5	6	17	118.5	87	150	73	6	140	Dissolved	Lundy et al. (2012)
Suburban roads	European data	65	10	120	960	20	1900	225	10	440	Dissolved	Lundy et al. (2012)
Ultra-urban	Mount Rainer, Md.	110			1180			220			Dissolved	Flint et al. (2007)
Urban	Millcreek, Ohio	94.8	13	279	4054.4	209	14786	16	13	21	Dissolved	Sansalone and Buchberger (1997)
Urban	Millcreek, Ohio	135	43	325	4274	459	15244	64.4	31	97	Total	Sansalone and Buchberger (1997)

		TSS				
Site	Site	Mean	min	max		
Pedestrian and cycle way, yard	Northern European	7.4			Total	Göbel et al. (2007)
Urban roads	European data	2705.5	11	5400	Dissolved	Lundy et al. (2012)
Residential roads high density	European data	811.5	55	1568	Dissolved	Lundy et al. (2012)
Residential roads low density	European data	155	10	300	Dissolved	Lundy et al. (2012)

Parking lot

		Cu (ug/L)			Zn (ug/L)			Pb (ug/L)				
Site	Site	Mean	min	max	Mean	min	max	Mean	min	max		
Car parks and commercial areas	European data	103	1	205	350.5	1	700	5.5	1	10	Dissolved	Lundy et al. (2012)
Carpark	Lund, Sweden										Dissolved	Deletic and Makisimovic (1998)
Parking areas	Birmingham, Alabama	11.00	1.10	61.00	86.00	6.00	560.00	2.10	1.20	5.20	Dissolved	Pitt et al. 1995
Parking lot	Review/global	11.8	2.7	35	77.2	12	317	4.3	1	15.9	Dissolved	Huber et al. (2016)
Storage areas	Birmingham, Alabama	250.00	1.00	1520.00	22.00	3.00	100.00	2.60	1.60	5.70	Dissolved	Pitt et al. 1995
Vehicle service areas	Birmingham, Alabama	8.40	1.10	24.00	73.00	11.00	230.00	2.40	1.40	3.40	Dissolved	Pitt et al. 1995
Parking lot	Review/global	40.7	5	220	201	39	620	23.1	2.5	66	Total	Huber et al. (2016)
Car park		80			400			137			Total	Göbel et al. (2007)

		TSS				
Site	Site	Mean	min	max		
Car parks and commercial areas	European data	138.9	7.8	270	Total	Lundy et al. (2012)
Carpark	Lund, Sweden		5	417	Total	Deletic and Makisim(
Parking areas	Birmingham, Alabama	110.00	9.00	750.00	Total	Pitt et al. 1995
Storage areas	Birmingham, Alabama	100.00	5.00	450.00	Total	Pitt et al. 1995
Vehicle service areas	Birmingham, Alabama	24.00	17.00	38.00	Total	Pitt et al. 1995

Highway

Site	Site	Cu (ug/L) Mean	min	max	Zn (ug/L) Mean	min	max	Pb (ug/L) Mean	min	max		
Highway low density	Review/global	23.3	5.7	64	76.9	5	191	1.3	0.01	3.1	Dissolved	Huber et al. (2016)
Highway high density, non urban	Review/global	34.6	4	100	204	8.6	577	12.8	12.8	12.8	Dissolved	Huber et al. (2016)
Highway high density, urban	Review/global	35.5	4.1	151	217	11	2118	3	0.8	7.4	Dissolved	Huber et al. (2016)
Highway	Weins, Germany	49			441			137			Dissolved	Stotz and Krauth (1994)
Highway	Weins, Germany	88			737			58			Dissolved	Stotz and Krauth (1994)
Highway low density	Review/global	60.7	13.3	140	306	32.3	1760	64.4	2.5	230	Total	Huber et al. (2016)
Highway high density, non urban	Review/global	84.4	23	430	385	52.5	2210	31.7	4.4	90	Total	Huber et al. (2016)
Highway high density, urban	Review/global	63.5	13	274	338	21	2234	33.1	1.4	220	Total	Huber et al. (2016)
Service road		86			400			137			Total	Göbel et al. (2007)
Motorway		65			345			224			Total	Göbel et al. (2007)

Site	Site	TSS Mean	min	max		
Highway	Weins, Germany	64.00			Dissolved	Stotz and Krauth (1994)
Highway	Weins, Germany	49.00			Dissolved	Stotz and Krauth (1994)
Service road		150			Total	Göbel et al. (2007)
Motorway		153			Total	Göbel et al. (2007)

