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Departamento de Cristalografía, Mineralogía y Química Agrícola

Characterization and effects of cross-linked potassium polyacrylate as soil amendment

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Memoria de Tesis Doctoral

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A mis padres,

Marisol y Javier

A mi esposa,

Carla

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“You'll never plough a field by turning it over in your mind.”

Irish proverb.

ABSTRACT

CHARACTERIZATION AND EFFECTS OF CROSS-LINKED POTASSIUM POLYACRYLATE AS SOIL AMENDMENT

Cross-linked potassium polyacrylate (Luquasorb®1280R) is a granular anionic superabsorbent polymer with the ability to absorb large amounts of water. The objectives of this study were the physicochemical characterization of the material and its effects when used as soil amendment together with the evaluation of the impact on agronomical parameters when it was applied to processing varieties of tomato (*Solanum lycopersicum* L.) grown under Mediterranean climate conditions. In order to reach the proposed objectives the following were investigated: swelling properties of the material and its limiting factors, the profile of the product as a cation exchanger, the impact of the polymer on pH, electric conductivity and hydric properties of sandy, loamy and clay soils and the effects on growth, yield and quality parameters on processing tomato under field experimental conditions. The polymer showed an average free swelling capacity of 280 g/g and 329 g/g measured with two different methods. Significant hygroscopic properties were shown by the material when relative humidity ≥63%. The absorption speed resulted significantly lower as bigger was the granule size distribution of the material. Swelling limiting factors were identified. The application of pressure on the polymer, the presence of ions in the media and the concentration of surface cross-linkers significantly affected the absorption and drying capacity of cross-linked potassium polyacrylate. The swelling ability of the polymer was maintained after repeated absorption-desorption cycles combined with the application of thermal stress. Significant amounts of soluble and exchangeable potassium were found in the product. The measured average cation exchange capacity of the material was 817 meq/100g. Cross-linked potassium polyacrylate was applied in different soils at dose rates of 0.2% and 0.4% w/w. The soil pH was buffered to 7 and the electric conductivity was increased in all cases. Furthermore water losses by evaporation were reduced and water holding capacity was significantly increased especially in the case of sandy and loamy soils when the material was applied at 0.2% w/w. No effects on soil texture were observed by the application of the polymer. The experimental results of the field trial series showed positive effect on crop establishment, plant growth and yield. Marketable yield (ripe fruits) was significantly increased in light-sandy soils by 20 and 17% at application rates of 3 and 6 g/row-m respectively. In the case of medium-loamy soils the marketable yield increase was 10, 14 and 13% at application rates of 3, 6 and 12 g/row-m respectively. No effects on yield were observed in heavy-clay soils. The studied characteristics and effects of cross-linked potassium polyacrylate (Luquasorb®1280R) as soil amendment could be of large socioeconomic importance in future implementation of sustainable agronomic practices with respect to the need of increasing yields within restricted agricultural lands.

RESUMEN

CARACTERIZACIÓN Y EFECTOS DEL POLIACRILATO POTÁSICO ENTRECRUZADO COMO ENMIENDA DE SUELOS

El poliacrilato potásico entrecruzado (Luquasorb®1280R) es un polímero superabsorbente granulado con la capacidad de absorber grandes cantidades agua. Los objetivos de este trabajo fueron la caracterización fisicoquímica del material y el estudio de sus efectos como enmienda de suelos, así como la evaluación del impacto en parámetros agronómicos de variedades de tomate de industria (*Solanum lycopersicum* L.) bajo condiciones de clima Mediterráneo. Para alcanzar los objetivos planteados se estudiaron las propiedades de hinchamiento del material y sus factores limitantes, el perfil del producto como intercambiador catiónico, el impacto del polímero en el pH, conductividad eléctrica y propiedades hídricas de los suelos, y los efectos en parámetros de crecimiento, rendimiento y calidad de tomate de industria en condiciones de campo. El polímero mostró una capacidad de hinchamiento libre promedio de 280 g/g y 329 g/g medida con dos métodos diferentes. Se observaron propiedades higroscópicas significativas cuando la humedad relativa fue ≥63%. La velocidad de absorción resultó significativamente menor cuanto mayor fue la granulometría. La aplicación de presión, la presencia de iones en el medio y la concentración de entrecruzante superficial, afectaron significativamente la capacidad de absorción y secado. Las propiedades de hinchamiento del polímero se mantuvieron después de repetidos ciclos de absorción-desorción combinados con estrés térmico. Se encontraron cantidades significativas de potasio soluble e intercambiable en el producto. La capacidad de intercambio catiónico del material fue de 817 meq/100g. Se aplicó el producto en diferentes suelos a dosis de 0.2% y 0.4% p/p. El pH de los suelos se amortiguó a 7 y la conductividad eléctrica aumentó en todos los casos. Las pérdidas de agua por evaporación se redujeron y la capacidad de retención de agua fue mejorada significativamente en el caso de los suelos arenosos y francos cuando se aplicó material a una concentración de 0.2% p/p. No se observaron efectos en la textura de los suelo. En los resultados de la serie de ensayos se observó un efecto positivo en el establecimiento del cultivo, en el crecimiento vegetativo y en el rendimiento. La producción comercial aumentó significativamente en suelos ligeros-arenosos en un 20 y 17% con dosis de aplicación de 3 y 6 g/m-lineal respectivamente. En el caso de suelos medios-francos la cosecha comercial aumentó en un 10, 14 y 13% a dosis de aplicación de 3, 6 y 12 g/m-lineal respectivamente. No se observaron efectos en rendimiento en suelos arcillosos. Las características y efectos estudiados del poliacrilato potásico entrecruzado (Luquasorb®1280R) como enmienda de suelo podrían ser de enorme importancia socioeconómica en la futura implantación de prácticas sostenibles relacionadas con la necesidad de incrementar las cosechas dentro de zonas agrícolas limitadas.

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List of ABBREVIATIONS & ACRONYMS

°C: Celsius degree (temperature)

AA: Acrylic Acid

AAm: Acrylamide

AAS: Atomic absorption spectroscopy

ANOVA: Analysis of variance

BASF: Badische Anilin und Soda Fabrik.

BBCH: Biologische Bundesanstalt, Bundessortenamt und Chemische Industrie

CEC: Cation exchange capacity

CO.: Company

EC: Electric conductivity

EDANA: European Disposables and Nonwovens Association.

ESEM: Environmental Scanning Electron Microscope.

FAO: Food and Agriculture Organization of the United Nations

FSC: Free swell capacity (g/g).

g: Gram

g/m-lineal: Gramos por metro lineal

g/row-m: Grams per row meter

GAA: Glacial Acrylic Acid

GmbH: Gesellschaft mit beschränkter Haftung (=private limited company)

HSD (Tukey´s): Honest Significant Difference

HW: Hygroscopic water

ICSHAM: Intercompany Committee for the Safety and Handling of Acrylic Monomers.

IFAPA: Instituto de Investigación y Formación Agraria y Pesquera de Andalucía.

IT: Information technology

IUPAC: International Union of Pure and Applied Chemistry.

K: Potassium element symbol

kg/ha: Kilograms per hectare

KPA: Potassium polyacrylate

L: Liter

LTD.: Limited Company

M: Molar concentration (moles per liter of solution)

meq: Milliequivalent

meq/L: Milliequivalent per liter

mg: Milligram

mq/L: Milligrams per liter

ml: Milliliter

N: Normal concentration (equivalents per liter of solution)

NCRCS: Natural Resources Conservation Service (USDA)

Na: Sodium element symbol

O.M.: Organic mater

p/p: peso/peso

p-value: probability of the null hypothesis

PAA: Poly(acrylic acid).

PAM: Polyacrylamide.

PCA: Principal components analysis.

pH: coefficient of acidity or alkalinity of an aqueous solution.

ppm: Parts per million (mg/liter)

®1280RL: Luquasorb®1280RL; large granule size.

®1280RM: Luquasorb®1280RM; medium granule size.

®1280RS: Luquasorb®1280RS; small granule size.

RH: Relative humidity (%)

RL: Luquasorb®1280RL; large granule size.

RM: Luquasorb®1280RM; medium granule size.

RS: Luquasorb®1280RS; small granule size.

SAP(s): Superabsorbent polymer(s)

SD: Standard deviation.

Site-Ref.: experimental site reference.

SNK: Student-Newman-Keuls (data analysis method)

UNESCO: United Nations Educational, Scientific and Cultural Organization

USDA: United States Department of Agriculture

w/v: weight/volume

w/w: weight/weight

WCI: Water content increase (%)

WPTC: World processing tomato council

CHAPTER I

GENERAL INTRODUCTION

1. 1. FUNDAMENTALS OF SUPERABSORBENT POLYMERS

1.1.1. Hydrogels and superabsorbent polymers; definitions.

Hydrogels are macromolecular cross-linked hydrophilic polymer chains with the ability to absorb water or aqueous fluids. The most commercially successful members of the hydrogel family are the superabsorbent polymers, also known as SAPs or superabsorbent hydrogels (Zhouriaan-Mehr *et al.*, 2010). While in general hydrogels can absorb up to about 10 g of water per gram of substance (Kabiri *et al*., 2011), superabsorbent polymers are able to imbibe water up to 1,000 grams of water per gram of polymer (Buchholz & Graham, 1998). Visual illustrations of commercial cross-linked potassium polyacrylate (Luquasorb®1280RL) granule in dry and water-swollen states are shown in Figure 1.1. In spite of the described differences it is common to equally use the terms hydrogel, superabsorbent hydrogel, superabsorbent polymer, SAP or superabsorber within the existing bibliography and publications. Due to this fact it was decided to use the acronym SAP (Super-Absorbent-Polymer) to indistinctly referring to all of them within this doctoral thesis.

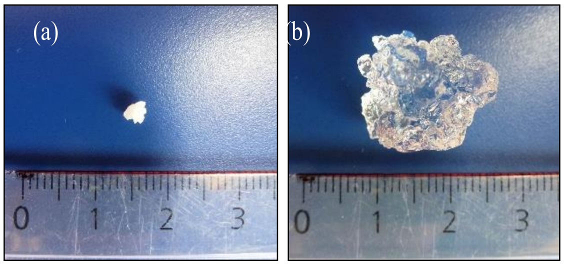


Figure 1.1 – Water absorption by Luquasorb®1280RL: (a) dry granule and (b) swollen hydrated particle. Ruler scale indicates millimeters and centimeters.

1.1.2. Evolution, history and market of superabsorbent materials.

The rise of SAPs can be explained as a classic case of material substitution replacing traditional absorbent materials such as cotton, paper, cloth fibers or cellulose fibers which were mainly used in hygiene products. First absorbent materials were divided into two groups: fiber masses and foams. The principal common characteristic to these materials is the presence of open space or pores within their structure (Sahed and Jog, 1991). The absorbency of classic absorbent materials is principally driven by the amount and the size of open space (porosity) so the water imbibition is inversely proportional to the bulk density of the material (Chatterjee, 1985). This means the higher is the value of bulk density the less open space is in the material structure and therefore the less water absorption is possible. However the classical absorbency rule based on bulk density is not followed by SAPs. Superabsorbent materials imbibe water by a combination of mechanisms (Hüttermann *et al.*, 2009): physical entrapment of liquids via capillary forces due to the macro-porous structure, hydration of functional groups and the dissolution and thermodynamically favored expansion of the macro-molecular chains limited by cross-linkages. Table 1.1 compares bulk density and water absorption capacity of some traditional absorbent materials and the commercial SAP Luquasorb®1280RM. These differences on absorption mechanisms leads to one major practical characteristic that excludes traditional absorbent materials from superabsorbent ones; SAPs will not release the absorbed water when they are squeezed (Zhouriaan-Mehr and Kabiri, 2008).

Table 1.1 – Bulk density and pure water absorbency of some traditional absorbent materials (Buchholz and Graham, 1998) and the commercial SAP Luquasorb®1280RM.

Absorbent Material	Bulk density (g/ml)	Water Absorbency (g/g)
Whatman No. 3 filter paper	3.424	1.8
Facial tissue	0.166	4.0
Cellulose acetate sponge	0.048	7.8
Polyurethane sponge	0.040	10.5
Wood pulp fluff	0.030	12.0
Cotton ball	0.018	18.9
Luquasorb®1280RM	~0.600*	~280.0*

*Values source: BASF data.

The first synthesis of a polymer as a water absorbent material was in 1938. It consisted in acrylic acid and divinylbenzene thermally polymerized in an aqueous medium (Kern, 1938). However it was in the late 1950s when the first hydrogel material was produced. First hydrogels (non-superabsorbent) were based on hydroxylalkyl methacrylate and derivative monomers with the ability to imbibe around 0.4 to 0.5 grams of water per gram of product. This first generation was used for developing contact lenses revolutionizing ophthalmology (Dayal *et al*., 1999).

A first commercial try of SAP was done in the 1970s by the Northern Regional Research Laboratory within the United States Department of Agriculture (USDA). It was developed a SAP produced by hydrolysis of starch-g-polyacrylonitrile (Taylor and Bagley, 1974). The elevated costs and very low strength at swollen state brought this product to fail in the market (Buchholz and Peppas, 1994).

Real commercial production of SAPs was started in Japan in 1978 for its use in feminine sanitary napkins. However, further developments took these materials to be widely used in baby diapers in Germany and France in the 1980s. These polymers replaced the cellulose fluff that was not able to retain as much liquid as SAPs under certain pressure causing a revolution in the personal hygiene industry (Brannon-Peppas and Harland, 1990). Due to this fact the development of SAP properties have being principally driven by this field of application during the last 30 years. Over 80% of the total SAPs sales were on infant diapers in 1995 (AMCOL, 1996).

According to the European Disposables and Nonwoven Association (EDANA) SAPs production was about 1.9 million tons in 2012. Furthermore it was reported a much more segmented picture for SAPs where hygiene/personal-care and construction were the major markets with 43% and 10% of sales respectively (EDANA, 2013). Other special markets have been developed for SAPs in the last decades. Further fields of application of SAPs are reviewed in the section 1.1.6.

1.1.3. Structure of superabsorbent polymers: absorption mechanism.

The structures of SAPs are based in long polymeric chains which are cross-linked by other small molecules or even single atoms forming a tridimensional net (Liu and Guo, 2001). Basic components of a SAP network are schematically shown in figure 1.2.

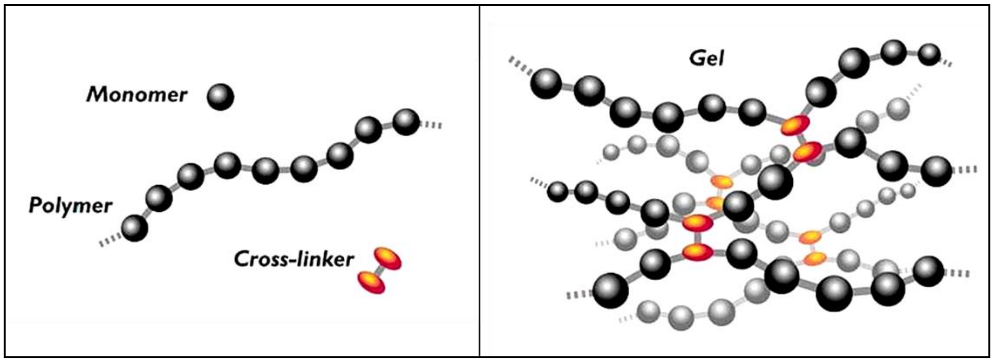


Figure 1.2 – Schematic representation of the fundamental components of a SAP and its tridimensional structure (gel). Source: BASF.

As discussed in section 1.1.2., the absorption mechanism of SAPs can be explained by different phenomena (Zohuriaan-Mehr and Kabiri, 2008). However, Buchholz and Graham (1998) simplified the absorption function to mainly a diffusive mechanism. Diffusion is a molecular physical phenomenon of transport where particles move in a random and non-organized manner into a media increasing the entropy of the system until reaching the equilibrium. The process of diffusion is explained by the Fick's Law (Equation 1.1). Diffusion flux is proportional to the minus gradient of concentration; it goes from regions of higher concentrations to regions of lower concentrations (Latorre *et al.*, 1996). Fick's Law for one spatial dimension is:

$$J = -D \cdot (\partial c / \partial x) \qquad \text{(Formula 1.1.)}$$

Where, J is the diffusion flux, D is the diffusion coefficient and $(\partial c / \partial x)$ is the concentration gradient. Thus aqueous solutions moves into a SAP particle because the fluid activity was initially lower in the interior of the particle. At the same time the polymer chains diffuse in an opposite direction to accommodate the volume of additional molecules (Bo *et al.*, 2012).

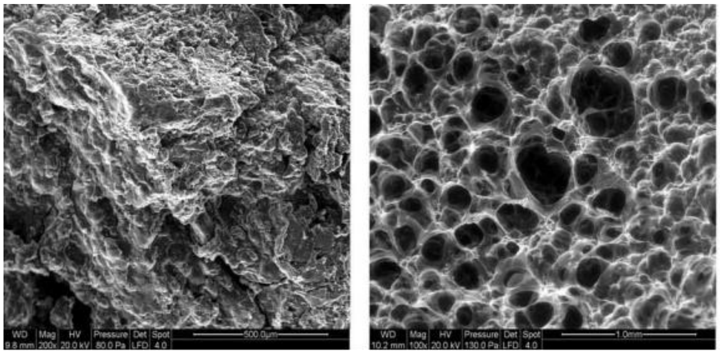


Figure 1.3 – ESEM images of a superabsorbent polymer in dry (left image) and swollen (right image) states (Bo *et al.*, 2012).

The diffusion of the polymer chains is slower not only because they are larger molecules than water but also because the swelling of the polymer is limited by the cross-linkers (Liu and Guo, 2001). In other words water moves with the purpose of balancing the concentration of molecules between the interior and exterior of the polymer (Ono *et al.*, 2007). It can be concluded that the absorption mechanism of SAPs is a combination of physical phenomena besides the gradient of chemical activity inside and outside the polymer according to Fick’s law.

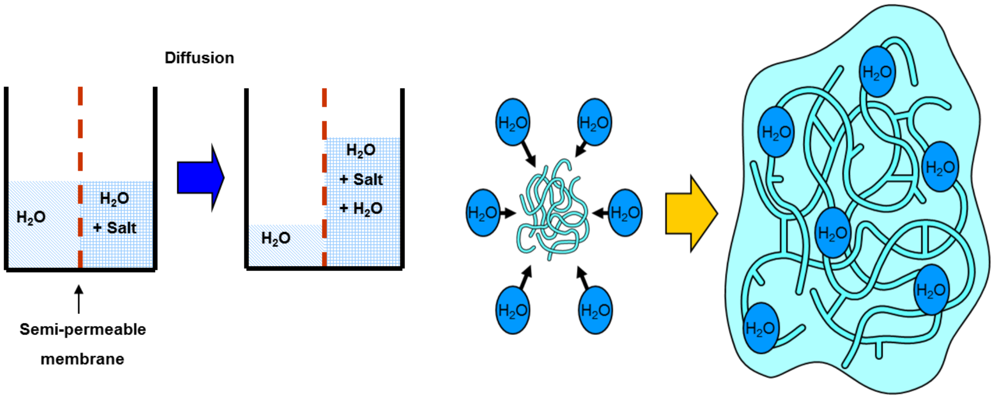


Figure 1.4 – Schematic comparison between classic osmosis where water diffuses to balance salt concentration and the absorption mechanism of a SAP particle. Source: BASF.

Once the basic structure and absorption mechanism is known, it is easier to understand the factors which might play a role in the absorbency properties of a particular SAP. The type and degree of cross-linking affect the swelling properties as these would impact the porous network space and the expanding capacity of the polymer chains when swelling (Xie *et al*., 2009). The presence of functional groups in the cross-linked polymer chains is also affecting the absorption properties. Buchholz and Graham (1998) discussed the polymer networks carrying dissociated ionic functional groups as the most efficient water absorbers.

1.1.4. Types of superabsorbent polymers.

1.1.4.1. Classification based on presence of ionic groups.

SAPs can be classified in basis of different aspects; a commonly accepted classification is based on the presence or absence of ionic or ionizable groups located in the cross-linked polymer chains (Zohuriaan-Mehr *et al*., 2008; Buchholz and Graham, 1998). With regards to this criterion SAPs are classified as non-ionic, ionic, amphoteric and zwitterionic.

1. Non-ionic

Non-ionic SAPs have no electrical charges or ionizable groups in their cross-linked polymer chains (figure 1.5). Polymers absorption mechanism is driven by energetic and entropic interaction with hydrophilic groups which are present along the polymer chains being solvated by water molecules through hydrogen bonds.

2. Ionic (cationic or anionic)

Ionic SAPs have ionic or ionizable groups in their cross-linked polymer chains and depending on the charge they are sub-classified on cationic or anionic (figure 1.5). The presence of ionic functional groups increases the absorption properties as ions are more strongly solvated than non-ionic functional groups. Furthermore, electrical neutrality is required so ions are neutralized with other ions of opposite charge (counter ions) which are also solvated. Within this type of superabsorbent polymers the main absorption mechanism is the osmotic pressure although energetic and entropic mechanisms still contribute. Majority of nowadays commercial superabsorbent hydrogels are anionic (EDANA).

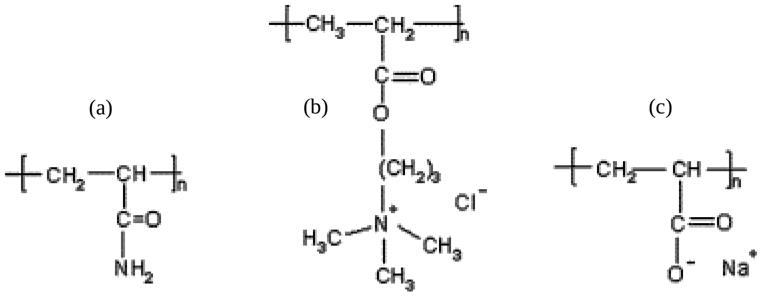


Figure 1.5 – Skeletal structure of monomer units used in SAPs being (a) non-ionic, (b) cationic and (c) anionic. (Saarinen *et al.*, 2008).

3. Amphoteric.

These SAPs have cross-linked amphoteric polymer chains which are defined as polymers containing both; cationic and anionic groups or corresponding ionizable groups (IUPAC, Gold Book, 1997).

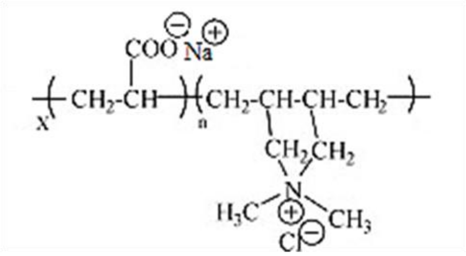


Figure 1.6 – Example of amphoteric chain of poly-(acrylic acid-co-diallyldimethylammonium chloride) SAP studied by Xu *et al*. (2005).

4. Zwitterionic.

These SAPs have cross-linked zwitterionic polymer chains which are defined as polymers containing both; ionic and cationic groups within the same structural repeating unit (IUPAC, Gold Book, 1997).

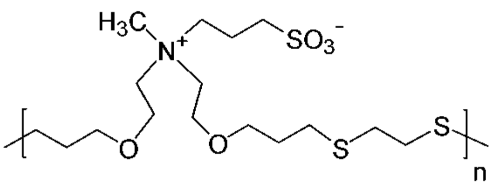


Figure 1.7 – Example of zwitterionic polymeric repeating unit of poly-thioether polymer (Anton and Laschewsky, 1995)

1.1.4.2. Classification based on type of monomeric units.

SAPs can be also classified based on the type of monomeric units used in the synthesis of their chemical structure. Based on this criterion Riccardo Po (1994) grouped most common SAPs as follows:

1. Cross-linked polyacrylate and polyacrylamide.
2. Hydrolyzed cellulose-polyacrylonitrile.
3. Cross-linked copolymers of maleic anhydride.

However according to available literature and publications SAPs can be easier classified in accordance to the origin of the monomers or polymers on which they are based. Following this criteria SAPs are grouped as synthetic, natural and hybrids (Zohuriann-Merh *et al*., 2008).

1. Synthetic superabsorbent polymers.

These are the most commercially used SAPs (Buchholz, 1994). The term “superabsorbent polymer” is normally referring to this type when no other specification is given. Synthetic SAPs are those ones normally produced from acrylic monomers such as acrylic acid (AA), salts of acrylic acid and acrylamide (AAm) (Fig. 1.8).

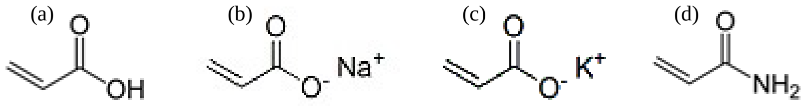


Figure 1.8 – Skeletal formula of most typical monomers used in the production of synthetic SAPs: (a) acrylic acid, (b) sodium acrylate, (c) potassium acrylate and (d) acrylamide.

This type of SAPs are known as having superior performance due to their gel strength, appropriate swelling capacity and re-swelling ability (Kabiri *et al*., 2011).

2. Natural superabsorbent polymers.

During last decade it has been increasing the number of publications regarding SAPs based on natural monomers or polymers. Some examples are SAPs based on polysaccharides like cellulose, starch, alginate, chitosan (Athawale and Lele, 2001; Zahng *et al*., 2014; Thibodeau *et al*., 2014; Ramos-Campos *et al*., 2015), cross-linked lignite humic acid (Cihlar *et al*., 2014) and/or proteins (Hwang and Damodaran, 1997).

3. Hybrid superabsorbent polymers.

Hybrid SAPs combine synthetic monomers with natural polymers. Some examples are SAPs based on synthetic monomers grafted onto polysaccharide (Kabiri *et al*., 2011), copolymerization of acrylamide onto kappa-carrageenan and gelatin-protein (Pourjavadi *et al*., 2009), beta-cyclodextrin- sodium acrylate and alginate (Huang *et al*., 2014) or the first developed superabsorbent polymer of starch-grafted-polyacrylonitrile by the USDA in the 1970s (Taylor and Bagley, 1974). Both natural and hybrid superabsorbent hydrogels offer several advantages such as better biodegradability, biocompatibility and lower raw material costs (Al *et al*., 2008).

1.1.4.3. Classification based on the field of application.

Another classification of superabsorbent polymers can be done based on their field of application. Most consolidate and emerging applications of SAPs are reviewed in the section 1.1.6.

1.1.5. Luquasorb®1280R: Cross-linked potassium polyacrylate.

Luquasorb®1280R (BASF, Germany) is the commercial name of a synthetic anionic SAP based on cross-linked potassium polyacrylate subject matter of this thesis.

Potassium polyacrylate polymer chains of Luquasorb®1280R are composed of monomeric units of potassium acrylate (potassium prop-2-enoate) and acrylic acid (prop-2-enoic acid) in a proportion of approximately 65% and 34.7% respectively (Figure 1.9). The polymer chains are cross-linked with 0.3% Pentaerythritol triallyl ether (Figure 1.10) commercially known as Neoallyl®P-30 (Daiso Co. Ltd, Japan).

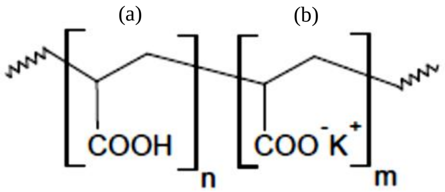


Figure 1.9 – Polymer chain scheme of Luquasorb®1280R with monomeric units of (a) acrylic acid and (b) potassium acrylate (n= 34.7%; m=65%).

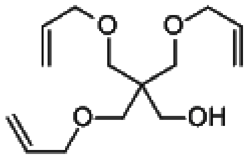


Figure 1.10 – Structure of pentaerythritol triallyl ether; cross-linker of Luquasorb®1280R

The synthesis of Luquasorb®1280R starts with the monomers preparation in a range between 15 – 45 ºC. Acrylic acid is the principal raw material. This weak organic acid is colorless liquid, double bonded with irritating acrid odor at room temperature and pressure which is soluble in water and most organic solvents. It easily polymerizes when exposed to light, heat or metals. To avoid strong exothermic polymerization of acrylic acid it is commercially necessary to add polymerization inhibitors (ICSHAM, 2000).

The commercial Glacial Acrylic Acid - GAA (BASF SE, Germany) used for producing Luquasorb®1280R contains hydroquinone mono-methyl ether (4-methoxyphenol) as polymerization inhibitor in a concentration of 200 ppm. For monomer preparation, acrylic acid is partially neutralized (Figure 1.11) with potassium hydroxide (KOH) in a mix tank which is jacketed by chilled water to remove the reaction heat. Final step in monomer preparation is the addition of the cross-linking agent.

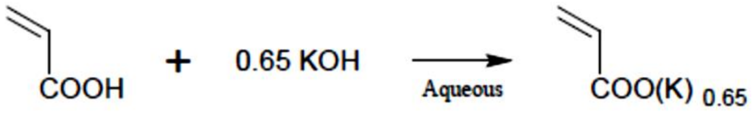


Figure 1.11 – Scheme of potassium salt formation by neutralizing acrylic acid. Potassium in brackets (K) $_{0.65}$ means that 65% of the acrylic acid is neutralized.

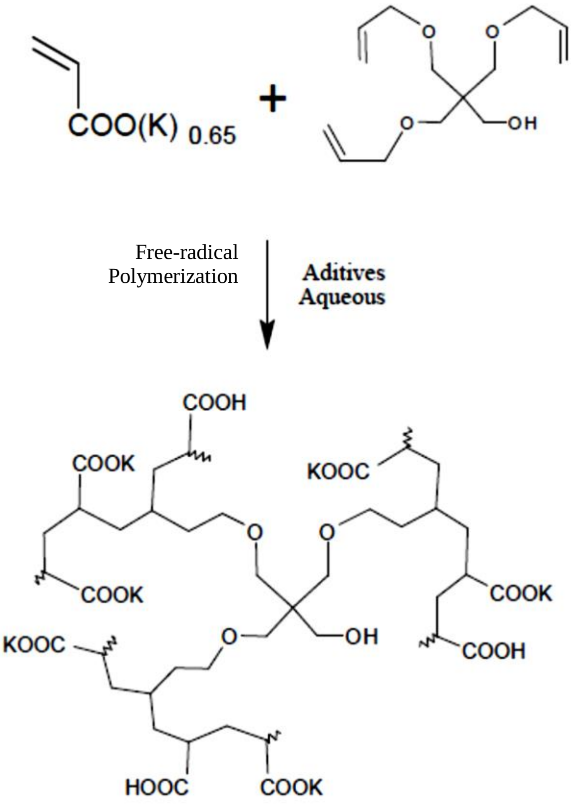


Figure 1.12 – Scheme of cross-linked polymerization of potassium acrylate (65%) cross-linked with pentaerythritol triallyl ether.

Luquasorb®1280R is prepared by free-radical initiated polymerization of acrylic acid and its potassium salt with the cross-linker Neoallyl®P-30 in aqueous solution from 0 – 90 ºC (Figure 1.12). This process is done in belt reactor which is essentially a buffer tank which allows continuous polymerization forming a gel. Gel drying at 160 – 180 ºC, milling and sizing at 40 – 70 ºC are the following steps before product conditioning for packaging (anti dust process by surface cross-linking). The resulting final material structure consists in a cross-linked network of flexible polymer chains with carboxyl and carboxylic acid potassium salt groups (Figure 1.13). Commercial product is presented in 3 different granule sizes; Luquasorb®1280RS (Small), Luquasorb®1280RM (Medium) and Luquasorb®1280RL (Large).

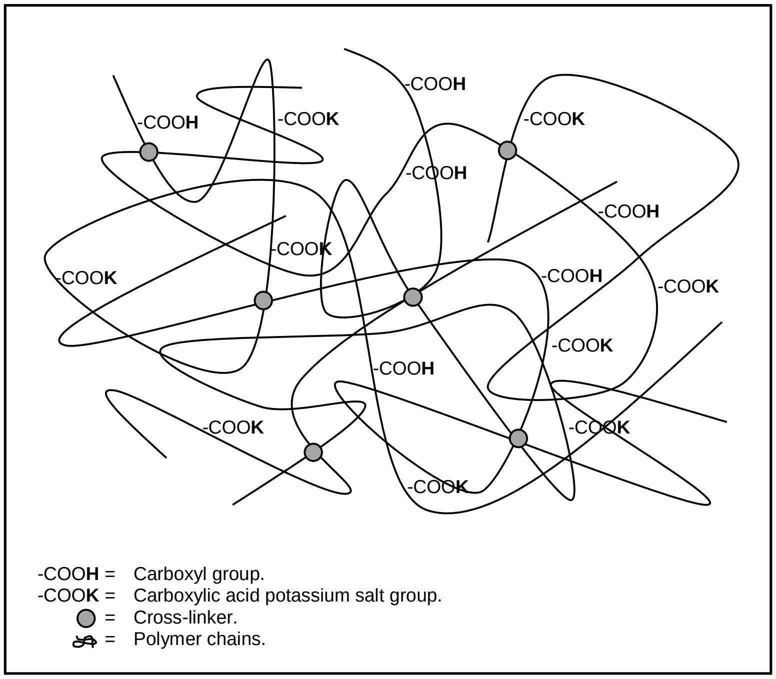


Figure 1.13 – Schematic representation of Luquasorb®1280R network structure.

1.1.6. Applications of superabsorbent polymers.

Personal hygiene products

Buchholz and Graham (1998) described many applications within the personal hygiene industry being the largest use of SAPs. The most well-known application within this field is their use in infant disposable diapers. First cores of disposable diapers were made of multiple layers of tissue paper which absorbed liquids by capillarity and stored them in the pores of the fibers. The use of SAPs revolutionized because under certain pressure SAPs are still able to absorb up to 30 times their weight in urine. Same technology has being used for adult incontinence products as well as feminine hygiene products (sanitary napkins). Some market data on hygiene application of SAPs is reviewed in section 1.1.2.

Medical and pharmaceutical use

Most medical application of SAPs are related to fluid management. In medicine SAPs are used to remove body fluids during surgery. For instance some SAPs based on carboxymethylcellulose (CMC) have the property of imbibing body fluids in the treatment of edemas (Sannino *et al*., 2003). SAPs has also being used for developing drainage bags (Ohta and Kuroiwa, 1999).

Within the field of pharmaceutics superabsorbent hydrogels were originally designed for gastric retention applications with the purpose of prolonging drug release in the stomach or intestine as specific drug delivery carriers (Chen *et al*., 2000; Singh, 2007).

Electronic and cabling

SAPs are widely used to isolate and protect different types of cabling. SAPs can prevent water from entering into the cable in case of damage or through junctions by forming a gel (gel-blocking effect). Swollen SAP gel blocks water influx by a combination of a controlled diffusion process together with an increase of swelling pressure (Wack and Ulbricht, 2007). Power and communication cables exposed to seawater or underground water can be protected when the coating is damaged (Buchholz and Peppas, 1994). Furthermore, a layer containing SAP in gel form can improve flame-retarding characteristics of cables (Sheu and Meeks, 2001).

Construction materials

Within the field of construction materials SAP composites are used as sealing materials to prevent water leakage through joints of construction block connections and pipes (Park and Kim, 2001). Such a component is commonly used in the construction of subways and underwater tunnels like the Eurotunnel connecting England and France (Sun *et al*., 2000). SAPs are also used as a concrete additive in construction applications to improve the internal curing of the cement process resulting in a better strength and durability (Chung, 2004).

Food Packaging

In packaging systems SAPs are used in absorbent airlaids for capturing juice and water from fresh foods or blood serum of meat (Baldwin *et al*., 2005). It has being also developed the application of SAPs for temperature and humidity control in perishable food packaging (Buchholz and Graham, 1998).

Other applications

The fabulous swelling properties of SAPs and their sensitivity to change in water content make them useful in many other applications such as part of different types of sensors based on humidity changes (Sawahata *et al*., 1995). Within the entertainment field SAPs are used as artificial snow in some skiing areas near Tokyo and Dubai (Taiji *et al*., 1998). SAPs are also used in cosmetic formulations to improve moisturizing effect of skin-creams, powders with talc to absorb perspiration or in a gel-form face masks (Buchholz and Graham, 1998). In other industries SAPs are used for dewatering adulterated fuel like gasoline or diesel and reducing the water content in crude oil (Po *et al*., 1994), as fire extinguishing and fire retardant materials (Asako *et al*., 2004), decorative purposes (Mudiyanselage and Necker, 2008), refreshing tissues (Sannino *et al*., 2006) or fragrance release systems (Po R. 1994).

Agricultural applications

Despite the application of SAPs in agriculture came out in the 1970s based on the idea of using these materials as soil amendment improving water holding capacity and therefore protect plants against abiotic stress (Buchholz and Peppas, 1994, Hüttermann *et al*., 1999), there have been developed parallel agricultural application of SAPs.

An application of SAPs in agriculture not related to the subject matter of this thesis is their use in controlled release systems for agrochemicals such as fertilizers (Liang *et al*., 2007, Rashidzahed and Olad, 2014), fertilizer additives like nitrification inhibitors (Minet *et al*., 2013) and crop protection products (Lehn *et al*., 2011; Zohuriaan-Mehr *et al*., 2010; Buczkowski *et al*., 2014). Controlled release formulations of agrochemicals with SAPs reduce the number of necessary applications as plants are able to take up the products in a more efficient way reducing losses by leaching (Kenawy, 1998; Ramos-Campos *et al*., 2015). Moreover SAP materials can be used as retaining materials in the form of seed additives, seed coatings or root dips (Abd El-Rehim *et al*., 2004). Other studies reviewed the use of SAPs as improvers of polluted soils (Hüttermann *et al*., 2009; Jelusic *et al*., 2014) or soil stabilizers reducing erosion problems (Han *et al*., 2007).

However the agricultural market covered only 2.1% of the total sales of SAPs worldwide in 2012 (EDANA). Deeper introduction with respect to SAPs in agriculture is given in the sub-chapter 1.2.

1.2. SUPERABSORBENT POLYMERS IN AGRICULTURE

1.2.1. The role of superabsorbent polymers in agriculture.

World population increased from 1,700 million in 1910 to nearly 7,200 million in 2014 while the forecast is reaching 9,500 million in 2050 (The World Bank, 2015). This inevitably means more food is needed (Jackson *et al*., 2001).

Recent studies estimate that global food demand will require an increase of 40% yield from main crops in the next 20 years while the cultivated land will increase only by 10% (Godfray *et al*., 2010). This can be translated into the necessity of improving crop yield per unit of land to match the increasing food demand. Improvement of yield will involve many biophysical and ecological aspects including plant abiotic stress alleviation like drought, salinity, heat, cold and nutritional deficiencies (Spiertz, 2012), Potential yield losses in agriculture by abiotic stress are estimated in about 50% in major annual crops (Wang *et al*., 2003).

