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Master Thesis

Comparison of water absorption and release properties of synthetic, hybrid and natural hydrogels and their potential as soil amendments.

Submitted by

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Affidavit

I hereby declare that I have authored this master thesis independently, and that I have not used any assistance other than that which is permitted. The work contained herein is my own except where explicitly stated otherwise. All ideas taken in wording or in basic content from unpublished sources or from published literature are duly identified and cited, and the precise references included.

I further declare that this master thesis has not been submitted, in whole or in part, in the same or a similar form, to any other educational institution as part of the requirements for an academic degree.

I hereby confirm that I am familiar with the standards of Scientific Integrity and with the guidelines of Good Scientific Practice, and that this work fully complies with these standards and guidelines.

Bolzano, 22.11.2021   Alexander DOVAS *(manu propria)*

Acknowledgements

Table of content

Abstract

Hydrogels have been used as soil amendments in order to increase the soil's water holding capacity. Most products are based on synthetic, hardly biodegradable polymers. Therefore, products created from natural, easily biodegradable polymers could represent a valid and environmentally friendly alternative. A synthetic hydrogel (Stockosorb®) was compared to a hybrid hydrogel (Polyter®, based upon cellulose and synthetic polymers) and to two newly developed products created from cellulose and lignin respectively. The aim was to assess the potential of natural and hybrid hydrogels as an alternative to synthetic products. Free swelling capacity, swelling velocity, the effect of mono- and divalent salt concentrations on swelling capacity and the change in water holding capacity over several wetting and drying cycles in soil were measured parameters. Furthermore, the efficiency of water release to drying soil was assessed by combined measurement of soil respiration and soil drying rate. Results indicate a high suitability of Polyter as an alternative to Stockosorb. Free swelling capacities of Polyter and Stockosorb were similar, whereas Cellulose, and especially Lignin, absorbed less water than abovementioned products. Increasing salt concentration decreased water absorption capacity of Stockosorb and Polyter, whereas natural hydrogels were not affected at all. Exposure to soil and wetting/drying cycles resulted in an initial decrease in water holding capacity for Stockosorb and Polyter, before values stabilized during subsequent measurements. Cellulose was very unstable, dissolving in water and being lost from the soil. The hydrogels released nearly all absorbed water to drying soil. Results suggest a high suitability of Polyter as an alternative to synthetic products. Cellulose proved to be unstable, breaking up and dissolving into water. Lignin absorbed the lowest amount of water compared to other products but could be useful if applied in high quantities.

Kurzfassung:

Hydrogele sind als Bodenzusatzstoffe in der Lage die Wasserspeicherkapazität von Böden zu erhöhen. Üblicherweise werden diese aus synthetischen, biologisch schwer abbaubaren Polymeren hergestellt. Aus diesem Grund wurden in den letzten Jahrzehnten auf natürlichen Polymeren basierende Produkte als umweltfreundliche Alternative entwickelt. In dieser Arbeit wurde ein synthetisches Hydrogel (Stockosorb®) mit einem hybrid-Hydrogel (Polyter®, basierend auf Cellulose und synthetischen Polymeren) und mit zwei neu entwickelten Produkten aus Cellulose bzw. Lignin verglichen. Ziel war es, das Potenzial von natürlichen und hybriden Hydrogelen als Alternative zu synthetischen Produkten zu bewerten. Gemessen wurden das Quellvermögen, die Quellgeschwindigkeit, die Auswirkung von Salzkonzentrationen auf die Quellfähigkeit und die Veränderung der Wasserhaltekapazität über mehrere Befeuchtungs- und Trocknungszyklen im Boden. Die Effizienz der Wasserabgabe an den Boden wurde durch Messung der Bodenatmung und der Trocknungsrate des Bodens bewertet. Die Ergebnisse deuten auf eine Eignung von Polyter als Alternative zu Stockosorb hin. Das Quellvermögen von Polyter und Stockosorb war ähnlich, während Cellulose und v.a. Lignin weniger Wasser absorbierten. Eine Erhöhung der Salzkonzentration reduzierte das Quellvermögen von Polyter und Stockosorb, zeigte jedoch bei Cellulose und Lignin keine signifikante Wirkung. Das Quellvermögen von Stockosorb und Polyter nahm nach Befeuchtungs- und Trocknungszyklen im Boden anfänglich ab, bevor sich die Werte bei späteren Messungen stabilisierten. Cellulose war instabil, löste sich in Wasser und wurde ausgewaschen. Die Hydrogele gaben fast das gesamte Wasser an den trocknenden Boden ab. Die Ergebnisse deuten auf eine Eignung von Polyter als Alternative zu synthetischen Produkten hin. Cellulose erwies sich als instabil und wurde ausgewaschen. Lignin hatte zwar das niedrigste Quellvermögen, könnte aber bei Anwendung in großen Mengen nützlich sein.

1. Introduction:

In 2017 global warming reached approximately 1°C above pre-industrial levels and was increasing at a rate of 0.2 °C per decade. Many regions experienced an increase in temperature way above the global average with warming over land being higher than over water (Allen et al., 2018). Especially Europe is subjected to faster increase in temperature, as mean temperature in the last decade was around 1.8 °C higher compared to pre-industrial levels (EEA, 2020).

Worldwide 1.2 billion people live in agricultural areas which are severely affected by water scarcity (FAO, 2020). Global warming will increase water shortages and the number of recurring droughts, therefore posing additional stress upon agricultural systems (FAO, 2020), which are responsible for 72% of global water withdrawals (UN-Water, 2020). These changes will significantly impact crop yields in rainfed and irrigated areas (Li, Ye, Wang, & Yan, 2009; Lobell et al., 2013; Ostrom, 1990).
Similarly to agricultural crops, also many forest sites have been severely impacted by increasing temperatures and resulting droughts, leading to global declines in forest productivity and tree survival (Allen et al., 2010; Zhao & Running, 2010).

One possible solution to combat the effects of drought and improve water retention capacity of soils has been identified in the application of hydrogels, chemical substances based on polymers, which are able to absorb great amounts of water (Puoci et al., 2008). When applied to the root zone of plants they retain irrigation- and rainwater, therefore increasing plant available water and reducing water loss (Hüttermann, Orikiriza, & Agaba, 2009). Although, one major issue speaking against the application of traditional hydrogels, which are usually synthesized from synthetic polymers, is the low biodegradability and high bioaccumulation potential in soil (Wilske et al., 2014). Therefore many environmentally-friendly, easily biodegradable hydrogels, based on natural polymers like cellulose, starch and chitosan have been developed in recent years (Ismail, Irani, & Ahmad, 2013; Spagnol et al., 2012; Wu, Zhang, Liu, & Yao, 2012).
In the following chapters different types of hydrogels, their application to soil and issues related to toxicity and biodegradability will be illustrated.

1.1 Hydrogels

Hydrogels (also called superabsorbent polymers) are networks of polymer chains which are held together by cross-links and can absorb great amounts of water without being dissolved (Braun, Harald, Rehahn, Ritter, & Brigitte, 2013; Kiatkamjornwong, 2007).

Technically there is a difference between the terms hydrogel and superabsorbent polymer (SAP). While hydrogels can absorb water up to 10 times their own weight (Kabiri, Omidian, Zohuriaan-Mehr, & Doroudiani, 2011), this number increases up to 1000 for superabsorbent polymers (Buchholz & Graham, 1998). Nonetheless the two terms are used interchangeably in the existing literature.

In this thesis, the word hydrogel will be used in order to refer to both of them.

1.2 Classification:

Hydrogels can be classified according to various criteria, depending on the characteristics being considered.

1.2.1 Classification based on origin:

Depending on the origin of the polymer building blocks three types of hydrogels can be distinguished:

- Natural hydrogels:
  Natural hydrogels are synthesized from natural polymers like polysaccharides (e.g., starch, cellulose, chitosan, natural gums) and polypeptides (Mondal & Haque, 2019).

- Synthetic hydrogels:
  Synthetic hydrogels are based on petrochemical substrates.
  Acrylic acid, its sodium and potassium salts (acrylates) and acrylamide are usually used in synthetic hydrogel production (Zohuriaan-Mehr & Kabiri, 2008).

- Hybrid hydrogels:
  In hybrid hydrogels, synthetic and natural monomers are combined. Hybrids based on several natural polymers have been developed, including cellulose (Wen et al., 2015), chitin (Liu et al., 2017), carrageenan (H. Hosseinzadeh, Pourjavadi, Mahdavinia, &

Zohuriaan-Mehr, 2005), lignin (Domínguez-Robles et al., 2018), starch (Qiao, Yu, Bao, Zhang, & Jiang, 2017) and plant protein (Zhang et al., 2011).

1.2.2 Classification based on ionic charge:

According to Peppas and Hoffman (2013), hydrogels can be classified according to the ionic charge of the backbone polymers. They differentiate between four different types:

Neutral hydrogels (being uncharged), anionic hydrogels (possessing negative charges only), cationic hydrogels (possessing positive charges only) and ampholytic hydrogels (consisting of positive and negative charges). The ionic charge of the polymers is an important factor influencing the absorption capacity of the hydrogels as it acts as a driver in the osmotic process (see chapter 1.3).

1.2.3 Classification based on type of cross-linking:

Two types of cross-links can be differentiated:

Chemically cross-linked hydrogels are characterized by covalent bonds between the structural units. In physically cross-linked hydrogels the network is based on non-covalent interactions, such as hydrogen bonds, dipole-dipole interactions and van der Waals forces, as well as molecular entanglements (Braun et al., 2013). Typical cross-linkers used in hydrogels vary from di-functional compounds such as N, N´-methylenebisacrylamide to tri- (1,1,1 trimethyolpropanetriacrylate) and tetra functional compounds (e.g., tetraallyloxyethane) (Kiatkamjornwong, 2007).

Physical bonds are very weak (only few kJ/mol) compared to chemical linkages (over 100 kJ/mol) (Mignon, De Belie, Dubruel, & Van Vlierberghe, 2019). Therefore, physical bonds result in quite unstable hydrogels because the links are easily destroyed under heat or pressure.

1.2.4 Classification based on morphology:

Hydrogels may also be classified according to their morphology. Forms may vary depending on the field of application, including granules (Shi et al., 2010), sheets (Patent No. 6,051,317, 2000), powders (Pelto et al., 2017) or fibers (Yabuki, Tanabe, & Fathona, 2018).

1.3 Absorption mechanism:

Important features required from hydrogels like high maximum absorption capacity (i.e., the maximum amount of water the hydrogel can take up) and good swelling kinetics (the velocity with which hydrogels absorb water until reaching maximum swelling capacity) are influenced by a variety of physical and chemical factors (Zohuriaan-Mehr & Kabiri, 2008).

The main force driving the hydrogels absorption is osmosis. Because of their internal ionic concentration osmotic pressure builds when the hydrogels get in contact with water, resulting in water uptake. The absorption is terminated when the restoring force of the polymer chains held together by cross-links equals the osmotic force (Koltzenburg, Maskos, & Nuyken, 2017). The number of ionic groups and other polar moieties (hydroxyl, carbonyl or amine functionalities) is directly proportional to the swelling capacity of the hydrogel (Mignon et al., 2019). Neutral hydrogels absorb water mainly by entropic and energetic interaction with hydrophilic groups of the polymer chains, which are solvated by hydrogen bonds (Sanz Gómez 2015). The presence of dissolved salts in the solution decreases both swelling capacity and swelling velocity by reducing the osmotic pressure gradient between the inside and outside of the hydrogel (Bo et al., 2012).

Also, the type and concentration of the cross-linker plays an extraordinary role in determining the hydrogels properties. A network with a low cross-linking degree results in a flexible material with high water absorption capacity. Too little cross-linking on the other hand leads to unstable gels, which may dissolve upon contact with water (Mignon et al., 2019). Too high cross-linking results in a hydrogel with reduced water absorption properties. The ratio of absorbed water of a chemically cross-linked hydrogel is often more than ten times that of a physically cross-linked gel, due to its stronger structure (Masuda & Ueda, 2014).

Moreover, parameters such as monomer and crosslinker types, porosity of the hydrogel, particle size, pH, temperature and ionic strength of the medium affect the performance (Zohuriaan-Mehr & Kabiri, 2008). Physicochemical processes like UV radiation and freeze-thaw cycles can also alter absorption capacity of the gels through polymer chain scission and fragmentation (Holliman, Clark, Williamson, & Jones, 2005).

Another factor significantly impacting the swelling of hydrogels is the amount of pressure exerted on them. This parameter is especially important when hydrogels are mixed into soil, as the soil load significantly limits the expansion and therefore absorption ability of the gel (Lejcuś, Śpitalniak, & Dabrowska, 2018).

1.4 Application as soil amendment:

Due to climate change, droughts are predicted to get increasingly severe in the future (Gornall et al., 2010). Hydrogels have been shown to represent a valid option to ameliorate water use efficiency in agriculture and forestry (Puoci et al., 2008).

Depending on the type of cultivation and hydrogel properties different methods of hydrogel application to soil have been used.

The most widely used application in agriculture is the direct mixing into the soil. This way is appropriate for very dense cultivations, ranging up to 180 plants per m^2. For cultivation of trees or bushes, which are not densely planted an application directly into and around the root-system has been preferred, either by injection, mixing into planting holes or by conditioning plant root systems before planting (Wróblewska, Dębicz, & Bąbelewski, 2012).

Hydrogels have proven to possess many potential benefits when used as soil amendments. They increase water holding capacity and reduce hydraulic conductivity of soils (Parvathy et al. 2014). Furthermore, they also ameliorate soil aeration by their expansion and contraction (Buchholz and Graham, 2004). Sometimes hydrogels are loaded with fertilizers, which are slowly and constantly released to plants, therefore increasing fertilizer use efficiency (Rabat, Hashim, & Majid, 2016; Sarmah & Karak, 2020).

Studies reported that soils amended with hydrogels had higher plant available water, subsequently leading to better plant growth (even under optimal water conditions), higher survival rate under water stress (Hüttermann et al., 2009) and greater yield (Yazdani, Allahdadi, & Akbari, 2007).

1.5 Toxicity and biodegradability:

Most commercially used hydrogels are based upon petroleum derivatives like polyacrylate and polyacrylamide (Saha, Sekharan, & Manna, 2020). Although polyacrylamide is not toxic, its degradation product acrylamide (Caulfield, Qiao, & Solomon, 2002) is a hazardous compound for the aquatic environment and for humans, being classified as carcinogenic (level 2) (WHO, 1985).

Biodegradation in soil of synthetic hydrogels was proven to occur very slowly. The main chain of a polyacrylate-based SAP degraded at a rate between 0.12 % in loam, 0.20% in sandy loam and 0.24% in loamy sand over a six months period (Wilske et al., 2014). Biodegradation by white rot fungi of polyacrylate was shown to be around 4 to 7 % for one year (Mai, Schormann, Majcherczyk, & Hüttermann, 2004). Most of the degradation occurred during the first month in both studies. This suggests that the degradation occurred mainly on the hydrogel surface on so-called "loose ends" and oligomers. This low degradation is due to the carbon-carbon backbone of polyacrylate polymers, the low solubility and high molecular mass obtained through cross-linking (Stahl, Cameron, Haselbach, & Aust, 2000). Holliman et al. (2005) describe the decomposition of polyacrylamide-based polymers in soil as a combination of biological (e.g. through amidases of microbes), chemical (UV light exposure) and physical (e.g. freeze-thaw) processes.

The possible toxicity of degradation products, low degradation rate and the production from non-renewable resources led to the development of more environmentally friendly alternatives. Hydrogels based on natural polymers like cellulose (Wu et al., 2012), starch (Ismail et al., 2013), chitosan (Spagnol et al., 2012) and lignin (Domínguez-Robles et al., 2018) have therefore been created. These products are more easily biodegradable by soil microorganisms as they are created from natural polymers. Wang et al. (2008) measured a degradation rate of 43% after 3 months for a SAP based on carboxymethyl cellulose. A starch-based SAP synthesized by Jin et al. (2013) displayed a degradation of 40 % after two months.

Overall, natural and hybrid SAPs can present a valid alternative to synthetic products due to lower production costs and greater environmental compatibility (Saha et al., 2020).

Nonetheless it should be considered that there is a conflict of interests between a possibly long functioning time and a good biodegradability of the hydrogel. The hydrogel should ideally

provide the plants with water for as long as they need and subsequently biodegrade. Obviously, this timespan varies strongly for different cultivars and application fields.