11.2 Appendix 2

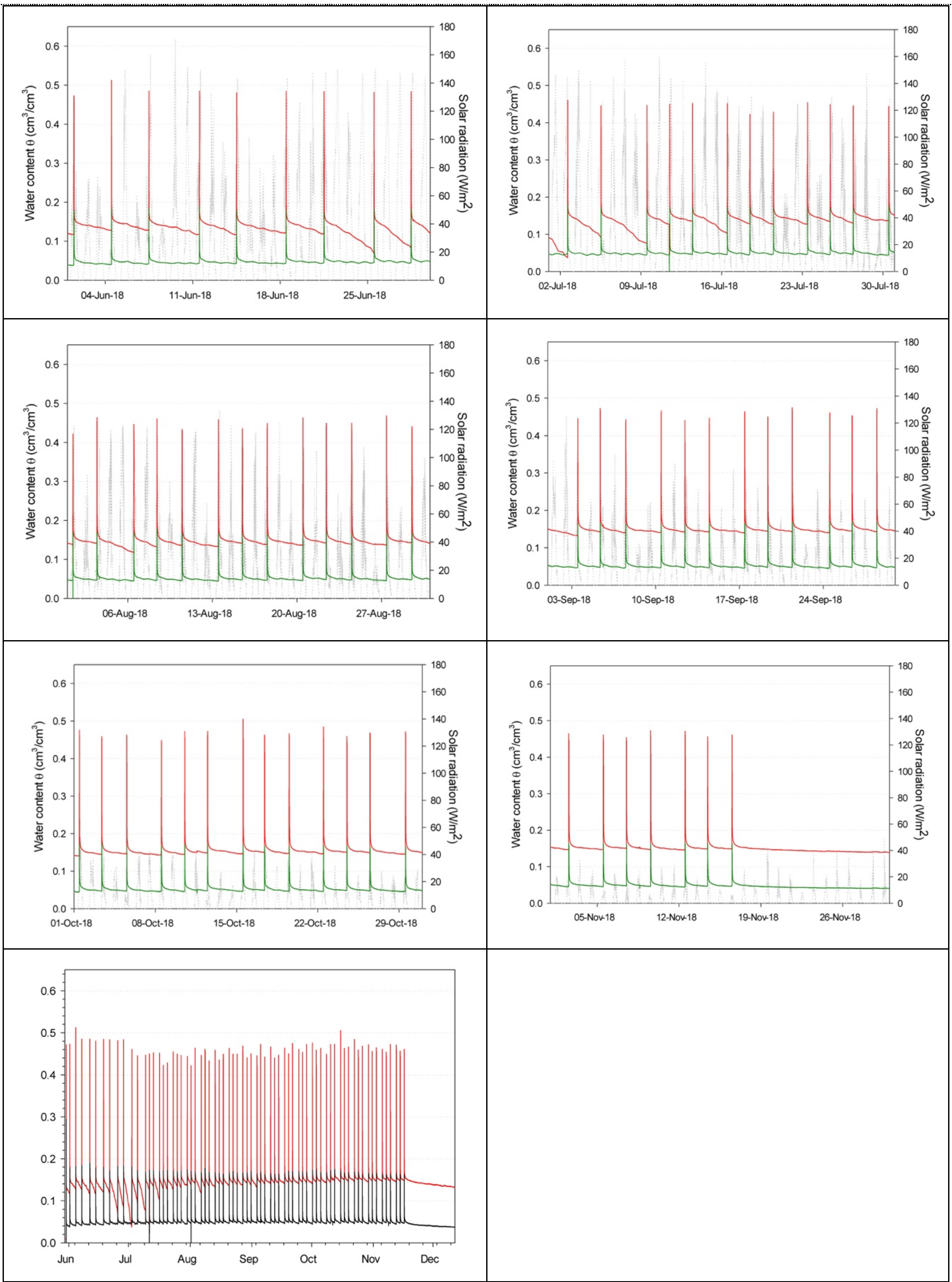


Figure 11-1 Moisture sensors installed in CoCa: in green the sensor installed in the top layer, in red the sensor installed in the deeper layer, temperature is the grey line

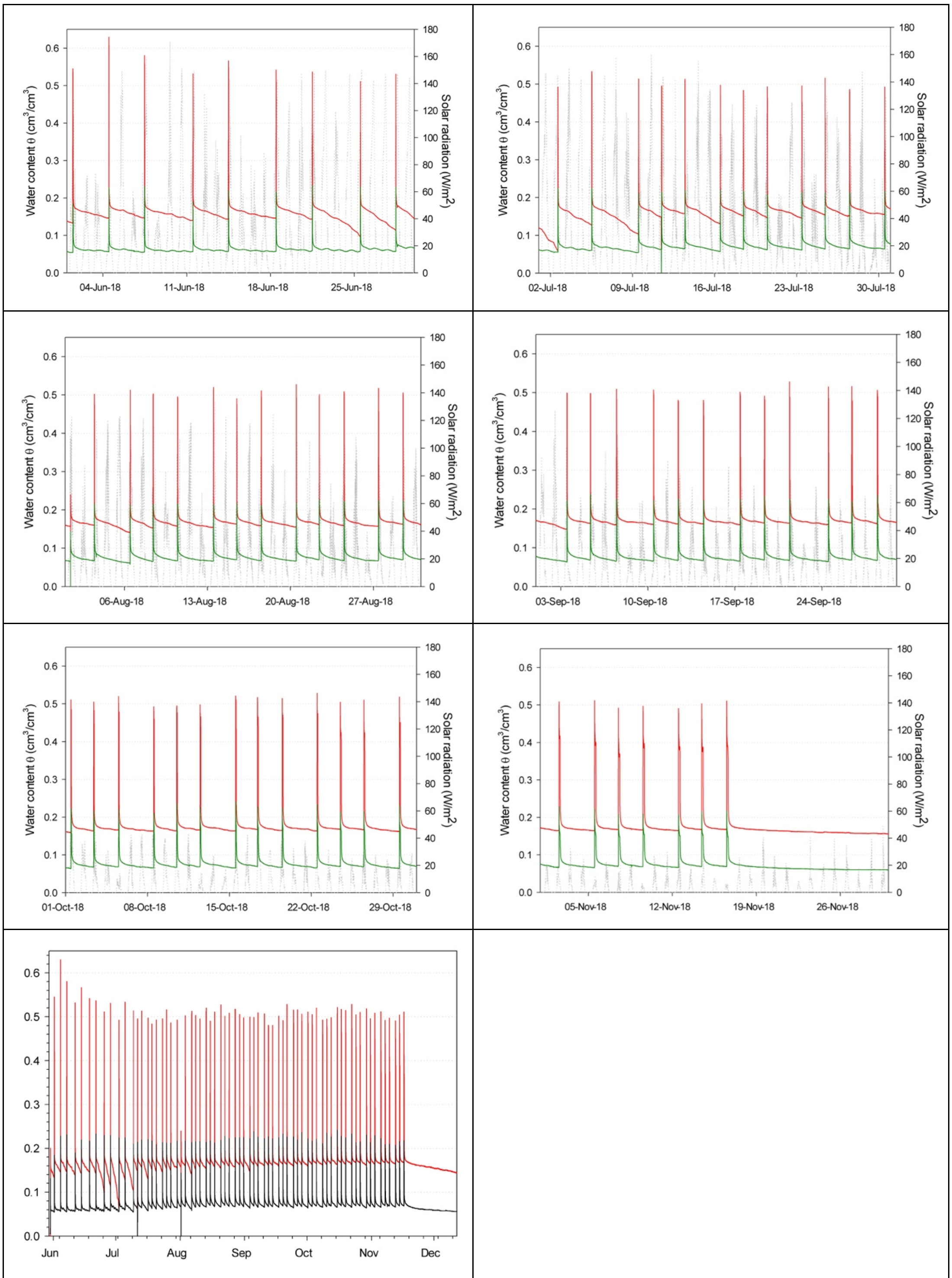


Figure 11-2 Moisture sensors installed in CoDe: in green the sensor installed in the top layer, in red the sensor installed in the deeper layer, temperature is the grey line