This global situation means that with the purpose of matching the increasing food demand worldwide, not only productivity should be increased but also the efficient use of limited resources like fertile lands and water (Spiertz, 2012). Food depends on agriculture and agriculture absolutely relies on water which is a limited resource. Fresh water from aquifers, soil pores, lakes, swamps and rivers constitute only about 0.01% of the total water on Earth (Postel *et al*., 1996). Irrigated agricultural land is 17% of the total cultivated area and 40% of the food in the world comes from irrigated lands (Postel, 2000). Furthermore, agriculture is the economic sector that consumes more fresh water with a 70% of the total resources over the 20% by industrial consume and 10% by human consume (UNESCO, 2009).

SAPs could play a role as soil amendments contributing to the increase of crop yields per unit of land (Wood and Johnson, 1991). At the same time, SAPs could contribute on more efficient use of limited resources as they could perform as reservoirs of water and nutrients (Bakass *et al*., 2002; Zohuriaan-Merh *et al*., 2008; Wu *et al*., 2008). This basic concept in combination with the problematic of water shortage and the need of a more efficient use of resources might explain the constant increase of research based on the potential use of SAPs in agriculture. Considering the number of published scientific papers related to SAPs in agriculture it can be easily deduced how this field of application has been principally investigated just during the last decade (Figure 1.15; Web of Knowledge).

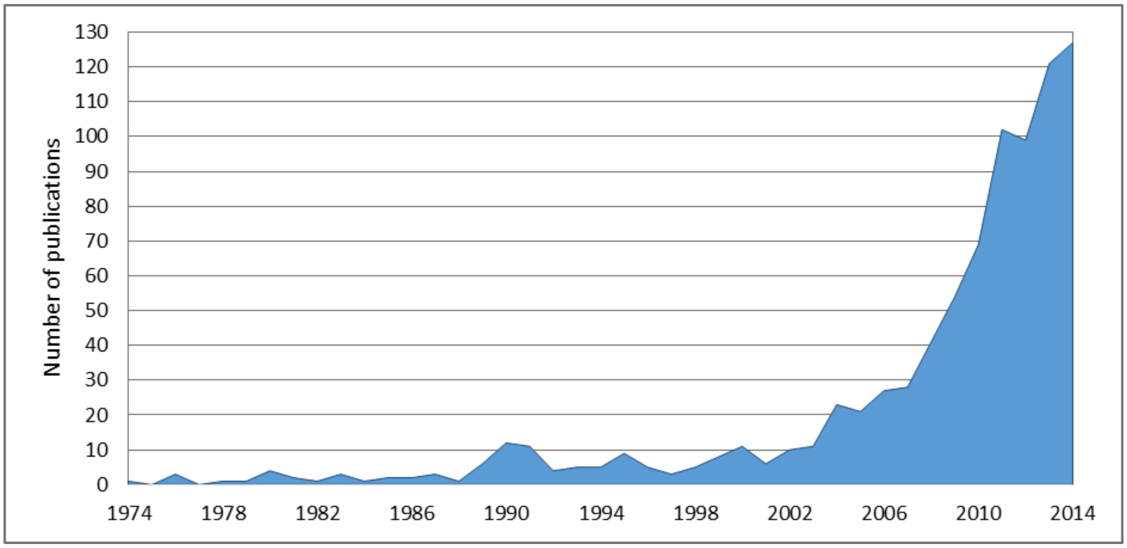


Figure 1.14 – Published items in each year on the topics "superabsorbent polymers" and/or "hydrogel" within the research area "agriculture" up to 2014. Citation report obtained from the Web of Knowledge (all data bases search).

1.2.2. Effects of SAP materials on soils and plants.

1.2.2.1. Effects on physical soil properties

SAPs have shown significant effects on improving some physical soil properties related to water when they are used as soil amendment mixed with the substrate. The role of water on the development of plants is known. Principal functions of water are transporting of mineral nutrients, maintenance of intracellular pressure, buffering plants against temperature fluctuations and its role in the photosynthesis which is mainly linked to crop productivity. Mekonnen and Hoekstra (2011) calculated the water footprints of primary crops being necessary 1600 m^3 for producing 1 ton of cereals, 1000 m^3 for 1 ton of fruits or 300 m^3 for producing 1 ton of vegetables.

Some studies from the 1980s showed and explained the physical impact of SAPs on soil properties (Table 1.2). SAP particles placed in pores of sandy soils permits to retain more water reducing the hydraulic conductivity and increasing the water-holding capacity (Parvathy *et al*., 2014). These effects on soil properties resulted higher water use efficiency (El-Hady *et al*., 1981; Tayel and El Hady, 1981; Azzam, 1985).

Table 1.2 – Effects of SAP on sandy soil physical properties and plant growth (Tayel and El-Hady, 1981).

Concentration of SAP (%)	Hydraulic conductivity (m/day)	Available water (%)	Transpiration ratio[1] (g/g)	Water use efficiency[2] (g/kg)
Control	9.75	1.85	1209.83	0.8265
0.05	9.00	2.16	1088.12	0.9190
0.1	7.25	3.12	1057.63	0.9455
0.15	6.32	3.92	889.81	1.1238
0.2	3.99	7.59	937.39	1.0668

[1] Weight of evapotranspirated water to produce 1g of dry matter.
[2] Weight of dry matter produced by 1 kg of water.

More recent publications confirmed the studies of Tayel and El-Hady from the 1980s. Banedjschafie and Durner (2015) showed a plant available water increase on sand from 0.005 for the untreated to 0.06 g/g for the treated with a SAP ratio of 0.3% w/w. Regarding hydraulic conductivity it has been shown its reduction in soils when increasing the concentration rate of SAPs (Andry *et al*., 2009). SAP materials reduces as well the largest pores of soils, especially in sandy soils (Abedi-Koupai *et al*. 2008). Hydraulic conductivity is responsible for the gravitational flow which means that the channels of losing water by percolation or evaporation are reduced by the use of SAPs. However other authors discussed that hydraulic conductivity initially increases and later on decreases by the effect of SAPs (Bhardwaj *et al*., 2007).

Other physical properties of soils are improved by the use of SAPs such as soil permeability, bulk density and structure (Abedi-Koupai and Asadkazemi, 2006). Furthermore, the expansion and contractions of the polymer particles due to the swelling and drying cycles increases the soil aeration especially in clay soils (Buchholz and Graham, 2004). According to Azzam (1985) SAPs can act as a soil ameliorator that transmits several properties from arable lands to poor sandy soils and substrates.

It can be concluded that the application of SAPs as soil amendment increases both, saturated and residual water so in general the water holding capacity of soil and thus the available water for plants (Bakass *et al*., 2002; Abedi-Koupai *et al*., 2008; Dorraji *et al*., 2010). The principal advantage coming from the positive effects on soil physical properties might be the potential benefit of reducing irrigation frequency and thus improving water management practices (Sivipalan, 2006; Zohuriaan-Mehr *et al*., 2010, Dorraji, 2010; De Carvalho *et al*., 2013).

1.2.2.2. Effects on chemical soil properties

Other agronomical effects of the applications of SAP materials in soils is related with a most efficient use of nutrients. As already discussed in the section 1.1.5, SAPs can act as a slow release system favoring the uptake of nutrients. SAPs can hold nutrients tightly delaying their dissolution (Wu *et al*., 2008; Liu *et al*., 2006). In this sense, less frequent applications are required and plants are still able to take up the required nutrients (Kenawy, 1998). A well-known example is the loss of about 40 to 70% of the urea fertilizer to environment. SAPs can be useful to reduce environmental pollution and improve the fertilizer efficiency by simply immersing the polymer in the fertilizer solution (Smith and Harrison, 1991). Some recent result confirms the ability of SAPs to conserve not only water but also nutrients and deliver them to the plants (Mao *et al*., 2011). Parvathy *et al*. (2014) showed an increase on macro, secondary and micro-nutrients in soils treated with SAP. This increase on uptake of certain nutrients leads in particular cases to better growth under salinity stress (Chen *et al*., 2014).

1.2.2.3. Effects on soil microbiology

Another effect which still not well explored is the impact of SAPs in soil microbiology. Some studies showed the depressed development of soybean seed microorganism by a SAP material (Knypl and Knypl, 1993) while other found the increase of nodulation of two actinorhizal plant species improving early growth (Kohls *et al*., 1999). In one study plant pathologists suggested that the addition of SAP material increased the bacterial aggressiveness (Lee *et al*., 2008). Some recent studies demonstrated and increase on bacteria and fungi counts in SAP amendment soils (Parvathy *et al*., 2014). More studies are needed in this area to increase the knowledge of the effects of SAP materials in soil microbiology.

1.2.2.4. Effects on plants and crops

Some studies reported that SAPs increase water availability for the plants inducing better plant growth, prolonging survival under water stress and drought conditions (Beniwal *et al*., 2010; Hüttermann *et al*., 2009) and as a consequence crop yield is enhanced (Dorraji, 2010). Some other positive effects have been demonstrated when using SAPs under watering limited conditions such as better crop establishment, growth and production on lettuce (Woodhouse and Johnson, 1991), improved growth and productivity in corn (Abd El-Rehim, 2004; Chu *et al*., 2006; Lentz and Sojka, 2009) and pepper (Lopez-Elias *et al*., 2013), improved drought tolerance and survival rate of *Pinus halepensis* (Hüttermann *et al*., 1999), increased germination and growth of soybean under lab, pot and field conditions (Knypl and Knypl, 1993), higher coffee seedlings quality (Marques *et al*., 2013), higher weight of ryegrass biomass (Burke *et al*., 2010), larger period of time until reaching the permanent wilting point in some ornamental plants (Firgure 1.15; Abedi-Koupai and Asadkazemi, 2006), improved photosynthetic performance of tree seedling (Jamnicka *et al*., 2013) and longer root system on maize plants (Mazen *et al*., 2015).

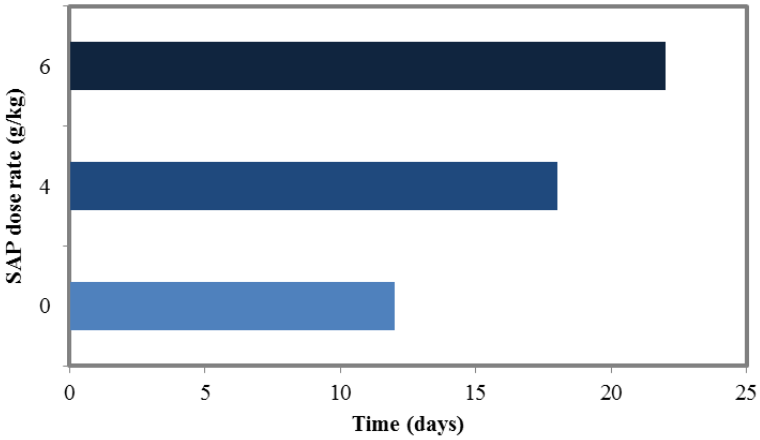


Figure 1.15 – Number of days to reach the permanent wilting point on untreated and treated plants with SAP (Abedi-Koupai and Asadkezemi, 2006).

Most of the positive results normally occurred when water availability was not optimal for plants and soils were drier than optimal (Buchholz and Graham, 1998). However some experiences showed also positive effects on growth and yield when applying SAP under standard irrigation or normal watering conditions (Figure 1.16).

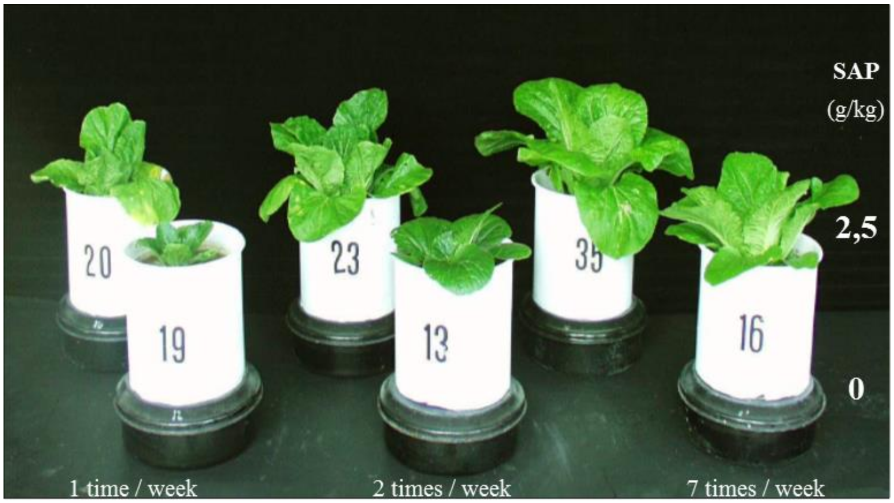


Figure 1.16 – Pot trial on lettuce with different irrigation regimens. Upper pots were treated with SAP. Positive effects are also visible at full irrigation regime. Source: BASF Crop Protection (Germany).

For instance yields of cabbage treated with SAP material increased about 10% compared to the control plot under similar watering conditions (Shimomura and Namba, 1994). In another study the produced biomass of ryegrass increased by 30% under normal watering conditions when soil was amended with SAP (Dorraji, 2010). It can be concluded that SAPs have also positive effects on plants when available water for the plants are optimal.

1.2.3. Limitation of SAP materials in agricultural systems.

Not always positive results coming from the effect of applying SAPs as soil amendments has been reported. In some cases it was found a negative effect on plant growth. Ingram and Yeager (1987) found a more pronounced decrease on the height of wheat plants as higher the applied rate of SAP material was. In other cases there was no significant effect found on the wilting point of plants treated with SAPs (Chatzoudis and Rigas, 1998). The conclusions by Frantz *et al*. (2005) suggest that the potential benefit of using SAPs is only significant in early stages of plant growth and there is limited or even no benefit in production parameters.

Al-Harbi *et al*. (1999) reported that SAPs lose efficacy over a period of time so this should be compensated by increasing dose-rates of application: SAPs in soils releases water with the increase of temperature and therefore losing it by percolation. However plant over-dose negative effects could lead to plant mortality when dose rates are too high (Sarvas *et al*., 2007).

The loss of efficacy reported by Al-Harbi *et al*. (1999) could be also explained by some known factors that generally affect the swelling capacity of SAPs and thus they could limit their application in the soil. It is known that the absorbency is negatively affected when SAPs are subjected to a certain pressure or load. In this way, SAP particles can be affected by the soil pressure when applied underground (Zohuriaan-Mehr *et al*., 2008). SAPs performance might be also negatively affected after several dry-wet cycles under different environments (Bai *et al*., 2013; Banedjschafie and Durner, 2015). The effect of dissolved salts on the swelling capacity of SAPs was widely discussed by Kanzanskii and

Dubrovskii (1992). According to the swelling mechanism SAPs swell much less in the presence of monovalent ions but even less in the presence of multivalent ions (Bowman *et al*., 1990; Taban and Naeini, 2006).

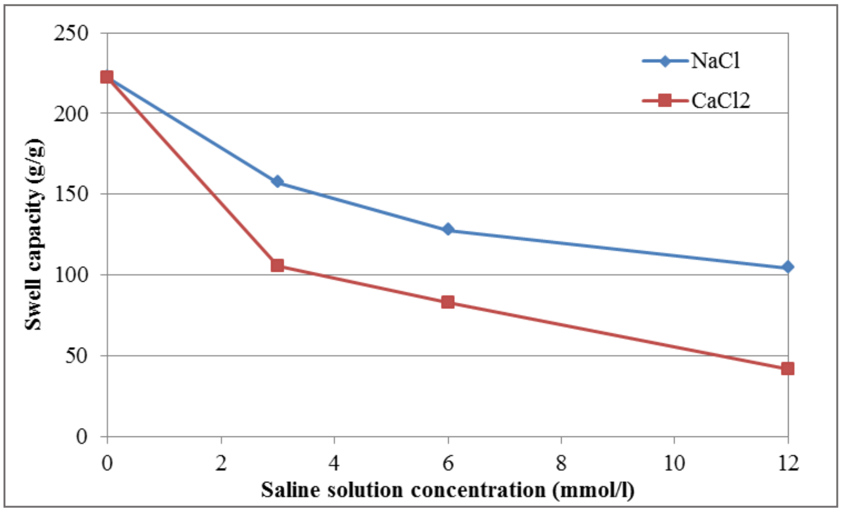


Figure 1.17 – Effect of the presence of increasing concentration of KCl and CaCl₂ solutions on the swelling capacity of a SAP. Source: Bo *et al*. (2012).

These ions can be naturally provided by the soil or by the use of fertilizers. Multivalent ions like Ca^{2+} or Fe^{3+} are able to act as additional crosslinkers collapsing the SAP structure (Chatzoudis and Rigas, 1999; Banedjschafie and Durner, 2015). Recent studies by reported not only effect of ions on the swelling capacity (Figure 1.17) but also the decrease of absorption velocity as ion concentration increases (Bo *et al*., 2012).

1.2.4. Application rates review.

Majority of the published studies about SAP materials including the testing of physicochemical properties in relation with soils and/or trials evaluating the effects on plants have used application mixtures of about 0.05% to 0.6% based on dry weight. According to the data of various authors, positive effects can be found at dose rates of 0.2% when SAP is applied to sandy soils in pots (Bakass *et al*., 2002; Johnson and Piper, 1997). Based on the water retention mode of action, Kazanskii and Dubrovskii (1992) calculated that it would be necessary to apply from 1 to 3 ton/ha of SAP in a soil layer of 35 cm to have about 10% of moisture increase (using SAP materials with an absorption capacity from 200 to 500 g/g). Due to the nowadays cost of superabsorbent materials, these rates are obviously not affordable to be used in field crops (Zohuriaan-Mehr *et al*., 2010).

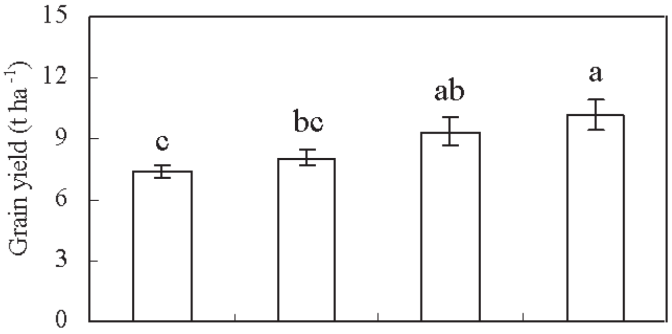


Figure 1.18 – Effects of applying 0, 5, 10 and 15 kg/ha of SAP (from left to right) on corn field trial (Mao *et al*., 2011).

In the other hand internal BASF trials carried out in 2009 and 2010 on processing tomato and corn showed positive effect at dose rates of 20 and 30 kg/ha applying the product in a localized way within the planting/sowing furrow. These results fits to those found in recent publications which reported significant response on plants using dose rates of 10 and 15 kg/ha with same application on corn trials (Mao *et al*., 2011) or significan yield increase on wheat at 20 and 40 kg/ha (Ashkiani *et al*., 2013). Other studies used SAP dose rates from 5 up to 15 kg/ha on corn, 60 kg/ha on *Avena sativa* and 30 kg/ha on wheat reporting positive effect in several parameter including yield (Islam *et al*., 2011), greater significant soil quality indexes in soybean-wheat cropping system at 5 kg/ha (Narjary and Aggarwal, 2014).

Based on the available knowledge about using SAPs in soil-plant systems and the fact that plants response as a syndrome or product of single effects it is difficult to think on casual relationships and that probably more than one single factor is involved in the the effects on crops.

1.2.5. Eco-compatibility: toxicity and degradability of SAP materials.

Eco-compatibility and biodegradability are crucial for the sustainable application of SAP materials in agricultural systems (Wilske *et al*., 2014). Having in mind that a completely natural based or natural-synthetic hybrid SAP have better eco-compatibility and biodegradability than completely synthetic ones (Al *et al*., 2008), this section is mainly focused on the last type.

Synthetic SAPs are considered as non-toxic compounds (Huttermann *et al*., 2009). All published studies on the toxicity of acrylate based SAPs shown that this substances have positive toxicological profile so they can be considered as environmentally compatible (McGrath *et al*., 1993; Haselbach *et al*., 2000; Fiume, 2002). Furthermore, it was found that polyacrylates have no negative influence or adverse effects on the soil microbiology from some forest (Basanta *et al*., 2002) or even improve their populations (Lee *et al*., 2008).

Regarding biodegradability and behavior in the soil there is limited literature and knowledge. Degradability is obviously dependent on the polymer chains of the polymer and the micro-flora. It was reported a variety of microorganisms and systems able to degrade the carbon chain of linear polyacrylates. The mechanism of biodegradation seemed to be similar to the degradation of fatty acids, linked to respiratory chains of bacteria (Kawai, 1995).

The depolymerization of acrylate polymers by White-rot Fungus has been studied (Sutherland *et al*., 1997; Stahl *et al*., 2000; Mai *et al*., 2004). White-rot fungus is considered as one woody-decay fungus which digests the moist wood. This fungus was able to degrade two synthetic cross linked acrylic polymers. The mineralization of the product (conversion to carbon dioxide) and fungus growth still increase when the amount of product added formed a gel by absorbing all the liquid culture media. Neither the polymers nor the degradation products were toxic to the fungus. Mineralization rate was low, however, the products were depolymerized into water soluble products in about 15 to 18 days. It could also be shown that most of the carbon of the polymer (>80%) was recovered in the fungal mycelia mat and therefore been converted to fungal metabolites (Sutherland *et al*., 1997). Other study shows that acrylate-polymers containing phenolic groups are more rapidly depolymerized by White-rot fungi than those with only aliphatic components (Mai *et al*., 2004) while biodegradation of this type of polymers works better under conditions that maximize solubilization (Stahl *et al*., 2000). The mineralization rates of some acrylamide-acrylic acid SAPs found was about 9% after 22 weeks when soils are inoculated with *Pleurotus ostreatus* (Wolter *et al*., 2002). Other authors found a degradation rate of 5.9% after 500 days in municipal compost for acrylate based SAPs (Stegmann *et al*., 1993).

Hayashi *et al*., (1994) described a first approximation to the degradation mechanism of polyacrylate polymer studying the microbial degradation of sodium polyacrylate. It was found that polymer chains with molecular weights of 1000, 1500 and 4000 degraded by two soil microorganisms in the level of 73, 49 and 20% respectively after two weeks. Polyacrylate chains of high molecular weight do not biodegrade as easy as small ones. Chains with molecular weight below 1,500 g/mol degraded completely as they can easily traverse the microbial cell membranes. Long chains must be firstly transformed into smaller ones before they completely degrade.

The resulting monomers and dimer material of the degradation is easily mineralized by microorganisms (Larson *et al*., 1997). The average decomposition rates of radioactively labelled cross-linked polyacrylates reported are normally in the range of about 1 to 9% in the period of one year. This is the same rate observed during the decomposition of organic matter in forest ecosystems. For example, the degradation of weed biomass in a coffee plantation on Sumatra reached of between 7 and 14% after four years (Watanabe *et al*., 2007) or the lignin moiety of needles was degraded by 13% after two years (Sjöberg *et al*., 2004). In the other hand recent studies modeled the degradation of SAPs exceeding 30% during 3 months under irrigated agriculture in arid climate and more than 10% under humid climatic conditions (Smagin *et al*., 2014).

As conclusion; despite on one hand SAPs might last few years in the soil until they completely degrade to carbon dioxide, methane, water and biomass under biochemical action (Holliman *et al*., 2005), SAPs can be considered as non-toxic and eco-compatible as they behaves like artificial humus (Ekebafe *et al*., 2013) or like organic litter entering the humus cycle (Eichhorn and Hüttermannet, 1994). However the exiting knowledge is coming principally from model/artificial experimental setups. Therefore it is questionable how good the existing tests might predict degradation under real field conditions and as a consequence further studies to better understand the short and long term degradation of SAPs in agricultural systems are still necessary.

1.3. MOTIVATION AND OBJECTIVES

1.3.1. Appraisal of the state of the art.

Multiple positive potential benefits of using SAPs in agriculture has been studied and reported during the last decade. A summary of these positive effects according to Zohuriaan-Mehr and Kabiri (2008) and Huttermann *et al*. (2009) is listed below:

- Reducing irrigation water consumption and the death rate of plants.
- Increasing the available water in the soil prolonging plants survival under water stress conditions.
- Reducing the evapotranspiration rate of plants.
- Inducing better growth rate.
- Reducing soil compaction by increasing aeration and microbiological activity in the soil.
- Improving fertilizer retention in the soil and thus increasing the fertilizer efficiency as well as preventing contamination of underground water.
- Preventing erosion improving soil stabilization.
- Mitigating polluted soils.
- Mitigating the effects of salinity.

In one hand SAPs have been developed for its use in agriculture mainly as water management tools. They can act as water reservoirs providing water to plants when needed and thus improving their establishment, growth, health and yields under drought or related abiotic stress conditions. Mode of action has been basically based on improving the water-holding capacity of soils. However to get this effect it is necessary to apply SAPs mixed with the substrate on an average rate of about 0.2% w/w or from 1 to 3 ton/ha under field conditions.

In the other hand, it has been described that SAPs also shows beneficial effects under standard irrigation or normal watering regimes. Furthermore some other lateral effects like nutrient retention properties or activation of the soil microbiology have been recently reported. In addition latest studies have shown positive benefits on crop yields when SAPs are applied in furrow within the seed/planting row at average dose rates of about 20 kg/ha.

The low rates of 20 kg/ha in combination to the reported limitations on swelling capacity of SAP materials when they are under soil pressure or aqueous saline conditions add a question mark to the nowadays accepted mode of action (water reservoirs). It seems that other unknown mechanisms might contribute to get positive effect by applying SAPs in agricultural systems.

Superabsorbent polymers have not yet developed its full potential in agriculture. Results from studies on the efficacy of superabsorbent in improving plant health or yield have been mixed. The existing published research on this field of application still being confused and not conclusive for three main reasons which are given below:

- Major part of available research has being done from the polymer science side without the agronomical thinking point of view.
- Published studies include a huge number of different products that differ on basic structural backbones, monomer origin, being from commercial or laboratory synthesized origin.
- The wide range of tested crops and varieties, experimental conditions, trials sites and locations, natural environments, mixing of soils and different evaluated parameters makes difficult to get a clear picture.

According to the literature review it is required a detailed and cross-disciplinary proof of concept approach from the agronomical and commercial perspective. A basic but wide study on just one referential product covering the overall view from the laboratory to the field is needed.

1.3.2. Hypothesis.

The application in a proper dose-rate of cross-linked potassium polyacrylate (Luquasorb®1280R) as a special soil amendment might improve soil physiochemical properties and therefore increase productions yield of crops grown under field conditions by making a more efficient use of soil resources.

1.3.3. Objectives.

This doctoral thesis main objective is to clarify and to increase to a certain extent the existing knowledge about the application of superabsorbent polymers in agriculture as soil amendments by characterizing, describing and evaluating the effects related to the application of cross-linked potassium polyacrylate with the corresponding design of experiments, tests and field trials. In a more specific manner this research work pretends to reach, within the possibilities, the following objectives:

1) Characterization, description and evaluation of cross-linked potassium polyacrylate physicochemical properties of agronomical interest for its application as soil amendment and its effects on soils properties.

2) Characterization, description and evaluation of the effects on agronomical parameters such as growth, yield and quality of crops grown under field conditions when using cross-linked potassium polyacrylate as soil amendment in Mediterranean climate areas.

3) Elucidating and opening new research areas which might be of interest to better understand the effects of applying superabsorbent polymers in agricultural systems and within the soil-plant interaction.

1.3.4. Work planning and thesis structure (outline).

Based on the complexity and the multidisciplinary work developed during the research part, this thesis has been structured with the purpose of facilitating the reading in alignment to the followed working plan. Research work was divided into 2 main working areas; physicochemical characterization together with the effects on soil properties (molecular level) and the effects on plants grown under field conditions (agronomical level). These two levels resulted in to the following chapters in alignment to the objectives of this thesis:

Molecular level: initial step followed was the physicochemical characterization of the superabsorbent polymer itself, in combination with soils and effects caused on those. Designed experiments and tests were based on existing physicochemical soil characterization methods. Selected methods were checked and adequately adapted to characterise hydrogels. Resulted chapter: PHYSICOCHEMICAL CHARACTERIZATION OF CROSS-LINKED POTASSIUM POLYACRYLATE AND ITS EFFECTS ON SOILS WHEN USED AS AMENDMENT.

Agronomical level: biological characterization field trial series were design to evaluate crop response to the application of cross-linked potassium polyacrylate as soil amendment under field conditions. Trial series were run on processing varieties of tomato in Spain and Italy. Resulted chapter: AGRONOMICAL TRIALS ON PROCESSING VARIETIES OF TOMATO (Solanum lycopersicum L.) IN MEDITERRANEAN CLIMATE USING CROSS-LINKED POTASSIUM POLYACRYLATE AS SOIL AMENDMENT.

1.3.5. Contributions by the proposed thesis.

In spited of the concept of using SAPs in agriculture came out in the beginning of the 70’s, this topic has been studied in very limited cases. Furthermore the number of publications regarding this concept has being increasing in a considerable way during the last years which makes this thesis be backed by the world agro-scientific community trends.

The global demand, driven by a world population increase, of reaching higher crop yields within the same land space needs to fit with sustainable agricultural practices; better use of soil resources (water and nutrients). Reducing abiotic stress is one of the main pillars to be secured in order reduce yield losses. In this way SAPs could play an important role in the near future.

The main proposed objective to be reached in this study covers a complete characterization of the effects from the lab to the field. The creation and adaptation of methodology for physicochemical and biological characterization of SAPs and the generation of knowledge on understanding how this product performs might be the base for a future development of new superabsorbent polymers with an agriculture-focus design. Furthermore this doctoral thesis pretends to open the doors for new research fields within the application of SAPs in agricultural systems.

CHAPTER II

PHYSICOCHEMICAL CHARACTERIZATION OF CROSS-LINKED POTASSIUM POLYACRYLATE AND ITS EFFECTS ON SOILS WHEN USED AS AMENDMENT

2.1. INTRODUCTION TO CHAPTER II

Cross-linked potassium polyacrylate is a superabsorbent polymer (SAP) with the ability of absorbing water or aqueous fluids (Buchholz & Graham, 1998) and therefore with potential of been used as a soil amendment for improving soil physical and chemical properties (Chapter I, sections 1.2.2.1 and 1.2.2.2).

The content of this chapter covers three main themes:

Water absorption properties of the polymer

The first two main topics of this chapter consist in the evaluation of the absorption and drying properties of a commercial cross-linked potassium polyacrylate product (Luquasorb®1280R) and the assessment of some swelling limiting factors that might play a role in soil-SAP systems such the presence of salts (Bo *et al*., 2012) and the impact of soil pressure (Zohuriann-Mehr *et al*., 2008).

Nutrient retention properties of the polymer

In a following section, knowing the ability of some SAPs to retain nutrients (Wu *et al*., 2008) and deliver them to the plants (Mao *et al*., 2011), this chapter appraises the inherent nutrient content of the product while elaborates a first approximation to a cationic exchange profile of cross-linked potassium polyacrylate including kinetics and selectivity.

Effects of the polymer on basic soil properties

The last segment of this chapter approaches the assessment of the effects of adding cross-linked potassium polyacrylate on soil properties. On one hand those soil properties known of importance for nutrient availability such as pH and electric conductivity (Navarro-Blaya & Navarro-Garcia, 2003) are covered. On the other hand those properties related to the water availability for plants such as soil texture, field capacity and wilting points (Brouwer *et al*., 1985) are studied in soil-SAP mixture systems.

2.2. MATERIALS & METHODS

2.2.1. Materials

2.2.1.1. Cross-linked potassium polyacrylate

As material source of cross-linked potassium polyacrylate for the experiments it was used the commercial product Luquasorb®1280R (BASF, Germany). It presented as irregular white opaque hard solid granules (Figure 2.1).

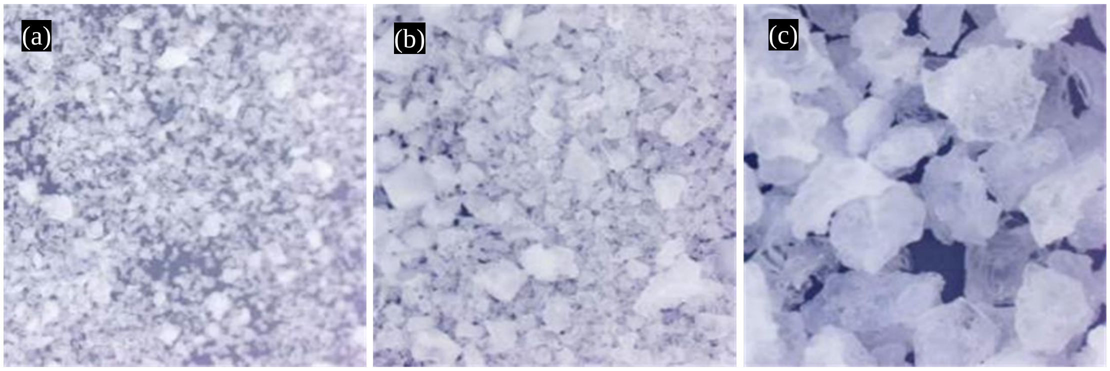


Figure 2.1 – Pictures taken with a microscope of the three granulometries of Luqusorb®1280R: (a) RS (45 – 500 um); (b) RM (150 – 850 um) and (c) RL (300 – 1800 um)

Luquasorb®1280R is commercially available in 3 different granulometries: RS (small), RM (medium) and RL (large) (Table 2.1). The three of them were used within the physicochemical characterization and the medium size one was used for the biological characterization and agronomical field trials.

Table 2.1 – Particle size distribution (%) of Luquasorb®1280RS, ®1280RM and ®1280RL.

Distribution	®1280RS (%)	Distribution	®1280RM (%)	Distribution	®1280RL (%)
< 45 µm	< 1	< 45 µm	< 1	< 300 µm	<1
45 – 150 µm	< 25	45 – 150 µm	5	300 – 600 µm	24
150 – 300 µm	20 – 50	150 – 300 µm	20	600 – 850 µm	39
300 – 500 µm	25 – 65	300 – 600 µm	45	850 – 1000 µm	19
500 – 850 µm	< 1	600 – 850 µm	28	1000 – 1800 µm	15
> 850 µm	< 0.1	> 850 µm	< 1	> 1800 µm	<1

**Data source: BASF Care Chemicals division.*

Based on available data for hygiene purposes of Luquasorb®1280R provided by BASF, physicochemical properties of the three granulometries do not differ significantly with the exception of the swelling velocity (Table 2.1.). Detailed properties of the RS, RM and RL products is included in Annex I, table AI.1.

2.2.1.2. Artificial substrates

Silica sand

For some of the experiments it was used commercial dry silica sand (Sales del Centro S.L., Spain) due to the low nutrient and water retention properties. Silica sand is composed of silicon dioxide (SiO2) and its appearance is white/transparent sand granules. Silica sand is chemically inert and heavy material (high density). Detailed chemical analysis is included in Annex I, table AI.2

Table 2.2 – Properties of the silica sand used for the experiments.

Property	Silica Sand
General chemical formula	SiO_2
Granulometry (mm)	0.5 – 1
CEC – Cation exchange capacity (meq/100g)	< 1
Bulk density (mg/ml)	1600
Real density (mg/ml)	2650

**Data source: Sales del Centro S.L.*

2.2.1.3. Natural soils

Three natural soils situated in the province of Seville (Spain) were selected, based on their different textures, for the evaluation of the effects of cross-linked potassium polyacrylate on its properties. Two of the selected soils were situated at BASF experimental farms in Utrera and El Coronil while the third one was from a commercial farm closed to the village Maribañez. Samples were collected manually in a randomized way within each sampling area with the help of a spade. Sampling depth was from 0 to 40 cm in all the sites (superficial layer). Soils were stored in plastic sacks under room temperature until their use for in the corresponding experiments. In the following pages soils will be referred as “Soil 1 = Sandy soil = Utrera”, “Soil 2 = Loamy soil = Coronil”, and “Soil 3 = Clay soil =

Maribañez". Detailed analysis of the soil can be found in the Annex I, table A1.3. Basic relevant characteristics of these soils are described in the following lines.

Soil 1 - Sandy soil, Utrera.

Sandy soil samples were taken from the south-western part of the experimental plot number 16 (latitude: 37.207606; longitude: -5.817903) of the BASF Agricultural Research Station in Utrera (Figure 2.2). The content of sand, silt and clay of the soil is 85%, 10% and 5% respectively. This soil contains a high percentage of sand, pH near to neutral and has a low content on nitrogen, calcium, magnesium and organic matter. Despite it has high content on phosphorous slight more acid pH is needed to make it plant available as pH of the soil is 7.15 (Annex I, table AI.3).

Figure 2.2 – Aerial view of the Plot 16 of the BASF Agricultural Research Station in Utrera and soil sampling area. **Picture source: Google Earth Pro. Picture date: 05.09.2011*

Soil 2 – Loamy soil, El Coronil.

Loamy soil samples were taken from the southern part of the experimental plot number 2 (latitude: 37.086664; longitude: -5.612003) of the BASF Agricultural Research Station in El Coronil (Figure 2.3). The content of sand, silt and clay of the soil is 57%, 14% and 29% respectively. This soil has a high pH what could affect the availability of nutrients but in the other hand it contains a good level of organic matter. (Annex I, table AI.3).

Figure 2.3 – Aerial view of the Plot 2 of the BASF Agricultural Research Station in El Coronil and soil sampling area. **Picture source: Google Earth Pro. Picture date: 18.04.2013*

Soil 3 – Clay soil, Maribañez.

Clay soil samples were randomized taken (Figure 2.4) from San Isidro farm located in Maribañez (latitude: 37.133117, longitude: -5.881822). The content of sand, silt and clay of the soil is 33%, 16% and 50% respectively. This area has an alkaline and slightly salty soil with low content of organic matter. Analysis showed an extremely high content on sodium and calcium and poor levels of nitrogen and phosphorous (Annex I, table AI.3).

Figure 2.4 – Aerial view of the plot belonging to the commercial farm San Isidro in Maribañez and soil sampling area. **Picture source: Google Earth Pro. Picture date: 13.09.2011*

2.2.2. Methods: SAPs physicochemical characterization

2.2.2.1. Swelling parameters

Swelling by absorbing aqueous solutions is the principal basic property of SAP materials. A set of experiments were carried out with the purpose of characterizing the swelling properties of cross-linked potassium polyacrylate including; free swelling capacity, swelling and drying kinetics and hygroscopicity.

a) Free swelling capacity (FSC).