1.6 Aim and research questions:

The aim of the thesis was to compare a synthetic hydrogel (Stockosorb®) to a hybrid hydrogel (Polyter®, based upon cellulose and synthetic polymers) and to two newly developed products made of cellulose and lignin respectively, in order to assess the potential of the natural and hybrid gels as environmentally friendly alternatives to synthetic products.
Following research questions were addressed:

- How do swelling kinetics differ between the different hydrogels and what is their maximum swelling capacity?
- What is the impact of various mono- (NaCl) and divalent (CaCl2) salt concentrations in the swelling solution on swelling capacity of the hydrogels?
- How is water holding capacity of the hydrogels impacted by several wetting and drying cycles when they are exposed to soil and soil microorganisms? Do natural and hybrid hydrogels have a stronger reduction in water holding capacity compared to synthetic products due to higher biodegradability?
- What is the water release capacity of the various hydrogels? Is the absorbed water released to surrounding soil when it dries out, therefore prolonging the time of microbial respiration compared to a control sample?

2. Materials and methods:

2.1 Investigated hydrogels:

Following hydrogels were the object of this master's thesis:

Stockosorb: Stockosorb is a fully synthetic hydrogel produced by Stockhausen GmbH, a daughter company of Evonik Operations GmbH. According to the product safety datasheet it consists to over 95 % of cross-linked potassium polyacrylate, which is hardly biodegradable under aerobic conditions. Grain sizes were up to 2 mm.

Polyter: Polyter is a hybrid hydrogel developed by Green Legacy GmbH. According to the product data sheet (version 1.1) it consists mainly of cross-linked cellulose, up to 25% of potassium polyacrylate and also includes NPK fertilizer (8.5%). Two granulometries of Polyter were tested. A fine granulometry (subsequently referred to as "fine Polyter") with particles of up to 2 mm, and a coarse granulometry (subsequently referred to as "coarse Polyter") with particle sizes up to 5 mm.

Lignin hydrogel: A newly developed, granular hydrogel consisting completely of lignin. It was developed at the Institute of Environmental Biotechnology at the University of Life Sciences, Vienna by Univ. Assoc. Prof. Dr. Gibson Stephen Nyanhongo, Georg Gübitz, Andreas Ortner and Sabrina Bischof. In this thesis it will be referred to as "Lignin".

Cellulose hydrogel: A new hydrogel, developed by Green Legacy GmbH, based fully on cellulose. The product was very heterogenous, but mostly in sheet morphology. Particles ranged from 0.3 to 1.5 cm in length and were up to 3 mm in thickness. It will subsequently be referred to as "Cellulose".

Both, the Lignin and the Cellulose hydrogels are prototypes and not yet commercially available.

Figure 1: Tested hydrogels from left to right: Stockosorb, Cellulose, Lignin and fine grained Polyter.

2.2 Experimental soil:

Soil used for the experiments was a silty clay loam which was sieved at 2 mm. Maximum water holding capacity of the soil was 34%. Detailed informations on the soil are reported in the supplementary material of Lak et al. (2020).

Used sand was washed quartz sand with a particle size distribution of 0.9 to 1.2 mm.

2.3 Experimental setup:

Five different experiments were carried out in order to assess the swelling and deswelling properties of the investigated hydrogels.

2.3.1 Influence of salt concentration on swelling capacity:

The effect of mono (NaCl) and divalent (CaCl2) salt solutions on the swelling capacity of different hydrogels was assessed.

Screws with a 3 mm diameter were screwed into the bottom of 50 ml centrifuge tubes at a depth of approximately 1.5 cm. Hydrogels were filled into the centrifuge tubes.

0.1 g of Stockosorb, fine grained Polyter and coarse grained Polyter, 0.2 g of Cellulose and 1 g of Lignin were added to the tubes.

Solutions of 0, 100, 500, 1000, 2000 mg/l NaCl and CaCl2 respectively were prepared with distilled water. Subsequently, the tubes were filled up to the 45 ml mark with the prepared solutions. Hydrogels were left soaking for five hours. Subsequently excess water was dripped through a circular filter paper (Whatman 589/1), which was fixed at the top of the tubes with an elastic, by turning the tubes upside down and removing the bottom screw to let air in. After

one hour of dripping the bottom screws were reinserted, the filter papers removed, and the samples weighed. Each treatment (hydrogel x salt concentration) was replicated three times.

Calculations:

Before performing calculations, the weight of hydrogels was corrected based on the percentage of hygroscopic water present in the products before measurement.

Retained water (ml) per g of hydrogel:

$$WHC = (THG - T - HG) * 1/HG$$

WHC= water holding capacity (ml of water retained by 1 g of hydrogel)
THG= total weight (tubes, dry hydrogel, water) after five hours of soaking (g)
T= weight of the tube and inserted screw (g)
HG= dry hydrogel weight (g)

2.3.2 Swelling kinetics:

Out of quadratic 50 micrometer mesh forms (8cm x 8cm) triangular bags were formed by folding the mesh and sealing the bottom through plastic melted by an impulse heat sealer.
0.05 g of Polyter fine, Polyter coarse and Stockosorb, 0.07 g of Cellulose and 1 g of Lignin were filled into the mesh-bags. The bags were subsequently sealed. For every hydrogel three replicates were prepared.
Five Tupperware-boxes were filled with 1 l of distilled water. Every box was filled with bags containing one specific hydrogel. After 1, 2, 5, 10, 20, 30 minutes and 1, 2, 3, 4, 5 and 24 hours the bags were taken out, excess water dripped for five minutes and the sample subsequently weighed.

Calculations:

Before calculations the weight of hydrogels was corrected based on the percentage of hygroscopic water present in the gels before measurement.

Retained water (ml) per g of hydrogel:

$$WHC = (BHG - B - HG) * 1/HG$$

ml/g= water holding capacity (ml of water retained by 1 g of hydrogel)
BHG= total weight (bags, hydrogel, water) after soaking (g)
B= weight of the bag (g)
HG= dry hydrogel weight (g)

2.3.3 Change in water absorption capacity after re-wetting:

In two experiments the change in water holding capacity of the hydrogels was measured, when the product was exposed to soil and soil microorganisms and subjected to several wetting-drying cycles.

2.3.3.1 Bags method:

The soil was sieved to 2 mm and 1.5-2 kg were filled into Tupperware boxes. The soil was wetted to 60% of its field capacity.

Fine grained Polyter, Cellulose, Stockosorb and Lignin were sieved to 0.8 mm and 0.09 g of product weighed into mesh bags, which were created following the procedure presented in chapter 2.3.2. The hydrogel was mixed with 10 (+- 0.1) g of sand. Subsequently, the bags were sealed at the top.

For each treatment five replicates were prepared. In addition, five controls containing only 10 grams of sand were made.

A 1:10 soil solution was prepared by mixing 1 kg of soil and 9 l of water for 2 hours.

Determination of the hydrogels water absorption capacity occurred through wetting of the bags for four hours in the prepared soil solution and subsequent dripping of excess water for 2.5 hours by laying the bags onto grids elevated from the floor. Then, the bags were buried into soil containing Tupperware (8-10 bags per box). The boxes were closed and stored at 20°C. Every two weeks the boxes were opened in order to aerate the soil.

After 3, 9, 15, 21 and 27 weeks the bags were taken out of the soil and water holding capacity measured following the abovementioned procedure. Change in water holding capacity was calculated as percentage of the first measurement.

Figure 2: Tupperware boxes containing hydrogel samples

Figure 3: Triangular mesh bags containing sand and hydrogel during the dripping process

Calculations:

As the hydrogels and sand were not completely dry, the dry weight and percentage of water content were calculated by drying them at 105 °C for 24 hours. The dry weight was used in following calculations.

Determination of field capacity of sand (%):

$$FC = (SFC - B - S)/((SFC - B)/100)$$

FC= field capacity of sand (%).

SFC= weight of sand, water and bags at field capacity (g).

B= weight of mesh bag (g)

S= weight of dry sand (g)

Determination of water retained by 1 g of hydrogel:

$$WHC = (BHG - B - HG - (S + ((S/(100 - FC) * FC)) * 1/HG$$

WHC= water holding capacity (ml of water retained by 1 g of hydrogel)

BHG= total weight (bags, hydrogel, sand, water) at field capacity (g)

B= weight of the mesh bag (g)

HG= dry hydrogel weight (g)

S= weight of sand (g)

FC= mean field capacity of sand (%)

Determination of percentage in relation to first measurement:

$$\% = SM/(FM/100)$$

%= percentage of water retained in proportion to first measurement (100%)
SM= second measurement (ml/g)
FM= first measurement (ml/g)

2.3.3.2 Tubes method:

In a second experiment a different method was used to test the changing water holding capacity of hydrogels over time and over several wetting-drying cycles. Hydrogels tested were Polyter (fine and coarse granulometry), Stockosorb, Cellulose and Lignin.

Screws with a 3 mm diameter were screwed into the bottom of 50 ml centrifuge tubes at a depth of approximately 1.5 cm.

Soil was sieved to 2 mm. 10 g of soil and 10 g of sand were mixed, and 13 g of this mixture were filled into the prepared centrifuge tubes. Hydrogels were added to the soil/ sand mixture in following amounts:

Polyter (0.25 g), Stockosorb (0.35 g), Cellulose (0.5 g), Lignin (2.5 g). Values were calculated based on results obtained from a preliminary experiment in order to get similar water holding capacities across the samples.

The remaining 7 g of sand and soil were added on top. This upper soil layer should prevent the hydrogels from being pressed out of the soil during swelling.

Samples with Polyter, Stockosorb, Lignin and controls containing only sand and soil, were replicated 10 times, Cellulose was replicated 5 times.

Samples were filled with water up to the 45 ml mark (approximately 4 cm above soil surface) and left at room temperature for 15 hours. Subsequently excess water was dripped through a circular filter paper (Whatman 589/1), which was fixed at the top of the tubes with an elastic, by turning the tubes upside down and removing the bottom screw to let air in (Figure 4). After four hours of dripping the bottom screws were reinserted, the filter papers removed, and the samples weighed. Samples were left to dry at room temperature until being rewetted and dripped again following abovementioned procedure.

Measurements occurred after 4, 7, 10, 13, 16 and 19 weeks.
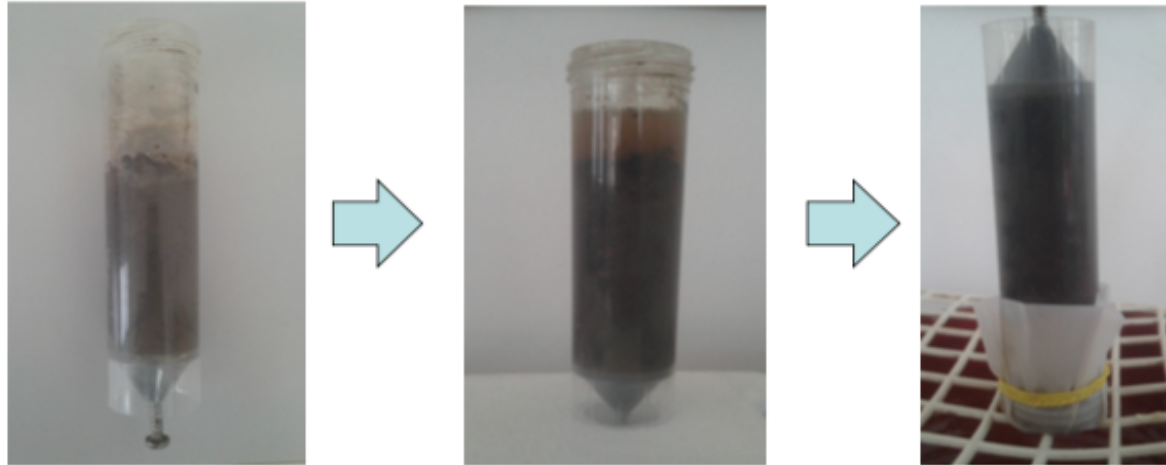
Figure 4: Procedure for water holding capacity assessment using centrifuge tubes method. Dried sample →wetting→dripping

Calculations:

Same formulas as for the bags experiment (chapter 2.3.3.1) were used. Weight of bags was replaced by weight of tubes and dry weight of sand was replaced by dry weight of the sand/soil mixture.

2.3.4 Water release capacity

Soil was wetted to 60 % of its field capacity and stored for 3 weeks in closed Tupperware boxes. This step was necessary in order to stabilize microbial respiration, which is known to increase very strongly immediately after a re-wetting a dry soil, compared to a soil which has been kept moist (Orchard & Cook, 1983).

50 grams of previously wetted soil were filled into plastic cups. 0.4 g of Polyter (coarse and fine), 0.5 g of Stockosorb, 0.8 g of Cellulose and 3 g of Lignin were mixed into the soil. 30 grams of soil were added on top of the samples in order to avoid that hydrogels swelled outside of the soil. The samples were filled with water and the gels left soaking for 15 hours. Excess water was decanted by gently turning the cup. For each hydrogel four replicates were prepared.

Samples were placed upon a machine developed for repeated measurement of sample weight and efflux of different gases, such as carbon dioxide and methane, in order to be able to monitor how gas efflux changes when the samples dry (Figure 5).

The machine consisted of a turning table with 10 plates on which the samples were placed, a scale for measuring sample weight and a cylinder, which enclosed the sample being measured.

The cylinder was connected to a Picarro G2131-i gas analyzer, measuring carbon dioxide, methane and water vapor.

The machine was programmed remotely through a wireless connection using a PC.

CO2 efflux was measured for eleven minutes for each sample. Measurements were conducted over the timespan of a week, totaling 84 measurements for each sample.

Measured data was transferred and stored through a wireless connection on a remote PC.

The apparatus was placed in a climate chamber at a constant temperature of 25 °C and at 60 % relative humidity.
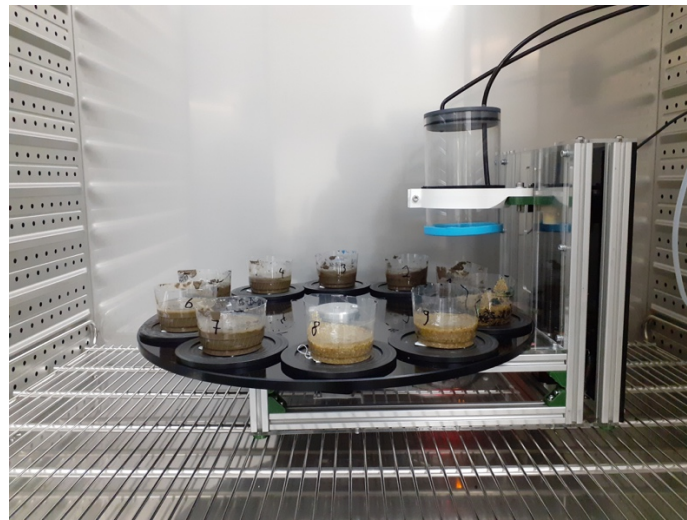
Figure 5: Samples placed upon turning plate before respiration measurement.

Data evaluation and calculations:

Respiration intensity was calculated by linear regression of CO2 concentration over time. CO2 in ppm was converted to μg CO2-C m^{-3} by following equation (Comeau, Lai, Cui, & Hartill, 2018):

$$Cf = \frac{P * Mwc * 1000}{R * T}$$

Cf= conversion factor (ppm to μg CO2-C m^{-3})

P= air pressure (kPa)

Mwc= molar mass of carbon

R= gas constant (8.314)

T= incubation air temperature (K)

Subsequently the CO2-C efflux was calculated on soil area basis by following formula (Comeau et al., 2018):

$$F = \frac{S * Cf * Hs * 3600 * 10^{-6}}{A}$$

F= gas efflux on soil area basis (g CO2-C m^2 h^{-1})
S= slope of the linear regression (ppm)
Cf= conversion factor
HS= headspace in measurement cylinder
3600= conversion from seconds to hours
10^{-6} = conversion from μg to g
A= area of the sample surface

Water content present in the samples was calculated in ml/g soil and as percentage of the controls initial water content (100%).

Sixth order polynomial functions were fitted to the data (water content and respiration) and predicted values calculated by the function. In order to get more accurate predictions polynomials were fitted starting from 70 hours.

To detect the effect of hydrogels on soil moisture and respiration, hydrogel samples were compared to the controls.
A threshold value was established for which the water content was assumed as constant, not decreasing more than 0.05 % of the soils field capacity per hour. The respiration value of the control at that given time was taken as threshold value by which the prolonged microbial activity in hydrogel samples was calculated. The difference in time between the control and the hydrogel samples reaching that value was considered as the time microbial activity was prolonged by the water released by hydrogels.
By correlation analysis the relationship between prolonged evaporative loss and prolonged microbial activity was assessed, in order to determine if the water released was also made bioavailable.