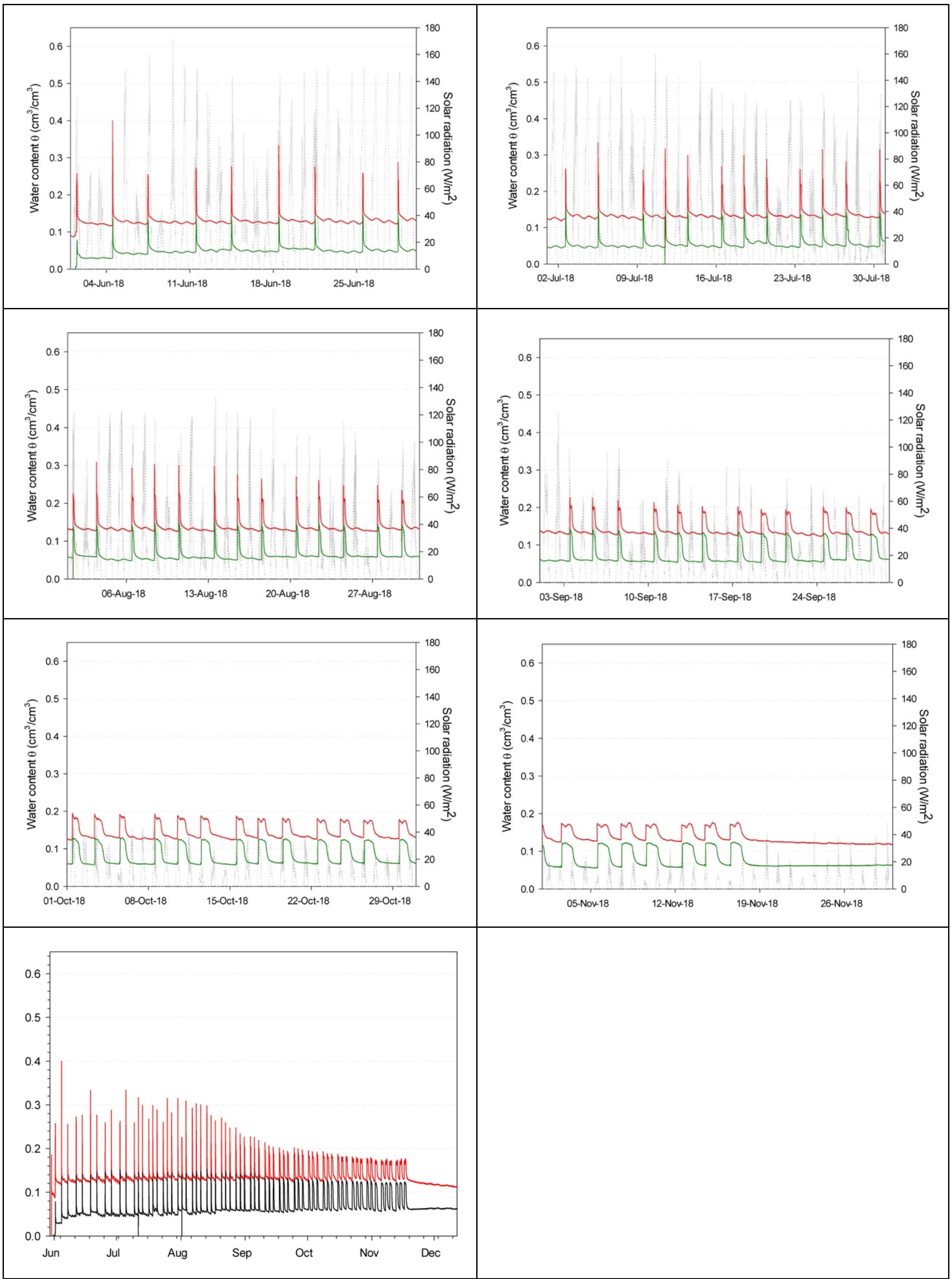


Figure 11-3 Moisture sensors installed in CoNP: in green the sensor installed in the top layer, in red the sensor installed in the deeper layer, temperature is the grey line

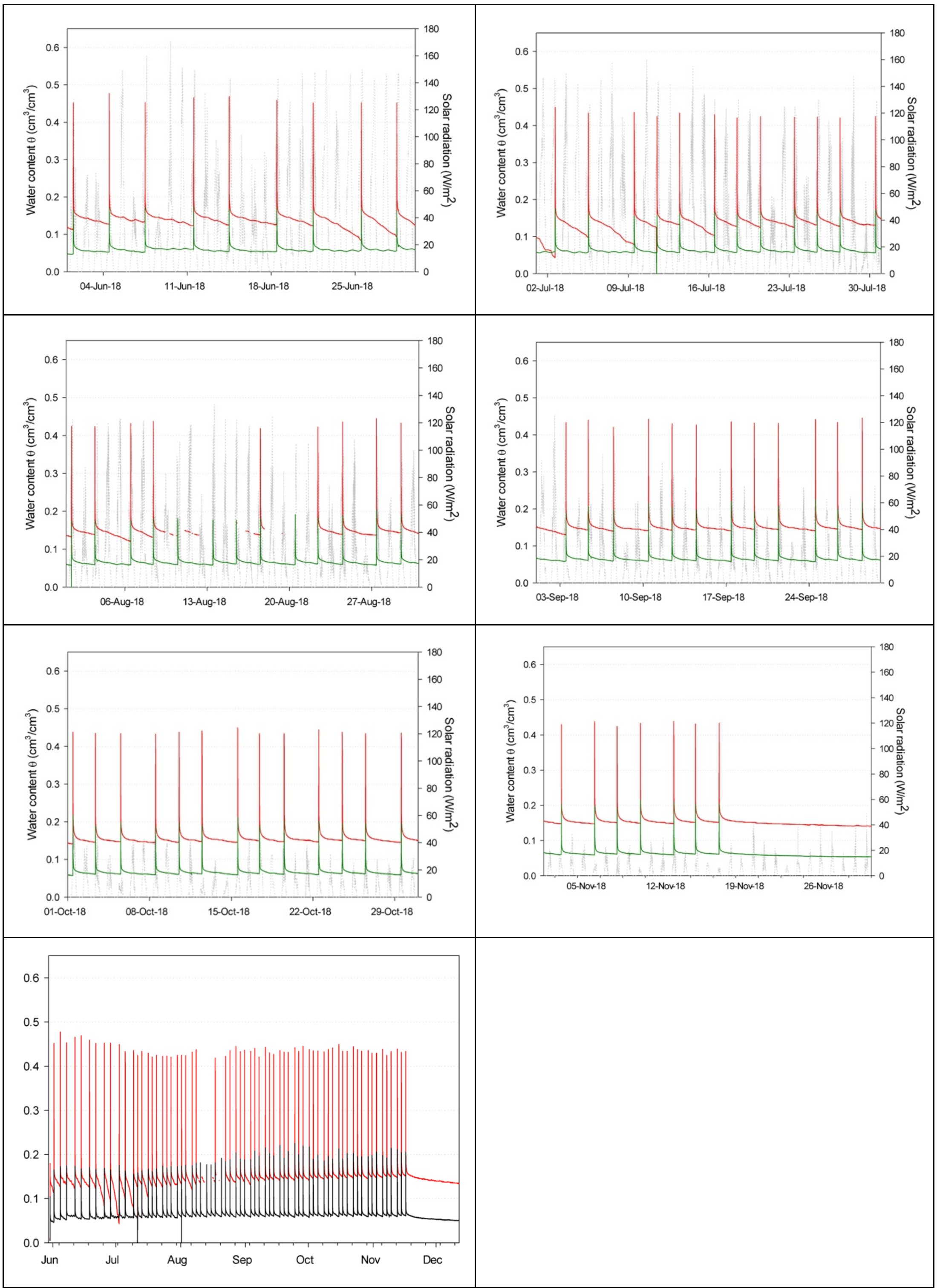


Figure 11-4 Moisture sensors installed in AmCa: in green the sensor installed in the top layer, in red the sensor installed in the deeper layer, temperature is the grey line