The free swelling capacity (FSC) of a SAP refers to the maximum volume of aqueous solution that can be absorbed by a polymer under free swelling conditions. FSC is normally expressed in grams of absorbed aqueous solution per gram of substance (g/g) and it was determined by 2 different gravimetric methods.

Filtration Method

50 mg of dry hydrogel were dried in an oven at 105 ºC for 24h to eliminate any possible hygroscopic water. After this period of time, the product was weighed obtaining the dry weight “W_1”. Then, dried sample was submerged into a beaker containing 100 ml of distilled water to start the swelling process. After one hour, the resulting gel was filtered during 10 minutes. The obtained gel was added again to another 100 ml of distilled water. These steps were repeated for a third time to ensure maximum swelling capacity of the polymer. The experiment was replicated by 3 obtaining an average FSC value. Filtrate was weighed after the last filtration process obtaining the wet sample weight “W_2”. FSC was calculated by the following formula:

$$FSC = (W_2 - W_1) / W_1 \qquad \text{(Formula 2.1)}$$

FSC = Free swell capacity, expressed in grams of water per gram of product

P_1 = mass, expressed in grams, of the dried sample.

P_2 = mass, expresses in grams of the wet samples after filtration.

Oven Method

50 mg of product were weighed and place into paper teabags produced by PTG Unionpack Lohnabfüllung GmbH, Germany (Figure 2.5). Paper teabags properties included in Annex I, table AI.4. Then, samples were laid on beakers containing 100 ml of distilled water to start the swelling process. After one hour the teabags containing the product were removed and hanged diagonally for 10 minutes to remove the excess of water. Same process was repeated two times more using beakers with 100 ml of renewed distilled water to ensure that maximum swelling capacity was reached. After this, teabags containing the sample were open and a portion of the obtained gel was weighed (W_{gel}) on a previously dried ceramic crucible of known mass (W_c). The whole system was dried in an oven for 24 hours at 105 ºC. The experiment was replicated by 3 obtaining an average FSC value. The resulting dried system weight was recorded (W_d). FSC was calculated by the following formula:

$$FSC = [(W_{gel} + W_C) - W_D] / (W_D - W_C) \qquad \text{(Formula 2.2)}$$

FSC = Free swell capacity, expressed in grams of water per gram of product

W_{gel} = Mass, expressed in grams, of the gel before drying.

W_C = Mass, expressed in grams, of the ceramic crucible.

W_D = Mass, expressed in grams, of the crucible and sample after drying.

Figure 2.5 – Two phase paper teabags used in the experiments (PTG Unionpack Lohnabfüllung GmbH, Germany)

b) Swelling kinetics.

Swelling kinetics refer to the velocity of absorption. In other words, the time needed for a SAP to reach its maximum swelling capacity. Knowing the polymer absorption kinetics might help to understand the behaviour of the polymer in the soil and how quick it captures water from the surrounding. To carry out this experiment paper teabags system were used (Figure 2.5). 50 mg of SAP were weighed into teabags by 10 times. Each teabag was submerged into a separated 400 ml beaker containing 100 ml of distilled water. Each sample was removed from the water at different timing for measuring free swelling capacity (Page 45). Teabags were pulled out at the following timing; 10 seconds, 30 seconds, 1, 3, 5, 10, 20, 40 and 60 minutes until getting similar swelling capacity by the three studied granulometries. The experiment was replicated by 3 obtaining average values for each sampling time. Results were plotted in graphs (Figure 2.6) representing swelling capacity versus time of measurement. The resulting curve reaches a constant value equivalent to its maximum swelling capacity.

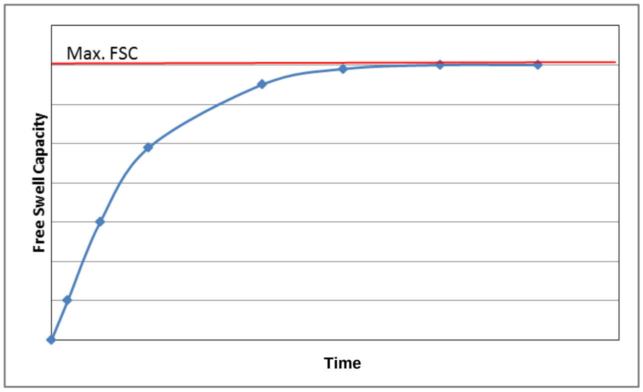


Figure 2.6 – Example of the resulting graph representing the swelling kinetics curve.

c) Drying isotherms.

Drying isotherms are related to the velocity of drying at a constant temperature. In other words, the time needed for a SAP to become completely dry from its maximum swelling capacity. Knowing the drying isotherms of SAPs might help to understand how much water still in the polymer by the pass of time and how important the losses of water by evaporation are.

Polymer samples were brought to maximum swelling capacity by saturating them with distilled water for 24 hours. After this time, 50 grams of the resulted gel was weighed in previously dried ceramic crucibles of known mass. These crucibles containing the samples were introduced in an oven for drying under different temperatures (25, 40, 80 and 105 ºC). For each temperature sample masses were weighed at different timings of 5, 10, 30, 60 minutes, 2, 4, 8, 24, 48 and 72 hours. The experiment was replicated by 3 obtaining average values of the remaining water in the polymer for each sampling time. Results were plotted in graphs (Figure 2.7) representing the remaining water content versus time at a fixed temperature.

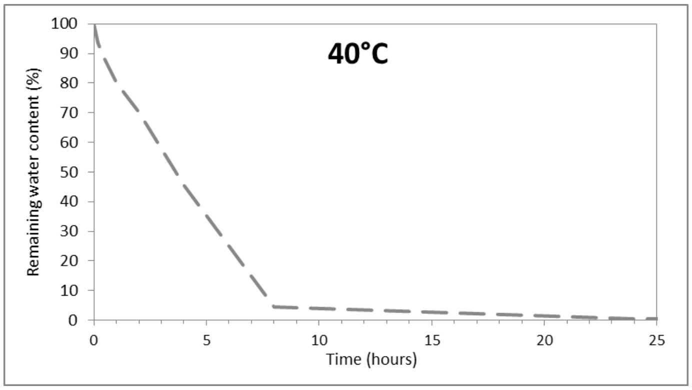


Figure 2.7 – Example of the resulting graph representing a drying isotherm at a constant temperature.

d) Hygroscopicity.

Hygroscopicity of a product is the capacity to attract and hold water molecules from the air. It is the equilibrium moisture content after being exposed to air humidity under given conditions (GEA, 2005). This property is highly important regarding transportation and packaging of SAPs. Furthermore knowing how hygroscopic a product is might help to better understand how to handle it with regards to field applications. The measurement was done by gravimetric method weighing a SAP sample which was summited to different humidity atmospheres. Mass measurements were done after 1, 2, 3, 4, 5, 6, 8 hours and 1, 5, 12, 15 and 30 days of exposition ($W_{t=i}$). It was used closed plastic trays containing approximately 1 cm thickness of specific saturated solutions and distilled water to create different humidity environments (Figure 2.8). Hygroscopicity was measured at 35, 63, 86 and 100% humidity using saturated solution of $CaCl_2$, NH_4NO_3, KCl and just distilled water respectively (Annex I, table AI.5). Triplicate samples of approximately 25 mg ($P_{t=0}$) were standing on red plastic caps on top of the base of a petri-dish avoiding direct contact with the solutions (Figure 2.8). SAP samples were previously dried at 105 ºC for 24 hours in an oven to remove the already hygroscopic water.

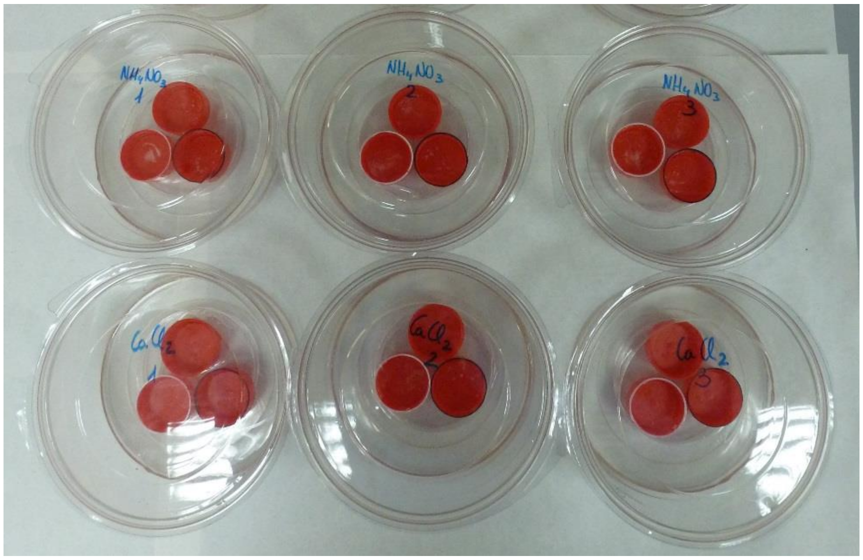


Figure 2.8 – Overview of the used system for measuring hygroscopicity of SAP samples.

The hygroscopic water captured by the polymer at a certain time was calculated by the following formula:

$$HW_{t=i} = W_{t=i} - S - P_{t=0} \qquad \text{(Formula 2.3)}$$

$HW_{t=i}$ = Mass, expressed in grams, of hygroscopic water content.
$W_{t=i}$ = Mass, expressed in grams, of the cap and the sample at time ‘i’.
W_{cap} = Mass, expressed in grams, of the cap stand.
$P_{t=0}$ = Mass, expressed in grams, of the dried polymer sample at initial time.

2.2.2.2. Experiments for evaluation of swelling limiting factors

Some limiting factors affecting the swelling capacity of SAPs like pressure (Zohuriaan-Mehr *et al*., 2008) or salinity (Kanzanskii and Dubrovskii, 1992) has been described in literature. A set of experiments were carried out with the purpose of evaluating the negative impact of pressure (soil depth), thermal stress and ions concentration on the swelling ability of cross-linked potassium polyacrylate.

a) Swelling capacity at different soil depth.

The water absorbed by cross-linked potassium polyacrylate at different depths in soil columns was measured for evaluating the impact of pressure on the swelling capacity of the polymer. For the preparation of the soil columns it was used 1 litre graduated cylinders. The cylinders were marked and filled with pre-washed silica sand as artificial substrate due to its chemical inert properties avoiding any other possible factor influencing the swelling capacity of the polymer.

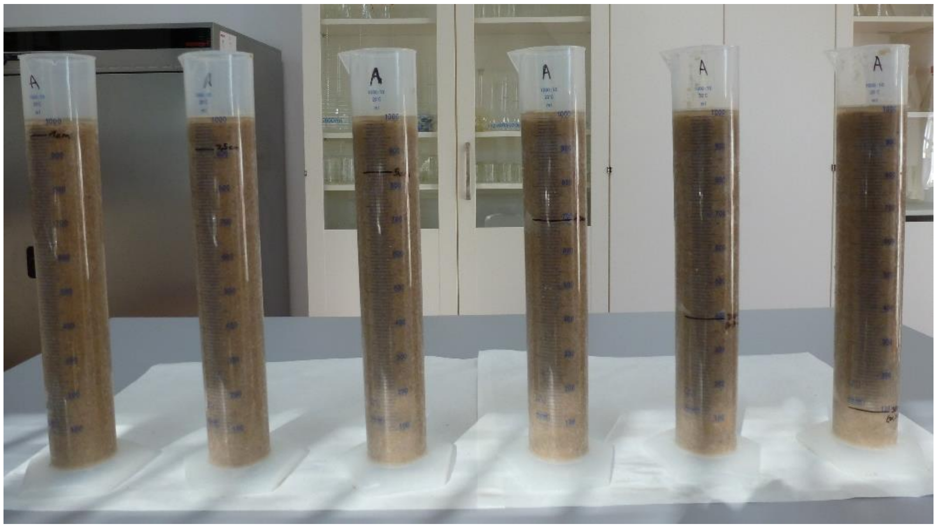


Figure 2.9 – Silica sand columns used for evaluating the impact of pressure on swelling properties of cross-linked potassium polyacrylate.

SAP samples were dried during 24 hours in an oven at 105 ºC before weighing approximately 50 mg into paper teabags (Figure 2.5). The teabags containing the polymer samples were placed at different depths (0, 1, 2.5, 5, 10, 20 and 30 cm) within the soil columns. Afterwards each soil column was filled with distilled water making sure that a supernatant of about 2 – 5 mm remains visible on the top of the graduated cylinder. The excess of water was needed to ensure that the reduction of swelling capacity was not driven by of lack of free water within the system.

After 1 hour samples were removed from the columns. A portion of the resulting gels were taken to determine the content of water using the oven method described in the section 2.2.2.1. The experiment was replicated by 3 obtaining average values for each sampling depth. Results were plotted in graphs representing the swelling capacity versus depth and/or pressure (Figure 2.10).

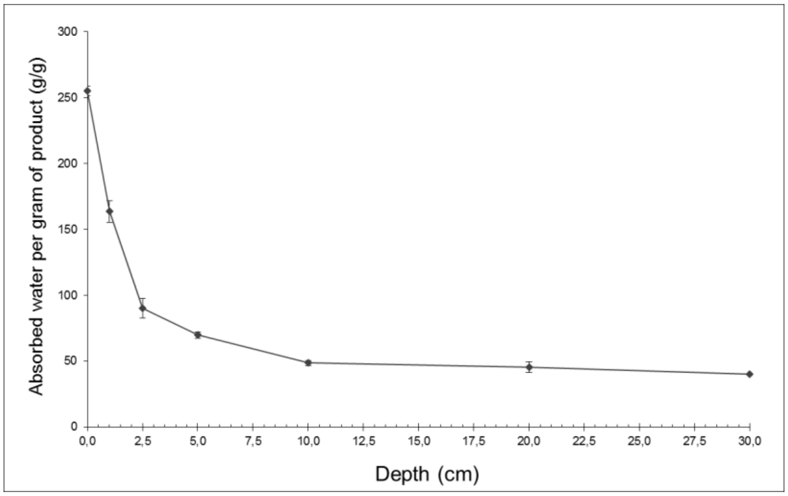


Figure 2.10 – Example of the resulting curve representing absorbed water per gram of product at different soil depth.

b) Swelling capacity vs. thermal stresses.

To understand how the swelling performance of cross-linked potassium polyacrylate is modified under thermal stress it was measured the absorption capacity on a cycle of 8 times submitting fully hydrated samples to low and extremely high temperatures. For extremely high and low temperatures effects it was considered 105 °C and -20°C. The method consisted in measuring free swelling capacity using the oven method (section 2.2.2.1) but in this case the gel was frozen for 24 hours at -20 °C before the drying process at 105 °C. After drying in the oven same dried polymer sample was used again to fill another teabag a start again until completing 8 dry-wet-frozen-heat-dry cycles (Figure 2.11). The experiment was replicated by 3 obtaining average values for each cycle.

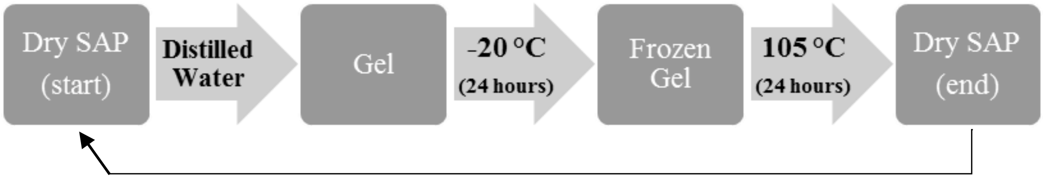


Figure 2.11 – Schematic representation of one thermal stress cycle followed to determine the effects on the swelling capacity of cross-linked potassium polyacrylate.

c) Swelling capacity vs. ions concentration.

In order to understand the impact of ion concentrations on the absorption capacity of cross-linked potassium polyacrylate it was studied the effect of different salt solutions containing monovalent divalent and trivalent cation but as well the effect of commercial fertilizers used in fertigation. With this purpose it was selected sodium chloride (NaCl), calcium chloride ($CaCl_2$) and iron chloride ($FeCl_3$) as salts (Annex I, table AI.6). As commercial fertilizer it was selected Hakaphos®Verde and Hakaphos®Naranja produced by COMPO GmbH, Germany (Annex I, table AI.7).

Salinity curves

Approximately 50 mg of Luquasorb®1280RM were weighed inside paper teabags (Figure 2.5). After this process each teabag was submerged into 100 ml of salt solution. Salt and fertilizer concentrations tested were 0, 100, 500, 1000, 1500 and 2000 mg/L. After one hour the teabags containing the samples were removed from the solutions and hanged diagonally for 10 minutes to eliminate the excess of water and then weighed. The wet mass of the teabags was estimated as a constant with a value of 0.996 grams ~ 1 gram. The experiment was replicated by 3 obtaining average values for each salt/fertilizer concentration. The swelling capacity in salty solutions was calculated by the following formula:

$$SC_{salt} = (W_{g+t} - K) - W_{dry} / W_{dry} \quad \text{(Formula 2.4)}$$

SC_{salt} = Swelling capacity, expressed in grams of salt solution per gram of product.

K = constant, expressed in grams, of the wet weight of the paper teabags equal to 0.996 ~ 1.

W_{g+t} = Mass, expressed in grams, of the hydrated gel and wet teabag.

W_{dry} = Mass, expressed in grams, of the dried polymer sample at initial time.

Absorption-drying cycles in salty solution

In addition to the absorption curves it was established a parallel experiment to measure the effect on swelling capacity of cross-linked potassium polyacrylate after several absorption-drying cycles in salty solutions. For this purpose 1 g of Luquasorb®1280RM was weighed and brought to its maximum swelling capacity using distilled water and solutions of NaCl and $CaCl_2$ in concentrations of 50 and 200 mg/L respectively. These concentration values are half of the recommended concentration limits in irrigation water by the FAO.

After full hydration in the solutions product was removed, filtered and brought to a system consisting in a scale within a drying oven at 40 °C. The scale was connected to a computer so the weight of the product was recorded every 5 hours during the drying process. After the samples were completely dry they were re-hydrated using same solutions again. The process was repeated 4 times.

2.2.2.3. Cationic interaction parameters

Some effects of SAPs on nutrient absorption, release and availability have been described in literature (Liu *et al*., 2006; Mao *et al*., 2011; Parvathy *et al*., 2014). A set of experiments were carried out with the purpose of evaluating the interaction of cations and cross-linked potassium polyacrylate including the determination of soluble and chemically linked potassium fractions, cation-exchange capacity and its kinetics, cationic affinity and nutrient release curves.

a) Determination of soluble and chemically linked potassium fractions.

Experiment 1 - Determination of the soluble-K fraction:

It was weighted exactly 100 mg of dry product in a 400 ml beaker. Then the polymer was hydrated with100 ml of distilled water and putted under shake at 180 rpm during 30 minutes. After this period the solution was filtered, levelled up to 100 ml and stored for its analysis. This process was repeated 2 times more to ensure that the entire soluble potassium fraction was removed. Resulting gel after filtration was used for continuing with the extraction of chemically linked potassium.

Experiment 2 - Determination of the chemically linked-K (from hydrated product):

The resulting gel samples from previous step were used. Exactly same operations were done like in process a.1 but using ammonium acetate 1 N as extractor solution with the idea of removing the chemically linked potassium in the polymer. The resulting filtrate was stored for its analysis.

Experiment 3 – Soluble and chemically linked K fractions (from dry product):

Same procedure of step a.1 was done but adding ammonium acetate 1 N as extractor solution directly to 100 mg of dry product. In this case the soluble fraction of potassium was not previously removed and the resulting filtrate would contain all the available potassium (soluble + chemically linked).

Each experiment was replicated by 3 obtaining average values for each potassium fraction. Potassium concentration was analysed in the resulting filtrates by atomic absorption spectroscopy.

b) Cation exchange capacity (CEC)

The cation exchange capacity (CEC) of a substance, substrate or soil is the number of exchangeable cations per dry weight that can be hold and available for exchange (Robertson *et al*., 1999).

To determine the CEC of cross-linked potassium acrylate it was used a modified method based on the acetate ammonium method by Rhodes (1982). This method was developed to obtain the total CEC on soils. It basically consists in the saturation of the sample with sodium cations using sodium acetate, washing the excess of sodium with ethanol and finally extracting the sodium cations by saturation with ammonium acetate. The concentration of extracted sodium was determined by atomic absorption spectrometry (AAS). Due to the swelling properties of the polymer the method was partially adapted for measuring CEC on superabsorbent polymers.

Step 1 - Saturation with sodium

It was weighed 100 mg samples of product into falcon tubes. Then it was added 33 ml of sodium acetate 1 N solution. Tubes were shaken for 30 minutes at 180 rpm and then centrifuged at 2800 rpm during 10 minutes. After centrifugation the supernatant solution was thrown away from each falcon and the addition of new ammonium acetate 1N is repeated. In total the process was done 3 times.

Step 2 – Washing of excess of sodium

To wash the excess of sodium it was used a solution of ethanol at 50% concentration following the same process as in step 1: 33 ml was added of solution to the samples within the falcon tubes, then shaking and centrifugation.

Step 3 – Extraction of the exchanged sodium

Last step was the extraction of the exchanged sodium using ammonium acetate 1N solution. The process was exactly as in previous steps with the exception that the supernatant solutions were reserved in volumetric flasks of 100ml to be analysed. After the last centrifugation and addition of the supernatant solution all the volumetric flasks were levelled up to 100 ml.

Step 4 – Analysis of extracted sodium and calculation of the CEC

The solutions containing the exchanged sodium were analysed by atomic absorption spectroscopy (AAS). Once the concentration of sodium was determined, CEC was calculated using the following formula:

$$CEC = ([Na] \cdot V \cdot 100) / (Peq_{(Na)} \cdot M) \qquad \text{(Formula 2.5)}$$

CEC = Cation exchange capacity, expressed in meq/100g.
[Na] = Concentration, expressed in mg/l, of sodium determined by AAS
V = Volume, expressed in L, of the solution where the Na concentration was measured.
$Peq_{(Na)}$ = Equivalent weight of sodium, expressed in eq/g.
M = Mass, expressed in grams, of the soil/product sample.

c) Exchange kinetics.

The aim of this experiment was to describe the cation exchange kinetics of cross-linked potassium polyacrylate using a monovalent (sodium, Na^+) and divalent (calcium, Ca^{2+}) cation. To evaluate the concentration effect on kinetics and being sure that all potassium is exchanged it was added 1.5 meq of each cation in different salt forms diluted in different volumes. In this way the product was immerse into different volumes of solution with different concentrations. Chlorides salts of the correspondent cation were used as source of sodium and calcium (Annex I, table AI.8). To prepare the solutions it was exactly weighed the mass of salts equal to 1.5 meq of cation in 400 ml beakers containing 100, 200 and 300 ml of distilled water. Therefore the concentrations of used solution were 15, 7.5 and 5 meq/l.

100 mg of Luquasorb®1280RM was added to the beaker containing the solutions. 1 ml aliquot of solutions before adding the product were considered time cero (T_0). Aliquots of 1 ml were taken from each beaker at 5, 10, 30 seconds, 1, 5, 10, 30 and 60 minutes. Potassium release was considered as the indicator of cation exchange. The

concentration of released K was analysed in the samples by atomic absorption spectroscopy (AAS). The velocity of cation-exchange was calculated by the following formula:

$$V_{ce} = \left[([K] \cdot v \cdot 100) / (Peq_{(Na)} \cdot M)\right] : t_i \qquad \text{(Formula 2.6)}$$

V_{ce} = Concentration, expressed in mg/l, of sodium determined by AAS
V = Volume, expressed in L, of the solution where the K concentration was measured.
$Peq_{(Na)}$ = Equivalent weight of potassium, expressed in eq/g.
M = Mass, expressed in grams, of the product sample.
t_i = Time, expressed in seconds.

d) Cationic affinity (selectivity).

In order to better understand the cross-linked potassium polyacrylate cation exchange profile it was evaluated the affinity or selectivity of the polymer for one or another cation. The process to characterise the cation affinity was divided into 2 steps.

Step 1 – Exchange of preferred cations by the polymer

It was exactly weighed 100 mg of RS, RM and RL in 400 ml beakers. Then 100 ml of previously prepared salt solution was added. The solution contained salts of Na^+ as monovalent, Ca^{2+}, Zn^{2+}, Cu^{2+}, Mg^{2+} and Mn^{2+} as divalent and Fe^{3+} as trivalent. The concentration referred to each cation in the solution was 0.5 meq/L. The selected salts are listed in the Annex I, table AI.9. After the addition of the solution to the polymer the system was shaken for 30 minutes at 180 rpm. Afterwards the gel was filtered and washed with a solution of ethanol in water at a concentration of 50% to remove supernatant solution containing not chemically linked cations.

Step 2 – Extraction of the exchanged cations from the polymer

In the second step of the experiment the exchanged cations were extracted from the gel obtained in the first step. The extraction was done by saturating the product using a solution of ammonium acetate 1 N. The extraction operation was done by adding 100 ml to the gel; shaking 30 minutes at 180 rpm and filtration. The operation was repeated 3 times to ensure the complete extraction of cations. The obtained filtrates were collected for analysing. The different cations were analysed by atomic absorption spectroscopy (AAS) for quantification of the cation selectivity of cross-linked potassium polyacrylate.

e) Potassium and exchanged cation release curves.

With the purpose of better understanding cross-linked potassium acrylate cation exchange dynamics it was studied the releasing potassium and other exchanged cations by the product. The study consisted of 2 different but linked experiment.

Experiment 1 – Potassium release curves

To obtain the potassium the release curves it was weighed approximately 100 mg of product in 50 ml plastic bottles (Figure 3.7). Afterwards 50 ml of salt solutions were added. The concentrations referred to the cations of the prepared solutions were 0, 2.5, 5, 10, 20, 40, 80 and 160 meq/L. The selected salts were chlorides, nitrates and sulphates of monovalent, divalent and trivalent cations (Annex I, Table AI.9).

Figure 2.12 – Plastic bottles used in the potassium release curves experiment containing in this case $CuSO_4$ solutions.

Bottles were closed and shaken for 30 minutes at 180 rpm. After this time the resulting gel-solution systems were filtered. Product residues after filtration were stored for the next experiment. In the other hand the exchanged potassium contained in the filtrates was analysed by atomic absorption spectroscopy (AAS). The experiment was replicated by 3 obtaining average values for each analysis.

Experiment 2 – Exchanged cation release curves

The gel samples obtained after filtration in the previous experiment were washed with 50 ml of ethanol solution in a concentration of 50%. This step was repeated 3 times to remove any supernatant cations not chemically linked to the polymer structure. Afterwards it was followed a similar process to the first experiment but adding an extractor solutions 50 ml of ammonium acetate at different concentrations to the gel samples. The concentrations referred to NH^{4+} of the extractor solutions were 0, 2.5, 5, 10, 20, 40, 80 and 160 meq/L. Closed bottles were shaken for 30 minutes at 180 rpm and then filtered. The obtained filtrates were analysed AAS. The experiment was replicated by 3 obtaining average values for each analysis.

2.2.2.4. Experiments to evaluate effects on soil properties

A set of experiments were carried out with the purpose of evaluating the effect of adding cross-linked potassium polyacrylate on soil properties of agronomical interest like pH, electric conductivity, water losses by evaporation, water retention curves and texture.

a) Determination and effects on soil pH

The pH is an indicator of the hydronium ion concentration (H_3O^+). It is considered of importance in characterization of agricultural substrates or soils due to its direct relation with the availability of mineral nutrients for plants (Navarro-Blaya and Navarro-García, 2003). The pH of the polymer and the effects on pH resulting of the addition of 0.2% and 0.4% w/w of cross-linked potassium polyacrylate to a sandy, loamy and clay soils were determined at 25ºC using an electrode Crison-5021T connected to a pH-meter Crison BASIC 20+ (Crison Instruments S.A., Spain). The pH was measured in dispersions of distilled water and calcium chloride 0.01M to correct the possible high content of salts.

pH of cross-linked potassium polyacrylate.

In hygiene industry pH of superabsorbent polymers is measure in a sodium chloride 0.9% solution of 5g/l of polymer. This value has an interest if we are talking about fluid in contact with the polymer which reaches that high salt concentration. For agricultural purposes the pH of the product itself once the gel is formed has more interest as roots will grow in or around spots of the hydrogel. This gel containing water could have certain effects on pH influencing nutrient absorption.

In the case of KPA alone pH was measured submerging the electrode in a saturated solution of product. For the preparation of the gel 100 mg of polymer were weighed into a 100 ml beaker. Water was added up to reaching maximum swelling capacity but leaving 1 – 3 mm of supernatant on the top. Same procedure was followed using $CaCl_2$ solution. Then the electrode was submerged and pH value was recorded when stable. The experiment was replicated by 3 obtaining average values for the gel.

pH of soils and soil-gel systems

It was measure the pH of 3 soils: sandy (Utrera), loamy (Coronil) and clay (Maribañez) and the effect of adding KPA. The pH was measured in dispersions made with distilled water and calcium chloride 0.01M in a relation of 1:5. To prepare the samples, soils were air dried and sieved by 2 mm. 10 g of soil were weighed into a 100 ml beaker. Then 50 ml of water or calcium chloride were added. Before submerging the electrode for measuring pH the soil-solution dispersion were slightly shaking during 30 minutes. Same procedure was done on soil samples mixing hydrogel at 0.2 and 0.4% w/w. The experiment was replicated by 3 obtaining average values for each soil and soil-gel systems.

b) Determination and effects on soil electric conductivity (salinity)

Electric conductivity (EC) is a property of a material that quantifies the ability to conduct an electric current. This property is proportional to the content of soluble salts in a solution. In agronomy electric conductivity is used as an indicator of salinity of substrates and soils. A soil is considered salty when it has an excess of soluble salts affecting the normal development of plants.

The EC of the product and the effects on EC resulting of the addition of 0.2% and 0.4% w/w of cross-linked potassium polyacrylate to a sandy, loamy and clay soils were determined at 25°C using a conductivity cell Crison +Pt-1000 connected to an EC-meter Crison CM35 (Crison Instruments S.A., Spain). The used EC-meter reads electric conductivity as well as salinity and temperature.

Electric conductivity of cross-linked potassium polyacrylate

Same procedure as for measuring pH of cross-linked potassium polyacrylate was followed (Section 2.2.2.4-a). 100 mg of KPA were brought to its maximum swelling capacity by adding water and leaving a 1 – 3 mm supernatant on the top. Electrode was submerged in the saturated solution recording EC and salt content values when stable. The experiment was replicated by 3 obtaining average values for the gel.

Electric conductivity of soils and soil-gel systems

It was measured the electric conductivity on 3 natural soils: sandy (Utrera), loamy (Coronil) and clay (Maribañez). To measure soil conductivity it was weighed 10 grams of soil previously air dried and 2 mm sieved in 100 ml beakers. It was added 25 ml of distilled water and stirred for 30 minutes. Then 2 different EC values were measured: saturated value (measuring EC of the dispersion) and filtrated value (measuring EC of the supernant solution after 24 hours). Same procedure was done on soil samples mixing hydrogel at 0.2 and 0.4% w/w. The experiment was replicated by 3 obtaining average values for each soil and soil-gel systems.

c) Water losses by evaporation (drying isotherms)

This experiment pretended to quantify the water losses by evaporation of a sandy (Utrera), loamy (Coronil) and clay (Maribañez) soils and the effect of adding cross-linked potassium polyacrylate in a proportion of 0.2 and 0.4 % w/w. The correspondent soil samples and amended samples with KPA were saturated with water for 24 hours to ensure field capacity and maximum polymer absorption capacity. After his period, a sub-sample of 50 grams was weighed in ceramic crucibles of known mass. These crucibles containing the samples were dried under controlled room temperature (25°C). The losses of water by evaporation were quantified by weighing of the sample every 24 hours during 22 days. The experiment was replicated by 3 obtaining average values for each soil and amended soil sample. Results were plotted in drying isotherms (Figure 2.7) representing the remaining water content versus time at a fixed temperature of 25 °C.

d) Texture

The analysis of texture of a sandy, loamy and clay soils and the effect on texture resulting of amending the soils with cross-linked potassium polyacrylate at 0.2% and 0.4% w/w was carried out by the Bouyoucos method (Bouyoucos, 1936). This method is based on the time that particles of sand, silt a clay need to fall down from an aqueous suspension. To proceed with the analysis 40 grams of previously dried and sieved below 2 mm soil samples were transferred to plastic bottles of 0.5 L. The soil sample was then mixed with 100 ml of sodium polyphosphate (5% w/v) and 200 ml of distilled water. Plastic bottles were then closed and shaken vigorously for 30 minutes. Afterward the content from the bottles was transferred to 1 L graduated cylinders and brought to 1000 mL with distilled water. The resulting dispersion was stirring up and down 10 times with special bar and immediately a hydrometer and thermometer were placed in the cylinder. The temperature and reading of the hydrometer were recorded at 40 seconds after stopping stirring and 2 hours later. Same readings of temperature and density are done for a control without soil sample. Each experiment was replicated by 3.

Figure 2.13 – Set of materials used for the measurement of soil texture by the Bouyoucos hydrometer method.

The readings of density recorded from the hydrometer were corrected based on the temperature by the following formula:

$$Y_{corrected} = Y_i + (T_i \text{ x } 0{,}36 - 7{,}01) \qquad \text{(Formula 2.7)}$$

$Y_{corrected}$ = corrected density, expressed in g/l.
Y_i = density, expressed in g/l, of the hydrometer reading at a specific time.
T_i = temperature, expressed in Celsius grades, at a specific time.

The percentage of sand, silt and clay of the soil or amended soil samples were calculated by the following formulas:

$$\%Clay = (Y_{2h} – B_{2h} / M) \text{ x } 100 \qquad \text{(Formula 2.8)}$$

$$\%Silt = (Y_{40s} – B_{40s} / M) \text{ x } 100 - \%Clay \qquad \text{(Formula 2.9)}$$

$$\%Sand = 100 – (\%Clay + \%Silt) \qquad \text{(Formula 2.10)}$$

M = mass, expressed in grams, of the dry soil.
Y_{2h} = density, expressed in g/l, of the hydrometer reading after 2 hours.
B_{2h} = density, expressed in g/l, of the control after 2 hours.
Y_{40s} = density, expressed in g/l, of the hydrometer reading after 40 seconds.
B_{40s} = density, expressed in g/l, of the control after 40 seconds.

e) Water retention curves (pF)

The water retention curve of a soil describes the relation between the water content in the soil and the retaining strength of it. This curves are helpful to understand the water capacity retention of a soil but also how much of the retained water is plant available. These curves can be plotted as the water content versus pressure (Figure 2.14). Field capacity is considered to be the water content at a pressure of 0.33 bar (pF 2.5) while the wilting point is considered as the water content at a pressure of 15 bat (pF 4.2). The difference between both pressure points is considered as the plant available water.

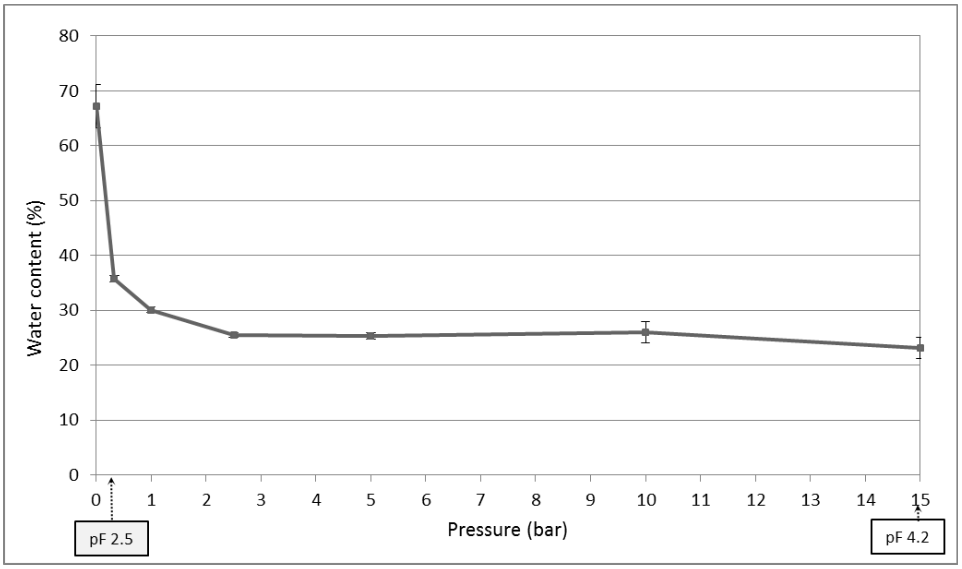


Figure 2.14 – Example of water retention curve of a soil obtained using Richards plates and pressure chamber.

The water retention curves for a sandy (Utrera), loamy (Coronil) and clay (Maribañez) soils and the effect on the curves when amend with cross-linked potassium polyacrylate at 0.2% w/w were determined with Richards plates and pressure chamber (Figure 2.15; Richards and Ogata, 1961). The selected pressure points for determining the water content of the samples were 0, 0.33, 1, 2.5, 5, 10 and 15 bar. The experiment was replicated by 6 obtaining average values for each soil and amended soil sample at each pressure point.

Previously dried and sieved below 2mm soil samples were transferred to plastic retaining rings on the top a Richard´s plate and brought to water saturation during 24 hours. Then the corresponding plate was placed in to the Richard´s chamber where the required pressure was applied until reaching the equilibrium. This is known when no more water flows out of an indicator plastic tube in the front of the chamber.