2.4 Statistical data analysis

Statistical data analysis was performed in R studio (version 1.1.463) and Microsoft Excel (version 16.43). Significant effects were tested by a two-way ANOVA. A two-way repeated measurements ANOVA was performed when same samples were repeatedly measured. For significant effects Bonferroni and Games-Howell post hoc tests were carried out. Due to high differences between hydrogels in absolute absorption values and variation within hydrogels probably due to measurement inaccuracies, homogeneity of variance was not always given (measured by Levene test). When samples were measured on a percentual scale, variance between and within samples was attributed to measurement inaccuracies and homogeneity of variance assumed. In this case Bonferroni post hoc tests were carried out. When samples were measured on an absolute scale (ml/g) variance differed very strongly between hydrogels. In this case the Games-Howell post hoc test was used.

3. Results

3.1 Overview swelling capacity

The maximum swelling capacities per gram of hydrogel obtained by the different methodologies described in chapters 2.3.1., 2.3.2, 2.3.3.1 and 2.3.3.2 are shown in Table 1 and in Appendix Figure 1.

Table 1: Water retention of different hydrogels (ml/g) measured using different methods.

Method	Stockosorb		Polyter fine		Polyter coarse		Cellulose		Lignin	
	mean (ml/g)	SD	mean (ml/g)	SD	mean (ml/g)	SD	mean (ml/g)	SD	mean (ml/g)	SD
Bags (H2O)	294.7 aA	4.7	374.4 aA	28.7	288.7 aA	16.3	40.2 abB	26.7	5.3 aB	0.3
Tubes (H2O)	218.3 bA	5.4	185.8 bAB	12.1	173.8 bB	8.5	32.9 abC	7.4	5.1 aC	0.3
Bags (sand+soil solution)	114.9 cA	12.4	103.2 cB	7.7	NA	NA	44.8 bC	4.6	15.7 bD	2.1
Tubes (soil solution)	171.3 dA	1.1	118.1 dB	4.4	95.3 cB	7.3	35.3 abC	4.6	5.0 aD	0.3
Tubes (soil+H20)	42.9 eA	2.6	50.9 eB	3.3	49.0 dB	3.1	27.1 aC	5.2	6.9 cC	0.6

Significant differences ($p \leq 0.05$) between methodologies are displayed by different small letters, between hydrogels by different capital letters. Calculation by Games-Howell post-hoc test *mean: mean value of absorbed water per gram of hydrogel. *SD: Standard deviation.
Methods: *Bags (H2O): Bags with deionized water (2.3.2); *Tubes (H2O): Tubes with deionized water (2.3.1); *Bags (sand+soil solution): Bags filled with sand and soaked with soil solution (2.3.3.1); *Tubes (soil solution): Tubes with soil solution (2.3.1); Tubes (soil+H2O): Tubes filled with soil and soaked with H2O (2.3.3.2)

Overall Lignin absorbed the lowest amount of water, followed by Cellulose. Polyter and Stockosorb performed similarly, with some variations based on measurement methodology, but generally absorbing more water than the natural hydrogels.

Methodology had a significant impact on water absorption for Polyter (fine and coarse) and Stockosorb. There was a significant difference between measurements carried out in mesh bags and in tubes with deionized water, with samples in mesh bags absorbing significantly more water. Furthermore, soil solution decreased water absorption significantly. Lowest absorptions occurred when hydrogels were buried in soil.

Lignin was not as strongly influenced by the measurement method. The only significant increase was measured when the hydrogel was buried in soil.

For Cellulose as well absorption capacity did not vary strongly between the measurement methods. The only difference was found between samples soaked in bags and soil solution and samples buried in soil, with the latter absorbing significantly less water.

3.2 Effect of salt concentration on water absorption

Results of the effect of different concentrations of NaCl and CaCl2 on swelling capacity are shown in Figure 10 and Appendix Tables 5,6 and 7.
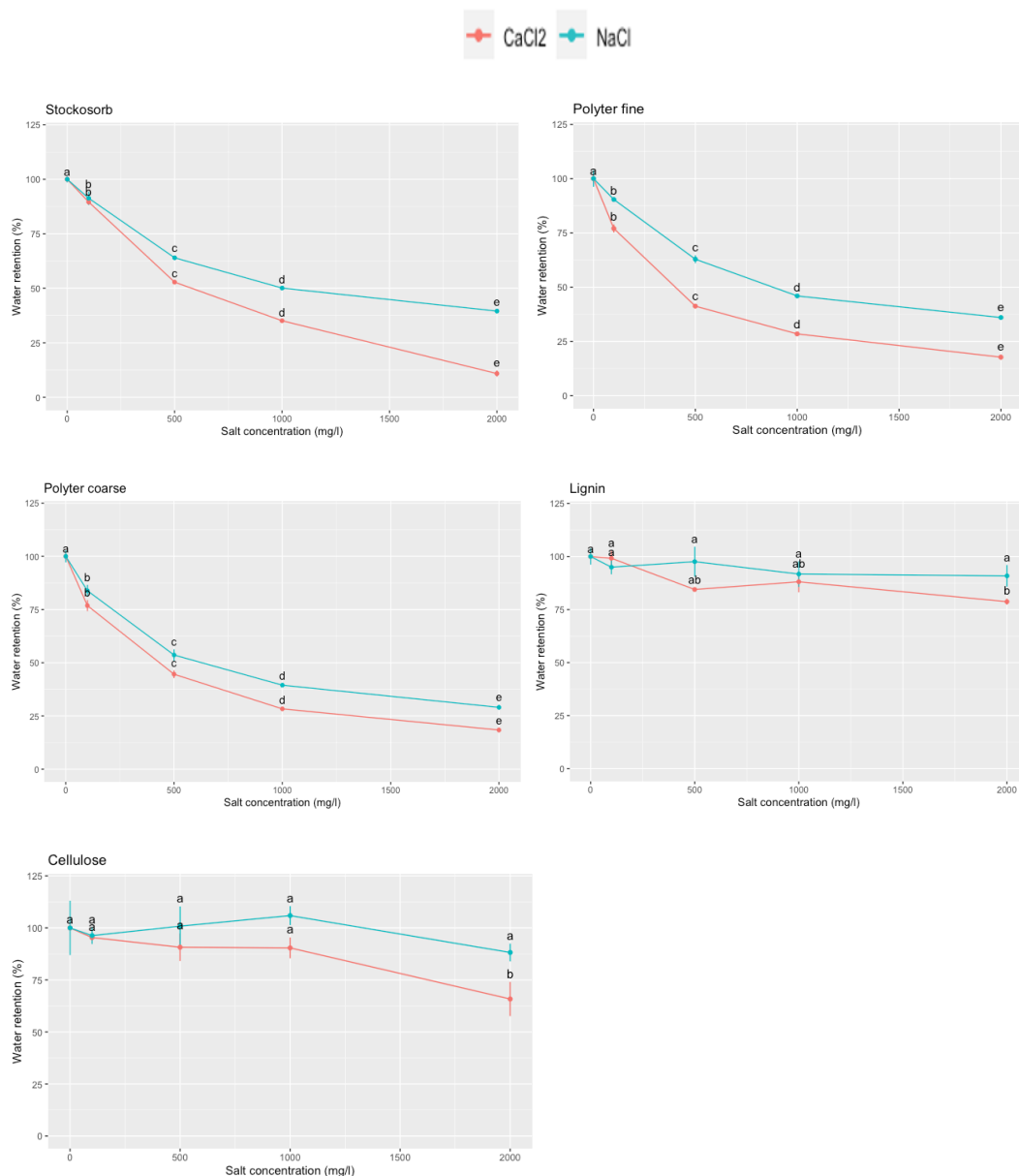
Figure 10: Mean values of water retention of five different hydrogels at varying concentrations of NaCl and CaCl2 as percentage to absorption in deionized water. Bars represent standard errors. Significant differences between different concentrations are displayed by different letters. Calculation by pairwise comparison of means. Adjustment of confidence intervals and p values by Bonferroni method.

In NaCl solutions Lignin and Cellulose were not significantly affected by increasing salt concentrations.

Fine grained Polyter, coarse grained Polyter and Stockosorb followed similar curves, with significant decrease in water holding capacity at each concentration.

After a concentration of 500 mg/l Stockosorb, Polyter coarse and Polyter fine absorbed a statistically lower percentage compared to Lignin and Cellulose.

Similarly to NaCl the increase in CaCl2 concentration as well had no significant effect on Lignin and Cellulose, except for concentrations of 2000 mg/l, where significantly less water was absorbed compared to measurements in deionized water.

Stockosorb, fine and coarse grained Polyter decreased their water retention capacity significantly at each concentration.

Absorption was not significantly different between Stockosorb and Polyter with one exception at 100 mg/l where Polyter absorbed significantly less water. Lignin and Cellulose absorbed significantly higher percentages compared to Stockosorb and Polyter at concentrations higher than 500 mg/l.

Differences between NaCl and CaCl2 solutions for each hydrogel are presented in Appendix Table 7.

Water absorption capacity for fine and coarse grained Polyter was significantly higher in NaCl solution at all concentrations.

For Stockosorb the amount of retained water was significantly lower in CaCl2 solutions starting from a concentration of 500 mg/l.

The only significant difference between NaCl and CaCl2 for Cellulose was at 2000 mg/l.

3.3 Swelling kinetics

Results of the experiment on swelling velocity of the various hydrogels are displayed in Table 2 and Appendix Figure 2.

Table 2: Results and statistical analysis of water absorbed by five different hydrogels after given time periods.

Time (hrs)	Stockosorb mean (%)	SD	Polyter fine mean (%)	SD	Polyter coarse mean (%)	SD	Cellulose mean (%)	SD	Lignin mean (%)	SD
0.017 (1 min.)	8.98 aA	0.81	8.94 aA	1.07	2.21 aA	0.61	11.45 aA	3.31	40.32 aB	0.92
0.033 (2 min.)	31.19 bA	2.98	28.71 bA	2.21	6.03 aB	1.03	27.49 abA	9.61	55.95 abC	2.78
0.083 (5 min.)	60.75 cAB	4..44	48.75 cAC	3.26	13.89 abE	1.62	36.81 bcC	13.72	66.30 bcB	1.30
0.167 (10min.)	77.13 cdA	2.04	67.01 dA	5.44	26.24 bcB	3.00	43.42 bcdC	15.92	75.75 cdA	0.61
0.333 (20 min.)	83.39 deA	1.01	76.36 deA	6.14	37.55 cdB	4.58	50.23 cdB	20.11	78.40 cdA	2.98
0.5 (30 min.)	88.50 deA	1.36	82.79 defA	6.22	48.30 deB	4.91	53.55 cdB	19.32	85.42 deA	2.57
1	91.64 deA	2.25	86.09 efA	4.83	62.08 efB	6.45	60.53 deB	24.14	88.13 deA	3.30
2	96.58 eA	2.19	88.18 efAB	8.06	76.40 fgBC	6.57	72.45 efC	34.50	99.39 eA	5.30
3	99.28 eA	2.91	92.11 efAB	7.03	88.34 ghAB	5.81	77.65 efB	38.20	98.62 eA	5.76
4	98.40 eA	2.87	91.95 efAB	5.37	91.72 ghAB	2.63	80.48 fB	40.67	97.54 eA	5.70
5	98.01 eA	1.33	94.63 fA	6.13	93.15 ghAB	4.46	79.75 fB	44.75	101.71 eA	4.75
24	100 eA	2.60	100 fA	6.84	100 hA	1.79	100 gA	58.55	100 eA	3.47

Significant differences (p ≤ 0.05) within each column are displayed by different small letters within each row by different capital letters. Calculation by pairwise comparison of means. Adjustment of confidence intervals and p values by Bonferroni method. *mean: mean percentual value of absorbed water. *SD: Standard deviation.

The hydrogels differed in terms of absorption velocity.

Stockosorb, fine grained Polyter and Lignin absorbed most of their total swelling capacity in the beginning.

Lignin had already absorbed 40% of total water in the first minute. The following increase was steady. After 30 minutes the increase was not significant anymore.

Stockosorb and fine grained Polyter swelled at similar pace, although Stockosorb was a little bit faster. Increase was not significant anymore after half an hour for fine grained Polyter and after 20 minutes for Stockosorb.

Coarse grained Polyter swelled at a slower, more constant pace compared to the fine granulometry but after two hours there was no significant difference anymore between the two.

Similarly to coarse grained Polyter also Cellulose swelled rather slowly compared to the other hydrogels, but it proved to swell for a longer time period. The increase between five and twenty-four hours was of nearly 20%.

3.4 Change in water absorption capacity after re-wetting:

3.4.1 Bags method

Results of the relative change in water holding capacity of the hydrogels are shown in Figure 8 and Appendix Table 2.
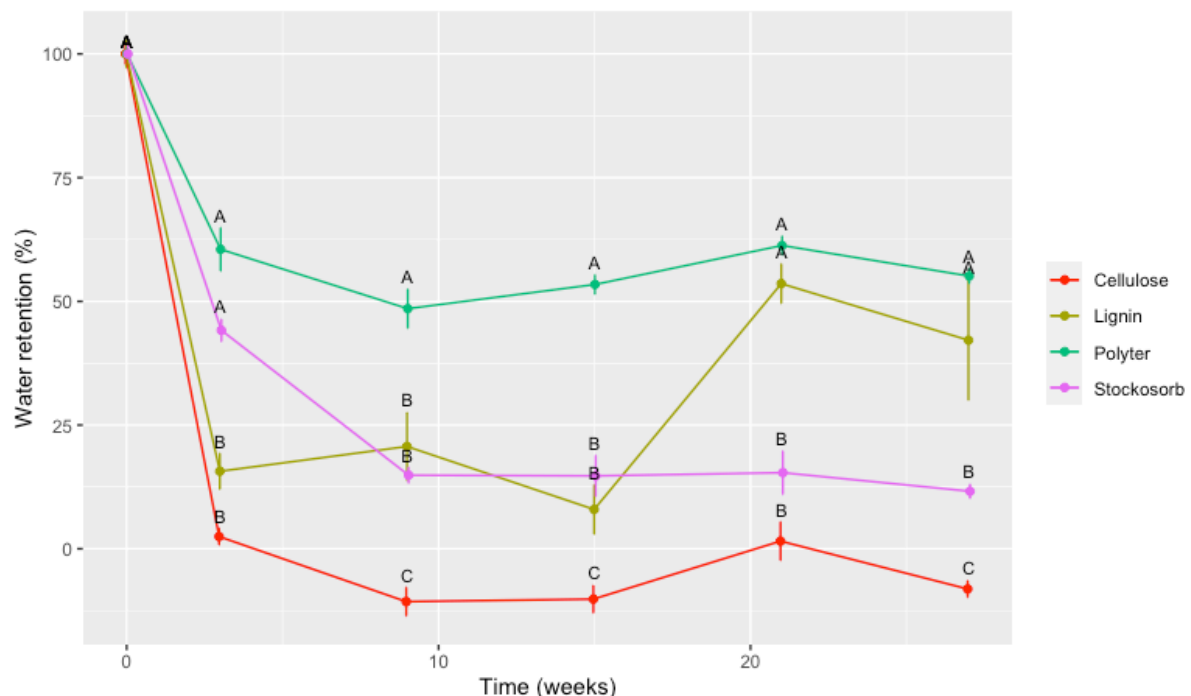
Figure 8: Mean values of water retention after rewetting (% of initial absorption) at given time periods for four different hydrogels. Significant differences between hydrogels are displayed by different capital letters. Bars represent standard errors. Method: Bags

The decrease between first and second measurement was significant for all hydrogels.

Cellulose lost nearly all of its water holding capacity.

Fine grained Polyter had a significant loss after three weeks but stabilized during subsequent measurements at around 50-60%.

Stockosorb had a significant reduction after three and nine weeks and stabilized at approximately 14% of its initial capacity.

For Lignin the results should be interpreted with care, as the amount of Lignin added to the samples resulted in very low water absorption. A lot of the variation could therefore be explained by measurement inaccuracies. There probably is some decrease in water holding capacity from the first to the subsequent measurements as there are no values reaching 100%, but it does not seem possible to identify a specific pattern linked to temporality.