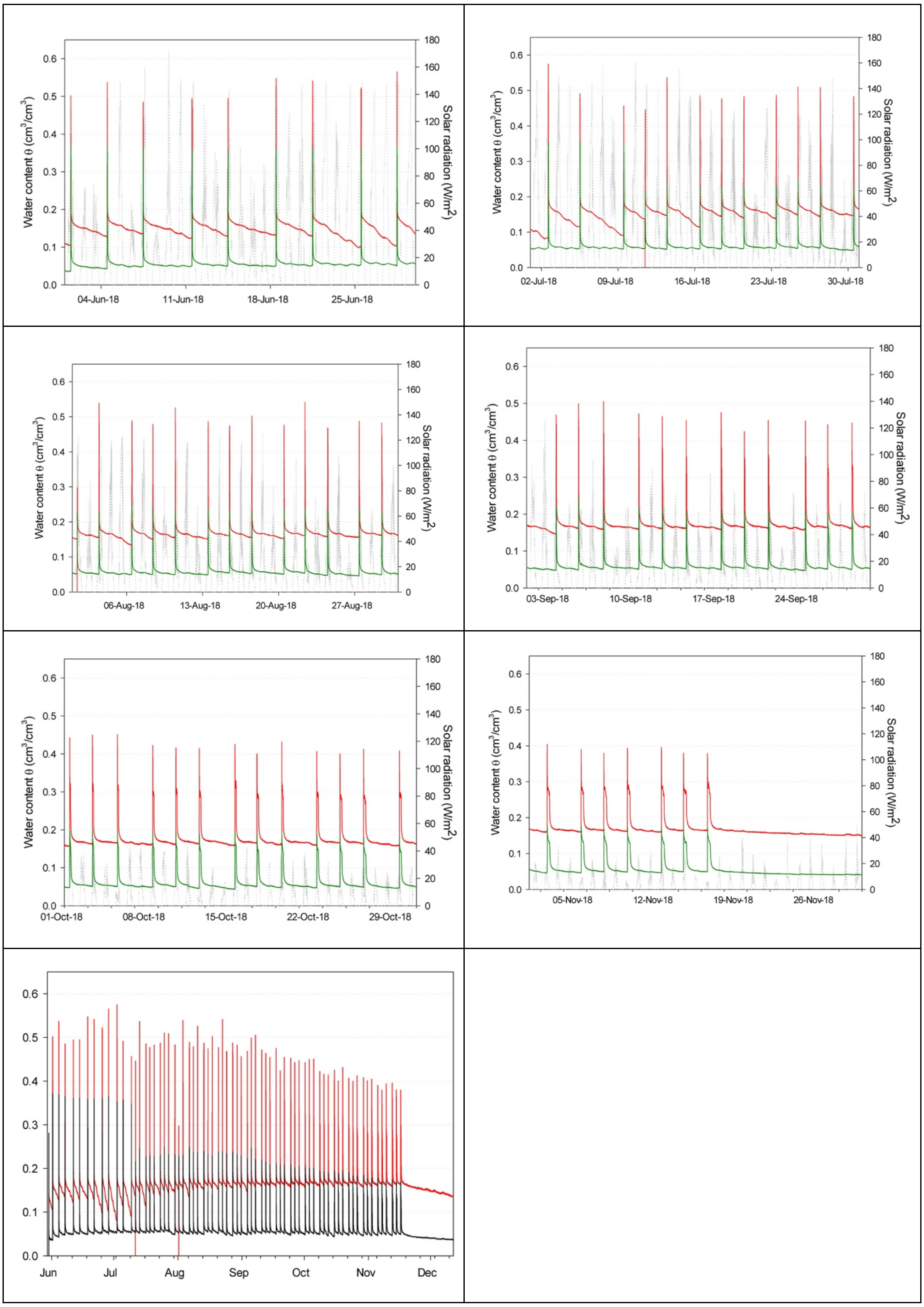


Figure 11-5 Moisture sensors installed in AmDe: in green the sensor installed in the top layer, in red the sensor installed in the deeper layer, temperature is the grey line