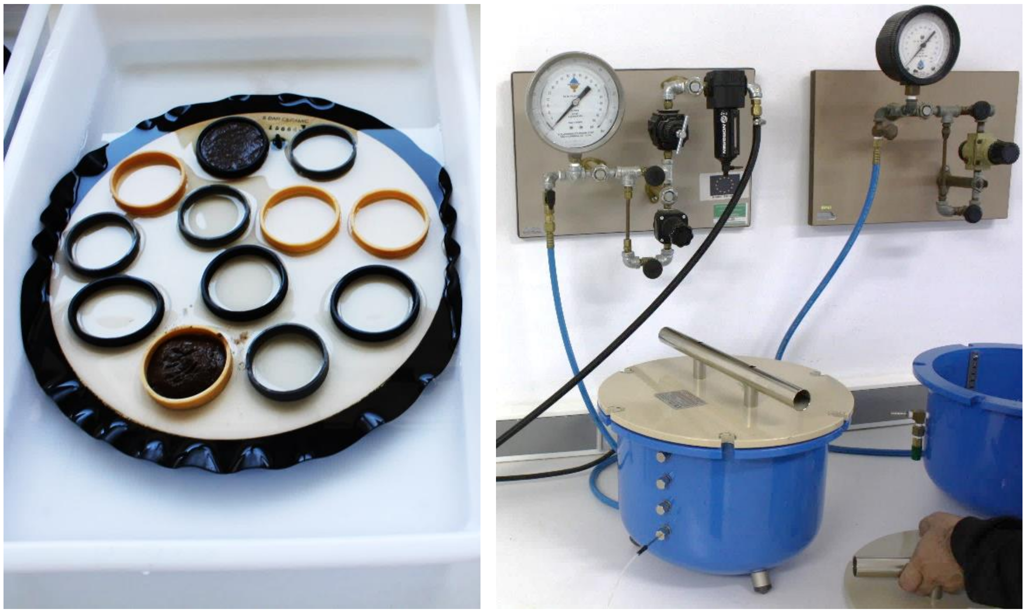


Figure 2.15 – Porous plate with plastic rings for soil samples (left) used within the Richards pressure chamber (right) for the determination of water retention curves (Richards and Ogata, 1961).

Once this is finished soil and amended soil samples were weighed (W_1). Afterwards samples were dried for 24 hours recording the weight after this period of time (W_2). The soil water content at a certain pressure was calculated by the following formula:

$$W_{cont} = [\ (W_1 - W_2) / W_2\ ] \times 100 \qquad \text{(Formula 2.11)}$$

W_{cont} = water content, expressed in %, of soil sample at certain pressure.
W_1 = mass, expressed in grams, of the wet soil sample.
W_2 = mass, expressed in grams, of the dried soil sample.

2.2.3. Data analysis and statistics

All data, parameters and experimental results from this chapter were statistically treated by an analysis of variance (ANOVA) first and then by multiple comparison Tukey´s HSD (Honestly-significant-difference) test with a confidence coefficient of 95% ($p \leq 0.05$). Error bars in all figures represent standard deviation (SD).

2.3. RESULTS AND DISCUSSION

2.3.1. Swelling properties of cross-linked potassium polyacrylate.

2.3.1.1. Free swelling capacity, velocity of absorption and hygroscopicity.

Results of the free swelling capacity quantification by both; filtration and oven method (section 2.2.2.1-a) for three different granulometries of Luquasorb®1280R (section 2.2.1.1), are shown in the Table 2.3.

Table 2.3 – Results and statistical analysis of free swelling capacity (FSC) of cross-linked potassium polyacrylate.

Method	Luquasorb®1280RS		Luquasorb®1280RM		Luquasorb®1280RL	
	FSC (g/g)	SD	FSC (g/g)	SD	FSC (g/g)	SD
Filtration method	270.87 bA	9.65	285.99 bA	0.92	281.75 bA	12.83
Oven method	315.19 aB	9.80	338.92 aA	8.05	331.86 aA	5.49

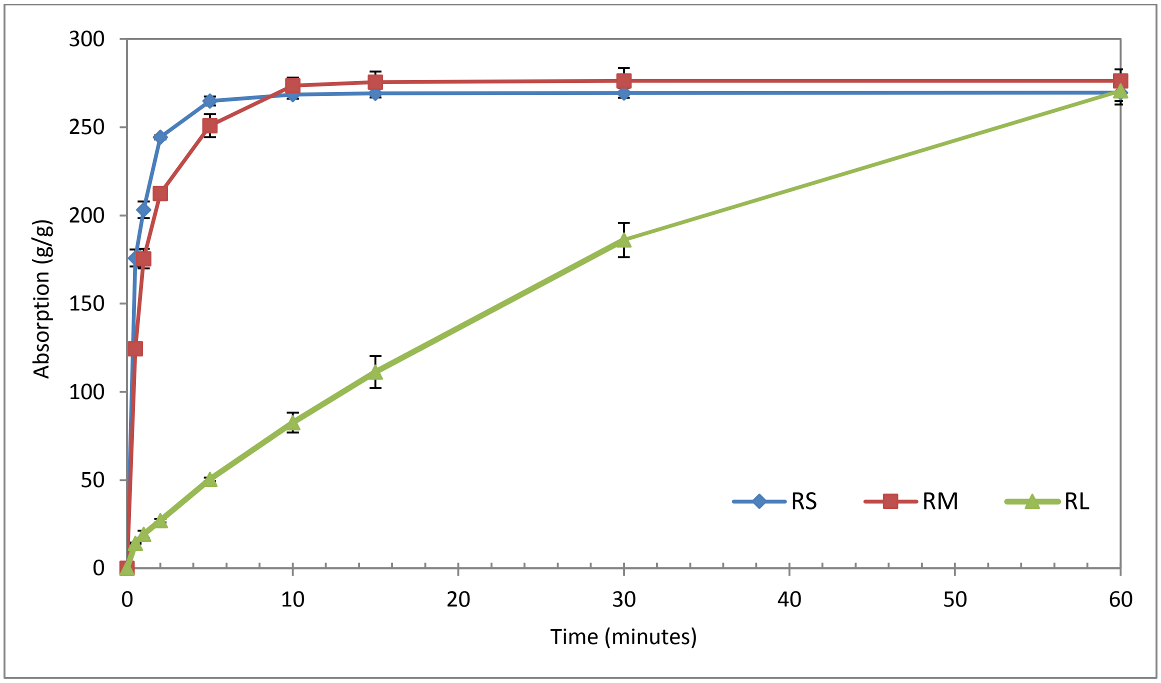
*Different letters indicate significant differences at $P \leq 0.05$ within columns (small letters) and within rows (capital letters) by Tukey´s HSD test. *FSC: Free swell capacity expressed in grams of absorbed water per gram of product. *SD: standard deviation value.

According to Buchholz and Graham (1998) the swelling capacity of SAPs is influenced by the type and degree of cross-linker, the gradient of concentration inside and outside the polymer and presence functional groups. In this case only the granule size distribution was different between RS, RM and RL granulometries so differences were not expected. However the ®1280RS resulted in not significant but lower FSC measured by filtration method and significantly than the other two sizes when measured with the oven method.

Significant differences between both methods were observed obtaining higher values of FSC with the oven method for all the granulometries. Methods resulted in high correlation with a coefficient of 0.9998. The lineal adjustment was very good with $R^2 = 0.9996$ following the equation “$y=1.5613x – 107.77$” being “y” the FSC obtained by the oven method and “x” the FSC obtained by the filtrate method (Annex II. Figure AII.4). Higher values on the oven method might be explained by possible losses of gel and/or soluble extractable polymers after each of the single filtrations (section 2.2.2.1-a).

With regards to the speed of absorption under free swelling conditions it was observed a big differentiation between the three granulometries being faster the RS followed by the RM and far away by the RL (Figure 2.16).

Figure 2.16 – Representation and comparison of the time needed by the three granulometries of Luquasorb®1280R to reach their maximum swelling capacity on distilled water.



*Error bars represent standard deviation. *RS: smallest granule size. *RM: medium granule size. *RL: bigger granule size.

Table 2.4 – Results and statistical analysis on absorbed water per gram of cross-linked potassium polyacrylate after certain period of time under free swelling conditions (FSC).

Time (minutes)	Luquasorb®1280RS		Luquasorb®1280RM		Luquasorb®1280RL	
	Absorption (g/g)	SD	Absorption (g/g)	SD	Absorption (g/g)	SD
0.5	175.85 dA	4.85	124.51 eB	3.33	14.27 fC	0.40
1	203.16 cA	4.73	175.51 dB	5.48	19.27 fC	2.05
2	244.27 bA	1.21	212.43 cB	2.57	27.08 fC	0.97
5	264.84 aA	2.52	250.96 bB	6.52	50.48 eC	0.98
10	268.44 aA	2.29	273.50 aA	4.54	82.63 dB	5.62
15	269.28 aA	2.45	275.51 aA	5.97	111.25 cB	9.15
30	269.44 aA	2.78	276.24 aA	7.31	186.08 bB	9.64
60	269.55 aA	4.78	276.28 aA	6.49	270.66 aA	7.84

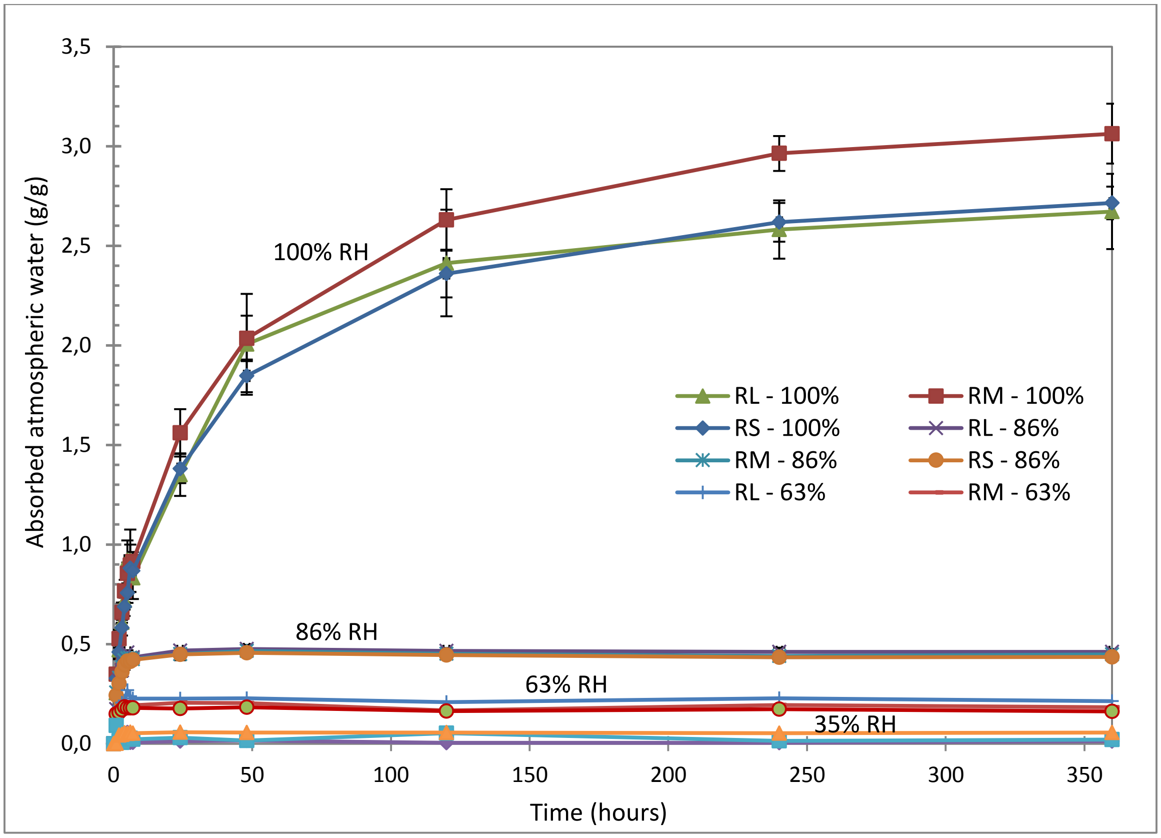
*Different letters indicate significant differences at $P \leq 0.05$ within columns (small letters) and within rows (capital letters) by Tukey´s HSD test. *SD: standard deviation value.

The smallest g (®1280RS) reached its maximum swelling capacity after 5 minutes of absorption while the medium one (®1280RM) did it after 10 minutes and the biggest (®1280RL) after 60 minutes (Table 2.4).

The significant differences on water absorption speed can be explained by differences on surface area of the particle sizes. In alignment to Das and Pourdeyhimi (2014) and the results from Casquilho *et al*. (2013), smaller granules have more surface area than bigger ones per volumetric unit of polymer and therefore more contact area with water and faster absorption of aqueous solutions.

2.3.1.2. Hygroscopicity.

Figure 2.17 – Representation of the absorbed atmospheric water by different samples of Luquasorb®1280R during 15 days under different relative humidity (%) conditions.



*Error bars represent standard deviation. *RS = smallest granule size, RM = medium granule size, RL = largest granule size. * RH = relative humidity expressed in %.

A summary of the results is represented in Figure 2.17. Under 35% relative humidity none of the granulometries showed a significant atmospheric water absorption. In the case of 63% relative humidity the absorbed atmospheric water was significantly increased for Luquasorb RS, RM and RL until reaching the equilibrium at about 0.17, 0.18 and 0.21 g/g after 3, 1 and 4 hours of exposition respectively. Similar results were obtained at 86% relative humidity were the equilibrium was reached at about 0.41, 0.43 and 0.46 g/g after 6 hours of exposition for RS, RM and RL respectively. Under 100% relative humidity conditions the granulometries showed significant absorption of atmospheric water which continued increasing until reach 2.71, 3.06 and 2.67 g/g for RS, RM and RL respectively after 360 hours (15 days) of exposition. Detailed results and statistical analysis are shown in Annex II (Tables AII.1-4).

Cross-linked potassium polyacrylate showed significant hygroscopicity when relative humidity was equal or higher to 63%. The atmospheric water absorption responded to the absorption mechanism of SAPs (Chapter 1.1.3.). In this way the higher was the concentration of atmospheric water the higher was the absorbed water.

2.3.1.3. Drying speed under conditions of constant temperature.

The obtained drying isotherms at 25, 40, 80 and 105 °C up to 25 hours of the three studied granulometries of Luquasorb®1280R are shown in Figures 2.18, 2.19 and 2.20. The drying behaviour of RS, RM and RL resulted similar. The remaining water content was stable at 25 °C after 25 hours and decreased faster as higher was the temperature. The drying isotherms at 40 °C showed two different drying phases; a fast drying phase (up to 8 hours) and a slow drying phase (until completely dry). Bakass *et al*. (2000) explained these two phases for a fixed temperature as a reduction on the drying speed derived of an increase in vapour pressure within the system. The obtained slopes of linear adjustment (Annex II, Figures AII.1-3) at 40 °C (fast drying phase), 80 °C and 105 °C are shown in the table 2.5.

Table 2.5 – Slopes of the linear adjustment for the drying isotherms of RS, RM and RL at 40, 80 and 105 °C.

Temperature	Luquasorb®1280RS	Luquasorb®1280RM	Luquasorb®1280RL
	Slope (linear adjust.)	Slope (linear adjust.)	Slope (linear adjust.)
40 °C	-10.828	-11.046	-11.552
80 °C	-31.992	-33.034	-33.583
105 °C	-50.106	-48.780	-48.758

Polymers were completely dry after 2 hours at 105 °C, after 4 hours at 80 °C and after 24 hours at 40°C. No statistically significant differences were found between the three cross-linked potassium polyacrylate granulometries.

Figure 2.18 – Drying isotherms for Luquasorb®1280RS at 25, 40, 80 and 105 °C.

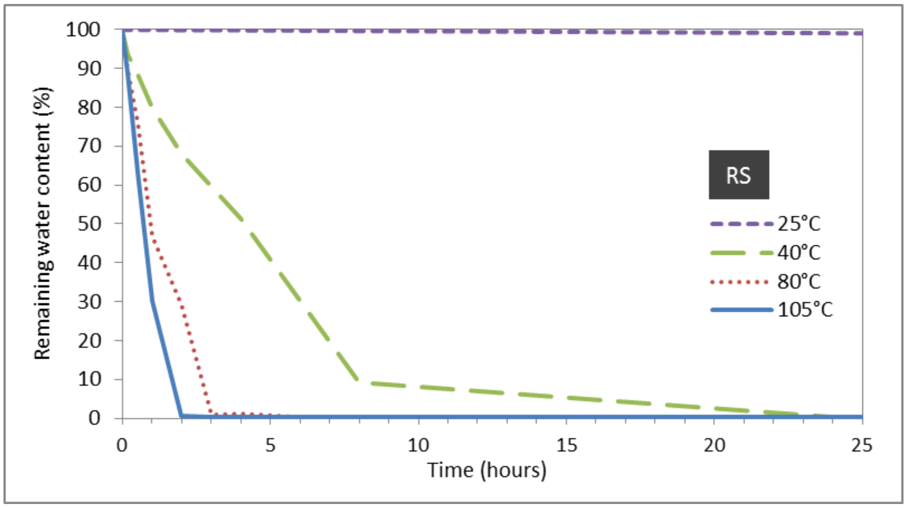


Figure 2.19 – Drying isotherms for Luquasorb®1280RM at 25, 40, 80 and 105 °C.

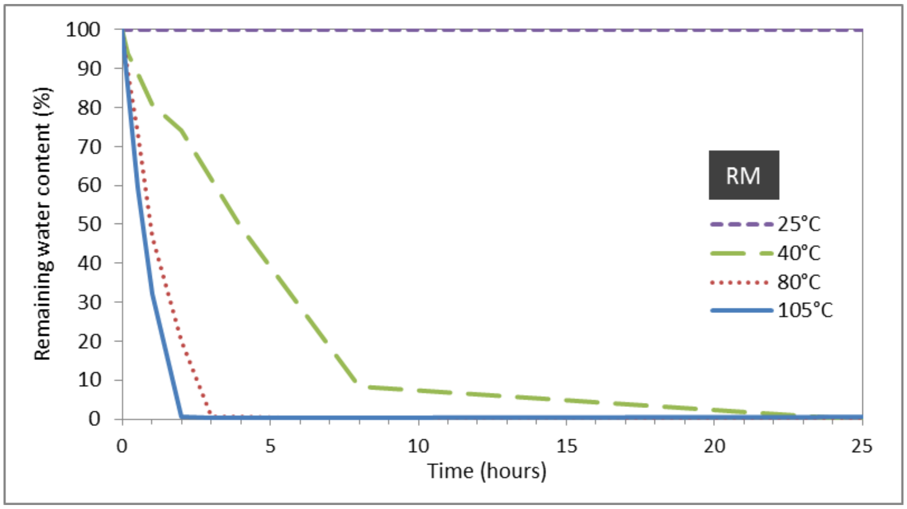
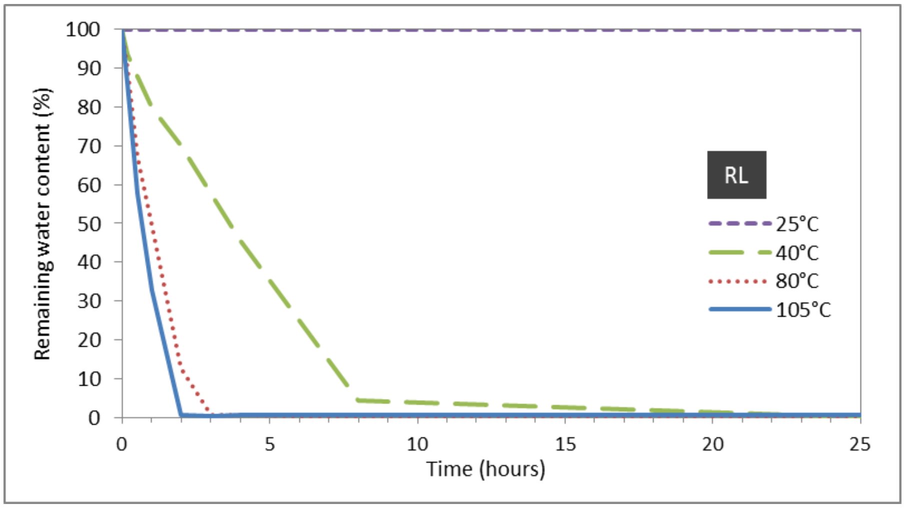
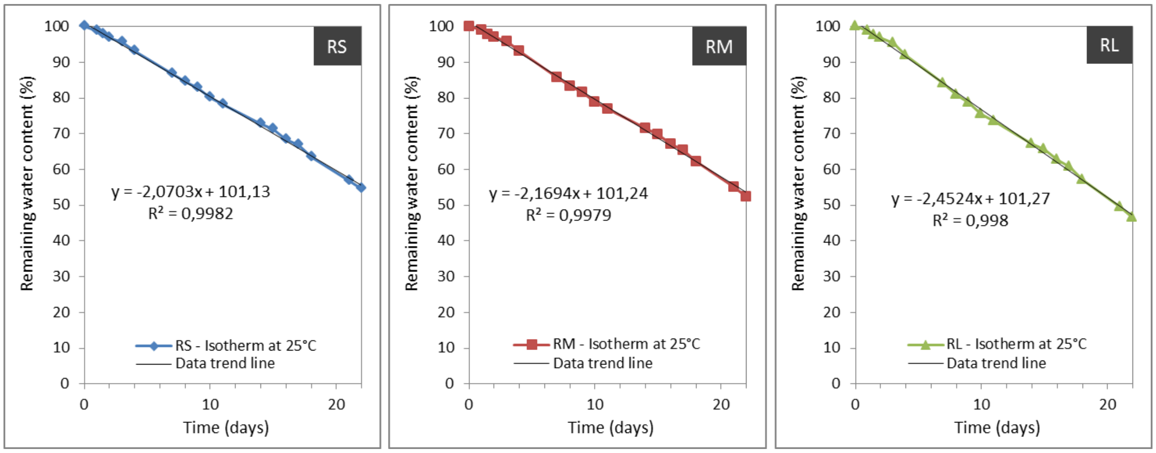


Figure 2.20 – Drying isotherms for Luquasorb®1280RL at 25, 40, 80 and 105 °C.



The obtained drying isotherms for RS, RM and RL at 25 °C during 22 days are shown in Figure 2.21. The drying behavior of the three granulometries was similar resulting in good adjustment to linear trendlines.

Figure 2.21 – Drying isotherms for the three granulometries (RS, RM and RL) of Luquasorb®1280R at 25ºC.



*RS: smallest granule size. *RM: medium granule size. *RL: biggest granule size.

The drying speed of RS was slightly slower than RM and then followed by RL with slope values of -2.07, -2.17 and -2.45 respectively for the trend lines of the remaining water content versus time. The complete drying time of RS, RM and RL at 25 °C degrees was estimated as 48.8, 46.7 and 41.3 days respectively, assuming a single phase drying process following the linear adjustment. In alignment to the conclusions of Bakass *et al*. (2000) these results showed a clear influence of the temperature on the drying speed of the polymer.

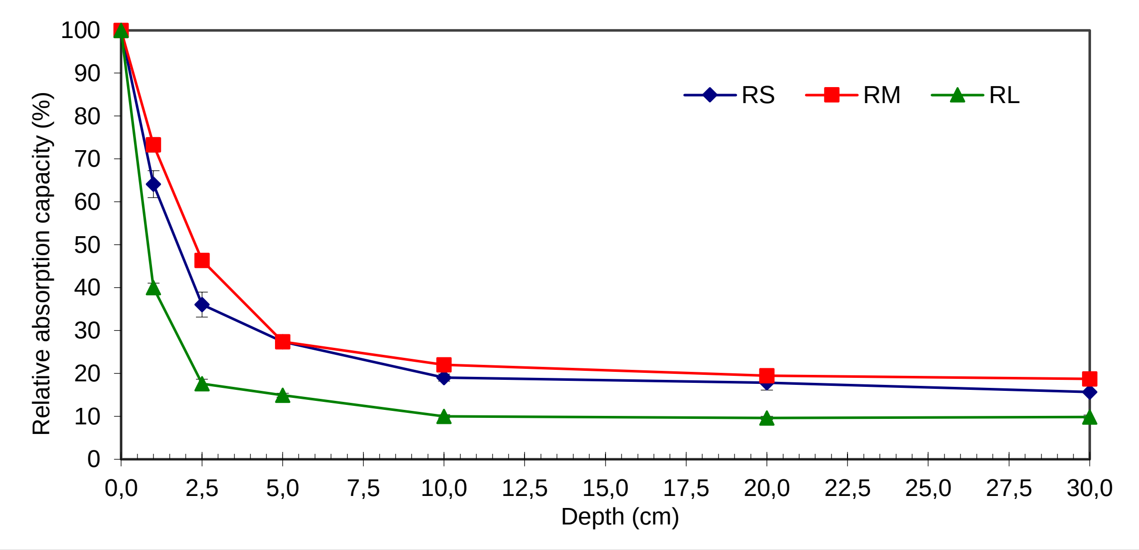
The slight differences on drying speed (RS < RM < RL) contradicting the expected order due to the surface area of the particles, might be the consequence of two effects: in one hand, the internal pressure is higher as bigger are the gel particles, so while water evaporates from the surface of the particles the diffusion of water from the core of the gel to the outside is expected to be faster (Wack and Ulbricht, 2007). In the other hand, a lower concentration of surface cross-linkers on bigger particles due to the last production process step might facilitate the evaporation of water in comparison to smaller particles.

2.3.2. Swelling limiting factors.

2.3.2.1. Effect of pressure on the swelling capacity.

The swelling capacity of the three tested granulometries of Luquasorb®1280R resulted significantly reduced when samples were submitted to an increasing depth and therefore increasing pressure (Figure 2.22).

Figure 2.22 – Absorption per gram of product (g/g) under increasing depth within a silica sand soil column.



*Error bars represent standard deviation. *RS: smallest granule size. * RM: medium granule size. *RL: bigger granule size.

Table 2.6 – Results and statistical analysis on the relative swelling capacity at different depth.

Depth	Pressure/weight of wet soil (kg)	Luquasorb®1280RS		Luquasorb®1280RM		Luquasorb®1280RL	
		Relative Abs. Cap. (%)	SD	Relative Abs. Cap. (%)	SD	Relative Abs. Cap. (%)	SD
0 cm	0	100.00aB	1.41	100.00aA	0.32	100.00aA	1.43
1 cm	0.035	64.11bB	3.14	73.31bA	1.69	40.03bC	1.01
2.5 cm	0.085	36.04cB	2.94	46.35cA	0.41	17.63cC	1.00
5 cm	0.175	27.36dA	0.91	27.411dA	1.50	14.89dB	0.44
10 cm	0.350	19.03eB	0.81	22.00eA	0.53	9.97eC	0.39
20 cm	0.700	17.80eA	1.66	19.48fA	0.85	9.62eB	0.39
30 cm	1.050	15.691eB	0.19	18.74fA	0.77	9.82eC	0.46

*Different letters indicate significant differences at $P \leq 0.05$ within each column (small letters) and within each row (capital letters) by Tukey´s HSD test. *Relative Abs. Cap.: Absorption capacity in relative values. *SD: standard deviation value.

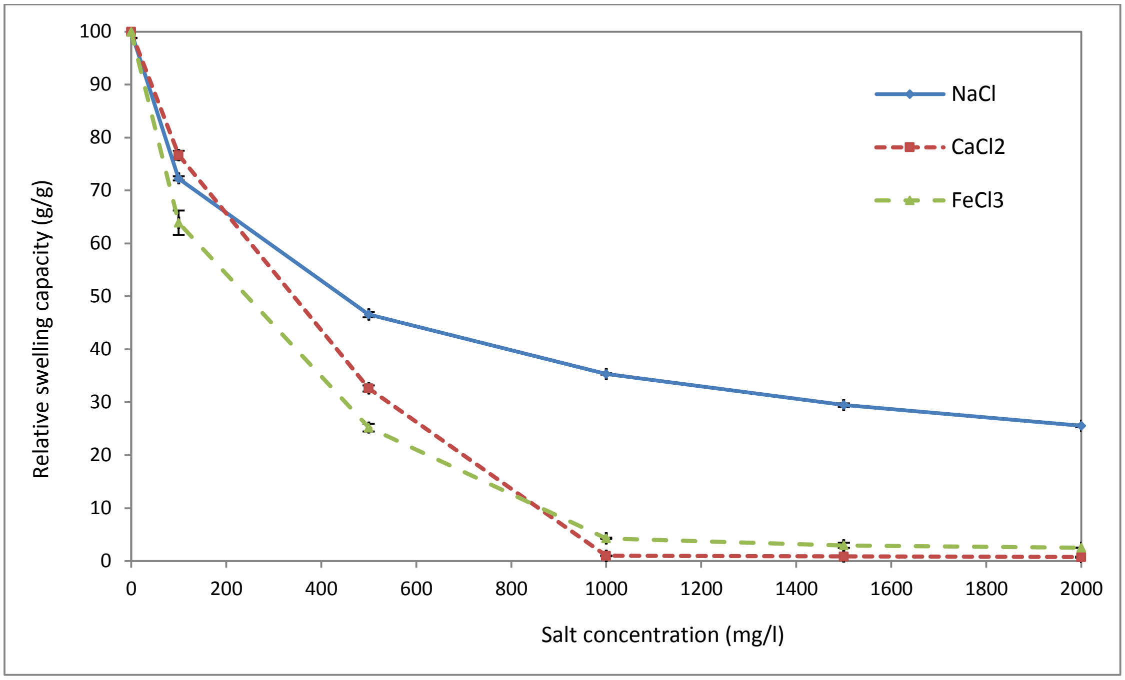
The reduction on the swelling ability of cross-linked potassium polyacrylate under applied pressure could be explain as a restriction of the polymer chains to diffuse in the opposite direction to the water movement. The expansion ability of the polymer accommodating the volume of additional molecules explained by Bo *et al*. (2012) resulted significantly different between the three tested granulometries at different depth being the largest granules (RL) the more affected.

RS, RM and RL reached a minimum swelling capacity at approximately 10 cm depth (0.350 kg of pressure) with values of 19.03, 22.00 and 9.97 respectively where the absorption capacity was not affected anymore by the applied pressure. As the specific gravity of the three granules is the same (Annex I, Table AI.1) the significant differences on the minimum swelling capacity could be only explain by the different ability of the polymers to expand accommodating water molecules within the used system. Therefore porosity of the utilized substrate might have an influence on the obtained results.

2.3.2.2. Effect of salt concentration on the swelling capacity.

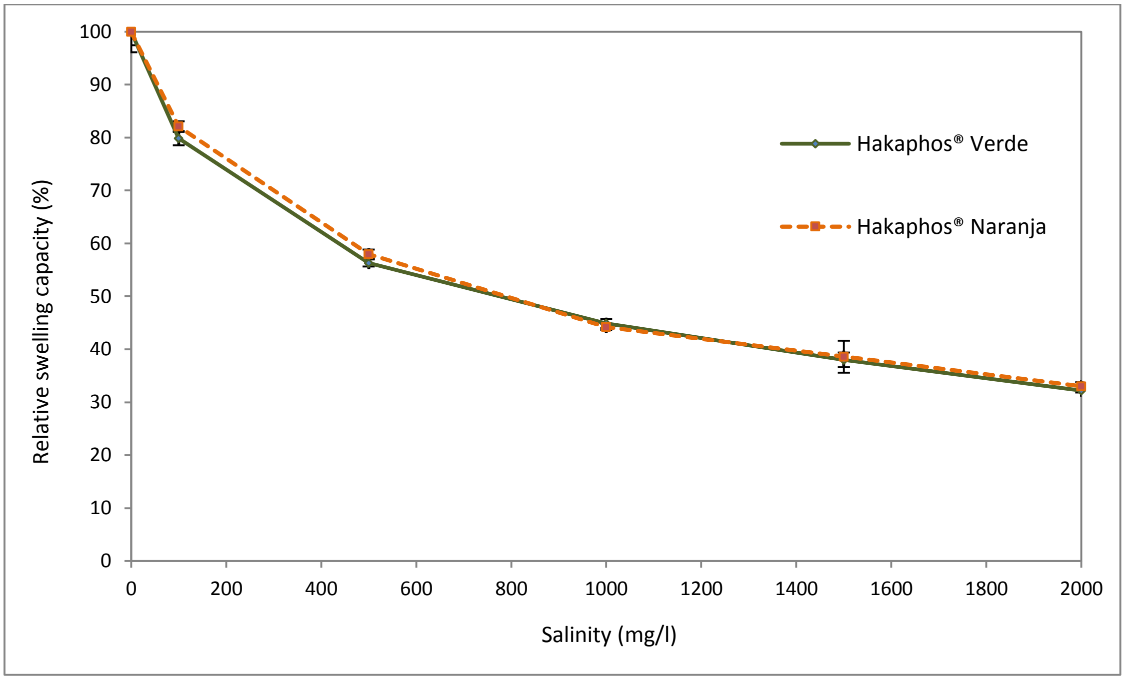
The results of quantifying the effect of an increasing concentration of chloride salts and two commercial soluble fertilizers to the relative absorption capacity of Luquasorb®1280RM are represented in Figure 2.23 and Figure 2.24.

Figure 2.23 – Relative free swelling capacity (%) of Luquasorb®1280RM under different concentrations of monovalent (NaCl), divalent ($CaCl_2$) and trivalent ($FeCl_3$) salts.



*Error bars represent standard deviation.

Figure 2.24 – Relative free swelling capacity (%) of Luquasorb®1280RM under different concentrations of two commercial NPK soluble fertilizers.

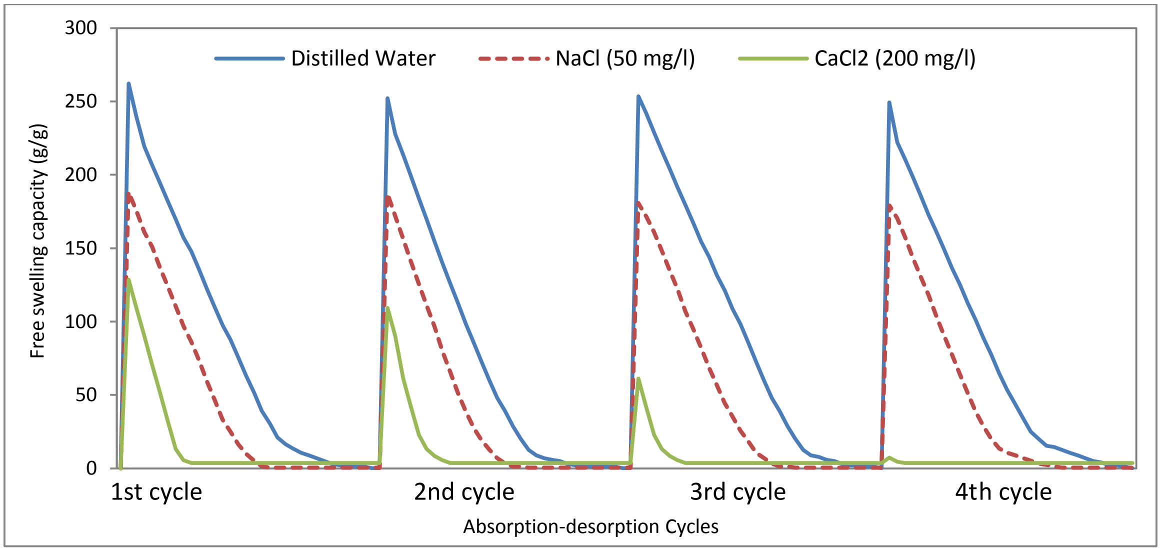


*Error bars represent standard deviation.

As expected from the results of Kazanskii and Dubrovskii (1992) and Bo *et al*. (2012), the swelling capacity of RM was significantly reduce by the presence of dissolved salts (Annex II, table AII.6). The effect on reducing absorption ability was stronger as higher was the concentration of salt. Furthermore it was more pronounced in the case of the multivalent salts ($CaCl_2$ and $FeCl_3$) than with the monovalent (NaCl). The significant differences caused by the addition of different salts can be explained by two effects described by Bowman *et al*. (1990) and Chatzoudis and Rigas (1999): by differences on the solution ionic strength being $FeCl_3 > CaCl_2 > NaCl$ (Annex II, figure AII.5) and by the collapse of the SAP structure by the presence of multivalent cations.

The effect of both commercial soluble fertilizers on the swelling ability was less pronounced but similar to NaCl. No significant differences were found between both fertilizers despite the concentration of certain cations were different in the case of ammonium nitrogen, potassium and magnesium (Annex I, table AI.8). Bowman *et al*. (1990) described that anions has less influence than cations on the swelling capacity of SAPs. Despite the total concentration of nutrients is higher in Hakaphos®Verde, the concentration of cationic elements in Hakaphos®Naranja is higher. In this way both effects might compensate resulting in no differences.

Figure 2.25 – Representation of absorption-desorption cycles of Luquasorb®1280RM using distilled water and two saline solutions at half of the concentration recommended by the FAO for irrigation water.



The results of absorption-desorption cycles using distilled water, NaCl and $CaCl_2$ solutions are shown in Figure 2.25. After four cycles the absorption capacity of RM was maintained in the case of distilled water. In the case of NaCl the absorption capacity was lower than in distilled water but as well stable. In the case of $CaCl_2$ the FSC of the polymer was lower after each absorption-desorption cycle. These results are in alignment to those by Chatzouids and Rigas (1999) showing that multivalent cations like Ca^{2+} can chemically interact with the polymer net performing as crosslinkers. After each cycle Ca^{2+} collapsed the SAP structure inhibiting the expansion of the polymer chains and therefore reducing the swelling capacity (Figure 2.25).

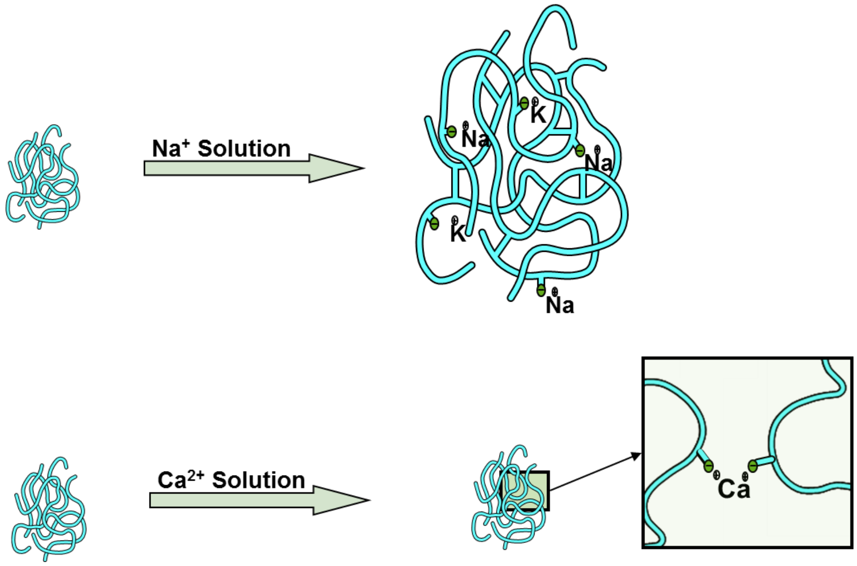


Figure 2.26 – Schematic representation of the effects on the basic structure of a SAP when swelling in the presence of a monovalent and divalent cations. Ca^{2+} acts as a crosslinker inhibiting the swelling properties of the polymer net.