Therefore, Polyter had the smallest reduction in relative water absorption capacity after 27 weeks, being able to still absorb 55% compared to the first measurement. Stockosorb still absorbed 11%. Cellulose did not absorb any water at all.

3.4.2 Tubes method

Results for change in water holding capacity using the tubes methodology are displayed in Figure 9 and Appendix Table 3.
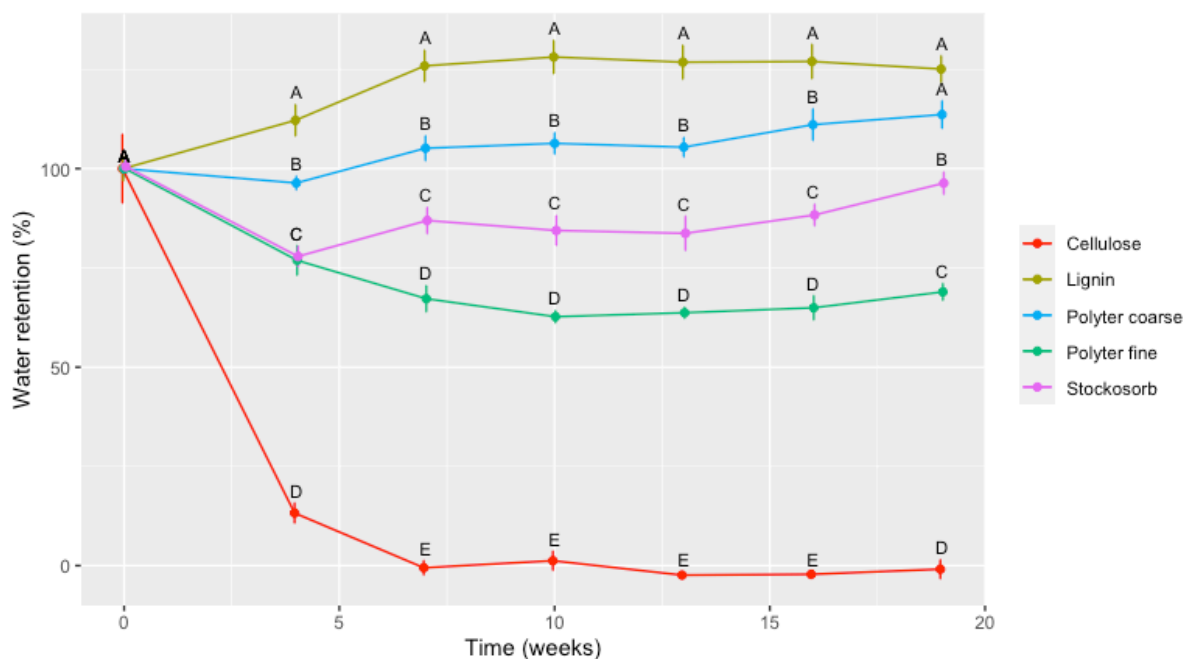
Figure 9:Mean values of water retention after rewetting (% of initial absorption) at given time periods for five different hydrogels. Bars represent standard errors. Different letters display significant differences between the hydrogels. Calculation by pairwise comparison of means. Adjustment of confidence intervals an p-values by Bonferroni method. Method: Centrifuge tubes.

Overall, Cellulose displayed the strongest decrease in water holding capacity, followed by fine grained Polyter and Stockosorb. Coarse grained Polyter and Lignin showed an increase in water holding capacity, which was not significantly different after the last measurement (week 19). For Stockosorb the decrease in water holding capacity was significant between the first and subsequent measurements, except for the last two.

Fine grained Polyter showed a significant decrease after 4 weeks but stabilized afterwards, resulting in a similar pattern as in the measurements conducted with the mesh bags (3.4.1).

Coarse grained Polyter didn't show significant changes from the first measurement up until week 19. Water holding capacity at week 19 although was significantly greater than during the first measurement.

Cellulose, similarly to the bags experiment, lost nearly all of its water holding capacity after the first measurement, resulting in water retention values close to those of the control.

Mean water retained by Lignin increased after 4 and 7 weeks, before showing some sort of stabilization.

3.5 Water release capacity

Stockosorb, Polyter, Lignin and Cellulose increased water availability to soil.

Depending on the initial water retention, hydrogels were able to prolong the time until water content in the samples stabilized (i.e., decrease in water content <0.05% per hour) (Figure 11).
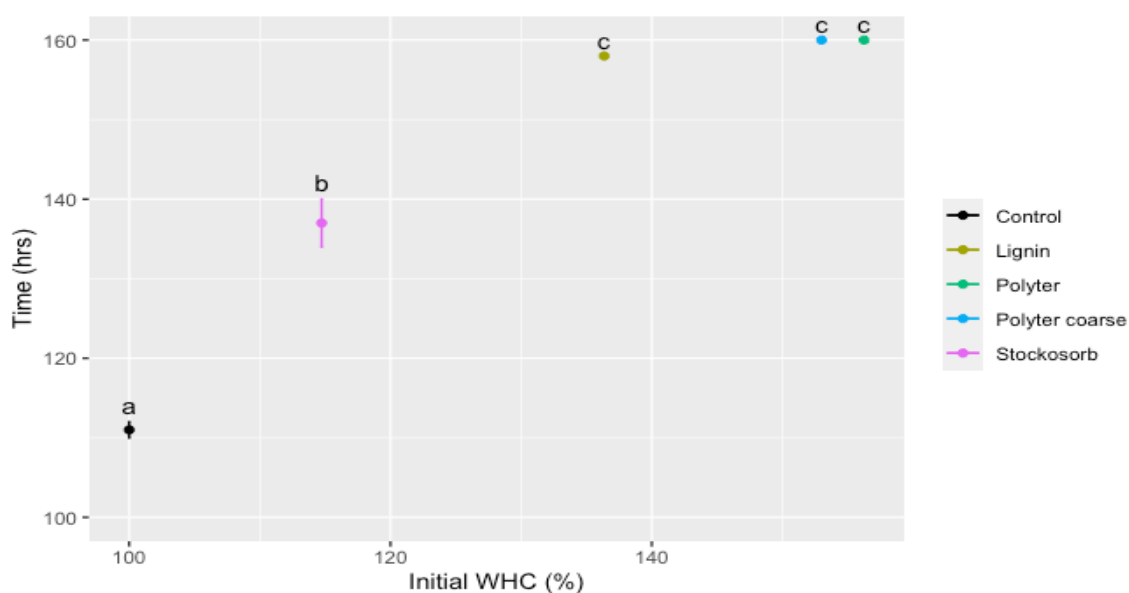
Figure 11: Time until water content stabilized (i.e., the evaporation rate was lower than 0.05% per hour). Cellulose was excluded from the figure, as the decrease in water content was 0.18 % and therefore still higher than the set threshold value of 0.05%. Bars represent standard errors. Different letters indicate significant differences in duration of water release between hydrogel samples. Calculation by pairwise comparison of means. Adjustment of confidence intervals and p values by Bonferroni method.

Higher initial water holding capacity resulted in longer water release. Lignin, although absorbing significantly less water than Polyter fine and Polyter coarse, displayed nearly equal

time of water release. Cellulose did not stabilize during the measured time period as there was significantly more water in the Cellulose samples compared to other samples after 168 hours (Figure 14), resulting in a mean evaporation rate of 0.18 % per hour, therefore being still higher than the threshold value set for the hourly decrease (0.05%). This despite the fact that the initial water holding capacity was of 136.5 % and therefore equal to that of Lignin and significantly lower than that of Polyter fine and coarse (Appendix Table 11).

Also, microbial activity was positively affected by increased water retention. Longer evaporation resulted in a longer period of microbial activity (Figure 12). The increased period of microbial activity was estimated by assessing the moment the hydrogel samples reached the respiration value of the Control when water content stabilized. This threshold value was determined as 0.00064 g CO_2-C/m2 /h.

For Stockosorb and Lignin water content and microbial activity stabilized approximately at the same time. Polyter fine and Polyter coarse stabilized microbial activity slightly before water content. Time water content stabilized and time the respiration reached the threshold value correlated strongly, with a Pearson Correlation factor of 0.98 (Figure 13). This suggests that the absorbed water was made bioavailable.

As the evaporation rate (mean decrease of 0.18 % per hour) and the overall water content was higher in the Cellulose samples compared to the threshold value after 168 hours (decrease per hour <0.05%), also the microbial respiration did not reach the determined threshold value, as there was still enough water available to the microbes. Cellulose still respired at a rate of 0.00162 g CO_2-C/m2 /h, compared to the threshold of 0.00064. Therefore, Cellulose was excluded from Figure 12.
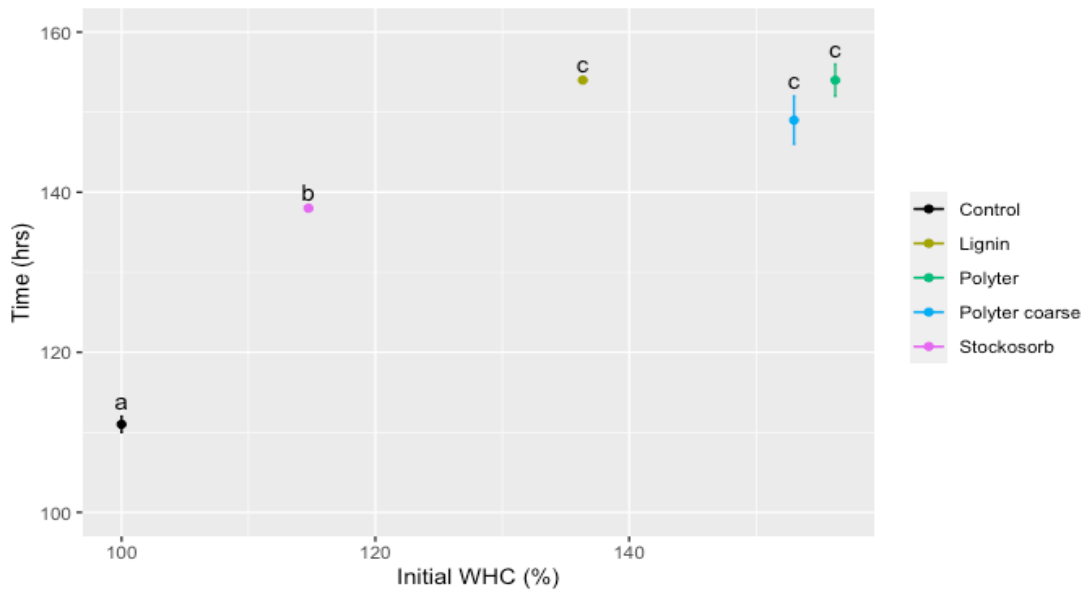
Figure 12: Time until microbial respiration reached threshold value (respiration value of the Control when the evaporative loss was lower than 0.05% WHC per hour for the first time, i.e. 0.00064 g CO2-C/m2/h). Cellulose was excluded from the figure as microbial respiration did not reach the determined threshold value after 168 hours (mean respiration was still 0.00162 g CO2-C/m2/h). Bars represent standard errors. Different letters display significant differences in duration of microbial activity between the hydrogel samples. Calculation by pairwise comparison of least square means. Adjustment of confidence intervals and p values by Bonferroni method.
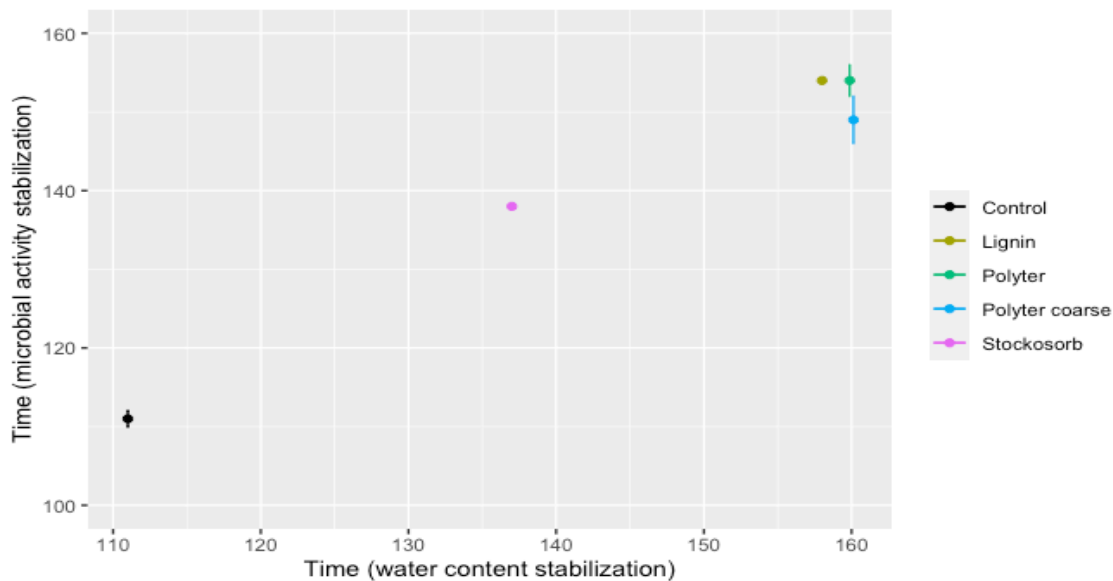
Figure 13: Correlation between time of water content stabilization (i.e., time where the evaporation rate was lower than 0.05% per hour) and time until microbial respiration reached threshold value (i.e., respiration value of the control when the evaporative loss was lower than 0.05 % WHC per hour for the first time). Cellulose was excluded from the figure as it did not reach neither of the two threshold values.

After one week Polyter (fine and coarse) and Stockosorb had reached approximately the same water content as the Control. All the absorbed water was therefore released by the gels. Cellulose had the highest amount of residual water due to a low evaporation rate. Lignin as

well had a (although not significantly) higher water content than the Control after one week with some residual water probably retained by the gel (Figure 14).

Figure 14: Residual water content of hydrogel samples after 168 hours. Bars represent standard errors. Different letters indicate significant differences between the samples. Calculation by pairwise comparison of least square means. Adjustment of confidence interval and p values by Bonferroni method.

Fitted curves of evaporative loss and microbial respiration over time are reported in Appendix Figures 7,8,9 and 10.

4. Discussion:

As the results in the swelling overview suggest (Appendix Figure 1 and Table 1) water absorption capacity of Stockosorb and Polyter d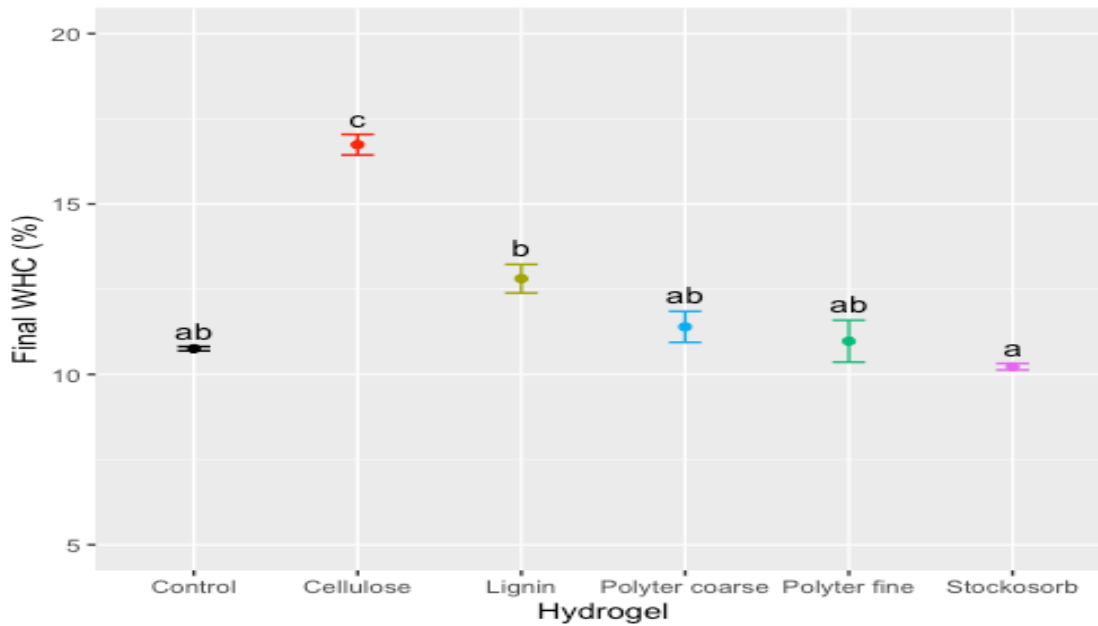iffered significantly depending on the used methodology, whereas Cellulose and Lignin were not strongly influenced. Various parameters could be responsible for the differences in absorption capacity at first wetting that were observed in the experiments.