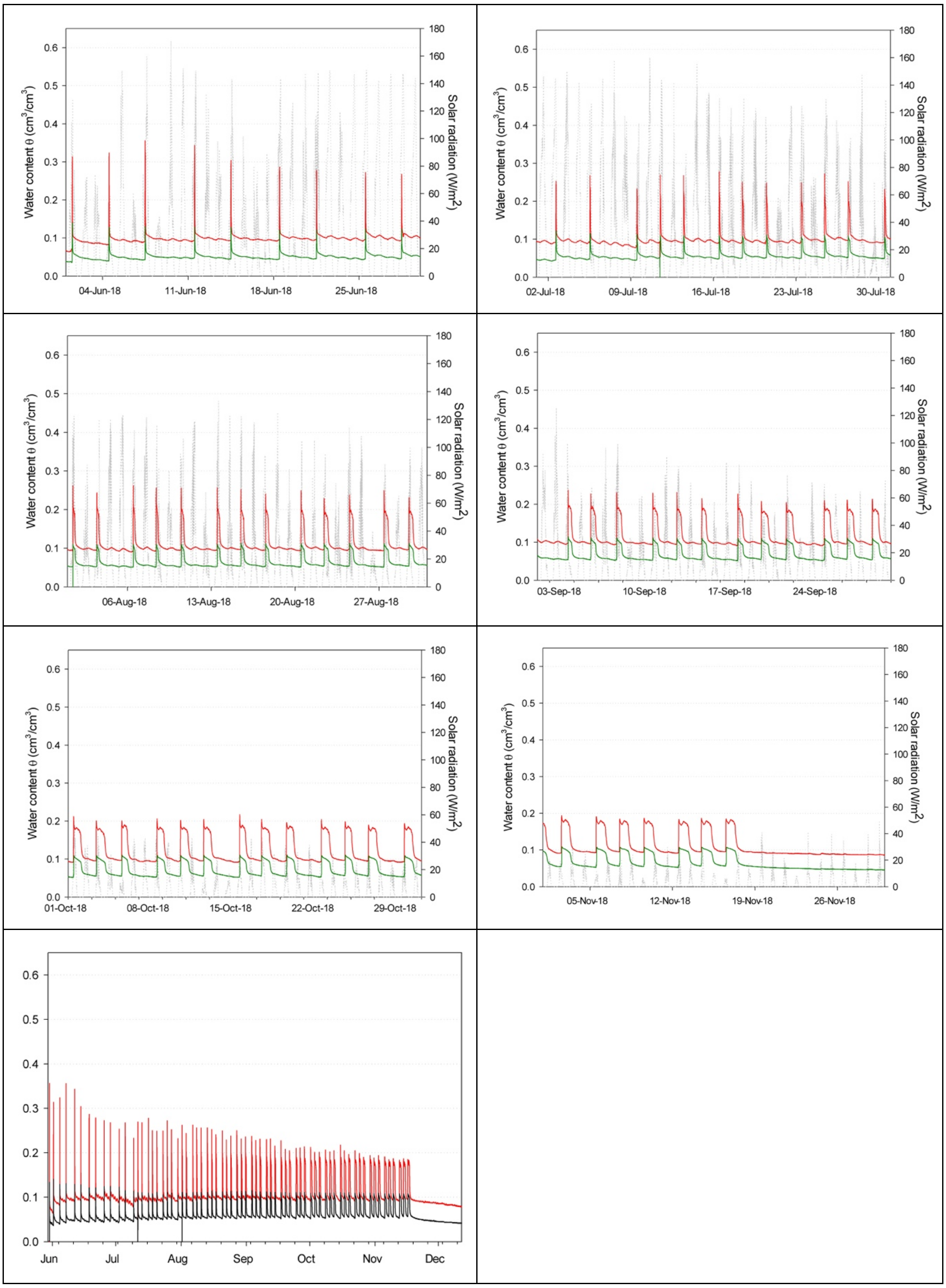


Figure 11-6 Moisture sensors installed in AmNP: in green the sensor installed in the top layer, in red the sensor installed in the deeper layer, temperature is the grey line

11.3 Appendix 3

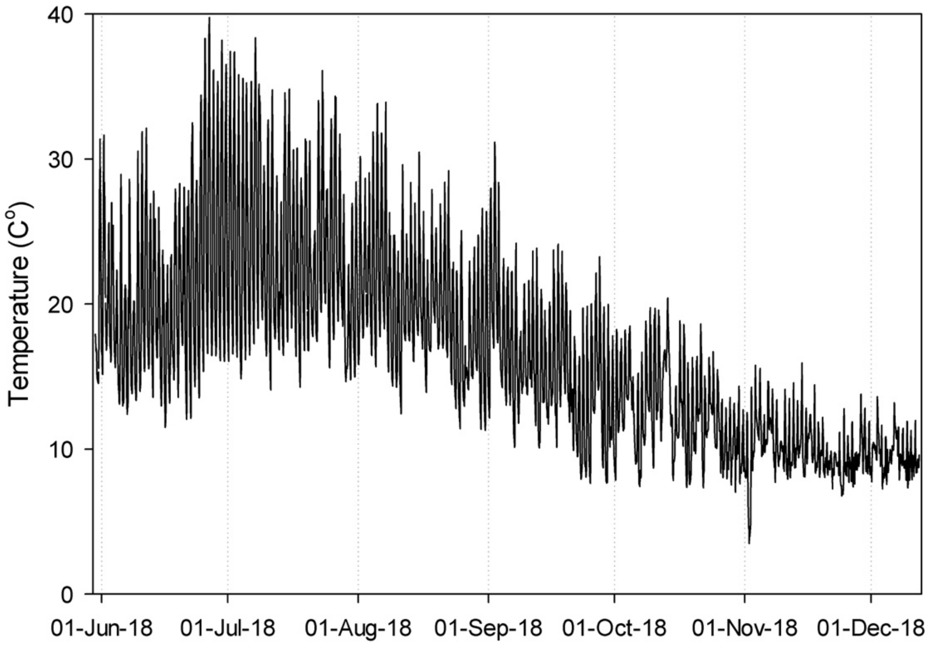


Figure 11-7 Temperature trend in the greenhouse from 30/05/18 to 12/12/18.

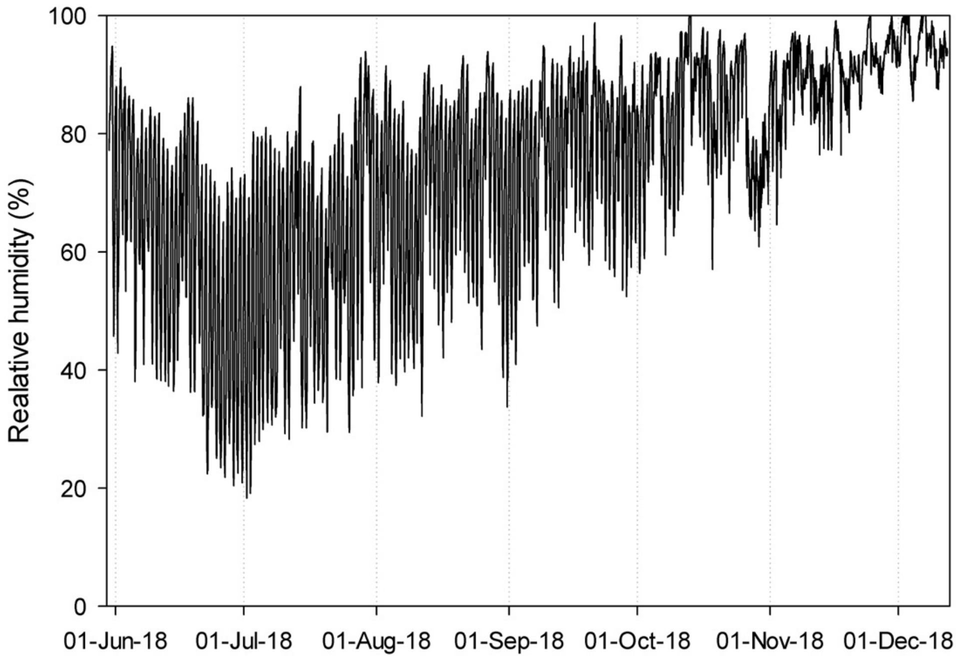


Figure 11-8 Relative humidity trend in the greenhouse from 30/05/18 to 12/12/18.