2.3.2.3. Effect of thermal stress on the swelling capacity.

Results on the measurement of the free swelling capacity of Luquasorb®1280R after submitting the samples to 8 thermal stress cycles resulted in not significant differences (Table 2.7). The FSC of all the granulometries resulted stable along the different cycles with average values of 259.24, 272.61 and 266.95 for RS, RM and RL respectively.

Table 2.7 – Results and statistical analysis on the effect on the free swelling capacity of Luquasorb®1280R after thermal stress cycles of low (-20°C) and high temperatures (105°C).

Cycle	Luquasorb®1280RS		Luquasorb®1280RM		Luquasorb®1280RL	
	FSC (g/g)	SD	FSC (g/g)	SD	FSC (g/g)	SD
0	257.31a	3.34	277.64a	7.33	261.22a	5.54
1	256.24a	2.76	273.89a	6.80	267.49a	2.90
2	261.56a	1.28	282.98a	2.01	272.78a	11.74
3	253.61a	9.64	258.87a	13.68	260.31a	5.68
4	253.39a	5.70	280.13a	8.56	258.85a	5.08
5	276.25a	8.46	282.43a	14.63	264.41a	13.93
6	262.73a	21.86	257.52a	5.85	261.29a	8.82
7	253.97a	17.23	268.78a	14.85	279.74a	2.63
8	258.14a	19.82	271.30a	17.68	276.44a	9.46

*Different letters indicate significant differences at $P \leq 0.05$ within each column by Tukey´s HSD test. *FSC: free swelling capacity expressed in grams of absorbed water per gram of dry product. *SD: standard deviation value.

Complementing the findings of Bai *et al*. (2013), where no significant differences in repeated water absorbency were found varying temperatures at more realistic field condition (50, 25 and -4°C), these results confirm that cross-linked potassium polyacrylate SAPs maintain excellent absorption capacity even after repeated absorption-desorption cycle under more extreme temperature.

2.3.3. Cationic exchange profile of cross-linked potassium polyacrylate.

2.3.3.1. <u>Soluble and chemically linked potassium.</u>

Results on the quantification of soluble and chemically linked potassium (section 2.2.2.3.-a, Experiments 1 and 2) are shown in the Table 2.8. The soluble fraction was significantly higher in RS and RM than in RL. However the determined chemically linked potassium fraction was significantly higher in RL than in RM and RS. Both fractions resulted in high correlation with a coefficient of -0.9991. The lineal adjustment had an $R^2 = 0.9991$ following the equation “$y=-3.8594x + 538.37$” being “y” the chemically linked potassium fraction and “x” the soluble potassium fraction (Annex II, Figure AII.6). The sum of the soluble and chemically linked fractions resulted in significant higher content of potassium in RL than RM and RS.

Table 2.8 – Results and statistical analysis on the water soluble and the chemically linked potassium fractions.

Potassium (K)	Luquasorb®1280RS		Luquasorb®1280RM		Luquasorb®1280RL	
	K (mg/g)	SD	K (mg/g)	SD	K (mg/g)	SD
Soluble	57.16a	2.16	51.39a	2.29	34.91b	9.71
Chemically linked (from swollen SAP)	318.88b	7.06	338.91b	4.62	404.02a	12.73

*Different letters indicate significant differences at $P \leq 0.05$ within each row by Tukey´s HSD test. *K(mg/g): potassium content expressed in mg of potassium per gram of cross-linked potassium polyacrylate. *SD: standard deviation value.

Table 2.9 – Results and statistical analysis on the total potassium content extracted from dry SAP.

Potassium (K)	Luquasorb®1280RS		Luquasorb®1280RM		Luquasorb®1280RL	
	K (mg/g)	SD	K (mg/g)	SD	K (mg/g)	SD
Total (from swollen SAP)	376.05aB	8.49	389.91aB	6.90	438.93aA	13.32
Total (from dry SAP)	257.05bA	5.02	249.85bA	5.90	261.39bA	4.38

*Different letters indicate significant differences at $P \leq 0.05$ within each column (small letters) and within each row (capital letters) by Tukey´s HSD test. *K(mg/g): potassium content expressed in mg of potassium per gram of cross-linked potassium polyacrylate. *SD: standard deviation value.

The surface cross-linking step in production results in a higher concentration of surface cross-linkers as smaller are the particles (higher surface area). The higher concentration of cross-linkers in the surface avoids the complete expansion of the external polymer chains causing a barrier effect. This might explain the significantly higher amounts of extracted potassium from swollen RL due to an easier entrance of ammonium ions within the gel to be exchanged by potassium. In the other hand when the total content of potassium was directly extracted from dry polymer (Section 2.2.2.3.-a, Experiment 3) no differences between granulometries were found (Table 2.9). Bowman *et al*. (1990) described the reduction of the swelling capacity in the presence of ammonium ion. Therefore extraction with concentrated ammonium acetate reduced the swelling capacity of the polymer and therefore the mobility of cations entering and going out of the net keeping potassium ions within the structure. It is important to remark that the results of potassium content extracted in the case swollen SAP were higher than the theoretically maximum content expected based on the chemical formula (354 mg/g). The over-content of potassium might be explained by a combination of the analytical error plus possible residual KOH out of the production.

2.3.3.2. Cation exchange capacity (CEC) and its kinetics.

The obtained results on the cation exchange capacity (CEC) for Luquasorb®1280R are shown in the Table 2.10. CEC resulted significantly higher in the case of RL in comparison to RM and RL samples. This might be explained by a lower concentration of surface cross-linkers as bigger are the particles which will then allowed an easier mobility of cations between the exterior and the interior of the gel particles.

Table 2.10 – Results and statistical analysis on the cation exchange capacity (CEC) of Luquasorb®1280R.

CEC	Luquasorb®1280RS		Luquasorb®1280RM		Luquasorb®1280RL	
	Average	SD	Average	SD	Average	SD
Meq/100g	794.77b	1.40	797.95b	5.42	858.00a	6.96

*Different letters indicate significant differences at $P \leq 0.05$ within each row by Tukey´s HSD test. *CEC: Cation exchange capacity expressed in cation milliequivalents per 100 grams of product (meq/100g). *SD: standard deviation value.

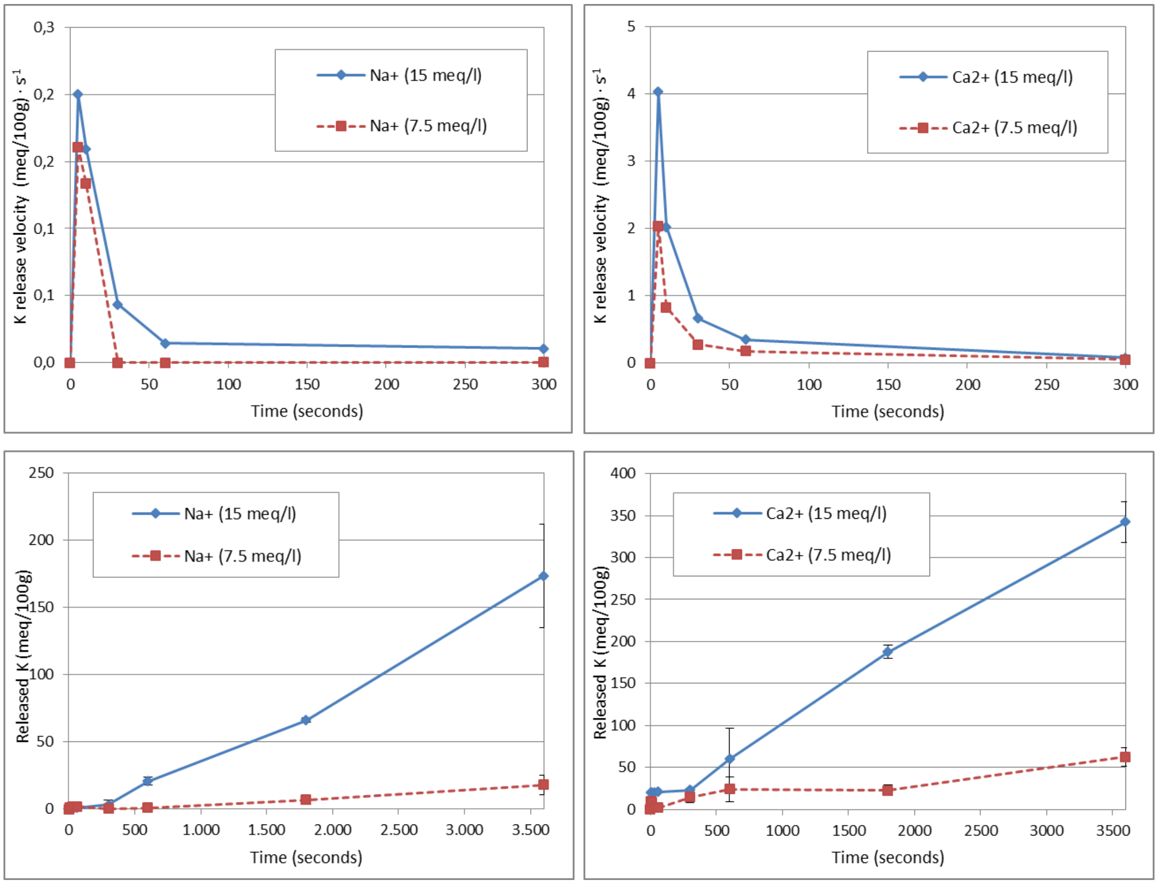
Based on the known values of CEC given by Rowell (1993) for soils and materials related to agronomy (Table 2.11) it can be considered that Luquasorb®1280R have a high cation exchange capacity widely overpassing the typical CEC values for organic matter.

Table 2.11 – Values of CEC for different soils and materials (Rowell, 1993).

Material	CEC (meq/100g)	Material	CEC (meq/100g)
Fine sand	0.8	Kaolin	3 – 15
Sand	1 – 4	Hydro mica	10 – 40
Loamy sand	2 – 12	Montmorillonite	29 – 150
Sandy loam	7 – 16	Vermiculite	100 – 150
Clay	4 – 60	Organic matter	130 – 500

With regards kinetics the velocity of exchange followed similar pattern for sodium and calcium (Figure 2.27). However it was significantly higher in the case of calcium reaching 4.03 (meq/100g)·s^{-1} after 5 seconds in comparison to exchange with sodium which reached the 0.19 (meq/100g)·s^{-1} after 5 seconds, both at the higher concentration. As well the cumulative exchanged potassium was significantly higher in the case of calcium (342.21 meq/100g) than sodium (173.57 meq/100g) after 1 hour at the higher concentration.

Figure 2.27 – Representation of the velocity and the cumulative number of milliequivalents of released potassium along the time by cationic exchange with sodium and calcium at different concentrations.



*Error bars represent standard deviation. *K released velocity: milliequivalents of released potassium per 100 grams of product and second. *K released concentration: milliequivalents of potassium released per 100 grams of product.

Both, the velocity of exchange and the cumulative release of potassium, were influenced by the concentration and the ionic strength of the exchanged cation. The higher was the concentration and ionic strength of the ion (Ca^{2+} > Na^{+}) the faster was the exchange and therefore the more potassium was released. The effect of the divalent cation (Ca^{2+}) on speed and exchange of potassium was much higher than the effect by the monovalent cation (Na^{+}). Detailed results and statistical analysis are shown in Annex II (Table AII.7).

2.3.3.3. Selectivity of exchangeable cations and their release curves

The obtained results on the exchanged-cation affinity for the three Luquasorb®1280R granulometries are shown in the Table 2.12. The three granulometries showed a similar affinity for the tested ions with slight numerical differences.

Table 2.12– Results and statistical analysis on the remaining exchanged cations for evaluating the selectivity of Luquasorb®1280R granulometries for some cations.

Cycle	Luquasorb®1280RS		Luquasorb®1280RM		Luquasorb®1280RL	
	Exchange (%)	SD	Exchange (%)	SD	Exchange (%)	SD
Na	36,31d	4,55	35,78d	1,25	27,26d	3,12
Ca	67,13c	15,55	71,39c	2,97	78,83c	5,83
Cu	75,62bc	0,84	82,29b	0,48	83,65abc	4,80
Mg	87,52ab	3,89	91,82a	0,83	89,33ab	1,50
Mn	92,52a	0,02	91,61a	0,21	90,94a	1,71
Zn	91,86a	0,08	90,64a	0,16	91,83a	1,69
Fe	75,47bc	2,13	83,25b	0,96	80,25bc	7,88

*Different letters indicate significant differences at $P \leq 0.05$ within each column by Tukey´s HSD test. *FSC: free swelling capacity expressed in grams of absorbed water per gram of dry product. *SD: standard deviation value.

Therefore the selectivity for the different granulometries of Luquasorb®1280R can be expressed by decreasing order of affinity as follows;

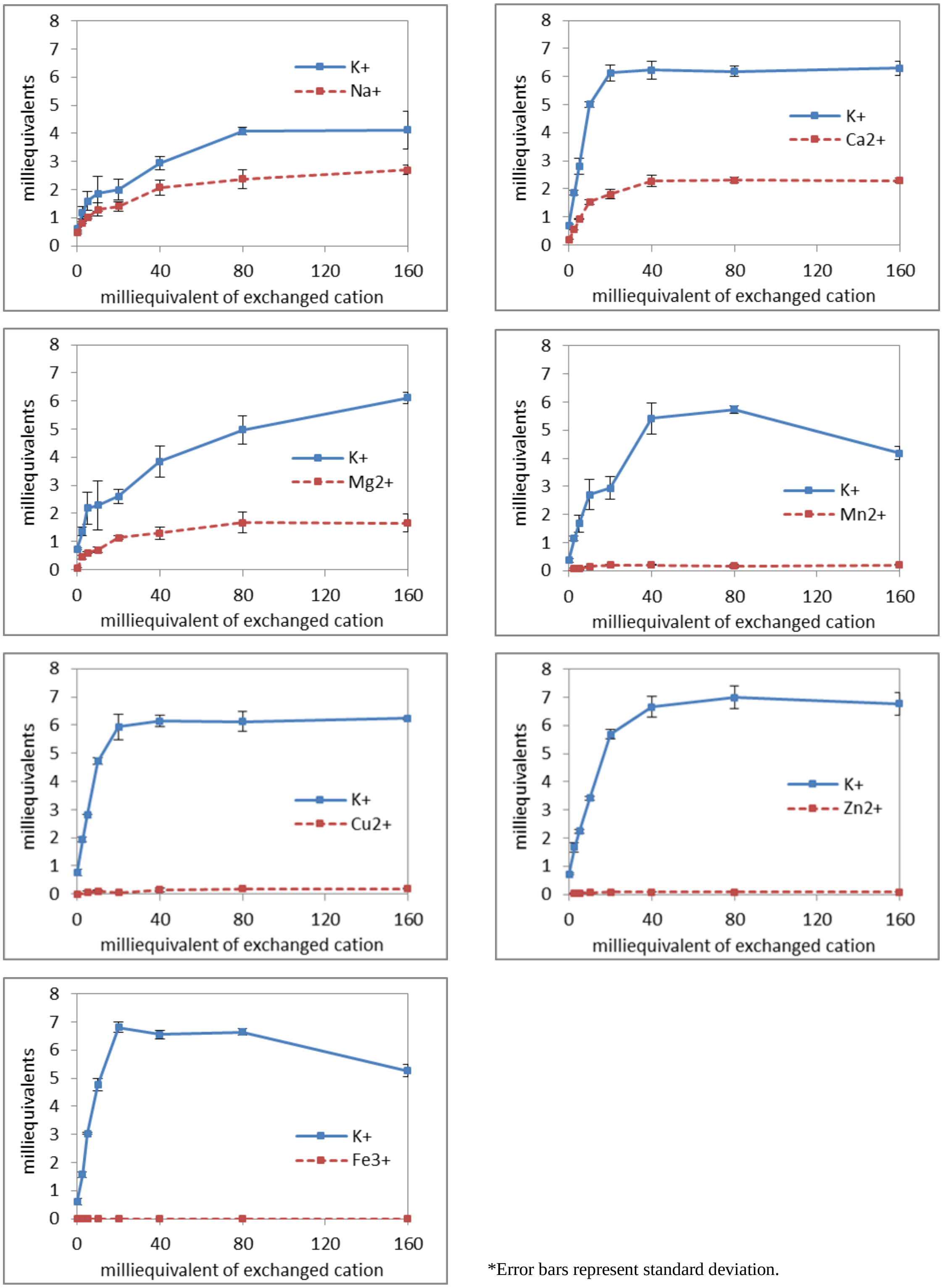
1280RS: $Mn^{2+} = Zn^{2+} \geq Mg^{2+} \geq Cu^{2+} = Fe^{3+} \geq Ca^{2+} > Na^{+}$

1280RM: $Mg^{2+} = Mn^{2+} = Zn^{2+} > Fe^{3+} = Cu^{2+} > Ca^{2+} > Na^{+}$

1280RL: $Zn^{2+} = Mn^{2+} \geq Mg^{2+} = Cu^{2+} \geq Fe^{3+} \geq Ca^{2+} > Na^{+}$

The obtained results contrast with those given by May and Philipp (1983). They reported the ion exchange selectivity for a cross-linked PAA where the resulted decreasing order of affinity was $Fe^{3+} > Cu^{2+} > Zn^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+} > Na^{+}$ at pH 5. However it was concluded the clear influence of pH on the order of cation affinity within the system. Solubility of salts is known to be higher as lower is the pH. This might explain general differences between different hydrogels like cross-linked polyacrylic acid (PAA) and cross-linked potassium polyacrylate (KPA). Furthermore a possible oxidation-reduction reactions of the metals might explain the observed differences, especially in the case of Fe^{3+} which might be reduced to Fe^{2+} behaving like a divalent ion in the solution. If the pH of the salt solution used was not acid enough the Further data on pH of KPA can be found in section 2.3.4.1.

Figure 2.28 – Released potassium curves for Luquasorb®1280RM by cationic exchange and the following release curve of the exchanged cation by ammonium acetate 1N.



*Error bars represent standard deviation.

When the release of potassium content from Luquasorb®1280RM was quantified by using the same cations but as independent salt solutions, the resulting curves (Figure 2.30) showed a higher exchange as higher was charge of the cation (monovalent < divalent < trivalent). The observed reduction on potassium release in the case of Mn^{2+} and Fe^{3+} might be explained by a stronger reduction on the swelling capacity and therefore reducing the mobility of the potassium cation from inside to outside of the gel.

The obtained curves from the release of the exchanged cations using ammonium acetate solution 1N (Figure 2.28) indicate how strong the different cations were bound to the polymer structure being $Fe^{3+} > Zn^{2+} > Cu^{2+} > Mn^{2+} > Mg^{2+} > Ca^{2+} > Na^{+}$. Detailed results and statistical analysis are shown in Annex II (Table AII.8-9).

2.3.4. Effects on soil properties when amended with Luquasorb®1280R.

2.3.4.1. Effect of KPA on pH and electric conductivity.

Values of pH for RS, RM and RL directly measured on saturated gel with distilled water and $CaCl_2$ 0.1M are shown in the table 2.13. Significant differences between both methods were found obtaining lower pH values when using $CaCl_2$ 0.1M as saturating solution.

Table 2.13 – Results and statistical analysis on the pH values for Luquasorb®1280R.

Solution	Luquasorb®1280RS		Luquasorb®1280RM		Luquasorb®1280RL	
	pH value	SD	pH value	SD	pH value	SD
Distilled water	7.02aA	0.04	7.12aA	0.03	7.07aA	0.03
$CaCl_2$ 0.1M	5.36bA	0.08	5.48bA	0.08	5.15bB	0.08

*Different letters indicate significant differences at $P \leq 0.05$ within each column (small letters) and within each row (capital letters) by Tukey´s HSD test. SD: standard deviation.

The cation exchange ability of the polymer might explain this differences as Ca^{2+} cations can be exchanged liberating potassium and protons H^{+} to the supernatant solution and therefore reducing pH. The significantly higher CEC value of RL (Section 2.3.3.2, Table 2.10) fit to the significant lower pH obtained when measured with $CaCl_2$. In the other hand, no significant differences were found between granulometries when using distilled water as suturing solution.

Table 2.14 – Results and statistical analysis on the pH values of three different soils and the effect of applying Luquasorb®1280RM at rates of 0.0, 0.2 and 0.4%.

Concentration	Soil 1		Soil 2		Soil 3	
	pH	SD	pH	SD	pH	SD
0.0% SAP	6.28b	0.07	8.00a	0.01	7.65a	0.02
0.2% SAP	6.36b	0.03	7.71b	0.04	7.51b	0.05
0.4% SAP	6.54a	0.02	7.54c	0.04	7.44c	0.01

Concentration	Soil 1		Soil 2		Soil 3	
	pH ($CaCl_2$)	SD	pH ($CaCl_2$)	SD	pH ($CaCl_2$)	SD
0.0% SAP	5.64a	0.05	7.51a	0,03	7.46a	0,03
0.2% SAP	5.42b	0.01	7.34b	0,07	7.37b	0,01
0.4% SAP	5.34c	0.03	7.07c	0,05	7.28c	0,01

*Different letters indicate significant differences at $P \leq 0.05$ within each column by Tukey´s HSD test. SD: standard deviation value.

The effect of applying increasing concentrations of Luquasorb®1280RM on the pH of the three soils was statistically significant (Table 2.14). When pH was measured using distilled water it was increased for soil 1 and decreased for soils 2 and 3 as higher was the polymer concentration. Higher content on salts (Table 2.16) and calcium carbonate (Annex I, Table AI.4) in soils 2 and 3 might explain a higher release of protons by the polymer to the media. In the case of using $CaCl_2$ as solution the pH was significantly reduced for the three soil as higher was the SAP concentration.

The resulted values of electric conductivity at 25°C and salinity measured in the saturated gel and the filtrate (supernatant) for RS, RM and RL are shown the table 2.15.

Table 2.15 – Results and statistical analysis on EC and salinity values for Luquasorb®1280R.

Media	Luquasorb®1280RS			Luquasorb®1280RM			Luquasorb®1280RL		
	EC 25ºC (µS/cm)	SD	Salinity (mg/l)	EC 25ºC (µS/cm)	SD	Salinity (mg/l)	EC 25ºC (µS/cm)	SD	Salinity (mg/l)
Saturated	149.25aA	13.22	70.20a	119.35aB	5.30	56.15a	47.67aB	6.47	22.31a
Filtrate	104.85bA	4.17	44.80b	88.23bB	6.31	41.43b	53.23aB	1.03	25.07a

*Different letters indicate significant differences at $P \leq 0.05$ within each column (small letters) and within each row (capital letters) by Tukey´s HSD test. *EC: Electric conductivity. *SD: standard deviation value.

Significant differences between measurements of EC and salinity in the saturated gel and the filtrate were found. The chemically linked potassium to the polymer will not dissolve resulting on lower EC and salinity values when measured in the supernatant solution. Furthermore the significant higher EC/salinity for RS > RM > RL fit to the content of soluble potassium (Section 2.3.3.1, Table 2.10).

Table 2.16 – Results and statistical analysis on the electric conductivity (EC) and salinity of three different soils and the effect of applying Luquasorb®1280RM at rates of 0.0, 0.2 and 0.4%.

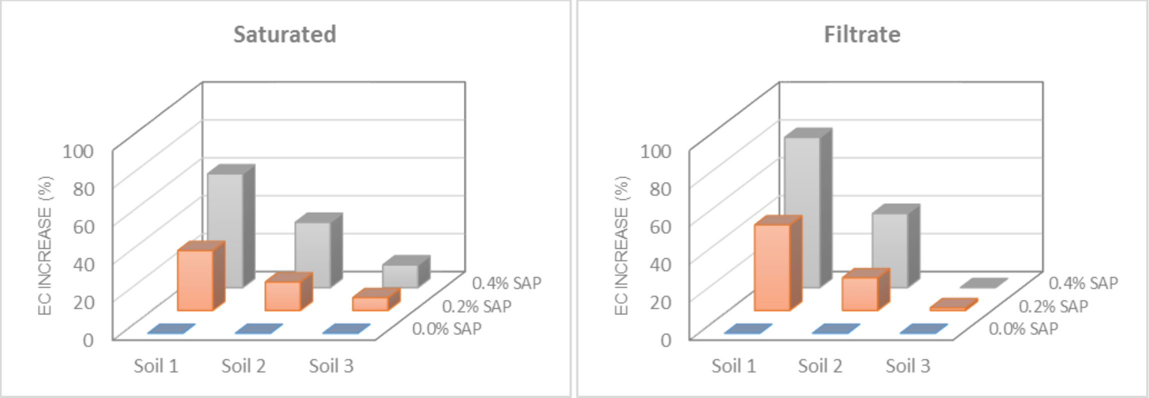
(Saturated)	Soil 1			Soil 2			Soil 3		
Concentration	EC 25ºC (µS/cm)	SD	Salinity (mg/l)	EC 25ºC (µS/cm)	SD	Salinity (mg/l)	EC 25ºC (µS/cm)	SD	Salinity (mg/l)
0.0% SAP	59.60c	0.53	27.90	93.57b	2.35	43.77	758.00c	21.07	367.67
0.2% SAP	79.37b	1.99	37.27	106.90ab	4.59	50.50	810.33b	9.71	393.00
0.4% SAP	96.47a	3.61	45.43	124.90a	12.44	58.73	849.00a	10.82	415.33

(Filtrate)	Soil 1			Soil 2			Soil 3		
Concentration	EC 25ºC (µS/cm)	SD	Salinity (mg/l)	EC 25ºC (µS/cm)	SD	Salinity (mg/l)	EC 25ºC (µS/cm)	SD	Salinity (mg/l)
0.0% SAP	62.43c	1.44	29.27	110.93b	4.47	52.17	808.00a	64.09	394.67
0.2% SAP	90.03b	3.79	42.27	129.47b	1.29	61.00	820.33a	43.43	400.33
0.4% SAP	108.00a	1.95	50.80	153.67a	14.61	72.47	798.67a	34.30	390.67

*Different letters indicate significant differences at $P \leq 0.05$ within each column by Tukey´s HSD test. *EC: Electric conductivity. *Saturated: EC measured in the saturated gel. *Filtrate: EC measured in the filtrate solution. *SD: standard deviation value.

The effect of applying Luquasorb®1280RM at increasing dose rates to soils 1, 2 and 3 was statistically significant when measuring EC in saturated soil solutions (Table 2.16). The higher was the polymer concentration the higher was increased the EC and therefore the salinity of the system. However when EC was measured in the filtrate it was significantly increase in soil 1, only at the higher dose in soil 2 and not significant at all in the case of the soil 3. Navarro-Blaya & Navarro-Garcia (2003) explained how a higher strength of a soil to retain exchangeable cations is related to a higher content of clay. In this way, the effect on the EC measured in the filtrate might be diluted (Figure 2.29) as higher was the EC and salinity of the soil as the result its ability to retain soluble potassium coming from the polymer due to a higher content of clay. Clay content was higher in soil 3 (50%) > soil 2 (29%) > soil 1 (5%), (Annex I, Table AI.4).

Figure 2.29 – Electric conductivity (EC) increase in % by addition of Luquasorb®1280RM to three different soils.



*EC: Electric conductivity. *Saturated: EC measured in the saturated gel. *Filtrate: EC measured in the filtrate solution.

2.3.4.2. Effect of KPA on water losses by evaporation

Obtained drying isotherms at 25°C for soil 1, 2 and 3 are shown in Figure 2.30. The drying kinetics are represented as the remaining water content (%) in the soil along time and relative to the initial water content. First 24 hours showed a fast reduction of humidity content which might be attributed to the supernatant water content that easily evaporates. Therefore a theoretical water retention capacity of soil can be defined as the remaining water content after drying 24 hours (Table 2.17).

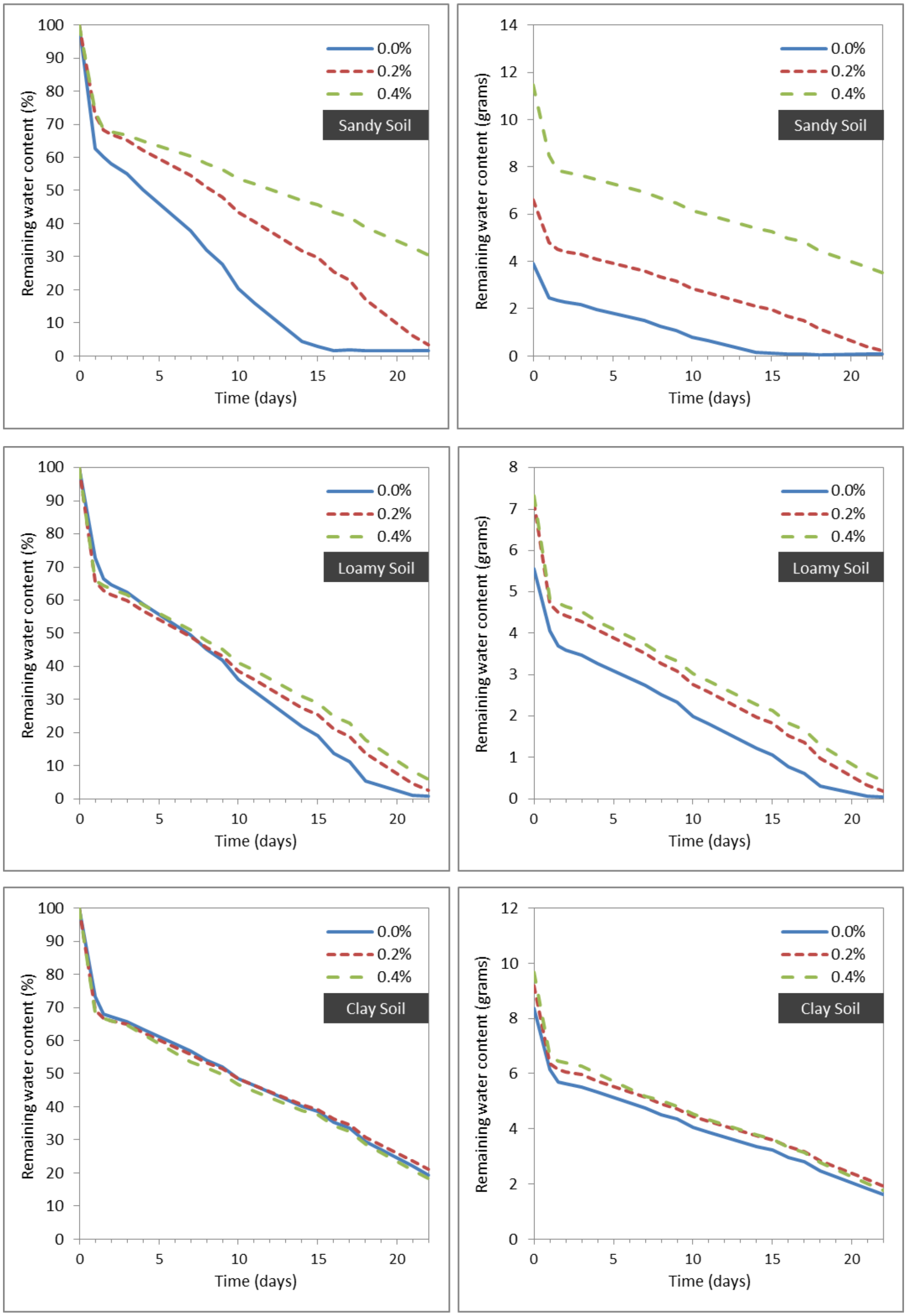
Table 2.17 – Results and statistical analysis on the remaining water content (g) in the system after 24h at 25°C.

SAP Concentration	Soil 1			Soil 2			Soil 3		
	Remaining water (g)	SD	WCI (%)	Remaining water (g)	SD	WCI (%)	Remaining water (g)	SD	WCI (%)
0.0%	2.46c	0.10	-	4.05b	0.28	-	6.14b	0.01	-
0.2%	4.81b	0.05	+95	4.71a	0.22	+16	6.37ab	0.18	+3
0.4%	8.48a	0.28	+244	4.84a	0.06	+19	6.64a	0.17	+8

*Different letters indicate significant differences at P $\leq$ 0.05 within each column by Tukey´s HSD test. SD: standard deviation. WCI: water content increase expressed in % with respect to the control.

The addition of increasing content of Luquasorb®1280RM to soils 1, 2 and 3 resulted in a significant increase of the water retention capacity. The water content increase (WCI) was more pronounce in the sandy soil (1) > loamy soil (2) > clay soil (3) after 24 hours at 25°C increasing exponentially with SAP concentration (Table 2.17).

Figure 2.30 – Drying isotherms at 25°C of three different soil types treated with 0.0, 0.2 and 0.4 % of Luquasorb®1280RM. Water content is expressed in remaining water content within the system in % (left diagrams) and grams (right diagrams).



*Sandy soil: soil 1. *Loamy soil: soil 2. *Clay soil: soil3.

The effect of the polymer on the drying kinetics was estimated by comparison between the slopes of a linear adjustment of the drying isotherms from 24h up to dry state. Resulted equations and the correspondent slopes are shown in Table 2.18. The lower is the value for the slope the faster the sample gets dry.

Table 2.18 – Equation and slopes of the drying isotherms for soil and SAP mixtures at 25°C after linear adjustment.

SAP Concentration	Soil 1		Soil 2		Soil 3	
	Equation	**Slope**	*Equation*	**Slope**	*Equation*	**Slope**
0.0%	$y=-4.32x+66.74$	**-4.3234**	$y=-3.52x+72.71$	**-3.5235**	$Y=-2.36x+72.67$	**-2.3658**
0.2%	$y=-3.17x+75.21$	**-3.1744**	$y=-2.99x+68.84$	**-2.9887**	$Y=-2.33x+70.86$	**-2.3335**
0.4%	$y=-1.88x+72.92$	**-1.8791**	$y=-2.84x+69.91$	**-2.8442**	$Y=-2.20x+71.15$	**-2.2207**

*Slope: value for the slope resulted of the equation after adjusting the drying isotherms to a linear model.

Results showed reduced losses by evaporation (drying) of the soil samples containing the polymer especially in the soil 1 followed by the soil 2 and soil 3. The effect was higher as higher was the concentration of Luquasorb®1280RM and the lower was the water retention capacity of the soil.

In one hand the experimental results showed that Luquasorb®1280RM increases the water holding capacity of especially sandy soils in alignment to the conclusions obtained by Hüttermann *et al*. (1999) who demonstrated the exponential increase of water retention capacity of a soil by the addition of a SAP being 0.2% and 0.4% the preferred concentrations. In the other hand the drying isotherms for mixtures of soil and polymer resulted to be similar to those obtained by Casquilho *et al.* (2013) when using sodium polyacrylate and Bakass *et al*. (2002) who used polyacrylic acid. In both cases it was possible to reduce losses by evaporation and preserving water longer in soils when those were amended with superabsorbent polymers.

2.3.4.3. Effect of KPA on soil texture

Obtained values of sand, silt and clay content expressed in percentage for soils 1, 2 and 3 when amended with increasing concentration of cross-linked potassium polyacrylate (KPA) are shown in the Table 2.19 and represented in a bar-graph in Figure 2.31.

Table 2.19 – Results and statistical analysis on textures values of a sandy, loam and clay soils when amended with concentration of 0.0%, 0.2% and 0.4% of Luquasorb®1280RM.

Soil 1	Sand content		Silt content		Clay content	
	% (w/w)	SD	% (w/w)	SD	% (w/w)	SD
0.0% SAP	86.7a	2.9	6.0a	1.3	7.4a	2.3
0.2% SAP	83.8b	3.3	10.4a	1.9	5.9a	3.2
0.4% SAP	84.6b	2.6	9.2a	3.1	6.3a	3.3

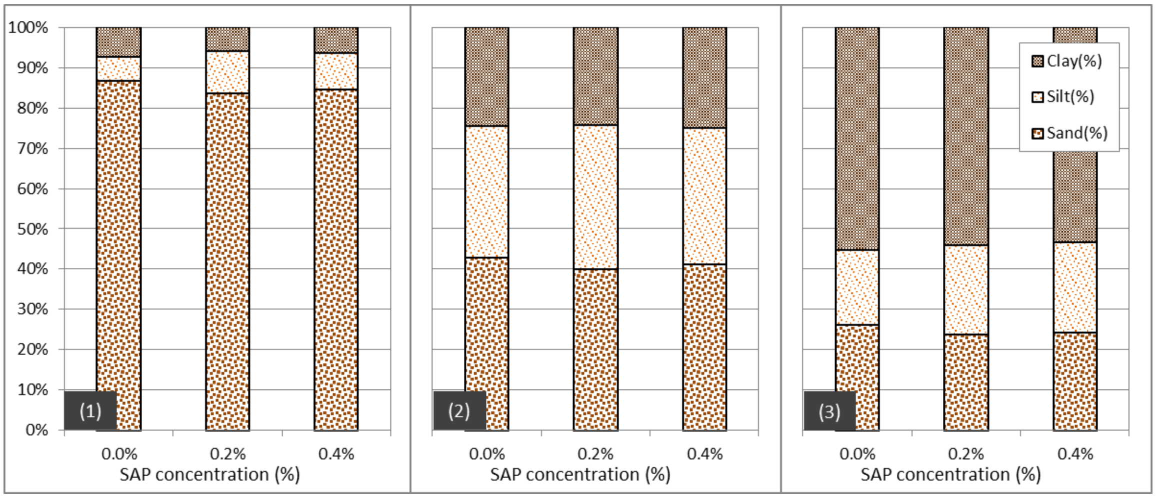
Soil 2	Sand content		Silt content		Clay content	
	% (w/w)	SD	% (w/w)	SD	% (w/w)	SD
0.0% SAP	42.9a	2.6	32.5a	5.5	24.6a	6.9
0.2% SAP	40.0a	3.3	35.9a	3.6	24.2a	5.6
0.4% SAP	41.3a	3.3	33.8a	3.3	25.0a	6.3

Soil 3	Sand content		Silt content		Clay content	
	% (w/w)	SD	% (w/w)	SD	% (w/w)	SD
0.0% SAP	26.1a	2.0	18.6a	1.4	55.2a	2.3
0.2% SAP	23.3a	2.3	22.1a	1.8	54.1a	4.0
0.4% SAP	24.5a	2.1	22.3a	3.3	53.3a	5.1

*Different letters indicate significant differences at $P \leq 0.05$ within each row by Tukey´s HSD test. *SD: standard deviation value.

Results showed a slight trend to increase the content of silt in all three tested soils but it was statistically not significant in any of them. In this way the contents of sand and clay were slightly reduced in all cases being significant only in the case of sand content of soil 1 (sandy soil). However, the addition of SAP should not modified a given proportion of clay, silt or sand of a soil. In this way the observed trends on the results might be the indirect influence of SAP on the density values measured by the Bouyoucos method (1936). Therefore it can be said that Luquasorb®1280RM did not significantly influence soil texture. These results contradict the claims by Abedi-Koupai and Asadkazemi (2006) who referenced that hydrophilic polymers like SAPs potentially influence soil texture.