It has been reported that pressure exerted on hydrogels significantly reduces their swelling capacity (Hossein Hosseinzadeh, 2013; Lejcuś et al., 2018; Salimi, Pourjavadi, Seidi, Jahromi, & Soleyman, 2010). Pressure was probably higher in centrifuge tubes compared to mesh bags, as the water column during swelling was higher and expansion was limited by rigid side walls. Also, pressure exerted by surrounding soil and sand resulted in a decrease in absorption capacity. Stockosorb and coarse grained Polyter, but especially fine grained Polyter seemed to be very susceptible to pressure exertion. Fine grained Polyter absorbed nearly double the amount of deionized water after five hours in mesh bags (value measured during the experiment on swelling kinetics after 5 hours) compared to centrifuge tubes (measured in the experiment on soil salinity). Cellulose as well absorbed less deionized water in the tubes compared to bags and even less when it was mixed into soil. The difference although was not significant. Interestingly, Lignin displayed significantly highest water absorption when it was buried in soil. As reported by Demitri et al., (2013) hydrogels can increase the porosity of the soil. Considering the amount of hydrogel added, it could be reasonable to assume that the Lignin hydrogel ameliorated the soil structure, creating a more porous soil which was able to retain more water.

Nonetheless, these results may serve as an approximation. A separate experiment measuring the absorption under load would be needed in order to measure the dependency between pressure and absorption.

Another factor that probably affected swelling capacity was the presence of ions. Particles swelling in soil or soil solution absorbed less than in deionized water.

This observation has been confirmed by the experiment conducted on the effect of mono- and divalent salts on the swelling behavior (Figure 10). Salinity had a strong effect on absorption properties of Stockosorb and Polyter. As reported by various authors, increasing salt concentration led to a significant reduction in swelling capacity of the hydrogels (Bo et al.,

2012; Buchholz & Graham, 1998; Zohuriaan-Mehr & Kabiri, 2008). Increasing salt concentration reduces the osmotic pressure gradient between the inside of the hydrogel and the solution, resulting in a lower amount of water absorbed (Bo et al., 2012).

Also, the reduction was significantly stronger for CaCl2 compared to NaCl solutions.

Many authors linked water absorption capacity to the ionic strength of the solution, being higher for divalent salts (CaCl2), compared to monovalent salts (NaCl) (Chatzoudis & Rigas, 1999; Kabiri et al., 2011). Additionally, multivalent cations, such as Ca2+, have been shown to act as cross-linkers between ionic sites and to collapse the polymeric structure, reducing the ability of the hydrogel to expand (Chatzoudis & Rigas, 1999). Moreover, Kaith et al. (2012) assumed that the increase in ionic charge led to an increase in cationic-cationic repulsion, which inhibited the movement of solution containing more ions into the polymer network.

Natural hydrogels were not strongly affected by increasing salt concentrations. The only significant decrease for Lignin and Cellulose was measured at concentrations of 2000 mg/l of CaCl2. A reason for this could be the fact that the natural hydrogels are neutral hydrogels with little or no anionic or cationic functional groups acting as drivers in the osmotic gradient and serving as additional cross-linking sites for multivalent ions. An increase in salt concentration therefore does not alter the main absorption mechanisms, which are entropic and energetic interactions with hydrophilic groups such as hydroxyls, carbonyls and methoxyls (Rico-García et al., 2020; Sanz Gómez, 2015).

Therefore, both factors, pressure and salinity, surely influenced the outcome in the different experiments for Polyter and Stockosorb, whereas Lignin and Cellulose were not so heavily affected. In order to get more precise insight on the correlation between these two factors experiments combining measurements under known pressure and with known ionic strength should be carried out.

The experiment conducted on swelling kinetics highlighted differences in absorption velocities of the hydrogels (Table 2).

Fine grained Polyter, Stockosorb and Lignin had no significant increase in water content after 30 minutes. Coarse grained Polyter swelled a lot slower compared to the fine-grained equivalent. This difference in swelling velocity might be led back to a lower surface to volume ratio for coarse Polyter due to bigger particle sizes (Mignon et al., 2019).

Overall Cellulose swelled at the slowest pace, but it has to be kept in mind that there was a strong difference in absorption between Cellulose samples. Some samples had reached maximum swelling after two hours, whereas another one still swelled consistently between five

and twenty-four hours absorbing more than double the amount of the other samples. In fact, there was still a significant increase of nearly 20 % between five and twenty-four hours of swelling. This might be explained by the fact that Cellulose particles were very heterogeneous in size and shape, with some particles absorbing more water than others due to this physical differences. This resulted in very high standard deviations. Statistical analysis should therefore be critically overthought.

In the two experiments carried out to assess the change in water holding capacity of hydrogels exposed to soil over several wetting and drying cycles, the change varied between the hydrogels and between the two methodologies used (mesh-bags method and tubes method) (Figures 8 & 9).

In the bags experiment Cellulose had the strongest reduction in water holding capacity, followed by Stockosorb and fine grained Polyter. Similarly to the bags experiment also in the tubes experiment Cellulose had the strongest reduction in water holding capacity, followed by fine grained Polyter and Stockosorb. Lignin and coarse grained Polyter had increased their water holding capacity compared to the first measurement.

Cellulose proved to be unstable, both in the mesh-bags and the tubes method. At the second measurement Cellulose had lost nearly all of its water holding capacity in both methodologies. In the tubes method, before re-wetting for the second measurement, the soil was topped by a slimy and jelly-like fluid, which did not evaporate. After re-wetting and dripping the water retained by the gel was close to zero. This leads to the conclusion that the gel was not stable and might have slowly broken up during the first weeks, losing its structure and creating a jelly-like fluid, which was then washed out through the filter during dripping. Similarly, also Cellulose in bags might have broken up and been lost to surrounding soil while being buried.

The complete loss of the product led to some mean absorption values to be lower than those of the Control. The calculation of mean percentage of water retained by the gel and statistical analysis has therefore little sense, as the percentage was calculated from the initial gel present in the bags, which was probably not present anymore during later measurements.

A reason for this instability of the Cellulose hydrogel might be a low cross-linking degree, which has been reported to influence the stability of hydrogels. A low cross-linking degree results in unstable gels which easily dissolve upon contact with water (Mignon et al., 2019).

Besides a low cross-linking degree also microbial degradation, which has been shown to be very high for natural hydrogels based on cellulose (Wang et al., 2008), could have had an impact in altering the hydrogels structure and therefore decreasing its functionality.

Fine grained Polyter and Stockosorb had a reduction in water holding capacity which preceded some sort of stabilization in absorption values in both methodologies.

The pattern was similar in both methodologies for fine grained Polyter, with a significant decrease in absorption capacity after three weeks (bags method) and after four and seven weeks (tubes method) and stabilization of absorption values around 50-60% (bags) and 60-70% (tubes). Stockosorb on the other hand lost nearly all of its water holding capacity after nine weeks in the bags experiment, stabilizing at absorption values between 10 and 15%. These results are in strong contrast with those obtained by the tubes method. Decrease in water holding capacity was not that pronounced, with values ranging between approximately 80 and 90% of initial absorption capacity.

According to existing literature different factors might be responsible for this initial reduction in water holding capacity. Overall, little research has been conducted on the effect of microbial degradation on water absorption capacity of the hydrogels. In one study conducted by Wilske et al. (2014) the polyacrylate main chain of a synthetic hydrogel degraded at a very low rate of 0.12-0.24% after 6 months. But one fourth to one half of total six-months degradation occurred during the first two weeks. This suggests that the degradation occurred mainly on the hydrogel surface on so-called "loose ends" and oligomers. In this same study a decreasing water holding capacity after some weeks of incubation was observed for hydrogels buried in sand. The authors explained it by the very low cation exchange capacity of sand and the resulting exposure of the hydrogel to cations, resulting in a collapse of the hydrogel structure. Similarly, also Holliman et. al (2005) observed the largest decrease in swelling capacity of soil-exposed gels after the first months of exposition. Considering the collapse of the hydrogel structure, also Sanz-Gómez (2015) reported a steady decrease in absorption after multiple swelling-deswelling cycles in multivalent ion solutions.

The microbial degradation rate for hybrid hydrogels has shown to be a lot higher (Jin et al., 2013; Wang et al., 2008) compared to synthetic hydrogels. This would theoretically explain the stronger loss in absorption capacity of fine grained Polyter compared to Stockosorb in the tubes method. On the other hand, the bags method resulted in opposite results. Stockosorb had a much stronger decrease in water absorption capacity compared to Polyter and to Stockosorb in the tubes method. One plausible explanation could derive from the fact that Stockosorb particles, similarly to the other hydrogels, were sieved to sizes smaller than 0.8 mm for the bags experiment but were overall actually smaller than the other gels, as the product contained a lot of "powdery" material. Smaller particle sizes result in higher microbial degradation rates due to higher surface to volume ratio. This could be the reason for a stronger loss in water

absorption capacity compared to the tubes methodology. Another reason might be that the sieved Stockosorb particles were unstable and pressed out of the mesh bag, as it was observed that some slimy substrate was present on the mesh after dripping. Parts of the hydrogel might have therefore been lost to surrounding soil after being buried in Tupperware boxes. The results from the tubes experiment are therefore believed to be more reliable in this case.

Results of these two hydrogels don't allow for a definitive conclusion on which factor, degradation or collapse of the structure, led to the decrease in water holding capacity and its subsequent stabilization. The results suggest that either the microbial degradation decreases after some weeks (as suggested by various authors above) or that ions collapse the hydrogel structure until reaching an equilibrium after some re-wettings. Probably the magnitude of the decrease results from a combined action of both factors. Additionally, a factor for the strong decrease of Stockosorb in the bags experiment could be the instability of the small particles, which might have been lost.

Lignin displayed different results in both methodologies used. In the bags method water absorption decreased, but was subject to huge, uncorrelated fluctuations. A substantial decrease during the first four measurements (until week 15) was followed by a significant increase in measurements five (21 weeks) and six (27 weeks). The results should be handled with care, as the amount of water absorbed by the hydrogel was very low. This is due to too little amount of hydrogel added to the samples in relation to its swelling capacity. The variation in calculated water absorption might therefore be a consequence of variation in water retained by the surrounding medium (sand). In the measurements conducted in tubes the water retention increased during weeks 4 and 7 and stabilized subsequently. Because of the amount of Lignin added (2.5 g), which was all allocated in the bottom half of the sample, dripping did not work properly, and the sample had to be gently disturbed with a spatula in order to allow for airflow during the first two measurements. This procedure and the subsequent turning of the sample has reallocated the gel along the whole soil-profile, reducing pressure on it and, as suggested by Demitri et al., (2013) by possibly creating a more porous soil structure, thereby increasing the water holding capacity of the soil-hydrogel matrix. Nonetheless, water absorption remained constant with no significant fluctuations after week 7, suggesting there was no reduction in water holding capacity due to microbial biodegradation after that time point.

Coarse grained Polyter, which was only measured by using the centrifuge tubes methodology, followed a similar pattern as the Lignin samples. Water holding capacity of the samples increased during later measurements. This is explained by the fact that some hydrogel particles moved out of the soil and settled on the soil surface, due to the slight, but repeated soil

movement when turning the samples. This might have reduced the pressure exerted on the hydrogel. As reported by Sanz Gómez (2015) a reduction in pressure on the hydrogels increases its absorption capacity. This fact makes it impossible to assess the effect of biodegradation on water retention of the gel, as the samples were too heavily disturbed.

Overall, both methodologies had its flaws and results should be critically overthought. In the bags experiments very small particles were used, as initially it was believed that smaller particles would increase the effect of microbial degradation, therefore making it easier to detect changes in water absorption capacity related to it. Especially for Stockosorb the use of this very small particles impacted the performance by reducing its water absorption capacity after re-wetting compared to the tubes experiment, where particles were not sieved. For Lignin too little product was added to the bags in order to be able to assess changes over time.

The tubes methodology on the other hand used samples which contained unsieved hydrogels, which was directly mixed into soil, therefore simulating the natural environment. A disadvantage of this method was the constant disturbance of the samples, with soil and hydrogel particles being moved during the dripping process. This has affected the position of the hydrogels, reallocating them along the soil profile and therefore probably impacting water absorption capacity. A methodology reducing soil disturbance as much as possible should therefore be developed.

Finally, it seems difficult to assess the effect of microbial degradation on the performance of the different hydrogels. As there clearly is a decrease in water holding capacity for Polyter, Stockosorb and Cellulose in both methodologies there are several factors that could have influenced the outcome. In order to get a better idea of the effect of microbial degradation on water absorption, degradation rate should be simultaneously monitored.

The last experiment assessed the capacity of the hydrogels to release the absorbed water to surrounding soil and to make it bioavailable.

Before discussing the results, it is worth mentioning that Stockosorb absorbed just approximately one fourth of the water compared to the other experiment where the hydrogels were directly buried in soil (tubes experiment, chapter 3.4.2), whereas Polyter, Lignin and Cellulose absorbed pretty similar quantities as in that experiment (Appendix Table 4 and 11). Stockosorb has been observed to swell strongly in a first phase but to release a great part of the water again afterwards. This phenomenon has been observed by Sakohara et al. (1990), for a synthetic hydrogel (sodium polyacrylate) swelling in electrolyte solutions. The gel swelled up to a maximum absorption, but subsequently shrank again. The authors explained the process

by electric forces acting on the gel. In the beginning functional groups of the synthetic hydrogel (-COONa) dissociate, with sodium ions distributing along the hydrogel/solution interface as a result of diffusion forces pushing the ions towards the solution and electrical attractive forces of the network keeping them back. The resulting electrical gradient between cations and anions forces the network to expand. In saline solutions an exchange between sodium ions and other cations occurs, which attach to the negatively charged -COO groups. This reduces the electrical force acting upon the gel and results in a release of previously absorbed water. The magnitude of the effect depends on the affinity of the cations present in the solution to -COO⁻ functional groups and on the concentration of salts in the solution. A higher ionic concentration in this experiment compared to the tubes experiment is assumed, as the soil/water ratio was way higher. As Stockosorb (potassium polyacrylate) presumably contains much more functional groups which can act as ion exchanger compared to the other hydrogels the effect of an increased ionic concentration was more pronounced, possibly also because of a high affinity of cations present in the solution to the functional groups.

The results of this experiment highlighted the fact that the capacity of the hydrogels to release the absorbed water to soil did not differ very strongly between them (Figure 14).

Polyter (coarse and fine) and Stockosorb reached approximately the same final water content as the Control. We can conclude that all absorbed water was released by the hydrogels. Lignin, although having a lower initial water content, provided water to soil for nearly as long as Polyter. This can be explained by a slower water release from the hydrogel to the soil and subsequently a flatter evaporation curve. Final water content of Lignin is slightly higher than that of the Control, implying that very small amounts of water were still retained by the gel. Cellulose samples had the highest final water contents after one week, because overall evaporation resulted to be slower than for other samples. The reason might be found in the instability of the gel, with parts of the hydrogel slightly dissolving into water and creating a jelly- like fluid. As suggested by Khalil et al. (2002), polymer additives (sodium carboxymethyl cellulose) reduce evaporation rate of water by increasing viscosity and therefore decreasing internal mass motion. Furthermore, the Cellulose hydrogel was analyzed after the completion of the desorption experiment. The particles had been completely deformed from their initial state, being present as a very thin layer attached to the soil matrix. One of the main reasons for hydrogel stability is the degree of cross-linking. Too high cross-linking results in decreased absorption capacity, whereas a low cross-linking degree leads to the instability of the gel (Mignon et al., 2019). Increasing the degree of cross linkages could therefore be a possibility

of increasing the gels stability. Nevertheless, the reduction in evaporation rate through dissolved polymers increased the time of water availability to soil. Therefore, for a one-time application Cellulose might be appropriate. For a repeated use it proved to be inadequate, deforming, dissolving and being washed out through additional irrigation.

The increase in water release through the hydrogels resulted in a prolonged time of microbial activity (Figure 13). From this correlation we can deduce that the released water was also made bioavailable to soil microorganisms, enhancing and prolonging their activity.