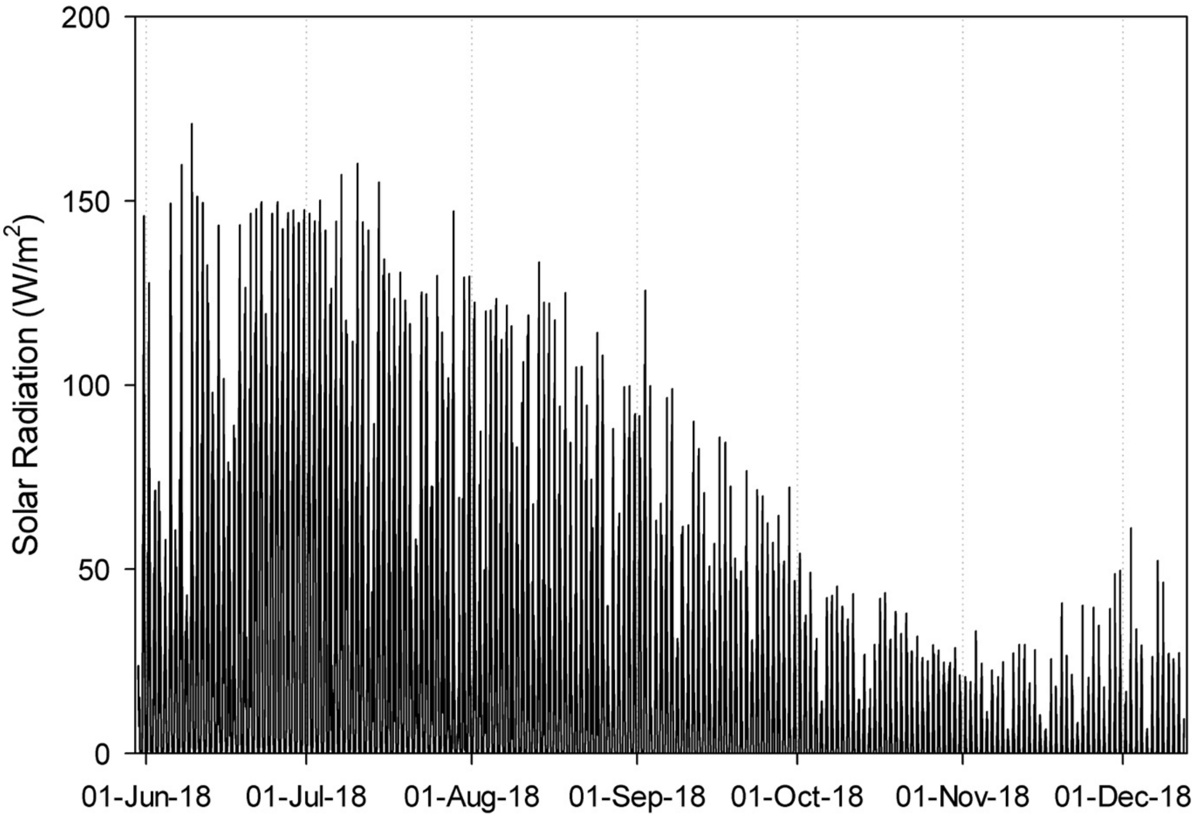
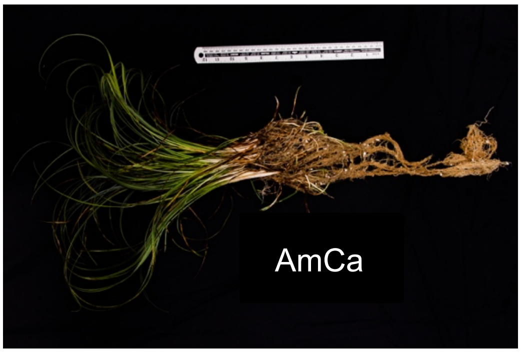


Figure 11-9 Solar radiation trend in the greenhouse from 30/05/18 to 12/12/18.

11.4 Appendix 4



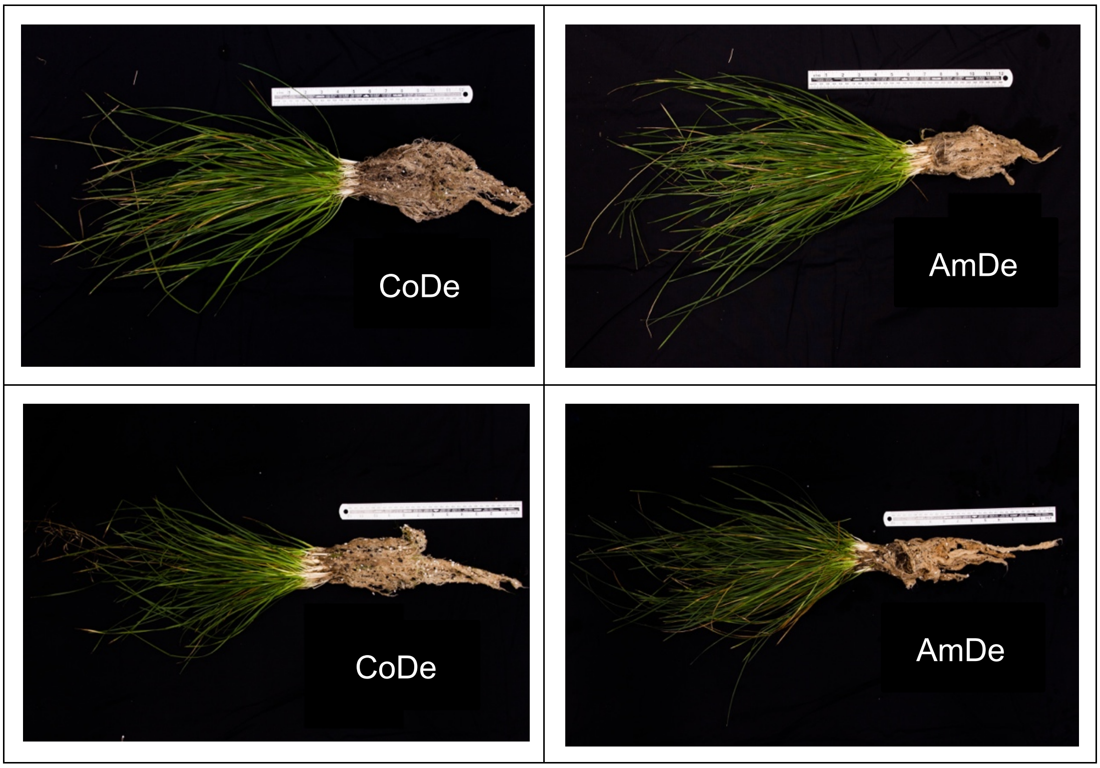
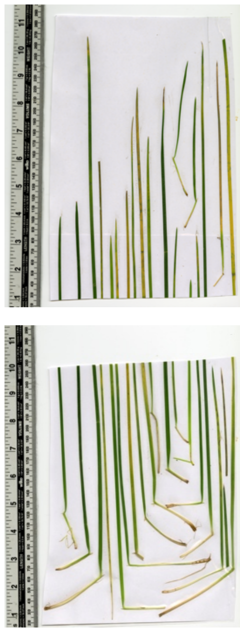
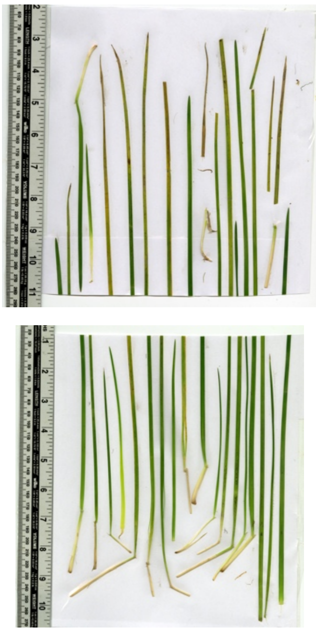
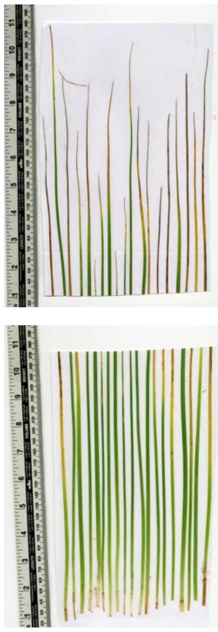