Figure 2.31 – Representation of the sand, silt and clay content of a sandy (1), loamy (2) and clay (3) soils and the effect on the texture properties when Luquasorb®1280RM is applied at 0.0, 0.2 and 0.4%.



*SAP: superabsorbent polymer.

2.3.4.4. Effect of KPA on soil moisture availability for plants

A summary of the obtained values for field capacity (pF 2.5) and wilting points (pF 4.2) for soils 1, 2 and 3 and their mixtures with Luquasorb®1280RM at 0.05, 0.1 and 0.2% are shown in Table 2.20. Detailed data of all pF points are shown in Annex II, Table AII.10.

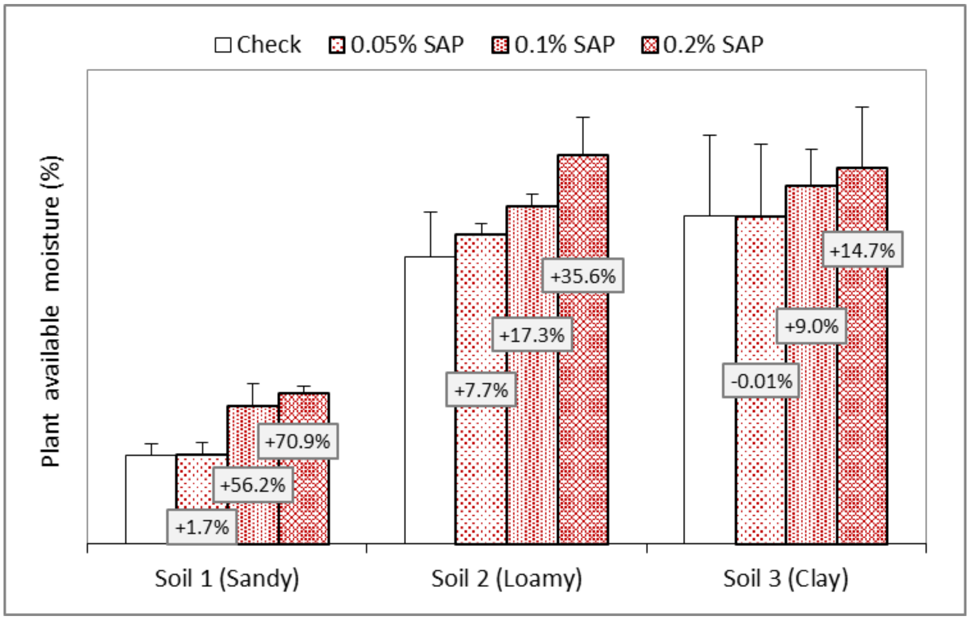
Table 2.20 – Results on field capacity, wilting point and plant available moisture of three soils 1, 2 and 3 and their mixtures with 0.05, 0.1 and 0.2% of Luquasorb®1280RM.

Soil samples	pF 2.5 Moisture (%)	pF 4.2 Moisture (%)	**Plants available moisture (%)**	Plants available water increase (%)
Soil 1 (Sandy)	5.80b	2.81a	**2.99b**	0.00
Soil 1 + 0.05% SAP	6.08b	3.04a	**3.04b**	+1.67
Soil 1 + 0.1% SAP	7.72a	3.25a	**4.67a**	+56.18
Soil 1 + 0.2% SAP	7.54a	2.43a	**5.11a**	+70.90
Soil 2 (Loamy)	19.32c	9.60a	**9.71b**	0.00
Soil 2 + 0.05% SAP	20.96b	10.50a	**10.46b**	+7.72
Soil 2 + 0.1% SAP	22.15ab	10.76a	**11.39ab**	+17.30
Soil 2 + 0.2% SAP	23.15a	10.00a	**13.15a**	+35.57
Soil 3 (Clay)	32.86b	21.78a	**11.08a**	0.00
Soil 3 + 0.05% SAP	33.78ab	22.64a	**11.04a**	-0.01
Soil 3 + 0.1% SAP	36.14a	24.06a	**12.10a**	+9.21
Soil 3 + 0.2% SAP	35.81a	23.10a	**12.71a**	+14.71

*Different letters indicate significant differences at $p \leq 0.05$ within each row by Tukey´s HSD test. *pF 2.5: field capacity. *pF 4.2: wilting point.

Field capacity of all tested soils was positively improved specially in soil 1 (sandy) followed by Soil 2 (loamy) and then by soil 3 (clay). Furthermore the obtained values were exponentially increased with the applied dose-rate being statistically significant in all cases at the higher dose (0.2%). Wilting points of the mixtures of soil and polymer were not significantly different to those of the soils. The calculated plant available moisture (Table 2.20, Figure 2.32) was significantly increase for soil 1 at SAP concentrations of 0.1 and 0.2% mixtures. In the case of soil 2 it was only significant at the highest dose and it was not improved at any dose for soil 3.

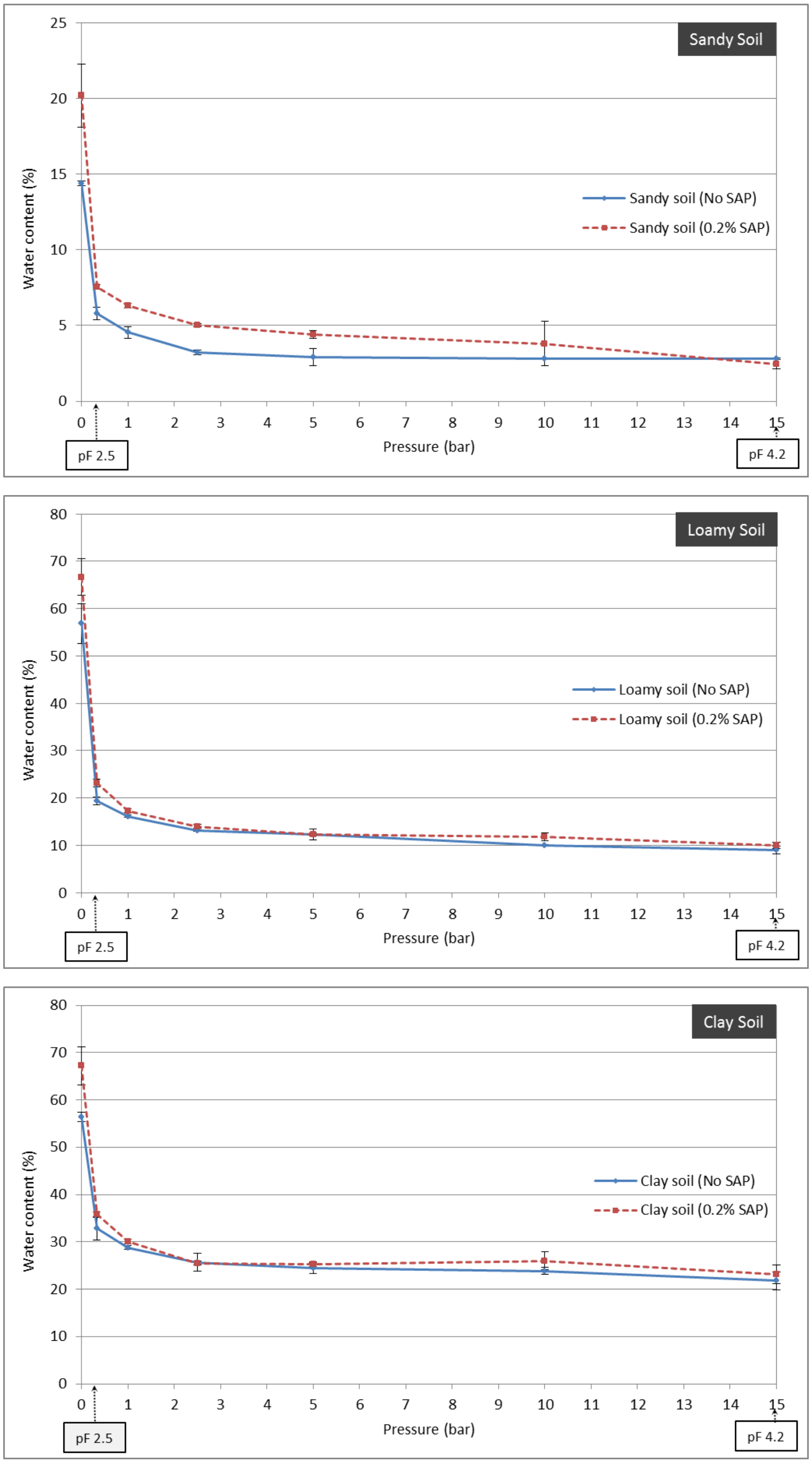
Figure 2.32 – Representation of plant available moisture (%) and the increase (%) when Luquasorb®1280RM is applied to soils 1, 2 and 3 at rates of 0.05, 0.1 and 0.2%.



*Error bars represent standard deviation. *SAP: Luquasorb®1280RM

Based on the experimental results showed in Annex II (Table AII.10) it was plotted the typical water retention curves for the three soils and the mixture of soil and Luquasorb®1280RM at the highest dose rate (Figure 2.33). In one hand it can be observed that the water retention capacity (water content, %) of the soil 3 (clay) resulted higher than in soil 2 (loamy) followed by soil 1 (sandy). In the other the addition of polymer at 0.2% significantly increase the water content at pressure-values of 0, 0.33, 1, 2.5, 5 and 10 Bar while for soils 2 and 3 it was significant only at 0 and 0.33 Bar.

Figure 2.33 – Water retention curves of soils untreated and treated with 0.2% SAP.



*Error bars represent standard deviation. *pF 2.5: field capacity. *pF 4.2: wilting point.

These experimental results supports those obtained by Hüttermann *et al*. (2009) and Agaba (2012) who showed that the positive increase on the field capacity of soils with the addition of cross-linked potassium polyacrylate was soil texture dependent being higher in sandy soils and much lower in the case of loamy and clay soils.

2.2. SUMMARY OF CHAPTER II

The conclusions obtained out of the experimental results from this chapter which main target is the characterization, description and evaluation of cross-linked potassium polyacrylate (Luquasorb®1280R) physicochemical properties of agronomical interest and its effect on soil properties when used as amendment, are summarised as follows:

Water absorption properties of the polymer

- The smallest granulometry of Luquasorb®1280R shows slightly lower swelling capacity compared to the medium and the bigger ones. The average water absorption capacity between all granule size-distributions of Luquasorb®1280R was 279.66 g/g using the filtration method and 328.25 g/g when using the oven method. The correlation coefficient between both methods was 0.9998.

- The speed of absorption of Luquasorb®1280R is faster as smaller is the granule size distribution. The smaller the granules are the higher the surface area is; therefore the faster is the velocity of water absorption. The smallest granulometry reached maximum FSC after 5 minutes, the medium one after 10 minutes and the biggest one after 60 minutes.

- Luquasorb®1280R shows hygroscopic properties to be considered in the storage and the agronomical application of the material. All studied granulometries showed significant absorption of water from the environment when relative humidity was equal or higher to 63%.

- The drying speed of Luquasorb®1280R is higher as higher is the environmental temperature and the bigger is the granule size distribution. The drying velocity of the polymer was significantly affected at 40°C by losing all the absorbed water after 24 hours. This drying profile of the product should be taken into account when applied under field conditions in arid and semi-arid climate with high temperatures.

- The drying speed was not significantly different between granulometries. However a small trend was observed being faster RL > RM > RS. The higher pressure within the big gel particles and the lower concentration of surface cross-linker over-compensated the water losses because of a smaller surface area.

- The swelling capacity of Luquasorb®1280R is significantly affected by pressure. The higher is the pressure on the granules the lower is the absorption capacity. Largest granulometry was more sensitive to pressure compared to the medium and the smallest, losing 90%, 78% and 81% of the absorption capacity with a soil pressure of 0.350 kg (10 cm depth) respectively.

- The swelling capacity of Luquasorb®1280R is significantly affected by the presence of salts in the aqueous media being more pronounce in the case of multivalent cations which perform as cross-linkers inhibiting the expansion of the polymer. The use of fertilizers, the salinity of the soil and the irrigation water might limit the absorption capacity of the polymer when used in agricultural systems.

- The submission of Luquasorb®1280R to extremely high (105°C) and low (-20°C) temperatures cycles (thermal stress) is not affecting the absorption ability of the polymer and therefore no impact on the performance is expected from this side in agricultural applications of the product.

Nutrient retention properties of the polymer

- Luquasorb®1280R contains a soluble potassium fraction which is higher the smaller is the granule size distribution and an exchangeable chemically linked potassium fraction which is higher the bigger is the granule size distribution. These potassium fractions are in a plant available form in the product and therefore might have a positive impact due to the role of potassium on the osmoregulation and improvement of the water stress tolerance in plants (Marschner, 2012).

- The cation exchange capacity (CEC) of Luquasorb®1280R is significantly high with an average value between all granule size distributions of 816.91 meq/100g. The CEC of the biggest granulometry was significantly higher than in the case of the medium and the smallest one. Based on this property the application of the polymer to agricultural systems might potentially improve the fertility of a certain soil.

- The velocity of cation exchange in Luquasorb®1280R exponentially increases with the concentration and the ionic strength of the exchanged cation.

- The cation exchange selectivity of Luquasorb®1280R is independent to the granule size distribution of the polymer. The cation selectivity of Luquasorb®1280R by decreasing order of affinity was: (Mn^{2+}, Zn^{2+}, Mg^{2+}) > (Fe^{3+}, Cu^{2+}) > Ca^{2+} > Na^{+}. In the other hand the bounding strength of the exchanged cations to the polymer is increasing as higher charge. The bounding strength of the studies cation to Luquasorb®1280R by decreasing order was: $Fe^{3+} > Zn^{2+} > Cu^{2+} > Mn^{2+} > Mg^{2+} > Ca^{2+} > Na^{+}$. The ability of the cross-linked potassium polyacrylate to retain and release nutrients might potentially increase the efficacy of some fertilizers and the reduction of nutrient leaching when used as a soil amendment.

- The cation exchange capacity of Luquasorb®1280R is affected by the swelling status of the polymer at the moment of the exchange and the concentration of surface cross-linkers. The higher is the swelling of the polymer and the lower is the concentration of surface cross-linkers, the easier is the mobility of a cation in/out of the gel and therefore the easier an exchange is plausible. Based on this, swelling limiting factors might have an impact on the nutrient retention and release properties of Luquasorb®1280R.

Effects of the polymer on basic soil properties

- The pH of soils seems to be buffered to neutrality (pH =7) when those are amended with Luquasorb®1280R. However in the presence of $CalCl_2$ (0.1M) the pH is reduced when soils are amended with the polymer by liberating protons to the media after cation exchange with calcium. No significant differences on pH values between granulometries were observed except for the largest one which was lower than other when measuring the pH on $CaCl_2$ media.

- The electric conductivity of soil and therefore their salinity is increased when those are amended with Luquasorb®1280R. The effect is higher the lower the concentration of salts is in the treated soils. The electric conductivity of Luquasorb®1280R was significantly lower in the largest granulometry followed by the medium and the smallest ones when measured in the saturated gel or the filtrate.

- The use of Luquasorb®1280R as a soil-amendment reduces water losses by evaporation and preserves water longer especially in sandy soils. Therefore the addition of cross-linked potassium polyacrylate to light soils in agricultural systems might help to increase the time between irrigations maintaining optimal moisture in the soil for longer periods. Furthermore the reduction of losses by evaporation might impact evapotranspiration levels and consequently the water needed to recover a soil into optimal humidity levels.

- The addition of Luquasorb®1280R to soils as an amendment does not affect the texture of soils at the studied concentrations. However results showed that the polymer seems to perform like silt particles. Saying that this might have a positive impact if concentrations are increased to a certain level by buffering very light or heavy soils to a medium-loamy texture.

- The use of Luquasorb®1280R as an amendment increases the field-capacity of soils and the content of plant available water, especially in sandy and loamy soils. Consequently the addition of cross-linked potassium polyacrylate to soils with low water retention capacity might be ideal to improve watering properties of those.

As an overall conclusion it can be said that the water absorption ability of Luquasorb®1280R and its positive impact on improving the hydric properties of soils make of this superabsorbent polymer an interesting amendment for agricultural purposes.

CHAPTER III

AGRONOMICAL TRIALS ON PROCESSING VARIETIES OF TOMATO (*Solanum lycopersicum* L.) IN MEDITERRANEAN CLIMATE USING CROSS-LINKED POTASSIUM POLYACRYLATE AS SOIL AMENDMENT

3.1. INTRODUCTION TO CHAPTER III

Cross-linked potassium polyacrylate is classified as a superabsorbent polymer (SAP) able to improve hydric properties of soils such as water holding capacity (Hüttermann *et al*., 2009) or reducing water losses by evaporation (Casquilho *et al*., 2013). Furthermore these products have the ability to retain nutrients (Wu *et al*., 2008) and deliver them to the plants (Mao *et al*., 2011).

Some of these effects has been proved in the Chapter II of this thesis at concentrations of 0.2% and 0.4%. Under field conditions these application rates would be equivalent to apply approximately 2 and 4 tons of polymer per hectare assuming a soil layer of 10 cm and a soil density of 1 kg/L. Nowadays these rates are economically not affordable to be used under field conditions (Zhouriaan-Mehr *et al*., 2010).

In the other hand positive effects on plant growth and yield of different crops were demonstrated when applying superabsorbent polymers in a localized way closed to the planting/sowing furrow at dose rates between 5 to 60 kg/ha (Mao *et al*., 2011; Islam *et al*., 2011; Ashkiani *et al*., 2013; Narjary and Aggarwal, 2014). In this way the application of superabsorbent polymers under field conditions might be an economically reasonable agronomical practice.

Based on these findings this chapter approaches the evaluation of the effects of applying cross-linked potassium polyacrylate at dose-rates between 10 to 80 kg/ha under field conditions. This study covers the evaluation of the effects on growth, yield and quality parameters of processing tomato varieties (*Solanum lycopersicum* L.). Processing tomato is an important high value crop typically grown under Mediterranean climate conditions in south European countries such as Italy, Spain, Greece and Portugal (WTPC, 2014). The World Processing Tomato Council reported that Italy and Spain were the two main producers in the Mediterranean area in 2014 with 4914000 and 2700000 tons respectively.

3.2. MATERIALS & METHODS

3.2.1. Field experimental sites

This study was set up following a field trial series approach. The trial series was composed of 12 individual experimental sites divided into the spring-summer seasons of 2011 and 2012 with 6 trials per campaign. These agronomical trials were run on transplanted varieties of processing tomato on commercial farms of Spain and Italy within typical growing areas for this crop (Table 3.1). Aerial images of the field experiment localizations are shown in the Annex III of this thesis (Figures AIII.1-AIII.2).

Table 3.1 – Location of the field experimental sites included in the study.

Site-Ref.	Country	Region	Province	Site	Position Lower Left Corner	
					Latitude (N)	Longitude (E)
ES11-01	Spain	Andalusia	Cadiz	Jerez-Las Pachecas	36.645556	-6.064167
ES11-02	Spain	Andalusia	Seville	Lebrija-BXII	36.905956	-6.123636
ES11-03	Spain	Andalusia	Cadiz	Jerez-La Isleta	36.645556	-6.097222
IT11-01	Italy	Piedmont	Alessandría	Pontecurone	44.947389	8.969778
IT11-02	Italy	Puglia	Foggia	Borgo Tressanti-A	41.398167	15.848042
IT11-03	Italy	Puglia	Foggia	Borgo Tressanti-B	41.394578	15.844350
ES12-01	Spain	Andalusia	Sevilla	Coria del Rio	37.245892	-6.011892
ES12-02	Spain	Andalusia	Cadiz	Jerez-Romanina	36.823333	-6.000000
ES12-03	Spain	Andalusia	Sevilla	Utrera	37.182250	-5.853012
IT12-01	Italy	Emilia-Romagna	Piacenza	Monticelli D'Ongina	45.068417	9.940694
IT12-02	Italy	Piedmont	Alessandría	Frugarolo	44.829917	8.647389
IT12-03	Italy	Emilia-Romagna	Piacenza	Ottavello-Rivergaro	44.949056	9.622639

*Site-Ref. = site reference. ES=Spain, IT=Italia, 11=2011, 12=2012. *Position = decimal coordinates.

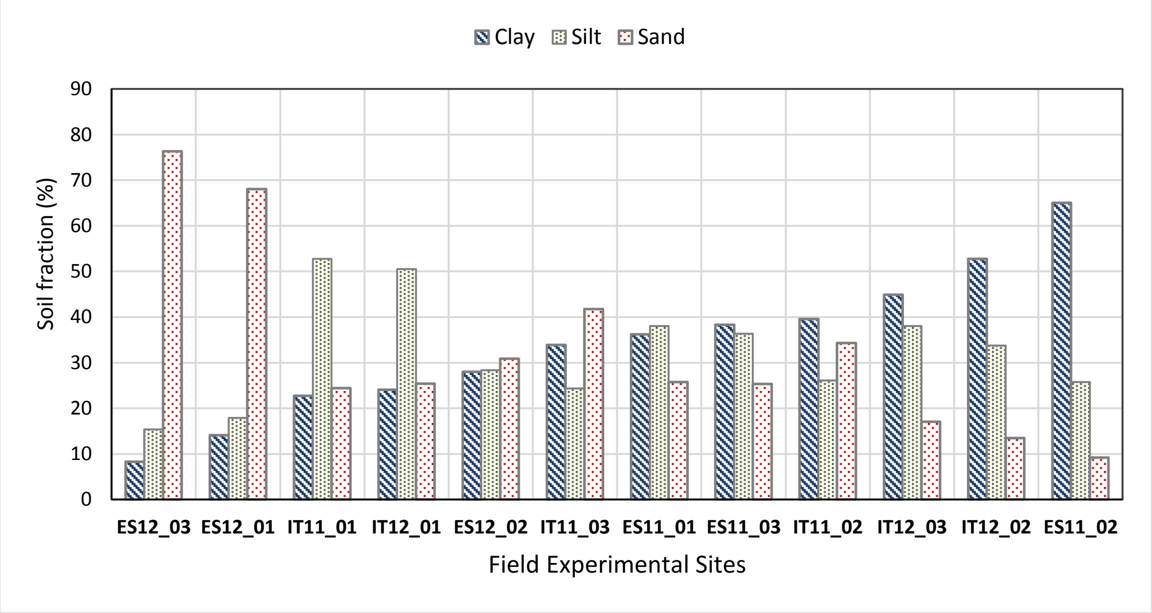
The selection of the field experimental sites was driven within the possibilities by two criteria; the selected farms should have an average medium to high productivity within their area and the total compilation of sites should have a range of different soil textures (Table 3.2, Figure 3.1) meaning light, medium and heavy soils (Figures 3.2).

Table 3.2 – Basic soil properties of the experimental field sites.

Site-Ref.	Soil Texture USDA Classification	Clay %	Silt %	Sand %	pH (H_2O)	OM %	CEC (meq/100g)
ES11-01	Clay loam	36.20	38.01	25.79	7.8	1.00	14
ES11-02	Clay	65.04	25.77	9.19	7.3	1.58	43
ES11-03	Clay loam	38.30	36.34	25.36	7.7	1.44	16
IT11-01	Silt loam	22.77	52.78	24.45	5.9	1.02	11
IT11-02	Clay loam	39.60	26.11	34.29	7.1	1.70	11
IT11-03	Clay loam	33.87	24.38	41.76	7.2	1.50	12
ES12-01	Sandy loam	14.08	17.89	68.03	5.0	1.83	7
ES12-02	Clay loam	28.00	28.33	30.87	8.0	1.03	26
ES12-03	Sandy loam	8.26	15.39	76.35	8.3	0.48	16
IT12-01	Silt loam	24.10	50.51	25.39	6.9	0.70	8
IT12-02	Clay	52.75	33.79	13.46	7.4	2.18	21
IT12-03	Clay	44.89	38.05	17.06	7.1	1.99	33

* Site-Ref. = Site reference. pH = acidity/alkalinity measured in water. *O.M. = organic matter. *CEC = cation exchange capacity.

Figure 3.1 – Content of clay, silt and sand of the soil from the field experimental sites.



*Experimental sites ordered by increasing clay content from left to right.

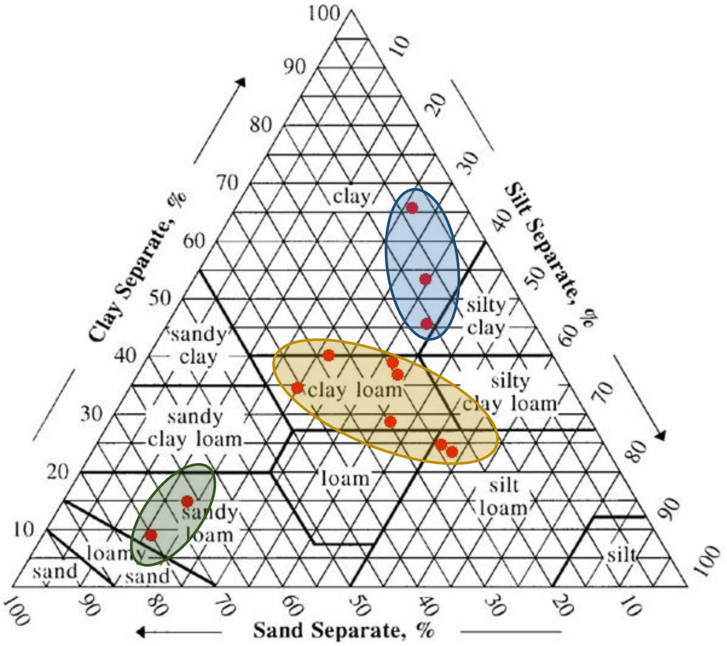


Figure 3.2 – Soils of the field experimental sites within the USDA soil texture triangle grouped by strength. Green = light; yellow = medium; blue = heavy.

All the experimental sites were situated on areas with Mediterranean climate and very similar weather conditions. Weather data was collected from the closest public weather station to the site being the average of annual rainfall of all sites 617 mm. Temperature during vegetative and generative periods of the crop was normal in all the sites with an average air temperature of 23°C and a similar variation between day and night of about 13°C. Detailed recorded weather data is shown in Annex III, Table AIII.1.

All the agronomical aspects (Table 3.3) of the field trials such as: soil preparation, selection of the seedlings variety, applications if crop protection products, basal fertilization, irrigation, fertigation, planting pattern, transplanting date and harvesting date followed the farmer practice in each of the experimental sites. With regards watering it was used surface auto-compensated drip irrigation system in all the sites. Furthermore all experimental sites used transplanted seedlings of commonly used processing varieties within each production area and year.

Table 3.3 – Varieties, planting pattern and transplanting/harvesting dates of the field experiments.

Site-Ref.	Variety	Planting Row Type	Distance (m) between		Density (plant/ha)	Planting Date	Harvest Date
			rows	plants			
ES11-01	Heinz 9694	Single	1.5	0.25	26,667	09/04/2011	08/08/2011
ES11-02	Albatros	Single	1.5	0.20	33,333	14/04/2011	04/08/2011
ES11-03	Albatros	Single	1.5	0.25	26,667	25/04/2011	27/08/2011
IT11-01	Enterprise	Single	1.5	0.22	30,303	19/05/2011	24/08/2011
IT11-02	Discovery	Twin	1.8	0.40	27,778	30/05/2011	30/08/2011
IT11-03	Discovery	Twin	1.8	0.40	27,778	30/05/2011	25/08/2011
ES12-01	Heinz 9661	Single	1.5	0.22	30,303	13/04/2012	06/08/2012
ES12-02	Albatros	Single	1.5	0.20	33,333	19/04/2012	22/08/2012
ES12-03	Juncal	Single	1.3	0.20	33,333	01/06/2012	24/09/2012
IT12-01	Heinz 3402	Single	1.5	0.22	30,303	31/05/2012	14/09/2012
IT12-02	Heinz 3406	Single	1.5	0.20	33,333	24/05/2012	10/09/2012
IT12-03	Heinz 3402	Twin	1.5	0.40	33,333	17/05/2012	31/08/2012

*Site-Ref. = Site reference.

3.2.2. Treatments and experimental design

3.2.2.1. Material, dose-rates and application

The material used in this study as source of cross-linked potassium polyacrylate was Luquasorb®1280RM (Chapter II, sub-chapter 2.2.1. section 2.2.1.1.). The applied dose rates of material were 0, 1.5, 3, 6 and 12 g/row-m (grams per row-meter) of granular material which corresponds to 0, 10, 20, 40 and 80 kg/ha considering a plantation pattern with 1.5 m between planting rows (Table 3.4).

Table 3.4 – Dose-rates equivalence between g/row-m and kg/ha depending on distance between planting rows.

Distance between Planting rows	Applied dose dose-rates of Luquasorb®1280RM			
	1.5 g/row-m	**3 g/row-m**	**6 g/row-m**	**12 g/row-m**
1.3 m	11.5 kg/ha	23.1 kg/ga	46.2 kg/ha	92.3 kg/ha
1.5 m	10 kg/ha	20 kg/ha	40 kg/ha	80 kg/ha
1.8 m	8.3 kg/ha	16.7 kg/ha	33.3 kg/ha	66.7 kg/ha

*g/row-m = grams per linear/row meter

The application of the product was done in furrow 10-15 cm below the soil surface and 5-10 cm offside the transplanting lines (Figure 3.3).

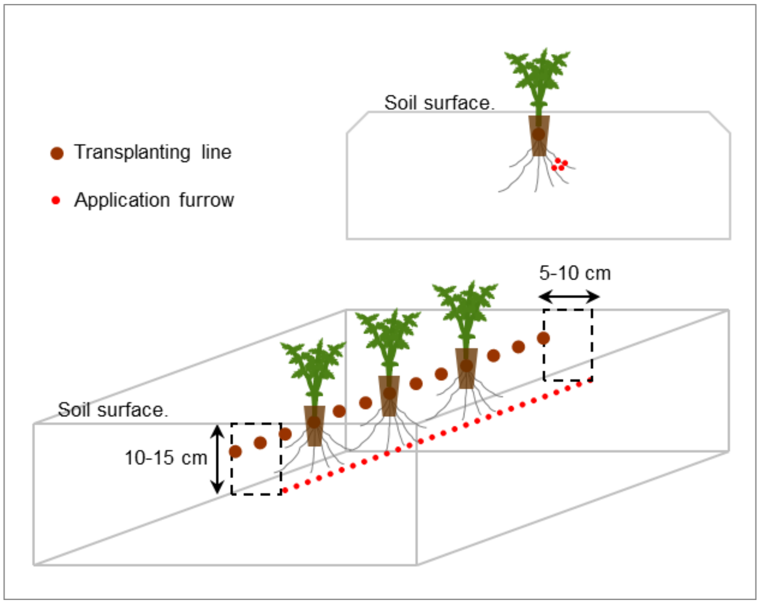


Figure 3.3 – Schematic representation of the localization of the product in the soil.

The tested material was applied at transplanting with the help of commercially available micro-granule applicators consisting of a hopper hitched to a planting machine and rubber pipes bringing the granules below the soil surface (Figure 3.4).

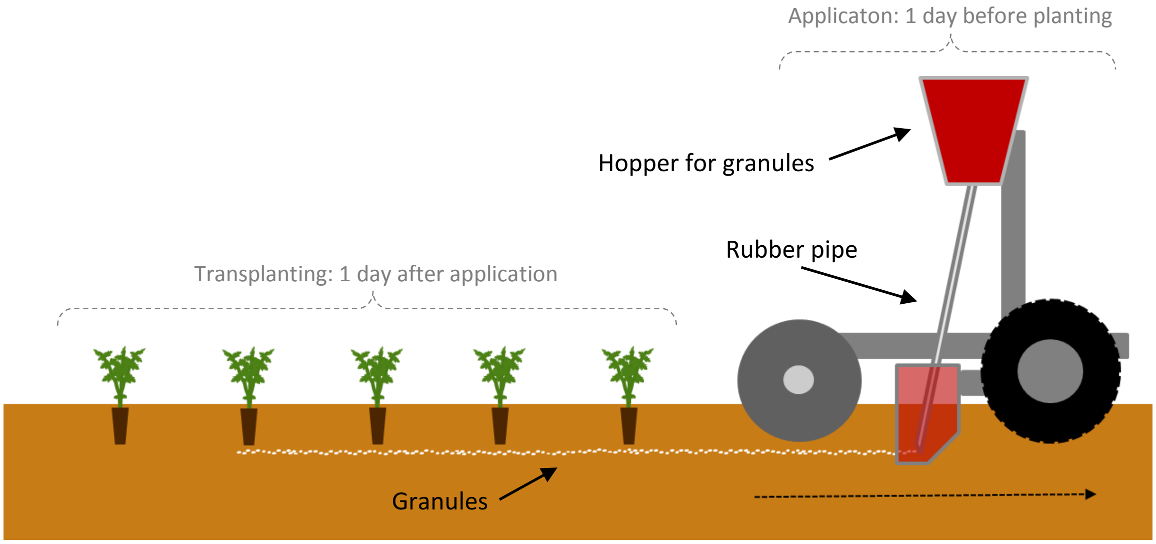
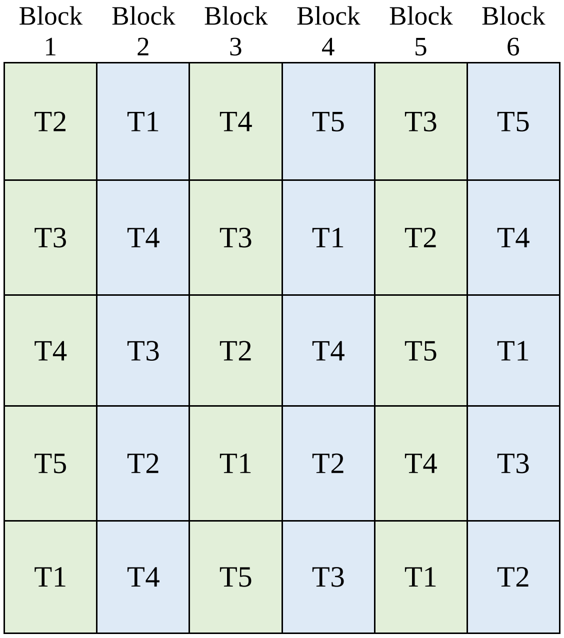


Figure 3.4 – Schematic representation of the application of ®1280RM with the help of a micro-granule applicator.

3.2.2.2. Experimental design of trials and individual plots

Each of the field experiments followed a complete randomized blocks design with 6 replications per treatment (Figure 3.5). Trial maps of each experiment and their randomizations are shown in Annex III, Figure AIII.3.



Block 1	Block 2	Block 3	Block 4	Block 5	Block 6
T2	T1	T4	T5	T3	T5
T3	T4	T3	T1	T2	T4
T4	T3	T2	T4	T5	T1
T5	T2	T1	T2	T4	T3
T1	T4	T5	T3	T1	T2

Figure 3.5 – Example of complete randomized block design with 6 blocks (ES11-01) being T1, T2, T3, T4 and T5 the treatments.

The individual experimental plots in all the sites consisted of 3 planting rows with a length of 6 meters. In this way experimental single plot sizes were 23.4, 27 and 32.4 m^2 for a plantation pattern with a distance between rows of 1.3, 1.5 and 1.8 m respectively. Furthermore all field sites had a minimum of three border rows at each side of the trial and a minimum of 3 m length buffer at the front and the back to reduce possible border effects related to plant growth on the experimental plots.

3.2.3. Agronomical assessments

All the assessments and evaluations carried out in this study were standardized on basis to the BBCH-scale for the following growth stages of the crop (Feller *et al*., 1995):

- BBCH 14-15: 4th-5th leaf of main shoot unfolded.
- BBCH 53-54: 3rd-4th inflorescence visible (first bud erect).
- BBCH 71-72: 1st-2nd fruit cluster: first fruit reached typical size.
- BBCH 88-89: 80-90% fruits have typical fully ripe colour.
- BBCH 99: harvested product.

To avoid possible contamination effects between neighbour plots, the first half row-meter at the beginning and the end of each row within a plot was not considered for any of the carried out evaluations. Therefore only 5 meters per row within the plots was considered a reliable sampling area.

3.2.3.1. Plant growth parameters

a) Plant population

This parameter is given as a density value of the number of alive plants per unit of area. Plant population was assessed at growth stages 14-15 and 53-54 of the BBCH-scale. It was calculated by counting the number of alive plants per experimental plot within the reliable sampling area divided by the sampling area.

b) Plant vigor

Plant vigor was assessed at growth stages 14-15 and 53-54 of the BBCH-scale. This relative assessment is done by rating from 0 to 10 the reliable sampling area of an experimental plot. The untreated plot in each block is always given value 5. Plots rated over 5 means more vigorous that the untreated plot and those rated lower than 5 means less vigorous than the untreated plot (0 = dead plants, 10 = double of control). This assessment is only used to evaluate small differences (10-20%) between plots (Bleiholder, 1997).

c) *Plant height*

Plant height was assessed at growth stage 53-54 in the BBCH-scale. Height was measured from the soil surface to the top of the plant canopy considering the youngest/highest branching in the main shoot. 10 plants within the reliable sampling area for each experimental plot were measured as subsamples. The average of the 10 subsamples was given as the plot height value. Obtained results were expressed in cm.

d) *Phytotoxicity*

Possible damage to the crop due to the treatments was evaluated along the crop cycle. Assessments were done at growth stages 13-15, 53-54 and 71-72 in the BBCH-scale. For the assessment of phytotoxicity it was considered changes in the development, mortality of plants, discoloration, yellowing, deformation or necrosis of leafs.

3.2.3.2. Yield parameters

For a proper evaluation of yield parameters, harvest was done manually in all the field experimental sites. Harvest was done at growth stage 88-89 in the BBCH-scale. The sampling unit was 5 row meters per plot selected from the most representative rows. The harvested plants per plot were from 20 to 25 plants depending on the plantation pattern of each site. Only homogeneous and plot representative rows were harvested within the reliable sampling area.

Figure 3.6 – Harvest and classification of fruits in one of the field experimental sites (ES12-01).

a) *Number of unripe, ripe and over-ripe fruits*

Harvested tomatoes were classified and separately counted as ripe, unripe and over-ripe (Figure 3.6). Obtained results were expressed in number of fruits per hectare (fruits/ha).

b) *Weight of unripe, ripe and over-ripe fruits*

All harvested tomatoes were classified and separately weighted as ripe (marketable yield), unripe and over-ripe (Figure 3.6). Obtained production data results were expressed in weighted tons per hectare (t/ha).

c) *Degrees Brix*

It was measured the content of soluble solids (sugar concentration) with the help of a manual refractometer in 10 ripe tomato fruit samples randomly picked from each harvested plot at growth stage 99 in the BBCH-scale. Final value per experimental plot was given as the average of the 10 subsamples. Obtained results were expressed in %.