Nonetheless, the hydrogels seemed to increase overall microbial respiration, probably because the hydrogels as well were subjected to degradation. Interestingly, also Stockosorb displayed a relatively high respiration rate. High respiration activity in Stockosorb may be due to a high number of residual monomers, which are quickly degraded by soil microorganisms (Oksińska, Magnucka, Lejcuś, & Pietr, 2016). Moreover, Cellulose and coarse grained Polyter had lower respiration rates compared to the other hydrogels, probably because of a lower surface to volume ratio.

Therefore, the results comparing the time of prolonged respiration should be critically overthought, as it could be that hydrogel inherent respiration influenced the outcome.

It has to be kept in mind that the results of the experiment are to be analyzed theoretically, and it does not mean that all the water is also plant available.

At 10% of the soils water holding capacity the suction forces of the soil might by far exceed the suction potential of plants, which might not be able to extract all the water from the hydrogel. This supposition has been confirmed by Saha et al. (2020), which analyzed several studies conducted to determine the increase in plant available water content by the addition of hydrogels. They found that an increase in field capacity also led to an increased water content at the permanent wilting point. This implies that a significant amount of water stored is not available to plants.

Under a practical perspective, analyzing the amount of released water at permanent wilting point should give more useful insight to the actual efficiency of the hydrogel to support plants with water.

5. Conclusion

The tested hydrogels have shown to differ between each other in various ways.

In terms of swelling velocity Lignin, Stockosorb and fine grained Polyter did not increase their water content significantly after thirty minutes, whereas coarse grained Polyter swelled significantly for three and some Cellulose particles still after five hours.

As Polyter and Stockosorb overall were able to imbibe way bigger amounts of water compared to Cellulose and especially Lignin, they were also very susceptible to factors like pressure exertion and salinity of the swelling solution. The latter was shown to reduce the swelling capacity of the synthetic and hybrid hydrogels a lot more than that of Cellulose and Lignin, which were not affected at all. Divalent salts (CaCl2) lead to a stronger reduction in water absorption capacity compared to monovalent ones (NaCl). This decrease might be explained by a reduction in the osmotic pressure gradient by increased salt content in the solution.

When measuring the change in water holding capacity, the tubes methodology showed that Stockosorb and the fine grained Polyter reduced their water holding capacity when they were mixed into soil and subjected to several wetting and drying cycles, with the latter displaying a stronger reduction. On the contrary Lignin and coarse grained Polyter increased water absorption, probably due to samples being too heavily disturbed during the measurements. The frequent turning of the samples has moved the hydrogel particles and reallocated them along and outside the soil profile, therefore influencing their water absorption capacity. The experiment should ideally be repeated trying to apply a design with lower sample disturbance. Cellulose had the strongest reduction in water holding capacity, as it was very unstable, dissolving and being washed out from the soil. The bags methodology gave similar results for Cellulose and fine grained Polyter compared to the tubes experiments but the measurements of Lignin (too little gel added) and Stockosorb (possible instability of the sieved particles) are not believed to be trustworthy.

It was not possible to assess with certainty which factor led to the decrease in water holding capacity of Stockosorb, fine grained Polyter and Cellulose. For Cellulose it is believed to be a too low cross-linking degree which usually results in unstable gels and their dissolution. But also microbial degradation might have had an influence in breaking up the gel. Polyter and Stockosorb may have reduced their capacity as result of the combined action of microbial degradation and a collapse of the hydrogel structure through additional cations present in the soil solution which acted as additional cross-linkers. In order to assess the effect of microbial degradation alone on reduction of water holding capacity microbial degradation rate should be

monitored simultaneously and possible effects like collapse of the hydrogel structure through cations estimated by a separate experiment.

All hydrogels were able to release nearly the entirety of the absorbed water to a drying soil and to make it bioavailable to soil microorganisms. This, although, does not imply that all the water will also be plant available as the suction forces of a soil at 10% of its water holding capacity might by far exceed those of plants. Further research will be needed to assess the increase of plant available water through hydrogel addition.

Overall, Polyter proved to be a valid alternative to a fully synthetic product like Stockosorb, absorbing great amounts of water and being able to release all of it. But similarly to Stockosorb it also seemed to be strongly influenced by factors like pressure and salinity.

Lignin absorbed very low amounts of water compared to the other hydrogels but it might be useful if applied in greater quantities. It should be further assessed if it possibly influences soil porosity and structure, therefore ameliorating also other soil properties.

Cellulose was unstable over longer periods of time as it dissolved in water. It is therefore not suitable to be used in practice with the exception maybe for one-time applications. Increasing its cross-linking degree could possibly be a solution to ameliorate the gels stability.

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7. Appendix:
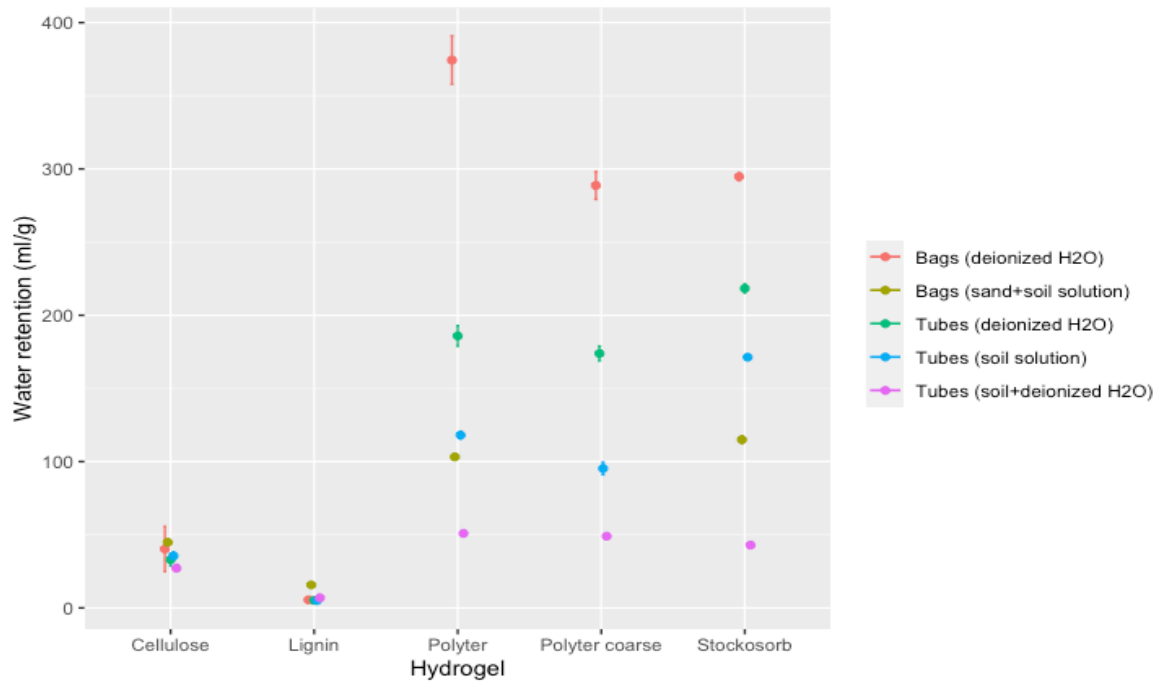
Appendix Figure 1: Mean values of water retention of five different hydrogels measured by different methodologies. Bars represent standard errors.
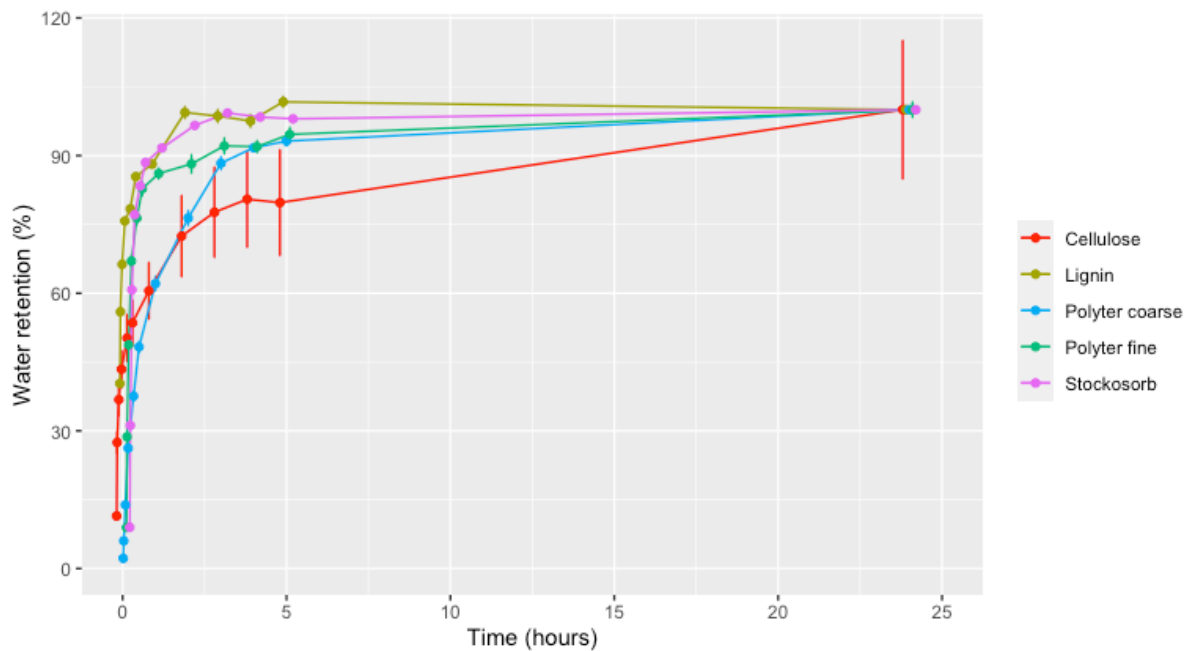
Appendix Figure 2: Mean absorbed water of five different hydrogels at given time periods. Bars represent standard errors.
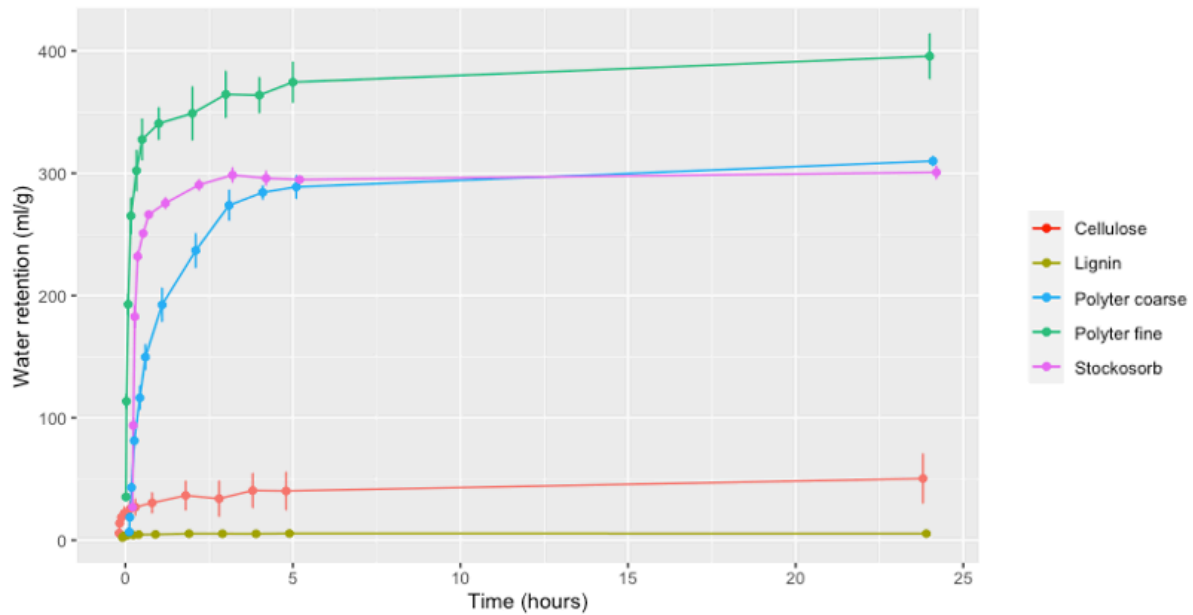
Appendix Figure 3: Mean absorbed water of five different hydrogels at given time periods. Bars represent standard errors.

Appendix Table 1: Results and statistical analysis of water absorbed by five different hydrogels after given time periods.

Time (hrs)	Stockosorb		Polyter fine		Polyter coarse		Cellulose		Lignin	
	mean (ml/g)	SD	mean (ml/g)	SD	mean (ml/g)	SD	mean (ml/g)	SD	mean (ml/g)	SD
0.017 (1 min.)	26.99 a A	2.87	35.38 aA	5.02	6.86 aB	2.24	5.77 aB	1.98	2.18 aB	0.06
0.033 (2 min.)	93.81 b A	10.62	113.6 bA	10.33	18.70 abB	3.77	13.86 aB	5.74	3.02 abB	0.18
0.083 (5 min.)	182.71 c A	15.81	192.87 cA	15.26	43.05 bcB	5.94	18.57 aBC	8.19	3.58 bcC	0.08
0.167 (10min.)	231.95 c A	7.28	265.14 cdA	25.48	81.33 cdB	11.02	21.90 aC	9.5	4.09 dC	0.04
0.333 (20 min.)	250.79 cd A	3.58	302.14 cdA	28.81	116.39 cdeB	16.81	25.33 aC	11.99	4.23 cdC	0.19
0.5 (30 min.)	266.14 de A	4.84	327.57 dA	29.16	149.71 defB	17.99	27.01 aC	11.53	4.61 deC	0.16
1	275.61 defAB	8.00	340.61 dA	22.63	192.43 efgB	23.67	30.52 aC	14.40	4.76 deC	0.21
2	290.44 ef A	7.78	348.90 cdA	37.72	236.79 fgA	24.11	36.54 aB	20.59	5.37 cdeB	0.34
3	298.55 def A	10.36	364.44 dA	32.90	273.82 gA	21.33	33.97 aB	25.14	5.32 cdeB	0.37
4	295.92 df A	10.21	363.80 dA	25.14	284.28 gA	9.66	40.59 aB	24.28	5.27 cdeB	0.36
5	294.74 f A	4.73	374.40 dA	28.71	288.73 gA	16.35	40.22 aB	26.70	5.49 deB	0.30
24	300.73 ef A	9.24	395.66 dA	32.00	309.95 gA	6.57	50.43 aB	34.94	5.40 eB	0.22

Significant differences ($p \leq 0.05$) within each column are displayed by different small letters, within each row by different capital letters. Calculation by pairwise comparison of means by Games-Howell test. *mean: mean value of absorbed water per gram of hydrogel. *SD: Standard deviation.

Appendix Table 2: Results and statistical analysis on percentage of absorbed water to initial water absorption at given time periods. Method: Bags.

Time (weeks)	Stockosorb mean (%)	SD	Polyter mean (%)	SD	Cellulose mean (%)	SD	Lignin mean (%)	SD
0	100 aA	10.81	100 aA	7.49	100 aA	10.34	100 aA	13.92
3	44.15 bA	5.03	60.51 bA	9.79	2.48 bB	3.73	15.67 bB	8.10
9	14.88 cA	3.55	48.53 bB	8.82	-10.67 bC	6.43	20.68 bA	15.29
15	14.73 cA	9.26	53.41 bB	4.35	-10.17 bC	6.14	7.95 bA	11.17
21	15.38 cA	9.76	61.29 bB	4.23	1.55 bA	8.66	53.59 cB	8.91
27	11.63 cA	3.16	55.12 bB	3.37	-8.12 bC	3.74	55.12 cB	27.03

Different letters within each column display significant differences at p ≤ 0.05 between different times. Calculation by pairwise comparison of means. Adjustment of confidence intervals and p values by Bonferroni method *mean: mean value of absorbed water. *SD: Standard deviation.

Appendix Table 3: Results and statistical analysis of hydrogel-absorbed water (%) at given time periods. Method: Tubes.