Figure 11-10 Pictures of plants after being washed.

CoCa	AmCa	CoCa
		

AmDe	CoDe	AmDe
		
CoDe	AmCa	CoCa
		

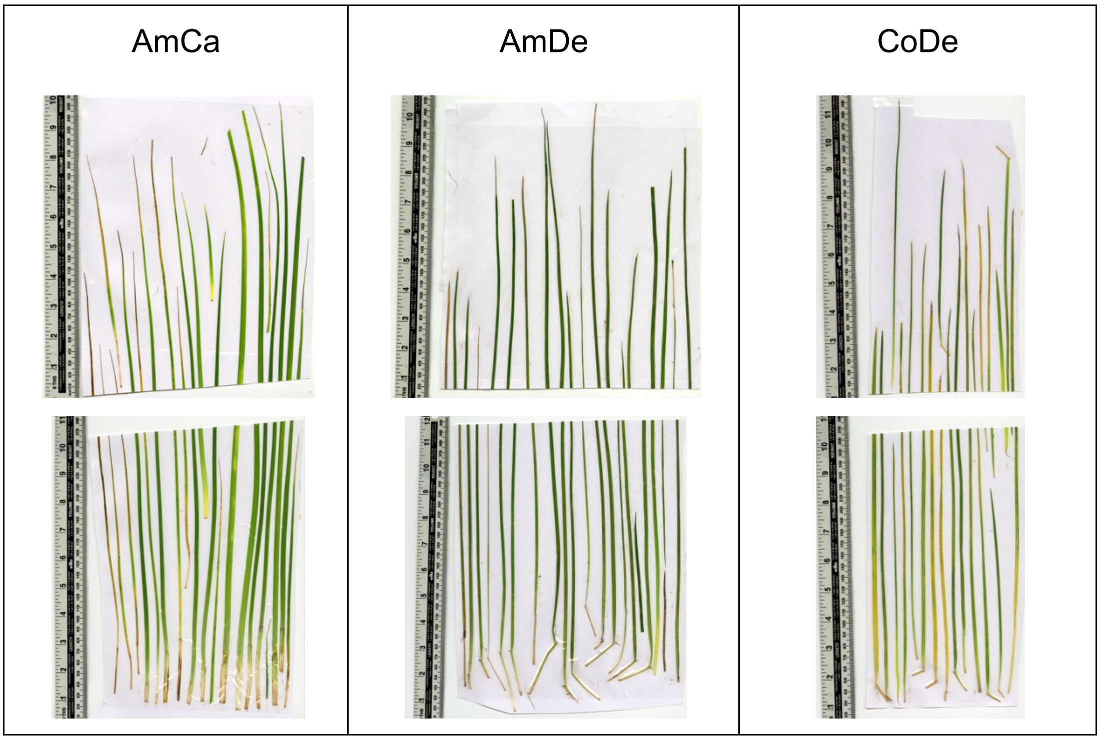
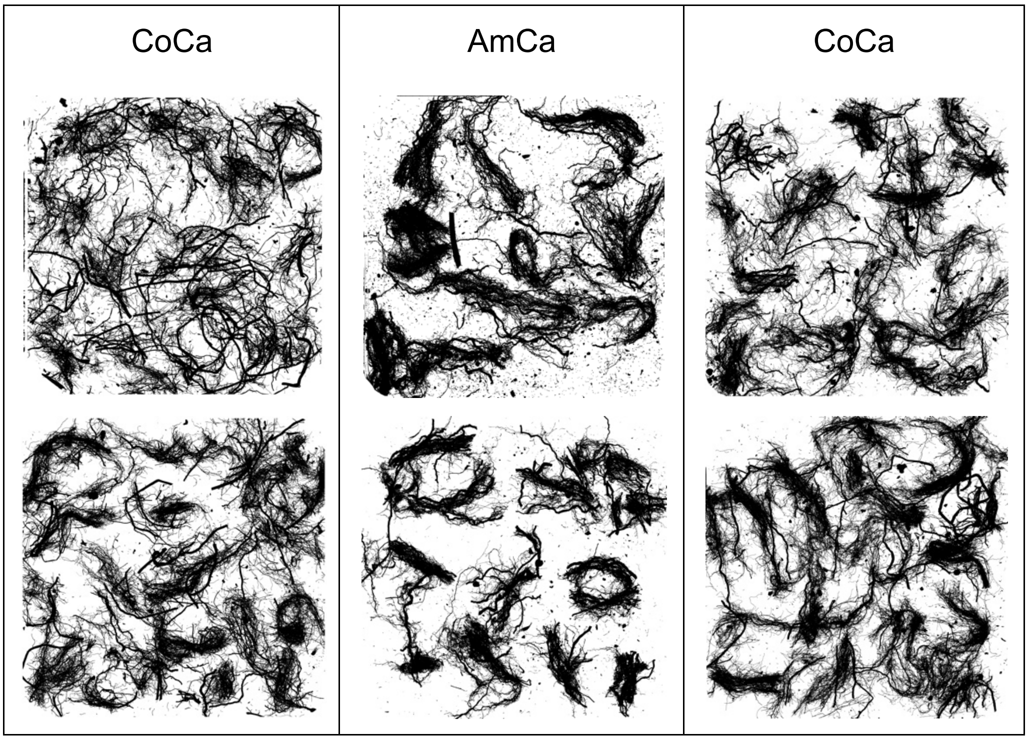
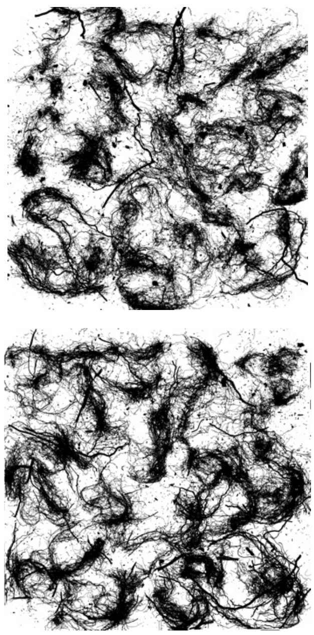
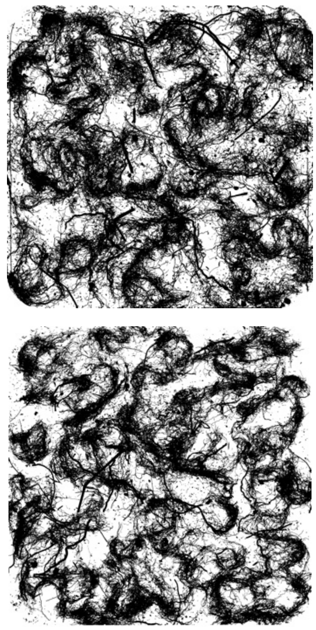
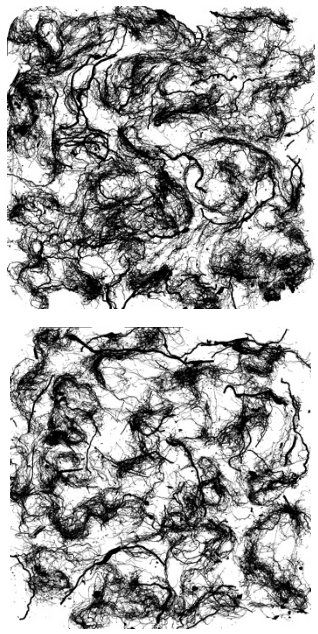
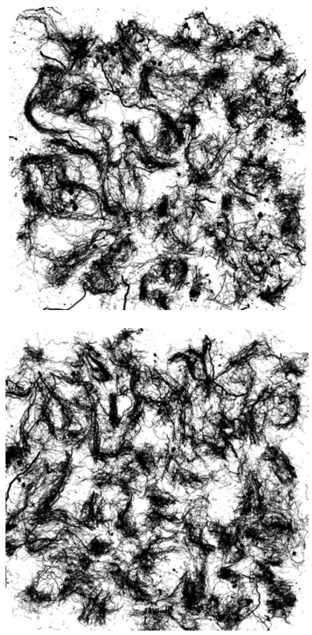
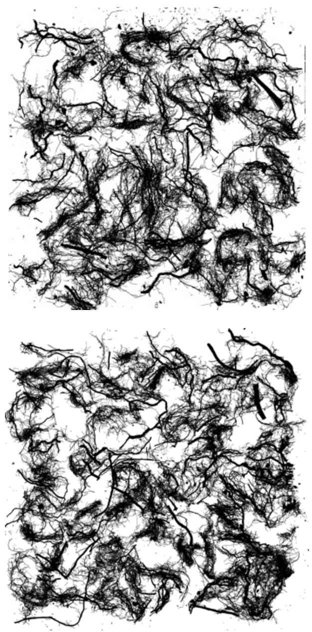