3.2.4. Maintenance of the field experiments

All field experiments were run under best local agronomical practices. The general maintenance of the field sites done by the farmers with regards irrigation, fertilization and pest and disease control was recorded for each experimental site. Weather conditions and any other observed phenomena were as well considered and recorded. All recorded parameters for each site are shown in Annex III.

3.2.5. Data analysis and statistics

For the design of the experimental protocols, creating the field randomizations, recording the assessments and statistically analyzing the data it was used a combination of the software ARM 9 (Gylling Data Management, Inc) and Spead MI (IPS Software GmbH).

Both IT tools permit to unify and guaranty the criteria of making the field experiments and furthermore they allow the analysis of more than one site jointly.

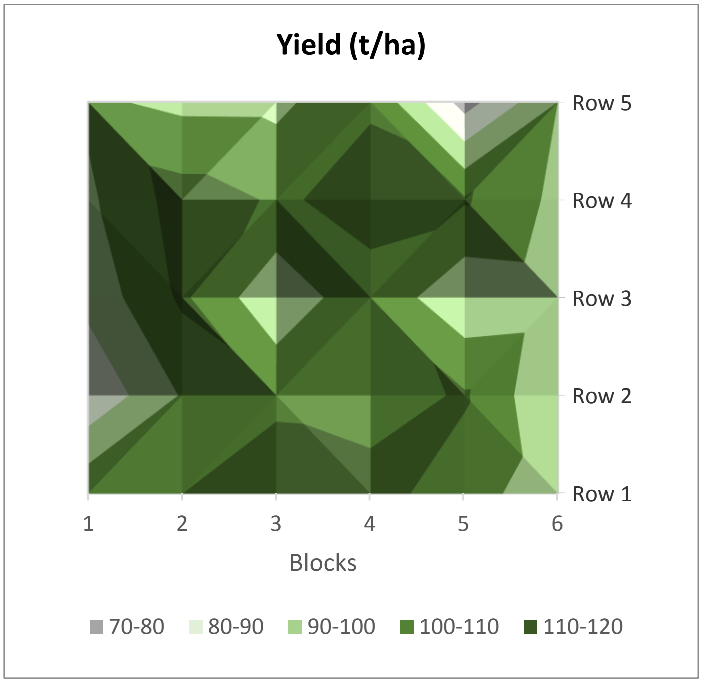


Figure 3.7 – Example of yield (ton/ha) data plotted in a surface graph for detection of field trends not covered by the block design.

Before running statistical analyses all experimental data was reviewed in order to identify typing errors or possible outliers. Data was plotted as 3D surface graphs to identify trends on the field experimental sites not covered by the block design (Figure 3.7). Possible identified outliers were afterwards statistically confirmed by Grubbs' test (maximum normed residual test). All the results out of the field experimental sites were statistically analyzed individually by site but as well as a summary of all sites by the Student-Newman-Keuls (SNK) test considering the complete randomized block design used. For the analysis of relations between results and experimental sites properties, Pearson´s correlation analysis and principal component analysis (PCA) were run with Excel 2013 (Microsoft) and the add-in software XLSTAT 2015 (Addinsoft).

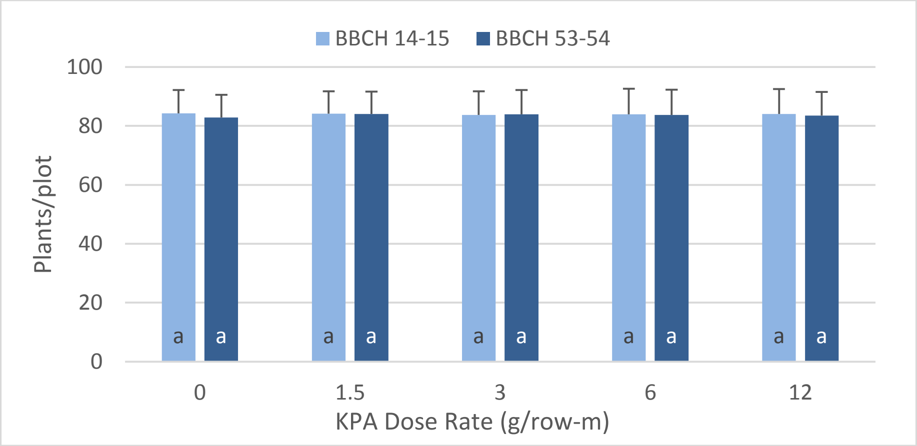
3.3. RESULTS AND DISCUSSION

3.3.1. Effects of KPA on plant growth parameters of processing tomato

3.3.1.1. Effects on plant population.

The addition of cross-linked potassium polyacrylate did not significantly affect the overall plant population density neither at growth stage 14-15 nor at 53-54 in the BBCH-scale (Figure 3.8). Plant population evaluations plotted in bar graphs for each field experimental sites are shown in the Annex III (Figures AIII.4 and AIII.5).

Figure 3.8 – Plant population (plants/plot) summary of all experimental sites (n=12).



*Error bars represent standard deviation. Different letters indicate significant differences at P ≤ 0.05 between bars of the same color by SNK-test.

However in the case of the experimental site IT11-02, where there was a significant mortality of plants due to natural reasons, Luquasorb®1280RM did significantly improve the maintenance of the plant population within the treated plots (Table 3.5).

Table 3.5 – Plant population results and statistics for the experimental site IT11-02.

BBCH	0 g/row-m		1.5 g/row-m		3 g/row-m		6 g/row-m		12 g/row-m	
	Plant /plot	SD	Plant/plot	SD	Plant/plot	SD	Plant/plot	SD	Plant/plot	SD
14-15	89.0aA	0.6	89.5aA	0.6	89.2aA	0.8	90.0aA	0.6	89.2aA	1.0
53-54	81.0bB	5.4	89.8aA	0.4	89.6aA	0.5	90.3aA	0.8	89.3aA	0.5

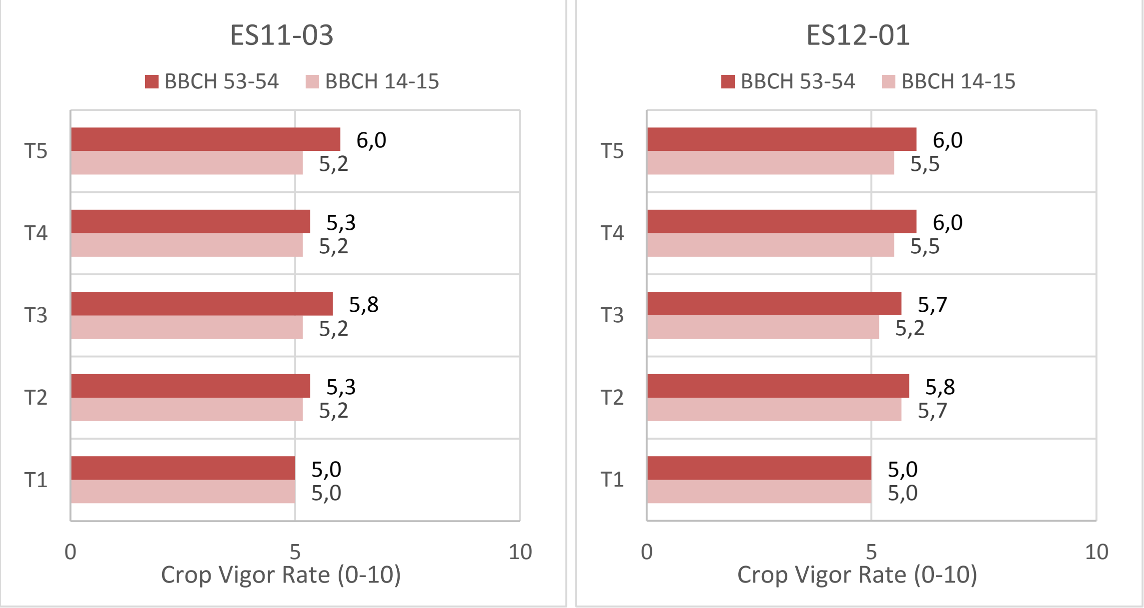
*SD = standard deviation. Different letters indicate significant differences at P ≤ 0.05 between rows (small letters) and between columns (capital letters) by SNK-test.

Differences on plant density between growth stages 14-15 and 53-54 in the untreated control might indicate mortality of plants related to bad tomato seedlings establishment. Therefore the obtained results on the site IT11-02 are in alignment to the claims of Woodhouse and Jonson (1991), Hutterman *et al*. (1999) or more recently Ashkiani *et al*. (2013) confirming a better seedlings establishment under limiting environmental conditions. Furthermore El-Sayed (1991) *et al*. demonstrated the efficacy of hydrogels to improve the survival to saline condition. In this way, the localized application of cross-linked potassium polyacrylate closed to the transplanted seedling might support the young plants under stress conditions.

3.3.1.2. Effects on plant vigor.

The overall treatments with Luquasorb®1280RM did not affect in general the crop vigor neither at growth stage BBCH 14-15 nor at BBCH 53-54. Detailed results for each field experimental sites are shown in Annex III, Table AIII.2. Only in the case of the case of two sites (ES11-03, ES12-01) there was a slight trends where crop vigor was improved in the plots treated with the polymer (Figure 3.9). Due to the rating character of the crop vigor assessment statistical analysis did not applied to the results.

Figure 3.9 – Crop vigor results at BBCH 14-15 and 53-54 for the experimental sites ES11-03 and ES12-01.

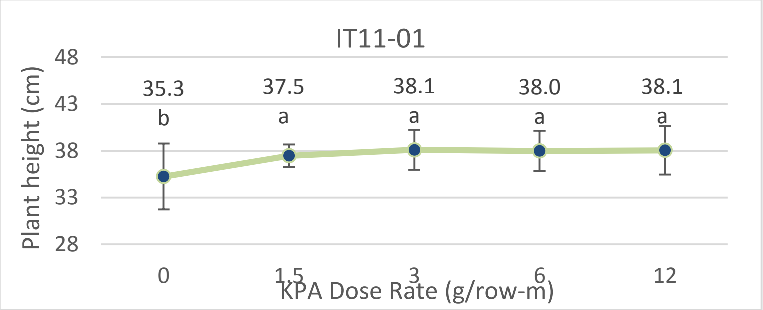


*T1 = 0 g/row-m; T2 = 1.5 g/row-m; T3 = 3 g/row-m; T4 = 6 g/row-m; T5 = 12 g/row-m.

3.3.1.3. Effects on plant height.

The assessment of plant height at growth stage 53-54 did not show significant differences between treatments within each single site with the exception of the experimental site IT11-01 (Figure 3.10). In this site, plant height was significantly increased in all the treated plots (1.5, 3, 6 and 12 g/row-meter) in comparison to the untreated control. Detailed results and statistics for each field experiment are shown in Annex III, Figures AIII.6 and AIII.7.

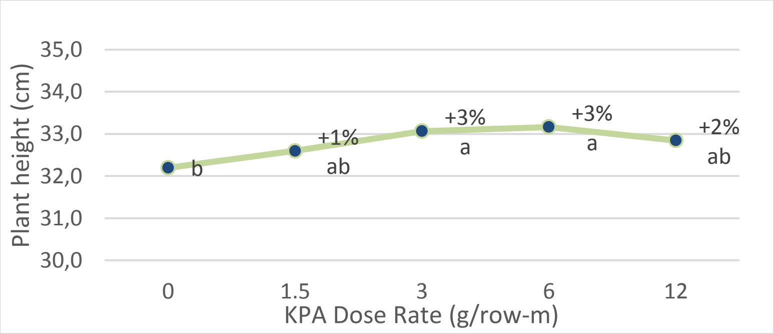
Figure 3.10 – Plant height (cm) at growth stage BBCH 53-54 in IT11-01.



*Error bars represent standard deviation. Different letters indicate significant differences between treatments at P ≤ 0.05 by SNK-test.

However the observed numerical positive trend found in some of the sites resulted in statistically significant differences between treatments when summarizing all sites together (Table 3.6). The application of 3 and 6 g/row-m of product significantly increased plant height compared to the untreated control by 3% in both cases (Figure 3.11).

Figure 3.11 – Summary of plant height (cm) for all sites (n=12).



*Error bars represent standard deviation. Different letters indicate significant differences between treatments at P ≤ 0.05 by SNK-test. *n= number of sites included in the analysis.

Table 3.6 – Results, statistics and relative increase compared to control of the measurements of plant height (cm) at growth stage BBCH 53-54 in all experimental sites (n=12).

Site-Ref.	0 g/row-m	1.5 g/row-m		3 g/row-m		6 g/row-m		12 g/row-m	
	Height (cm)	Height (cm)	Increase (%)	Height (cm)	Increase (%)	Height (cm)	Increase (%)	Height (cm)	Increase (%)
ES11-01	25.8a	25.3a	-2	26.2a	+1	26.7a	+3	26.0a	+1
ES11-02	25.3a	25.0a	-1	25.5a	+1	24.7a	-3	24.8a	-2
ES11-03	22.2a	22.5a	+2	22.5a	+2	22.7a	+2	23.7a	+7
IT11-01	35.3b	37.5a	+6	38.1a	+8	38.0a	+8	38.1a	+8
IT11-02	58.4a	58.6a	0	58.6a	0	58.9a	+1	58.2a	0
IT11-03	27.0a	26.3a	-2	26.5a	-2	26.2a	-3	26.0a	-4
ES12-01	32.6a	33.8a	+4	34.1a	+4	35.3a	+8	35.0a	+7
ES12-02	16.0a	16.4a	+2	16.2a	+1	15.9a	-1	16.4a	+2
ES12-03	28.1a	28.5a	+1	28.3a	+1	28.0a	-1	28.2a	0
IT12-01	34.4a	34.7a	+1	35.6a	+3	34.7a	+1	34.8a	+1
IT12-02	38.9a	39.5a	+2	40.6a	+4	42.0a	+8	39.6a	+2
IT12-03	42.3a	43.0a	+2	44.7a	+6	45.1a	+7	43.4a	+3
Average (n=12)	**32.2b**	**32.6ab**	+1	**33.1a**	+3	**33.2a**	+3	**32.8ab**	+2

*SD = standard deviation. Different letters indicate significant differences at P ≤ 0.05 between rows by SNK-test.

These observations made for processing varieties of tomato are in alignment to those made by Knypl and Knypl (1993), Abd El-Rehim (2004), Chu *et al.* (2006), Lenzt and Sojka (2009) or Mao *et al.* (2011) who reported better plant growth under field condition of different crops such as corn and soybean. Maboko (2006) reported as well significant increase of plant height on tomato plants treated with two different superabsorbent polymers.

3.3.1.4. Phytotoxicity assessments.

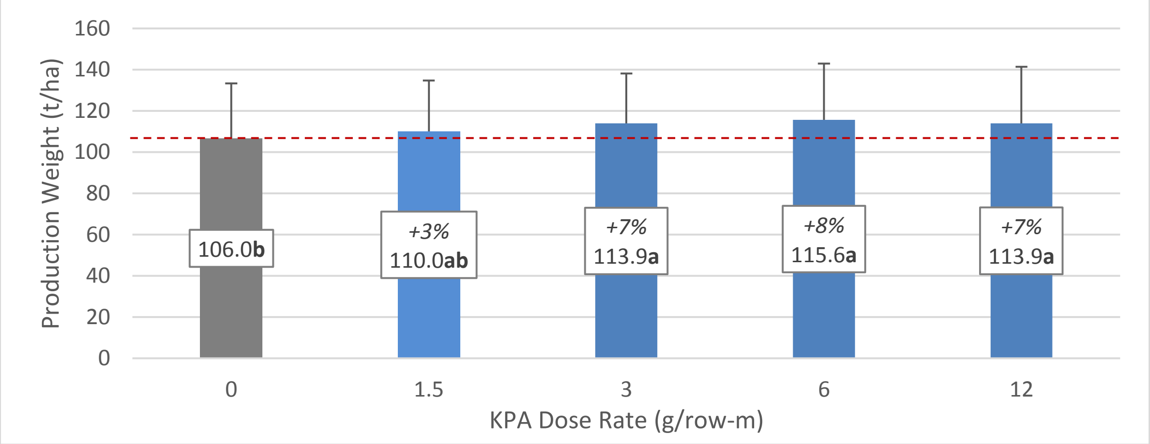
No damages on the crop were observed in any of the experimental fields during the whole crop cycle. The application of cross-linked potassium polyacrylate did not caused changes in the development, mortality of plants or discoloration, yellowing, deformation or necrosis on the crop leafs. No reports on plant damages caused by the application of superabsorbent polymers were found within the bibliography of this thesis. The development of specific studies for investigating possible phytotoxicity of cross-linked potassium polyacrylate might be of interest for further develop SAPs in agriculture.

3.3.2. Effects of KPA on yield of processing tomato

3.3.2.1. Production yields of the experimental sites.

The results and statistical analyses by yield classes for each individual experimental site are shown in bar graphs in figures 3.13 (sites from 2011) and 3.14 (sites from 2012). Due to the natural variability of processing tomato varieties and the limited number of replicates used in the individual field experiments there were no statistical differences between treatments in majority of the sites. Only field sites IT11-02 and IT12-02 showed significant differences between treatments on the marketable yield. However, when analyzing all the sites together, the application of cross-linked potassium polyacrylate did in average increase the total production yield of processing tomato (Figure 3.12) being significantly higher at applied dose-rates of 3, 6 and 12 g/row-m with a positive total production increase of 7, 8 and 7% respectively.

Figure 3.12 – Summary analysis of the total production yield average (t/ha) of all experimental sites (n=12).



*Error bars represent standard deviation (dispersion between experimental sites). Different letters indicate significant differences between treatments at P ≤ 0.05 by SNK-test. *n= number of sites included in the statistical analysis.

The principal driver of the total production increase was a significantly higher marketable yield which resulted significantly different to the untreated control at a rate of 6 g/row-m (Table 3.7). In the other hand the difference between treatments in the case of unripe and over-ripe tomatoes was not significant when summarizing all sites.

Table 3.7 – Summary of yield (t/ha) of marketable (ripe), unripe and over-ripe tomatoes of all sites (n=12).

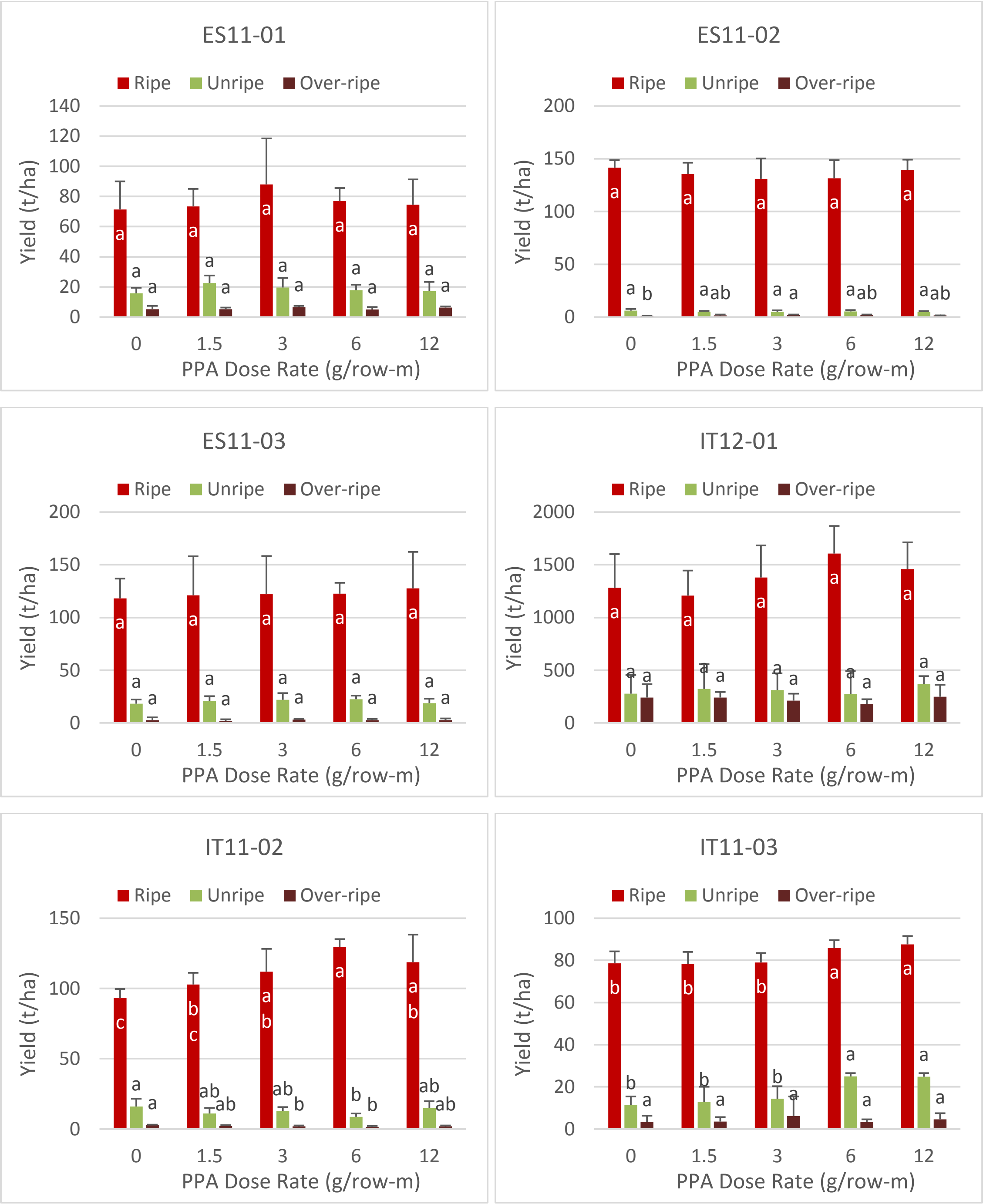
Fruits	0 g/row-m		1.5 g/row-m		3 g/row-m		6 g/row-m		12 g/row-m	
	t/ha	SD	t/ha	SD	t/ha	SD	t/ha	SD	t/ha	SD
Over-ripe	6.2a	3.9	6.5a	3.4	6.5a	3.4	6.5a	3.8	6.9a	4.1
Unripe	10.8a	5.7	11.9a	5.5	12.6a	4.0	11.6a	6.2	10.9a	4.7
Marketable	89.7b	27.8	92.1ab	29.4	95.1ab	29.4	97.1a	28.4	95.4ab	31.6

*SD = standard deviation. Different letters indicate significant differences between rows at $P \leq 0.05$ by SNK-test. *n= number of sites.

The obtained results showing a general positive effect of the polymer yield and marketable yield of processing tomato complement those obtained by Johnson and Pipper (1991). These authors proved that the total yield and especially the marketable yield were significantly improved when treating tomato plants grown under controlled conditions with 3 different types of superabsorbent polymers.

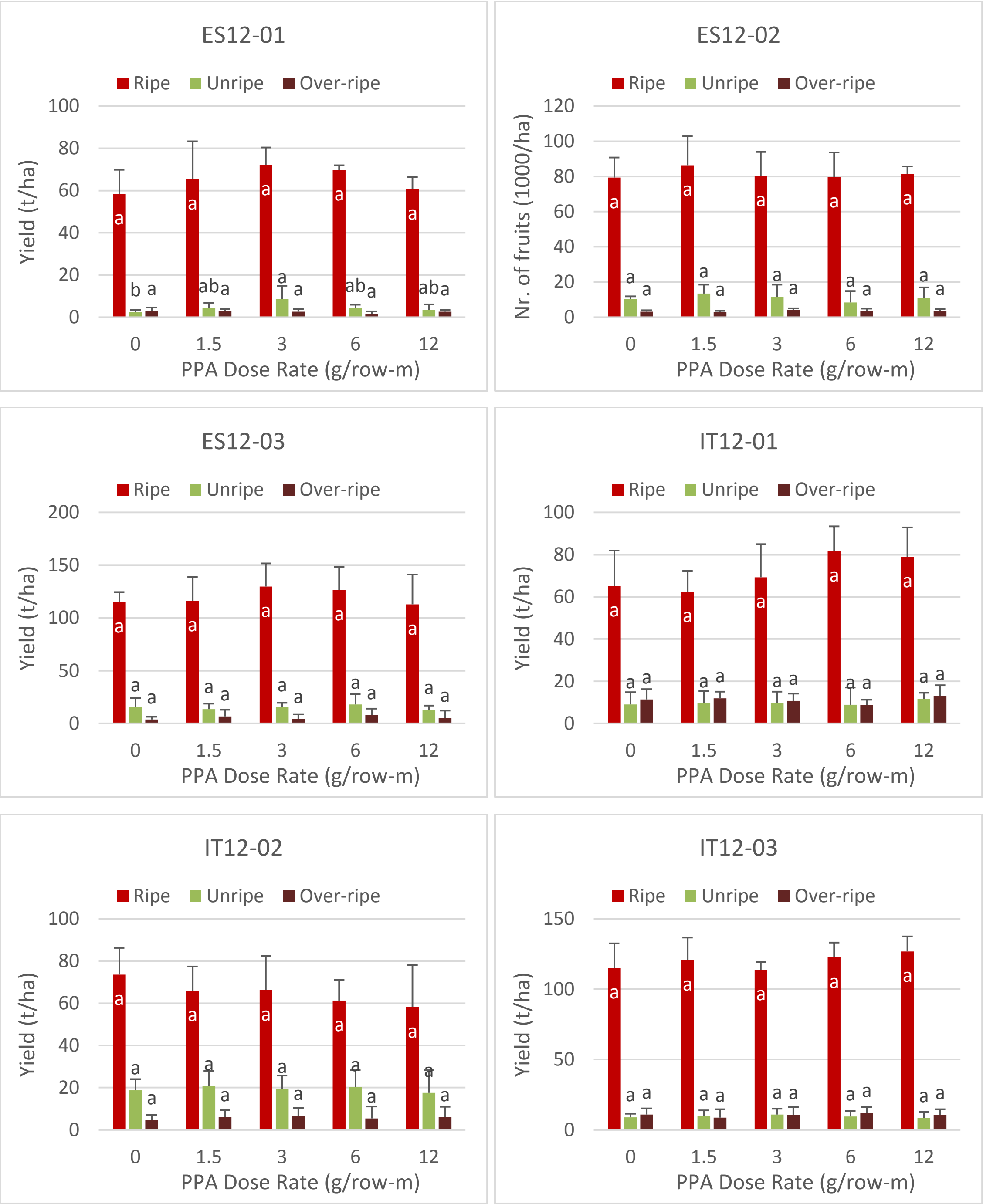
Within the marketable yield results of the individual experimental sites (Figures 3.13 and 3.14) there were found 3 different trends in general. In some of the sites there was a dose-response effect exponentially increasing as higher was the applied dose-rate (E.g. IT11-03, IT12-01). In other sites there was a kind of optimum dose-rate and an over-dose negative impact (E.g. ES12-01, ES12-03). In a third group of sites there was a negative impact exponentially increasing with the dose-rate of applied product (E.g. ES11-02, IT12-02). These different trends on the marketable yield results suggested that Luquasorb®1280RM performance was not independent to the experimental site where it was applied. Therefore correlation and PCA analyses might help to identify the origin of the different performance (section 3.2.2.2. of this sub-chapter).

Figure 3.13 – Yield (t/ha) of marketable, unripe and over-ripe fruits of the 2011 experimental sites.



*Error bars represent standard deviation. Different letters indicate significant differences between treatments within the same fruit class at P ≤ 0.05 by SNK-test.

Figure 3.14 – Yield (t/ha) of marketable, unripe and over-ripe fruits of the 2012 experimental sites.



*Error bars represent standard deviation. Different letters indicate significant differences between treatments within the same fruit class at P ≤ 0.05 by SNK-test.

3.3.2.2. Correlation and principal components (PCA) analyses.

The correlation coefficients of Pearson, resulting of the correlation analysis done between the marketable yield increase effect of the treatments and the characterization soil data of the experimental sites, are shown in the Table 3.8.

Table 3.8 – Pearson correlation coefficients (r) for the marketable yield increase and site properties.

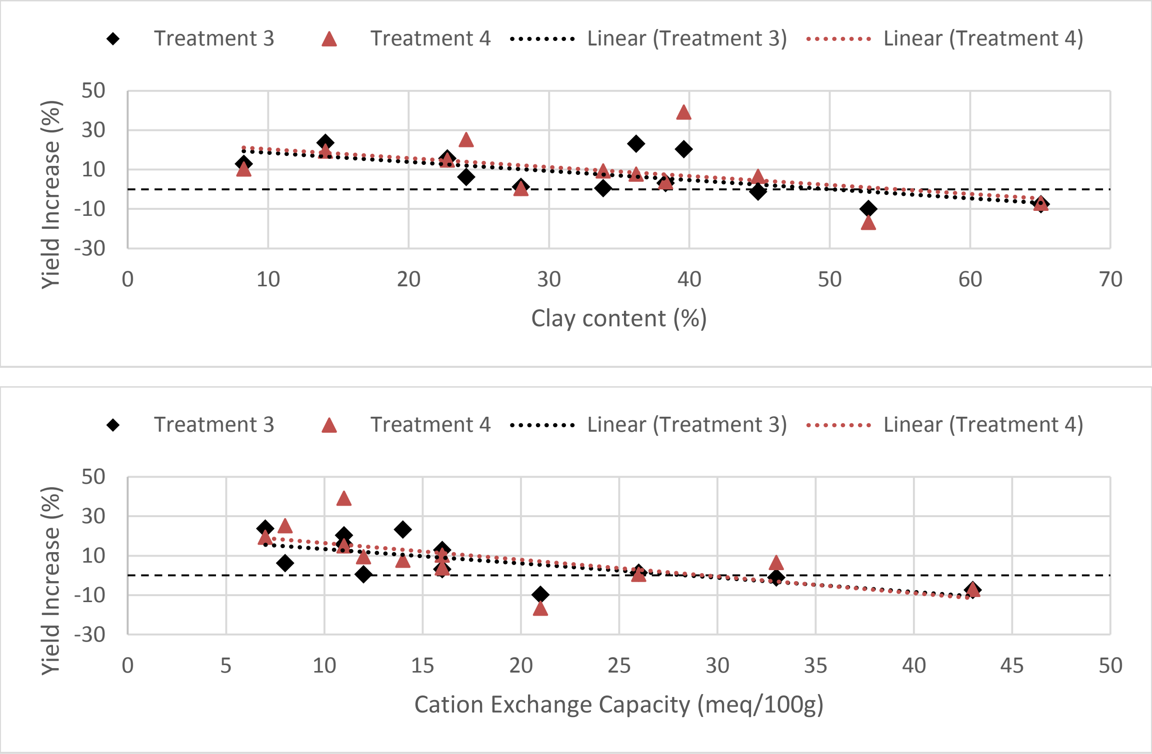
Parameters	Yield (untreated)	Treatment 2 (1.5 g/row-m)	Treatment 3 (3 g/row-m)	Treatment 4 (6 g/row-m)	Treatment 5 (12 g/row-m)	Average (T3-T4)
Clay content	0.477	-0.493	-0.638**	-0.498*	-0.260	-0.602**
Silt content	-0.288	-0.010	-0.057	0.061	0.324	0.009
Sand content	-0.186	0.345	0.558*	0.388	0.038	0.499*
Soil Strength	0.345	-0.482	-0.732***	-0.523*	-0.230	-0.663**
pH	0.479	-0.461	-0.372	-0.366	-0.258	-0.396
O.M.	0.084	-0.107	-0.338	-0.260	-0.263	-0.317
CEC	0.726***	-0.317	-0.678**	-0.631**	-0.402	-0.701***

Parameters	Clay content	Silt content	Sand content	Soil Strength	pH	O.M.	CEC
Clay content	1						
Silt content	0.107	1					
Sand content	-0.818***	-0.631*	1				
Soil Strength	-0.905***	-0.375	0.910**	1			
pH	0.231	-0.146	-0.150	0.203	1		
O.M.	0.607**	-0.165	-0.342	-0.535	-0.324	1	
CEC	0.701***	-0.127	-0.514*	-0.753**	0.363	0.292	1

*Statistically significant (*P ≤ 0.05, **P ≤0.025; ***P ≤ 0.001) by t-test. *Soil strength refers to light, medium and heavy soils.

Yield of the sites did only positively correlate with the CEC which might be explained as an indicator of fertility of a site. Treatments 2 and 5 did not result in any significant correlation to any soil parameter. In the other hand the effect on yield increase of treatment 3, treatment 4 and the average of them did have in common a significant correlation to the clay content, soil strength and soil cation exchange capacity (CEC). Treatment 3 did also significantly correlate to the sand content. The overall analysis showed a significant negative correlation between the effect of the treatments and soil texture related parameters such as clay content and soil strength (light, medium and heavy soils). Furthermore it was shown a significant negative correlation with the cation exchange capacity of the soils (CEC) which is linked to the soil texture and therefore to the clay content of a soil (Navarro-Blaya and Navarro-Garcia, 2003). Based on the graphs from Figure 3.15, it can be said that the positive yield effect by the application of Luquasorb®1280RM started to be consistent when the soil clay content was lower than 40% and the cation exchange capacity of the sites was lower than 20 meq/100g.

Figure 3.15 – Representation of yield increase (%) by treatments 3 and 4 against the clay content and cation exchange capacity of the soils.



*Linear = trend line adjusted to linear.

Pearson correlation coefficients between some of the basic soil parameters were significant (Table 3.8). Therefore it is suggested an existing relation between them. These results justified to run a principal components analysis (PCA) in order to explain the relation between the variables and better understanding the effect of cross-linked potassium polyacrylate on marketable yield when combining parameters in a reduced number of principal factors or components named as F1, F2, F3…etc. (Smith, 2002). For the PCA it was used the average value of T3 and T4 as the effect on yield by the polymer. Obtained factors out of the analysis, the explained variability and the contribution of each of the variables to the factors, are shown in Table 3.9.

Table 3.9 – Contribution (%) of the variables to the calculated principal components (F1, F2… etc.) in PCA.

Variables	F1	F2	F3	F4	F5	F6	F7	F8
T3-T4	**13.943**	8.015	0.288	43.965	28.816	4.793	0.119	0.063
Clay content	**20.795**	0.000	1.539	14.367	0.995	35.176	0.256	26.872
Silt content	1.373	**41.856**	19.963	3.010	0.772	8.199	1.170	23.658
Sand content	**18.032**	10.478	3.762	2.137	0.221	4.196	21.207	39.967
Soil Strength	**22.344**	1.750	0.028	0.468	0.011	6.397	62.669	6.333
pH	1.951	**26.311**	27.964	23.484	8.610	9.642	1.511	0.527
O.M.	6.784	1.045	**46.453**	3.500	11.448	21.564	8.292	0.914
CEC	**14.779**	10.545	0.004	9.069	49.127	10.033	4.777	1.666
Explained Variability	*52.870*	*19.382*	*16.714*	*5.179*	*4.135*	*1.204*	*0.371*	*0.145*

*T3-T4 = Average marketable yield increase of T3 and T4. Numbers in bold represent highest quadrate cosine for each variable.

The studied variables in the PCA can be explained by mainly 3 principal components or factors (F1, F2 and F3). F1 explains 52.87% of the variability followed by F2 and F3 with 19.38% and 16.71% respectively. In this way, by combining the calculated principal components F1 and F2 it is possible to explain 72.25% of the total variability of the experiments.

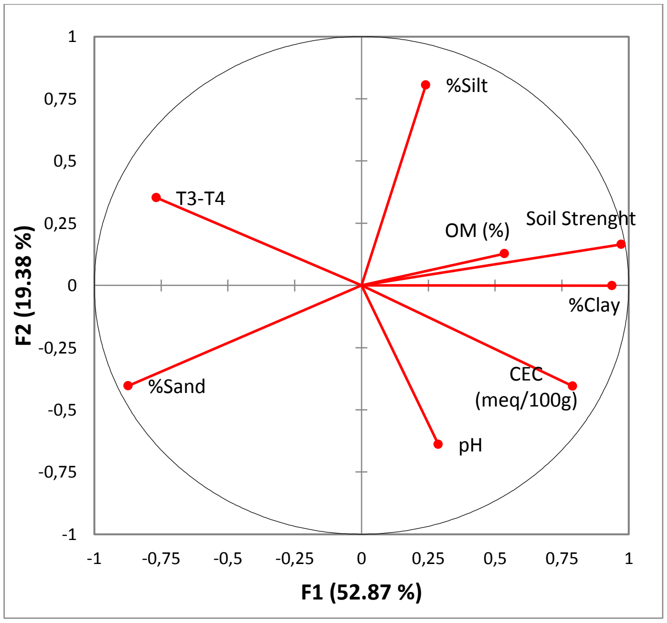
Table 3.10 – Pearson coefficient factors of correlation between the components and the variables.

Variables	F1	F2	F3	F4	F5	F6	F7	F8
T3-T4	**-0.768**	0.353	0.062	0.427	0.309	-0.068	0.006	-0.003
Clay content	**0.938**	-0.001	0.143	0.244	0.057	0.184	0.009	0.056
Silt content	0.241	**0.806**	**-0.517**	-0.112	-0.051	-0.089	-0.019	0.052
Sand content	**-0.873**	-0.403	0.224	-0.094	-0.027	-0.064	0.079	0.068
Soil Strength	**0.972**	0.165	-0.019	0.044	0.006	-0.078	0.136	-0.027
pH	0.287	**-0.639**	**-0.611**	0.312	-0.169	-0.096	-0.021	0.008
O.M.	**0.536**	0.127	**0.788**	0.120	-0.195	-0.144	-0.050	0.010
CEC	**0.791**	-0.404	0.007	-0.194	0.403	-0.098	-0.038	0.014

*T3-T4 = Average marketable yield increase of T3 and T4. Numbers in bold are statistically significant for n-2 degrees of freedom.