Time (weeks)	Stockosorb mean (%)	SD	Polyter fine mean (%)	SD	Polyter coarse mean (%)	SD	Cellulose mean (%)	SD	Lignin mean (%)	SD
0	100 aA	2.08	100 aA	2.10	100 abA	1.37	100 aA	8.64	100 aA	3.06
4	77.89 bA	7.63	76.89 bA	11.78	96.37 aB	5.47	13.25 bC	5.63	112.17 abD	11.84
7	86.93 bcA	9.91	67.23 bcB	10.37	105.13 abcC	9.88	-0.53 bD	4.02	125.87 bcE	11.86
10	84.41 bcA	11.22	62.70 cB	4.92	106.35 abcC	8.63	1.24 bD	5.36	128.11 cE	12.62
13	83.70 bcA	12.95	63.70 cB	4.39	105.40 abcC	7.79	-2.38 bD	1.71	126.81 cE	12.78
16	88.37 abcA	8.20	64.96 bcB	9.59	111.01 bcC	12.64	-2.19 bD	1.43	126.99 cE	12.96
19	96.33 acA	8.39	68.95 bcB	6.67	113.62 cC	11.00	-0.90 bD	5.23	125.07 bcC	10.00

Different letters within each column display significant differences at p ≤ 0.05 between different times. Calculation by pairwise comparison of least square means. Adjustment of confidence intervals and p values by Bonferroni method *mean: mean value of absorbed water per gram of hydrogel. *SD: Standard deviation.
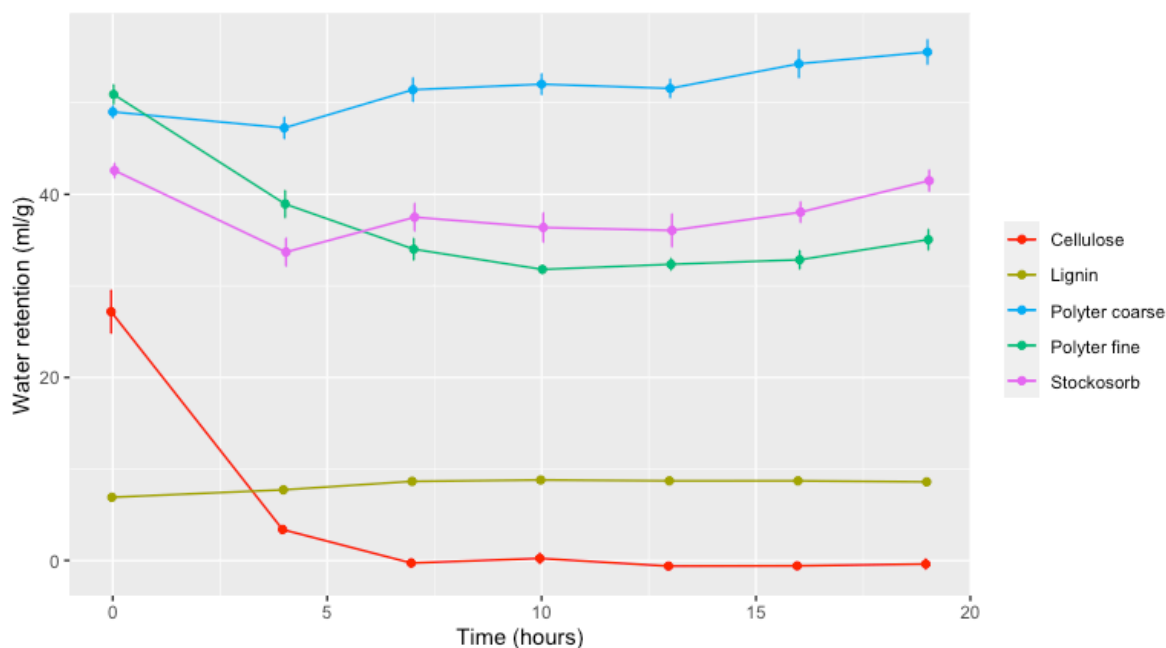
Appendix Figure 4: Mean values of water retention (ml/g), after rewetting at given time periods, for five different hydrogels. Bars represent standard errors. Method: Centrifuge tubes.

Appendix Table 4: Results and statistical analysis of hydrogel-absorbed water (ml/g) at given time periods. Method: Centrifuge tubes.

Time (weeks)	Stockosorb		Polyter fine		Polyter coarse		Cellulose		Lignin	
	mean (ml/g)	SD	mean (ml/g)	SD	mean (ml/g)	SD	mean (ml/g)	SD	mean (ml/g)	SD
0	42.47 abA	2.23	50.92 aB	3.37	49.00 abB	2.12	27.18 aC	5.25	6.90 aD	0.63
4	33.69 cA	4.60	38.94 bA	4.68	47.26 bB	3.72	3.38 bC	0.85	7.72 abD	0.84
7	37.50 bcA	4.52	34.00 bcA	3.74	51.42 abcB	4.12	-0.28 cC	0.10	8.64 bD	0.63
10	36.37 bcA	4.80	31.80 cA	1.38	52.03 abcB	3.63	0.23 cC	1.30	8.79 bDA	0.64
13	36.06 bcA	5.36	32.36 cA	2.06	51.57 abcB	3.17	-0.62 cC	0.44	8.70 bD	0.62
16	38.05 bcA	3.35	32.85 cB	3.20	54.27 acC	4.81	-0.59 cD	0.44	8.70 bE	0.43
19	41.50 bA	3.48	35.05 bcB	3.58	55.55 cC	4.25	-0.39 cD	1.25	8.59 bE	0.44

Significant differences ($p \leq 0.05$) within each column are displayed by different small letters, within each row by different capital letters. Calculation by pairwise comparison of means by Games-Howell test. *mean: mean value of absorbed water per gram of hydrogel. *SD: Standard deviation.

Appendix Table 5: Results and statistical analysis of the effect of different NaCl concentrations on absorption capacity of five different hydrogels (%).

Conc. (mg/l)	Stockosorb		Polyter fine		Polyter coarse		Cellulose		Lignin	
	mean (%)	SD	mean (%)	SD	mean (%)	SD	mean (%)	SD	mean (%)	SD
0	100A	2.48	100A	6.55	100A	4.91	100A	22.63	100A	6.62
100	91.30A	5.30	90.37A	0.62	83.82A	4.75	96.29A	6.94	94.96A	5.77
500	63.98A	1.7	62.86A	3.16	53.62A	4.61	100.83B	16.45	97.57B	12.21
1000	50.11A	0.52	45.94A	0.52	39.46A	1.32	105.92B	7.95	91.73B	10.49
2000	39.54A	1.48	36.00A	1.72	29.03A	1.97	88.19B	7.73	90.89B	8.88

Significant differences ($p \leq 0.05$) within each row are displayed by different capital letters. Calculation by pairwise comparison of means. Adjustment of confidence intervals and p values by Bonferroni method. *mean: mean percentage of absorbed water. *SD: Standard deviation.

Appendix Table 6: Results and statistical analysis of the effect of different CaCl2 concentrations on absorption capacity of five different hydrogels (%)

Conc. (mg/l)	Stockosorb		Polyter fine		Polyter coarse		Cellulose		Lignin	
	mean (%)	SD	mean (%)	SD	mean (%)	SD	mean (%)	SD	mean (%)	SD
0	100A	2.48	100A	6.55	100A	4.91	100A	22.63	100A	6.62
100	89.59A	2.20	77.02B	3.21	76.85B	4.45	95.37A	2.28	99.18A	6.00
500	52.83A	1.11	41.24A	1.61	44.06A	3.15	90.71B	11.42	84.45B	1.40
1000	35.12A	0.18	28.46A	0.95	28.32A	1.22	90.40B	8.67	88.09B	8.58
2000	10.90A	2.51	17.73A	1.97	18.38A	1.81	65.85B	14.23	78.71C	2.47

Significant differences ($p \leq 0.05$) within each row are displayed by different capital letters. Calculation by pairwise comparison of means. Adjustment of confidence intervals and p values by Bonferroni method. *mean: mean percentage of absorbed water. *SD: Standard deviation.

Appendix Table 7: Results and statistical analysis of the effect of different concentrations of NaCl and CaCl2 on absorption capacity of five different hydrogels.

Conc. (mg/l)	Polyter coarse					Conc. (mg/l)	Polyter fine			
	NaCl		CaCl2				NaCl		CaCl2	
	mean (%)	SD	mean (%)	SD			mean (%)	SD	mean (%)	SD
0	100aA	4.91	100aA	4.91		0	100aA	6.55	100aA	6.55
100	83.82bA	4.75	76.85bB	4.45		100	90.37bA	0.62	77.02bB	3.21
500	53.62cA	4.61	44.06cB	3.15		500	62.86cA	3.16	41.24cB	1.61
1000	39.46dA	1.32	28.32dB	1.22		1000	45.94dA	0.52	28.46dB	0.95
2000	29.03eA	1.97	18.3eB	1.81		2000	36.00eA	1.72	17.73eB	1.97

Conc. (mg/l)	Stockosorb					Conc. (mg/l)	Cellulose			
	NaCl		CaCl2				NaCl		CaCl2	
	mean (%)	SD	mean (%)	SD			mean (%)	SD	mean (%)	SD
0	100aA	2.48	100aA	2.48		0	100aA	22.63	100aA	22.63
100	91.30bA	5.30	89.59bA	2.20		100	96.29aA	6.94	95.37abA	2.28
500	63.98cA	1.7	52.83cB	1.11		500	100.83aA	16.45	90.71abA	11.42
1000	50.11dA	0.52	35.12dB	0.18		1000	105.92aA	7.95	90.40abA	8.67
2000	39.54eA	1.48	10.90eB	2.51		2000	88.19aA	7.73	65.85bB	14.23

Conc. (mg/l)	Lignin			
	NaCl		CaCl2	
	mean (%)	SD	mean (%)	SD
0	100aA	6.62	100aA	6.62
100	94.96aA	5.77	99.18aA	6.00
500	97.57aA	12.21	84.45abB	1.40
1000	91.73aA	10.49	88.09abA	8.58
2000	90.89aA	8.88	78.71bB	2.47

Significant differences ($p \leq 0.05$) within each row are displayed by different capital letters, within each column by different small letters. Calculation by pairwise comparison of means. Adjustment of confidence intervals and p values by Bonferroni method. *mean: mean value of absorbed water per gram of hydrogel. * SD: Standard deviation.
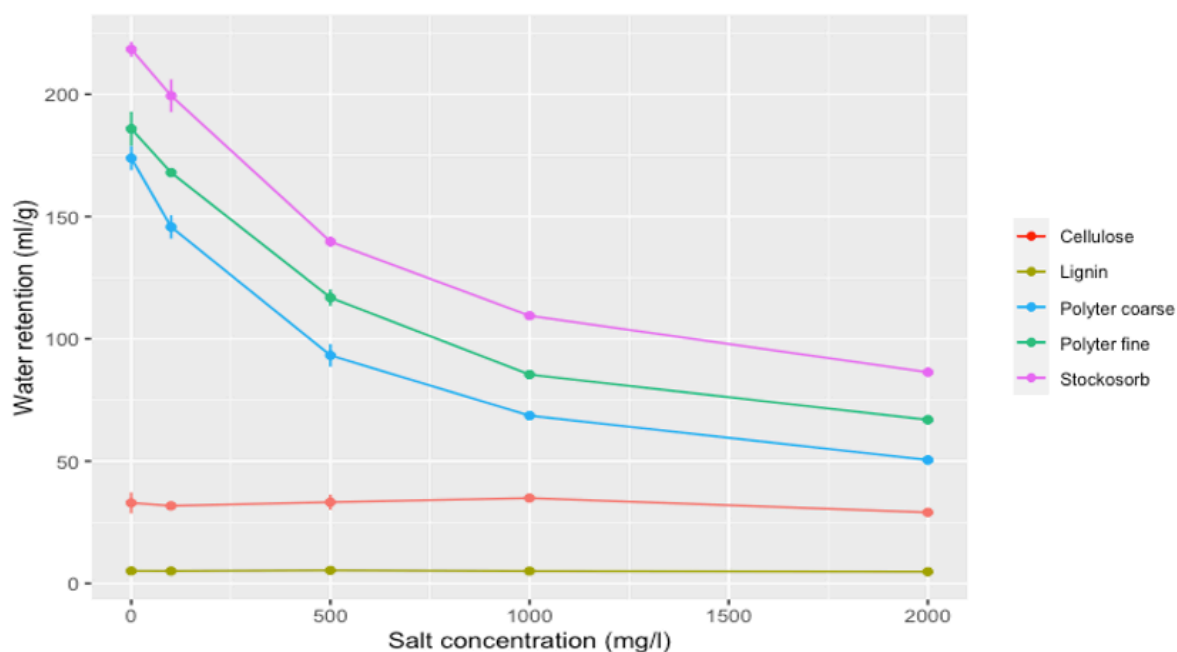
Appendix Figure5: Mean values of water retention of five different hydrogels at various NaCl concentrations. Error bars represent standard error.
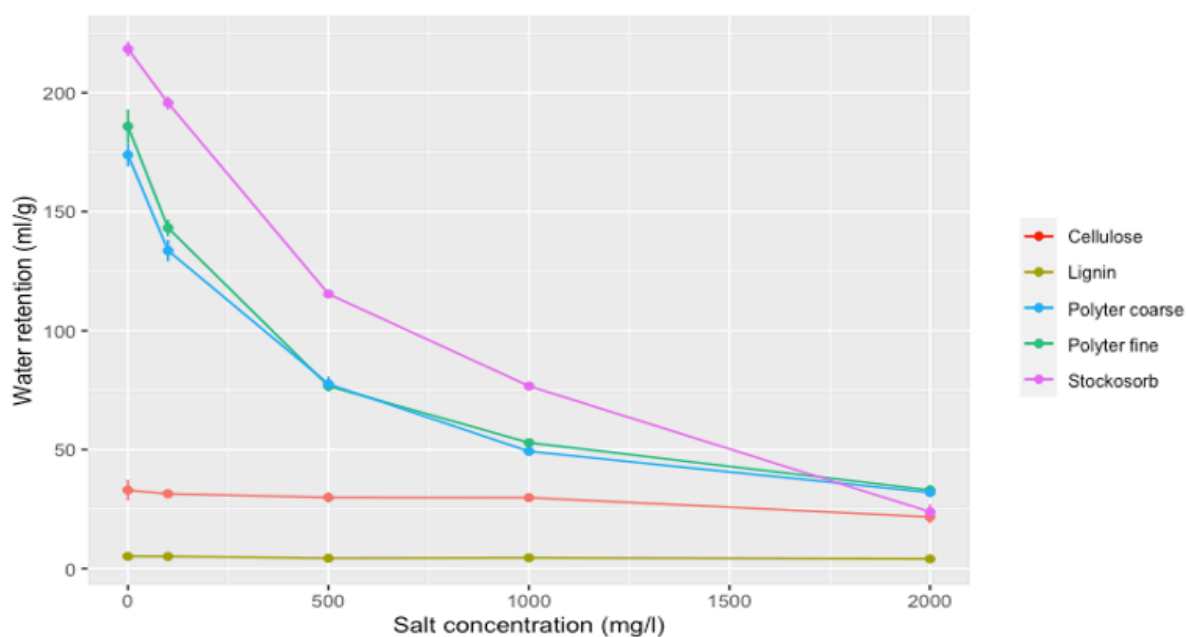
Appendix Figure 6: Mean values of water retention of five different hydrogels at various CaCl2 concentrations. Error bars represent standard error.

Appendix Table 8: Results and statistical analysis of the effect of different NaCl concentrations on absorption capacity of five different hydrogels.

Conc. (mg/l)	Stockosorb mean (ml/g)	SD	Polyter fine mean (ml/g)	SD	Polyter coarse mean (ml/g)	SD	Cellulose mean (ml/g)	SD	Lignin mean (ml/g)	SD
0	218.36 A	5.42	185.86 AB	12.18	173.86 B	8.54	32.95 C	7.46	5.12 C	0.34
100	199.38 A	11.57	167.97 AB	1.17	145.75 B	8.27	31.73 C	2.29	5.07 D	0.29
500	139.72 A	3.72	116.85 B	5.88	93.24 B	8.03	33.22 C	5.42	5.36 D	0.35
1000	109.43 A	1.14	85.40 B	0.10	68.61 C	2.31	34.90 D	2.62	5.05 E	0.22
2000	86.36 A	3.25	66.92 B	3.20	50.48 C	3.43	29.06 D	2.44	4.80 E	0.85

Significant differences ($p \leq 0.05$) within each row are displayed by different capital letters. Calculation by pairwise comparison of means by Games-Howell test. *mean: mean value of absorbed water per gram of hydrogel. *SD: Standard deviation.

Appendix Table 9: Results and statistical analysis of the effect of different CaCl2 concentrations on absorption capacity of five different hydrogels.