Figure 11-11 Scanned plants leaves (800dpi)



AmDe 	CoDe 	AmDe 
CoDe 	AmCa 	CoCa 

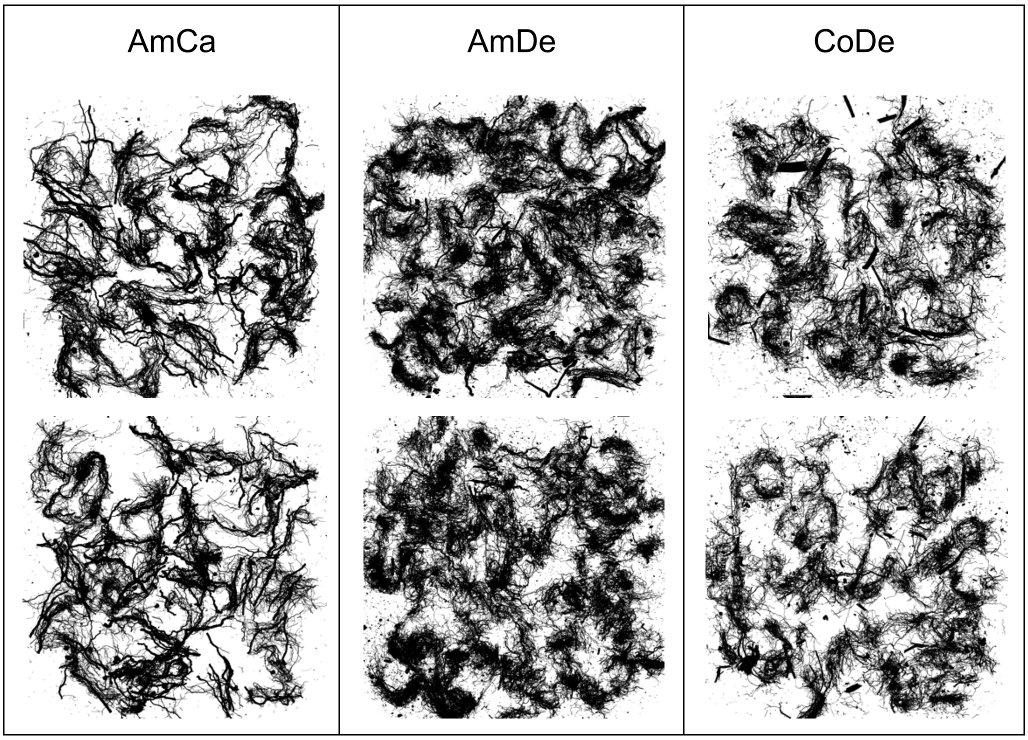


Figure 11-12 Scanner image (800dpi) of roots samples after thresholding analysis