Conc. (mg/l)	Stockosorb mean (ml/g)	SD	Polyter fine mean (ml/g)	SD	Polyter coarse mean (ml/g)	SD	Cellulose mean (ml/g)	SD	Lignin mean (ml/g)	SD
0	206.68 A	23.77	185.86 AB	12.18	173.86 B	8.54	32.95 C	7.46	5.12 C	0.34
100	195.64 A	4.81	143.16 B	5.98	133.62 B	7.74	31.42 C	0.75	5.08 D	0.31
500	115.37 A	2.43	76.66 B	2.99	77.55 B	5.48	29.89 C	3.76	4.33 D	0.07
1000	76.69 A	0.400	52.90 B	1.78	49.25 B	2.13	29.79 C	2.86	4.51 D	0.44
2000	23.80 AB	5.49	32.96 A	3.66	31.97 A	3.15	21.70 AB	4.69	4.03 B	0.13

Significant differences ($p \leq 0.05$) within each row are displayed by different capital letters. Calculation by pairwise comparison of means by Games-Howell test. *mean: mean value of absorbed water per gram of hydrogel. *SD: Standard deviation.

Appendix Table 10: Results and statistical analysis of the effect of different NaCl and CaCl2 concentrations on water absorption capacity of five different hydrogels.

Conc. (mg/l)	Polyter coarse NaCl mean (ml/g)	SD	Polyter coarse CaCl2 mean (ml/g)	SD
0	173.9 aA	8.54	173.9 aA	8.54
100	145.75 bA	8.27	133.62 bB	7.74
500	93.24 cA	8.03	77.55 cB	5.48
1000	68.61 dA	2.31	49.25 dB	2.13
2000	50.48 eA	3.43	31.97 eB	3.15

Conc. (mg/l)	Polyter fine NaCl mean (ml/g)	SD	Polyter fine CaCl2 mean (ml/g)	SD
0	185.9 aA	12.18	185.9 aA	12.18
100	167.97 bA	1.17	143.16 bB	5.98
500	116.85 cA	5.88	76.66 cB	2.99
1000	85.40 dA	0.10	52.90 dB	1.78
2000	66.92 eA	3.20	32.96 eB	3.66

Conc. (mg/l)	Stockosorb NaCl mean (ml/g)	SD	Stockosorb CaCl2 mean (ml/g)	SD
0	218.4 aA	5.42	218.4 aA	5.42
100	199.38 bA	11.57	195.64 bA	4.81
500	139.72 cA	3.72	115.37 cB	2.43
1000	109.43 dA	1.14	76.69 dB	0.40
2000	86.36 eA	3.25	23.80 eB	5.49

Conc. (mg/l)	Cellulose NaCl mean (ml/g)	SD	Cellulose CaCl2 mean (ml/g)	SD
0	32.9 aA	7.46	32.9 aA	7.46
100	31.73 aA	2.29	31.42 aA	0.75
500	33.22 aA	5.42	29.89 aA	3.76
1000	34.90 aA	2.62	29.79 aA	2.86
2000	29.06 aA	2.44	21.70 aA	4.69

| Conc. (mg/l)	Lignin NaCl mean (ml/g)	SD	Lignin CaCl2 mean (ml/g)	SD
0	5.12 aA	0.34	5.12 aA	0.34
100	5.07 aA	0.29	5.08 aA	0.31
500	5.36 aA	0.35	4.33 abB	0.07
1000	5.05 aA	0.22	4.51 abA	0.44
2000	4.80 aA	0.85	4.03 bB	0.13

Different capital letters display significant differences ($p \leq 0.05$) in water absorbed by hydrogels between NaCl and CaCl2 solutions at a given concentration. Calculation by pairwise comparison of means. Adjustment of confidence intervals by Bonferroni method. *mean: mean value of absorbed water per gram of hydrogel. * SD: Standard deviation.
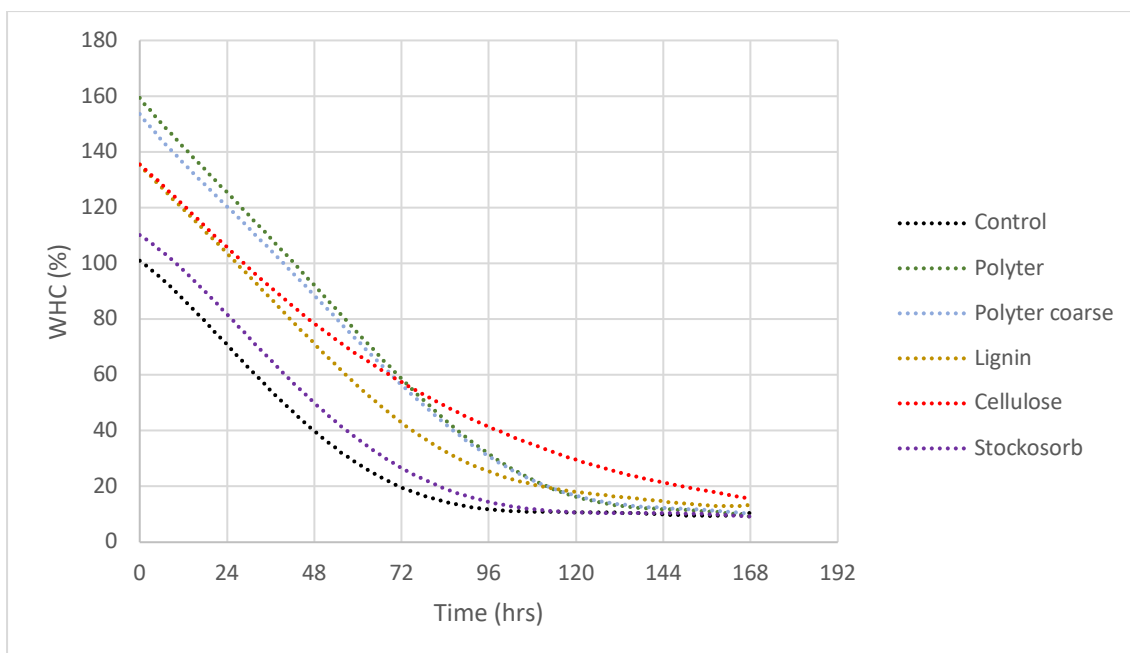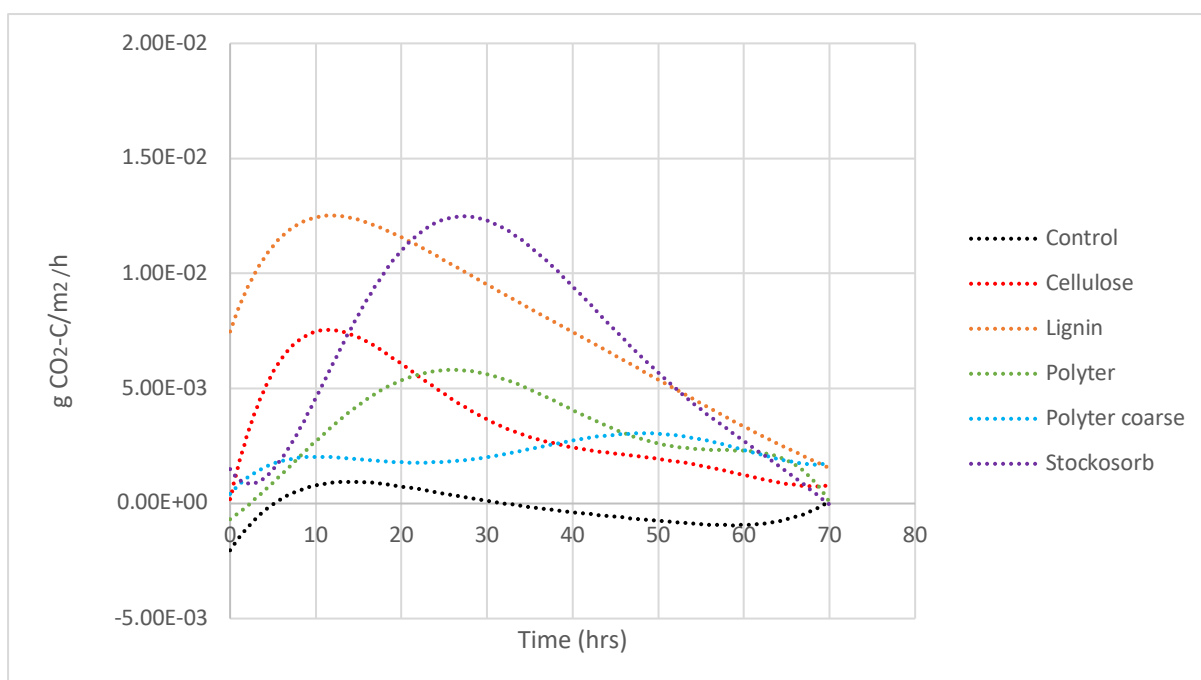
Appendix Figure 7: Drying kinetics of hydrogel and control samples over a one-week period.
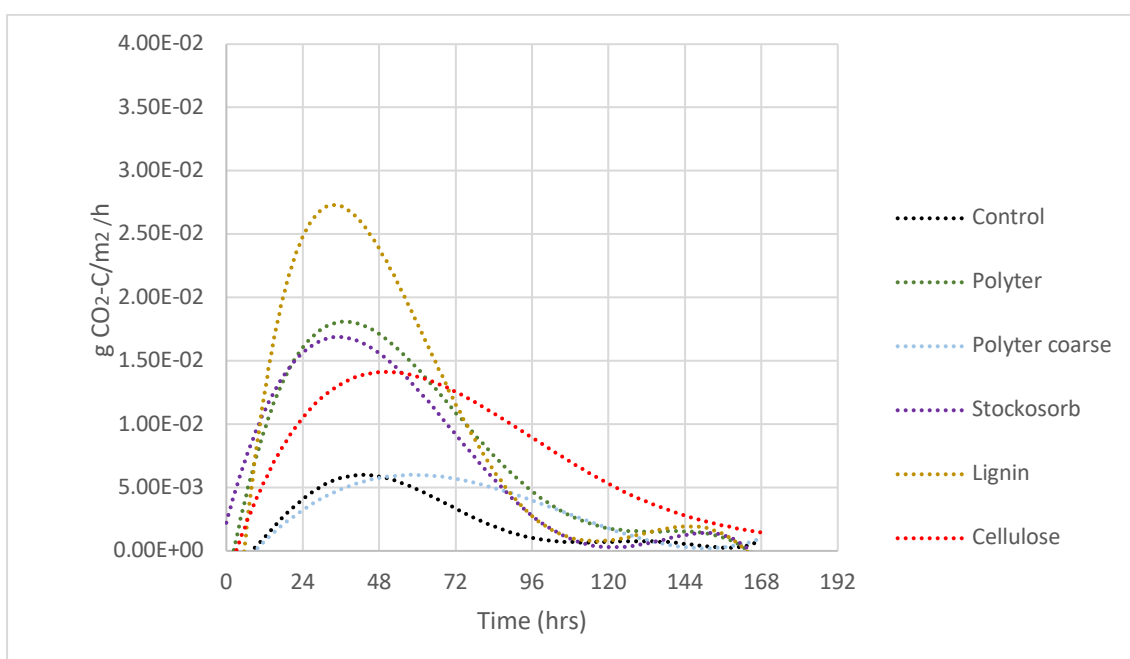
Appendix Figure 8: Microbial respiration measured for hydrogel and control samples over a one-week period.

56
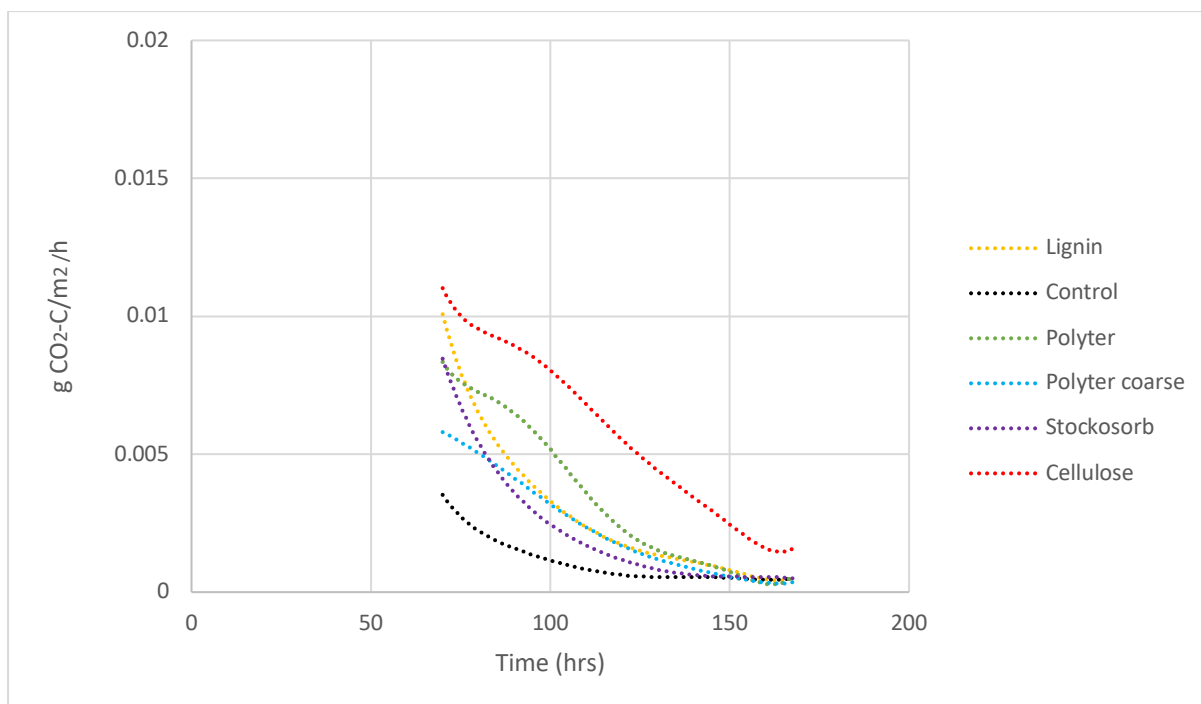
Appendix Figure 9: Respiration values predicted with sixth order polynomials after 70 hours for hydrogel and control samples.

Appendix Figure 10: Respiration values of pure hydrogel and control samples fitted by sixth order polynomials.

Appendix Table 11: Mean initial water contents in ml/g soil and as percentage to the control

	Control		Stockosorb		Polyter fine		Polyter coarse		Cellulose		Lignin	
	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
ml/g	0.49 a	0.008	0.558 ab	0.01	0.760 c	0.02	0.744 c	0.02	0.664 d	0.009	0.633 bd	0.014
%	100 a	0	114.7 a	3.00	156.2 b	4.19	152.9 b	4.25	136.5 c	2.00	136.3 c	4.47

Different letters display significant differences between hydrogels (p ≤ 0.05). Calculation by pairwise comparison of means. Adjustment of confidence intervals and p values by Bonferroni method.

Appendix Table 12: Time until water content stabilized (i.e., the evaporation rate was lower than 0.05% per hour), in relation to initial water content.

	Control		Stockosorb		Polyter fine		Polyter coarse		Lignin	
	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
Time (hours)	111 a	1.41	137 b	4.24	160 c	0	160 c	0	158 c	0

Different letters display significant differences (p ≤ 0.05). Calculation by pairwise comparison of means. Adjustment of confidence intervals and p values by Bonferroni method.

Appendix Table 13: Time until microbial respiration reached threshold value (i.e., respiration value of the control when the evaporative loss was lower than 0.05% WHC per hour for the first time).

	Control		Stockosorb		Polyter fine		Polyter coarse		Lignin	
	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
Time (hours)	111 a	1.41	138 b	0	154 c	2.82	149 c	4.24	154 c	0

Different letters display significant differences (p ≤ 0.05). Calculation by pairwise comparison of means. Adjustment of confidence intervals and p values by Bonferroni method.

Appendix Table 14: Mean final water contents in ml/g soil and as percentage to the control.

	Control		Stockosorb		Polyter fine		Polyter coarse		Cellulose		Lignin	
	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
ml/g	0.053 ab	0.001	0.049 a	0.001	0.053 ab	0.004	0.055 ab	0.003	0.081 c	0.002	0.062 b	0.002
%	10.75 ab	0.08	10.22 a	0.134	10.97 ab	0.869	11.39 ab	0.644	16.74 c	0.426	12.08 b	0.59

Different letters display significant differences (p ≤ 0.05). Calculation by pairwise comparison of means. Adjustment of confidence intervals and p values by Bonferroni method.