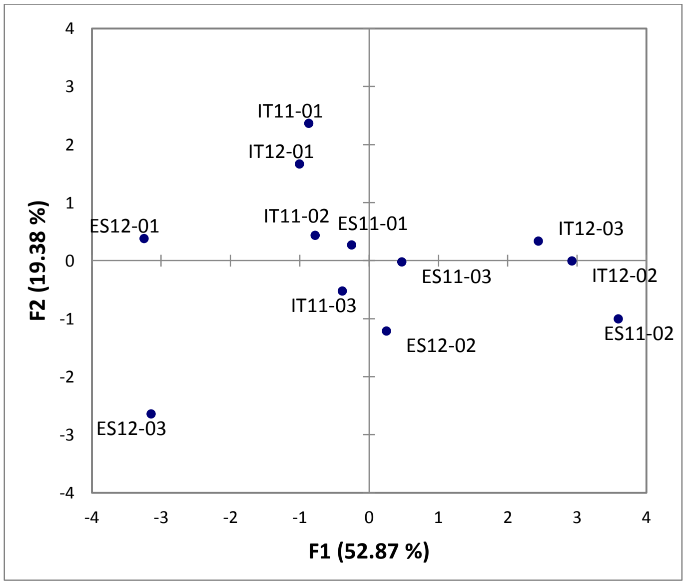
The variables contributing to the principal component F1 were clay content, sand content, soil strength and CEC together with the average yield increase of T3 and T4. In addition, factor F1 did significantly correlate to the organic matter content. Being F1 the factor explaining the majority of the variability (52.87%) the obtained results of the PCA confirmed those of the correlation analysis. In the other hand the remaining variables (silt content and pH) were explained by factor F2. The relation between variables and the contribution to F1 and F2 are represented in Figure 3.16. The experimental sites were represented in accordance to all studied variables in a 2-dimensional graph by plotting F1 versus F2 (Figure 3.17).

Figure 3.16 – Variables in axes F1 and F2 (72.25%)



*T3-T4 = Average marketable yield increase of T3 and T4

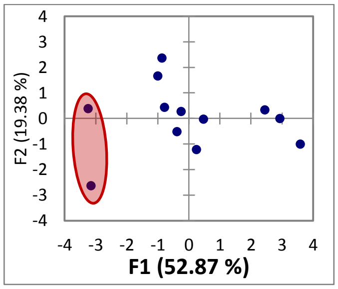
Figure 3.17 – Observations in axes F1 and F2 (72.25%)



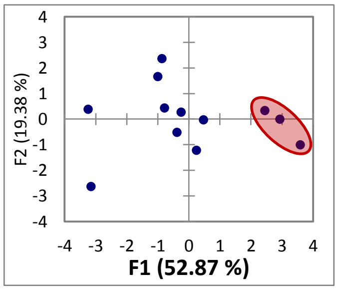
*Each point represents one experimental field site.

PCA results indicate that factor F1 is the best explaining the effect of cross-linked potassium polyacrylate on marketable yield. Based on this result three groups of sites can be distinguished with respect to F1:

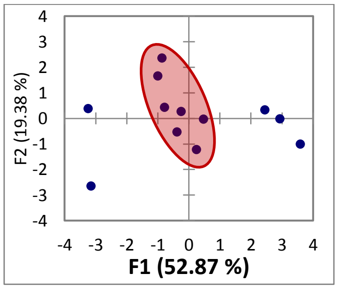
- Sites in the left side of the graph (ES12-01 and ES12-03) are those where the effect of the polymer was the highest. These sites have soils with high content of sand, low clay content and lower CEC and organic matter than the other groups. This group correspond to light-sandy soils.



- Sites in the right side of the graph (IT12-03, IT-02 and ES11-02) are those where the effect of the polymer was the lowest. These sites have soils with high clay content, low sand content and higher CEC and organic matter than the other groups. This group correspond to heavy-clay soils.



- Sites in the centre of the graph (IT11-01, IT12-01, IT11-02, ES11-01, IT11-03, ES11-03 and ES12-02) have intermediate soil properties between the other groups. This groups correspond to medium-loamy soils.

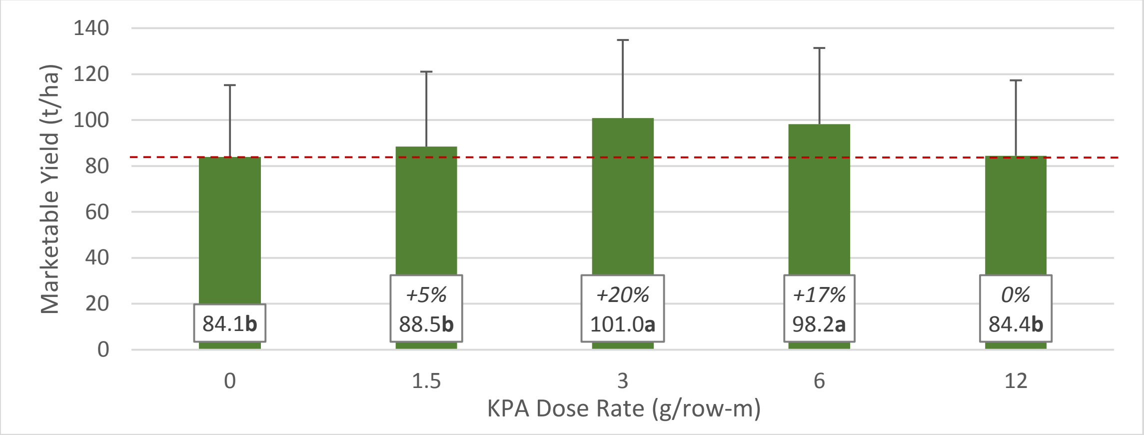


To explain differences between sites based on the factor F2 is questionable due to the low contribution of the yield effect variable (T3-T4) to it. Therefore PCA results suggest that the effect of cross-linked potassium polyacrylate on field sites should be higher the lighter is the soil texture, the lower is the cation exchange capacity and the poorer is the organic matter content of a soil.

3.3.2.3. Yield summaries by soil type.

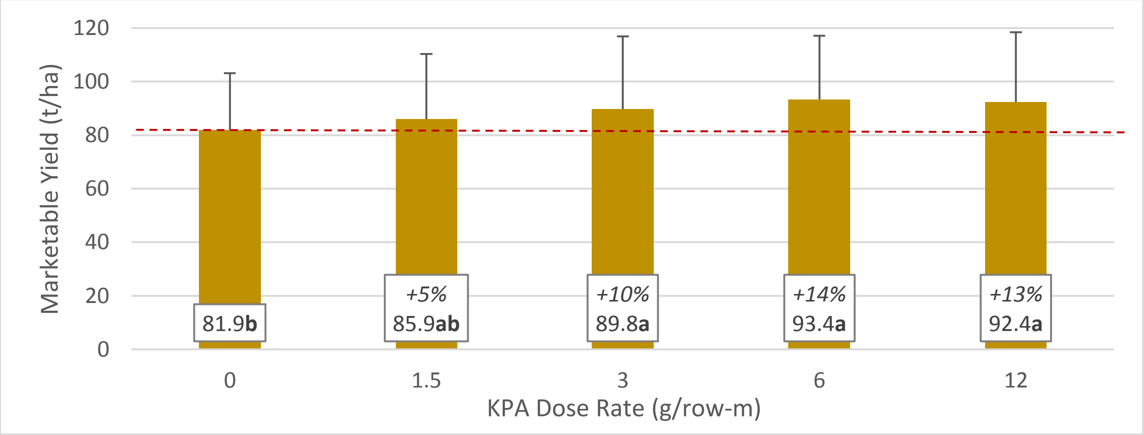
The results from the field trials on marketable yield were summarized by soil types (Figure 3.18 to 3.20) in accordance to outcome of the Pearson´s correlation and PCA analyses. The application of Luquasorb®1280RM on experimental sites with light-sandy soils (Figure 3.18) showed a significant yield increase of 20% and 17% with respect to the untreated control at a dose-rate of 3 and 6 g/row-m respectively. The lowest and the highest dose-rates did not increase significantly the marketable yield.

Figure 3.18 – Summary of marketable yield (t/ha) of experimental sites with light soils (n=2).



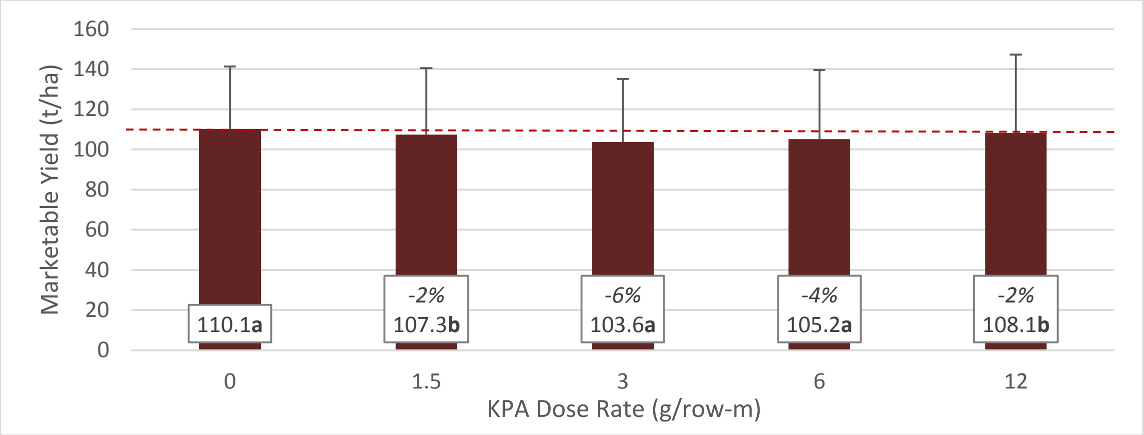
*Error bars represent standard deviation (dispersion between experimental sites). Different letters indicate significant differences between treatments at P ≤ 0.05 by SNK-test. *n= number of sites included in the statistical analysis.

Figure 3.19 – Summary of marketable yield (t/ha) of experimental sites with medium soils (n=7).



*Error bars represent standard deviation (dispersion between experimental sites). Different letters indicate significant differences between treatments at P ≤ 0.05 by SNK-test. *n= number of sites included in the statistical analysis.

Figure 3.20 – Summary of marketable yield (t/ha) of experimental sites with heavysoils (n=3).



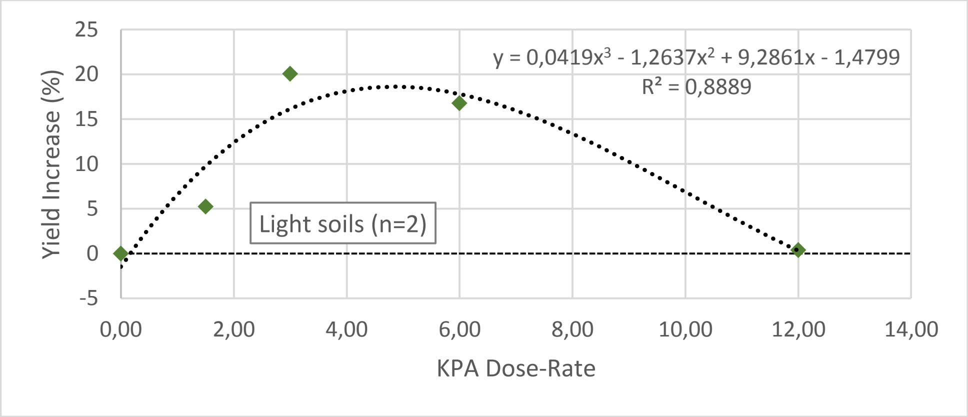
*Error bars represent standard deviation (dispersion between experimental sites). Different letters indicate significant differences between treatments at P ≤ 0.05 by SNK-test. *n= number of sites included in the statistical analysis.

In the case of the experimental sites with medium-loamy soils (Figure 3.19), the application of Luquasorb®1280RM showed a significant increase of marketable yield of 10%, 14% and 13% at applied dose rates of 3, 6 and 12 g/row-m respectively. In the other hand the results on marketable yield in heavy-clay soils (Figure 3.20) did not show any significant difference with respect to the untreated control at any of the applied dose-rates.

The obtained results out of the correlation and PCA analyses, showing a better performance of Luquasorb®1280RM as lighter is the soil, are in alignment to the observation made in the Chapter II. The effectiveness of the product to reduce water losses by evaporation and increase the plant available water was more pronounced in sandy and loamy soils. As well these experimental results supports those obtained by Hüttermann *et al*. (2009) and Agaba (2012) who demonstrated that the effects of using cross-linked potassium polyacrylate as amendment was soil texture dependent being higher in the case of light soils. Furthermore these results confirm the efficacy of applying cross-linked potassium polyacrylate at dose rates between 3 and 6 g/row-m (20-40 kg/ha) localized in furrow. These experimental results supports those obtained by Mao et al. (2011) who used 15-30 kg/ha on corn, Ashkiani *et al*. (2013) who proved significant yield increases at 20 and 40 kg/ha or Islam *et al*., (2011) who demonstrated positive yield increase on corn with application rates between 5 to 15 kg/ha.

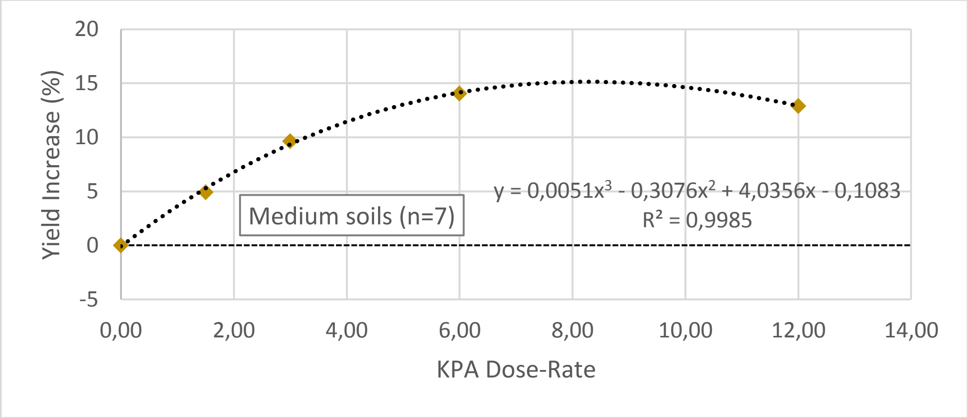
In the light-sandy and medium-loamy soils, where there was a significant effect of the product, the response to the dose-rate was different depending on the soil type (Figure 3.21 and 3.22). The lighter the soil was, the lower was optimal dose-rate to obtain a significant yield increase.

Figure 3.21 – Dose-rate response curves for light soils.



*Linear trends adjusted to a polynomial curve of order 3.

Figure 3.22 – Dose-rate response curves for medium soils.



Linear trends adjusted to a polynomial curve of order 3.

Based on the doses response curves and the previous statistical analyses it could be recommended an application dose-rate of cross-linked potassium polyacrylate between 3 and 6 g/row-m for light-sandy soils and between 6 and 12 g/row-m for medium-loamy soils.

3.3.2.4. Yield effects drivers.

Number of fruits

The difference between treatments on the overall number of average harvested fruits was not significant neither in the total amount nor classified by ripe (marketable), over-ripe or unripe classes (Table 3.10). However it was observed a general numerical trend to increase the number of harvested fruits when treated with cross-linked potassium polyacrylate in all fruit classes.

Table 3.11 – Average number (1000/ha) of harvested ripe, unripe and over-ripe tomatoes of all sites (n=12).

Fruit Class	0 g/row-m	1.5 g/row-m		3 g/row-m		6 g/row-m		12 g/row-m	
	Number (1000/ha)	Number (1000/ha)	Inc. (%)	Number (1000/ha)	Inc. (%)	Number (1000/ha)	Inc. (%)	Number (1000/ha)	Inc. (%)
Over-ripe	132.36a	133.5a	+1	134.8a	+2	141.3a	+7	136.0a	+3
Unripe	321.3a	364.4a	+13	365.8a	+14	345.76a	+8	336.7a	+5
Marketable	1473.6a	1496.0a	+2	1558.5a	+6	1560.3a	+6	1527.1a	+4

*Inc.(%) = Relative difference to the control. Different letters indicate significant differences between rows at P ≤ 0.05 by SNK-test.

Detailed results and statistics on harvested fruits by classes for each experimental site are shown in Annex III, (Figures AIII.8-AIII.9). Statistical differences between treatments were found in the experimental sites IT11-02, IT11-03 for all fruit classes and in the experimental site ES12-01 only in the case of unripe fruits.

Weight per fruit

The results of the calculation of the weight of per harvested fruit for all the experimental sites (n=12) and only for the sites with light and medium soils are shown in the Tables 3.12 and 3.13.

Table 3.12 – Summary of the calculated weight per fruit (g/fruit) of all experimental sites (n=12).

Fruits	0 g/row-m		1.5 g/row-m		3 g/row-m		6 g/row-m		12 g/row-m	
	g/fruit	SD	g/fruit	SD	g/fruit	SD	g/fruit	SD	g/fruit	SD
Over-ripe	47.9a	8.95	50.3a	10.8	57.3a	6.3	53.3a	7.9	55.2a	13.7
Unripe	39.1a	7.5	40.1a	4.2	40.4a	8.6	40.6a	8.6	40.3a	6.7
Marketable	63.7a	8.5	63.7a	6.9	64.6a	7.5	65.8a	9.5	63.8a	7.8

*SD = standard deviation. Different letters indicate significant differences between rows at P ≤ 0.05 by SNK-test.

Table 3.13 – Summary of the calculated weight per fruit (g/fruit) of the sites with light and medium soils (n=9).

Fruits	0 g/row-m		1.5 g/row-m		3 g/row-m		6 g/row-m		12 g/row-m	
	g/fruit	SD	g/fruit	SD	g/fruit	SD	g/fruit	SD	g/fruit	SD
Over-ripe	45.6a	13.5	48.9a	10.6	58.9a	24.7	52.2a	22.1	52.7a	21.4
Unripe	41.2a	10.7	42.7a	13.5	42.4a	11.8	43.3a	12.9	43.6a	12.8
Marketable	62.8b	11.5	62.6b	8.9	64.6ab	11.8	66.9a	12.2	64.4ab	9.6

*SD = standard deviation. Different letters indicate significant differences between rows at P ≤ 0.05 by SNK-test.

No statistical significant differences were shown when summarizing all the experimental sites together. The majority of the experimental sites did not show significant differences between treatments (Annex III. Table AIII.x) with the exception of the site IT12-03. However some clear trends were found to increase the weight per fruit in many of the sites resulting in significant differences of marketable fruits when summarizing the results excluding the experimental sites with heavy soils (Table 3.9).

These results suggests that marketable yield increase caused by the application of Luquasorb®1280RM is driven by the combination of two effects: higher weight per fruit in the case of marketable yield (ripe fruits) and the increased number of harvested fruits. In alignment to these observations, Johnson and Piper (1991) and Maboko (2006) reported that the application of different superabsorbent polymers significantly increased number and mass of tomato fruits grown in sandy soils.

3.3.3. Effects of KPA on fruit quality of processing tomato

Degrees Brix

The results of the measurements of soluble solids content (sugars concentration) on the marketable fruits are shown in the Table 3.14. Only one of the sites (IT11-03) showed significant differences between treatments. When the results were summarized for the analysis by soil types it was observed a significant increase of sugar concentration (%) at the applied dose-rate of 3 g/row-m compared to the untreated control in the sites with medium soils (Table 3.15). Even so differences between treatments were relatively small.

Table 3.14– Degrees Brix of the marketable fruits from all the experimental sites.

Fruits	0 g/row-m		1.5 g/row-m		3 g/row-m		6 g/row-m		12 g/row-m	
	°Brix	SD	°Brix	SD	°Brix	SD	°Brix	SD	°Brix	SD
ES11-01	4.21a	0.23	4.13a	0.38	4.31a	0.26	4.01a	0.24	4.00a	0.22
ES11-02	4.37a	0.41	4.50a	0.37	4.30a	0.28	4.23a	0.37	4.37a	0.29
ES11-03	3.85a	0.23	4.13a	0.12	3.97a	0.27	3.90a	0.11	3.92a	0.26
IT11-01	3.95a	0.10	4.03a	0.24	4.08a	0.08	4.03a	0.15	4.05a	0.19
IT11-02	5.07a	0.22	5.25a	0.16	5.32a	0.12	5.25a	0.23	5.30a	0.23
IT11-03	4.85b	0.05	5.28a	0.15	5.27a	0.27	5.17a	0.10	5.15a	0.12
ES12-01	4.63a	0.19	4.71a	0.09	4.48a	0.36	4.85a	0.17	5.09a	0.46
ES12-02	5.67a	0.41	5.55a	0.31	5.78a	0.64	5.70a	0.84	5.60a	0.89
ES12-03	4.40a	0.24	4.24a	0.52	4.30a	0.35	3.97a	0.29	4.00a	0.24
IT12-01	4.09a	0.28	4.11a	0.10	4.12a	0.17	4.20a	0.20	4.05a	0.17
IT12-02	5.01a	1.31	4.75a	0.42	4.70a	0.37	4.57a	0.43	4.56a	0.57
IT12-03	4.32a	0.18	4.38a	0.22	4.50a	0.30	4.47a	0.35	4.48a	0.26
Average (n=12)	4.53a	0.53	4.59a	0.52	4.62a	0.57	4.53a	0.59	4.55a	0.59

*SD = standard deviation. Different letters indicate significant differences between rows at P ≤ 0.05 by SNK-test. *n= number of sites.

Table 3.15 – Degrees Brix of the marketable fruits analyzed by soil type.

Soil Strength	0 g/row-m		1.5 g/row-m		3 g/row-m		6 g/row-m		12 g/row-m	
	°Brix	SD	°Brix	SD	°Brix	SD	°Brix	SD	°Brix	SD
Light (n=2)	4.52a	0.16	4.47a	0.33	4.57a	0.38	4.41a	0.62	4.55a	0.77
Medium (n=7)	4.53b	0.68	4.64ab	0.68	4.69a	0.74	4.61ab	0.74	4.58ab	0.73
Heavy (n=3)	4.57a	0.39	4.55a	0.19	4.50a	0.20	4.42a	0.17	4.47a	0.10

*SD = standard deviation. Different letters indicate significant differences between rows at P ≤ 0.05 by SNK-test. *n= number of sites.

In alignment to these experimental results, Maboko (2006) reported no significant effects on degrees Brix in sandy soils on tomato treated with two different superabsorbent polymers at two different dose-rates.

3.3. SUMMARY OF CHAPTER III

The conclusions obtained out of the experimental results from this chapter which main target was to evaluate the response of processing tomato (*Solanum lycopersicum* L.) to the application of cross-linked potassium polyacrylate (Luquasorb®1280RM) under field conditions, are summarised as follows:

Plant growth parameters

- The application of cross-linked potassium polyacrylate as soil amendment supported the crop establishment on transplanted tomatoes improving the survival rate of seedlings under crop limiting environmental conditions.

- The use of cross-linked potassium polyacrylate as soil conditioner under field conditions did not visually improve the overall crop vigor of processing tomatoes along the crop cycle. However it significantly increased plant height by 3% at applied dose rates of 3 and 6 g/row-m of cross-linked potassium polyacrylate.

Production yield parameters

- The application of cross-linked potassium polyacrylate improved the overall yield of processing tomatoes at a dose rates of 3 and 6 g/row-m driven by a significant increase of marketable yield (ripe fruits). Non marketable yields (over-ripe and green fruits) were not significantly affected by the application of the polymer.

- Correlation and PCA analyses indicated that that the positive effect of cross-linked potassium polyacrylate on marketable yields of processing tomato was higher on field-sites as lighter was the soil texture (light>medium>heavy), lower is the cation exchange capacity (CEC) and lower the of content organic matter.

- The effect on marketable yield by applying cross-linked potassium polyacrylate as soil amendment on processing tomato under field conditions was significant in light-sandy soils by 20 and 17% at 3 and 6 g/row-m respectively. Furthermore it was significantly increased in medium-loamy soils by 10, 14 and 13% at applied dose rates of 3, 6 and 12 g/row-m respectively while no effects on marketable yield were observed in the case of heavy-clay soils.

- The adjusted dose-rate response curves for cross-linked potassium polyacrylate indicated an optimal application rate between 3 and 6 g/row-m in the case of light-sandy soils and between 6 and 12 g/row-m in the case of medium-loamy soils.

- The principal observed drivers of the marketable yield increase on processing tomato when cross-linked potassium polyacrylate was applied as soil amendment in light-sandy and medium-loamy soils were the increasing number of fruits and the higher weight per fruits (mass).

Fruit quality parameters

- The application of cross-linked potassium polyacrylate on processing tomatoes grown under field conditions did not positively or negatively affect the concentration of soluble sugars (°Brix) of the marketable fruits and therefore production quality was not altered.

As an overall conclusion it can be said that; the observed positive effects on growth and yield of processing tomato varieties grown under field conditions due to the application of cross-linked potassium polyacrylate (Luquasorb®1280RM), when it was used at economically affordable dose-rates, position this superabsorbent polymer as a soil amendment of high interest for general agricultural purposes. The expansion to other crops of economical relevance under different climate environments as well as the study of the interaction of these amendments with nutrients under field conditions might be of interest to complement the results from this study.

CHAPTER IV

GENERAL DISCUSSION

GENERAL DISCUSSION

Characterization of Luquasorb®1280R as a superabsorbent polymer

The quantification of the absorption capacity of the three studied granulometries of cross-linked potassium polyacrylate (Luquasorb®1280R) resulted on values fitting to the existing definitions of superabsorbent polymers (Zohuriaan-Mehr and Kabiri, 2008). The free swelling capacity (FSC) average values of the three granulometries were 280 g/g and 329 g/g quantified by the filtration and the oven methods respectively. Furthermore the polymer was able to absorb water from the atmospheric humidity when the relative humidity was equal or higher than 63%.

The absorption speed was significantly higher the smaller was the granule size distribution of the polymer what can be explained by a larger surface area of the smallest particles (Casquilho *et al*., 2013; Das and Pourdeyhimi, 2014). The smallest, medium and biggest granules needed 5, 10 and 60 minutes respectively to reach the same swelling capacity. In contradiction, the drying speed of the polymer, highly influenced by the temperature, was slightly higher in the case of the biggest granule size distribution followed by the medium and the smallest. This contradiction might be explained by a higher internal pressure in biggest gel particles. While water evaporates from the surface of the granules the diffusion of water from the core of the gel to the outside should be accelerated (Wack and Ulbricht, 2007). In addition to that, the lower concentration of surface cross-linkers on bigger particles, coming from the last production process step, might facilitate the diffusion, and therefore evaporation of water, in comparison to smaller particles.

In alignment to the knowledge that SAPs swelling ability might be limited by the application of certain pressure (Zohuriaan-Mehr *et al*., 2008) Luquasorb®1280R did show same restrictions. The RS, RM and RL granulometries of the polymer reached a minimum swelling capacity at approximately 10 cm depth within a soil column filled with silica sand (0.350 kg of pressure). Differences between granulometries were found and explained by the different ability of the granules to expand and accommodating water molecules within the system, being RL more sensitive to pressure followed by RS and RM. Furthermore, Luquasorb®1280R absorption capacity was limited by the presence of monovalent or multivalent ions in alignment to several publications (Bowman *et al*., 1990; Chatzoudis and Rigas, 1999; Taban and Naeini, 2006; Bo *et al*., 2012). The reduction of the swelling capacity of Luquasorb®1280R was more pronounce the higher was the concentration of the ions and the higher was the charge of the dissolved cations. After different absorption-desorption cycles in the presence of monovalent and divalent cations it was observed an inhibition of the expansion of the polymer, demonstrating that multivalent cations can interact with the polymer net performing as cross-linkers. In the other hand, cross-linked potassium polyacrylate (Luquasorb®1280R) did maintain its swelling properties after repeated absorption-desorption cycles combined with thermal stress cycles of low (-20°C) and high temperatures (105°C) complementing the findings of Bai *et al*. (2013) who reported similar results at 50, 25 and -4°C.

Overall it can be said that the characterized swelling/absorption properties of cross-linked potassium polyacrylate (Luquasorb®1280R) fit within the expected profile of a classical anionic superabsorbent polymer from the water absorption point of view.

Characterization of Luquasorb®1280R as cation exchanger

The content of soluble and chemically linked potassium within the polymer (Luquasorb®1280R) was quantified. As average values of all granule size distributions, the measured content of soluble and exchangeable potassium in the polymer were 256 mg/g and 402 mg/g quantified from dry and swollen status. The analyzed potassium content was higher than the theoretical maximum content based on the molecular formula or potassium polyacrylate (354 mg/g). This might be explained by a combination of analytical error with a residual content of non-reacted KOH in the final product. In any case, the plant available potassium might be of high interest from the crop establishment point of view. The known role of this macro nutrient in the osmoregulation and improvement of abiotic stress tolerance in plants (Marschner, 2012) might help crops to better establish under critical environmental conditions.

Furthermore the total cation exchange capacity of the polymer was 795, 798 and 858 meq/100g for the granulometries RS, RM and RL respectively. Based on the CEC values given by Rowell 1993 of other materials like clay (4-60 meq/100g), vermiculite (100-150 meq/100g) or organic matter (130-500 meq/100g), it can be considered that Luquasorb®1280R has a remarkable high cation exchange capacity. The lower surface cross-linker concentration expected in the RL granulometry in comparison to RM and RL, coming from the final conditioning step in production, might explain the significant higher CEC by facilitating mobility of cations.

With regards the kinetics of exchange, the velocity was influenced by the concentration and the ionic strength of the exchanged cations. Furthermore cross-linked potassium polyacrylate (Luquasorb®1280R) showed a cation exchange selectivity independent to the granule size distribution with the following affinity ($Mn^{2+} > Zn^{2+}, Mg^{2+}$) > ($Fe^{3+}, Cu^{2+}$) > $Ca^{2+} > Na^{+}$. However when those cations were exchanged they bounded to the polymer with different strength, being difficult to be re-exchanged. By order of decreasing bounding strength the cations can be listed as follows: $Fe^{3+} > Zn^{2+} > Cu^{2+} > Mn^{2+} > Mg^{2+} > Ca^{2+} > Na^{+}$.

The cation exchange properties of Luquasorb®1280R were affected by the swelling status of the polymer at the moment of the exchange and the concentration of surface cross-linkers. The higher is the swelling of the polymer and the lower is the concentration of surface cross-linkers, the easier is the mobility of a cation to go in and out of the gel. Therefore the easier an exchange is plausible. Based on this, swelling limiting factors might have an impact on the nutrient retention and release properties of Luquasorb®1280R. Knowing this and the ability of multivalent cations to perform like cross-linkers it might be expected a reduction of performance of the polymer over time by collapsing the structure. Then the polymer would not be able to exchange cations anymore and it would dramatically reduce its water absorption capacity.

Despite the characterized limiting factors to the cation exchange properties, the use of cross-linked potassium polyacrylate might potentially increase the nutrient absorption efficiency under agronomical practices, at least during the crop establishment of a crop, in alignment with the claims of Wu *et al*. (2008), Mao *et al*. (2011) and Parvathy *et al*. (2014).

Luquasorb®1280R as improver of soil properties

The addition of cross-linked potassium polyacrylate (Luquasorb®1280R) to different soils resulted in two different effect on the pH. On one hand the increasing concentration of polymer buffered the pH to 7. In the other hand, the addition of the polymer acidified the soil in the presence of $CaCl_2$. The buffer effect of the polymer might be explain by its composition including acid and saline groups. In one hand, under alkaline soil conditions the polymer might retain cations and release protons reducing the pH of the media. In the other hand, under acid soils conditions the polymer might absorb protons by exchange with potassium increasing the pH of the media. In addition the effects on electric conductivity were studied. The addition of cross-linked potassium polyacrylate did increase electric conductivity. As expected the addition of the polymer, which is a potassium salt, increase salinity of the media and therefore electric conductivity.

With regards hydric properties of soils, the application of cross-linked potassium polyacrylate (Luquasorb®1280R), at dose-rates between 0.2 and 0.4% w/w, reduced water losses by evaporation preserving water longer in the soils. These results were in alignment to the studies of Bakass *et al*. (2002) and Casquilho *et al*. (2013). Furthermore it was demonstrated an increased water holding capacity and improved content of plant available water of soils when amended with cross-linked potassium polyacrylate (Luquasorb®1280R). These observations were in alignment to those of Huttermann *et al*. 2009 and Agaba (2012) who worked with the same polymer. It was also clarified that this effects are more pronounced in the case of sandy/light soils, followed by loamy/medium soils and very little in the case of clay/heavy soils. The obtained results clearly show the benefits on the general hydric properties of soils by applying cross-linked potassium polyacrylate (Luquasorb®1280R) at the studied dose-rates. Overall it can be said that cross-linked potassium polyacrylate (Luquasorb®1280R), applied at dose rated of 0.2% and 0.4% w/w, can be a highly recommended amendment for light/sandy substrates or soils with the purpose of improving the overall hydric properties.

Luquasorb®1280R as plant growth and yield enhancer

In one of the field experimental sites where some plant were lost after transplanting due to natural reasons, processing tomato (*Solanum lycopersicum* L.) plots treated with cross-linked potassium polyacrylate (Luquasorb®1280R) significantly maintained the plant population density. This buffering effect might be attributed to a better seedling establishment under unfavorable environmental conditions which has been reported by Woodhouse and Jonson (1991), Huttermann *et al*. (2009) and Ashkiani *et al*. (2013).

Despite differences on plant vigor were difficult to be observed on the field, it was possible to quantify differences when plant height was numerically measured. In alignment to several authors who reported better plant growth of different crops such as corn or soybean under field conditions (Knypl and Knypl, 1993; Abd El-Rehim, 2004; Chut *et al*., 2006; Lentz and Sojka, 2009; Mao *et al*., 2011), the application of the studied polymer significantly increased in average plant height of processing tomatoes (*Solanum lycopersicum* L.) by 3% at dose-rates of 3 and 6 g/row-m (20 – 40 kg/ha) when plant growth stage was 53-54 in the BBCH-scale.

The effects on marketable yield of processing tomato (*Solanum lycopersicum* L.) caused by the treatment of the crop with the studied polymer can be split by soil types if classifying them in light-sandy, medium-loamy and heavy-clay soils. Cross-linked potassium polyacrylate (Luquasorb®1280R) increased marketable yield by 20% and 17% in light-sandy soils when it was applied at 3 and 6 g/row-m (20 – 40 kg/ha) respectively and by 10%, 14% and 13% in medium-loamy soil when applied at 3, 6 and 12 g/row-m (20, 40 and 80 kg/ha) respectively. No significant yield increase effects were observed in the case of heavy-clay soils. In alignment to the experimental results obtained in this work and those reported by Hüttermann *et al*. (2009) and Agaba (2012) the effects of the studied polymer as amendment are soil texture dependent being more pronounced in light-sandy soils. Considering the polymer properties to work as water reservoir and cation exchanger, the obtained results fit to the known properties of light-sandy, medium-loamy and heavy-clay soils. The lighter is a soil the lower is the ability of that soil to retain water, the higher are the evaporation losses and the lower is the ability to retain nutrients. Therefore the effects of applying cross-linked potassium polyacrylate (Luquasorb®1280) are potentially higher on this type of soil.

The positive effect of the tested dose-rates of polymer (3 and 6 g/row-m) which are equivalent to 20 and 40 kg/ha and were applied in a localized way in the planting line, confirm the efficacy of using economically affordable rates under field conditions. This was already proven in tomato (Maboko, 2006) and other crops like corn (Islam *et al*., 2011; Mao *et al*., 2011) or wheat (Ashkiani *et al*., 2013). Based on the experimental results of the trial series the potential dose rate recommendation for light-sandy soils would be between 3 and 6 g/row-m (20 – 40 kg/ha) while for medium-loamy soils would be between 6 and 12 g/row-m (40 – 80 kg/ha).

Overall it can be said that the application of cross-linked potassium polyacrylate (Luquasorb®1280R) under field conditions, at dose-rates between 3 and 6 g/row-m, improved crop establishment, plant growth and marketable yield of processing tomato varieties (*Solanum lycopersicum* L.) complementing the observations made on this crop by Johnson and Piper (1991) and Maboko (2006).

Luquaosorb®1280R mechanism of action under field conditions.

Generally the application of superabsorbent polymers to agricultural systems is associated to the idea of increasing the water retention capacity of soils and substrates. Due to the ability to absorb large amounts of water these type of polymers might play the role of water reservoirs in the soil releasing when needed the absorbed water to the plants. This mechanism of action has been proven in this thesis by mixing cross-linked potassium polyacrylate (Luquasorb®1280R) with the soil at dose-rates between 0.2% and 0.4% w/w. This would mean that for the activation of this mechanism under field conditions it would be necessary to apply between 2000 and 4000 kg/ha of polymer if we assume, in a conservative way, the mixing of the polymer with a soil layer of 10 cm depth and a soil density of 1 kg/l. It seems reasonable to think that the application of these amounts under field conditions are difficult to be approached neither from the economical nor the application technology point of view.

However it has been demonstrated positive effect on crops grown under field conditions when applying superabsorbent polymers at much lower dose-rates. This study showed effects on crop establishment, plant growth and marketable yield of processing tomatoes (*Solanum lycopersicum* L.) using dose rates equivalent to 20 and 40 kg/ha applied in-furrow closed to the planting line.

Considering the application of 3 and 6 g/row-m and an absorption capacity of the polymer of 280 g/g, it would mean an extra water holding capacity of 0.56 and 1.12 L/m^2 respectively under ideal conditions. However it has been demonstrated that the absorption capacity of the polymer is affected by the application of pressure. In this way it can be assumed that the granules reduced their swelling capacity to approximately 30% of its maximum when applied at 10 to 15 cm below the soil surface. Furthermore it is known that the presence of soluble ions reduced as well the swelling capacity of the polymer. Being conservative it can be assumed an extra reduction of its swelling properties by 5% considering a low salinity environment. Therefore if it is recalculated, the application of cross-linked potassium polyacrylate (Luquasorb®1280R) in furrow, at 10-15 cm below the soil surface, under low salinity conditions at 3 and 6 g/row-m, would mean and extra water holding capacity of 0.14 and 0.28 L/m^2 respectively. Considering that the water necessary to produce 1 kg of tomatoes was estimated in 214 liters by Mekonnen and Hoekstra (2011) and that the average marketable production yield obtained in this study was of 90 t/ha, the increase of 0.14 or 0.28 liters per square meter can be considered negligible.

Furthermore, field experimental trials showed positive effects on marketable yield even under best local agronomical practices without water deficiencies. However, crops grown under field conditions have always to cope with unpredictable cycles of environmental changes. Abiotic stress events such as wind, heat, cold, water excess or irrigation deficiencies under high atmospheric demand cannot be controlled under field conditions. These natural phenomena affect the capacity of crops to reach their maximum yield potential.

Previously discussed results and estimations suggest that the mechanisms of action involved in the positive effects of applying this type of polymers, at economically feasible dose rates under field conditions, goes beyond the impact on the hydric properties of soils. In one hand, the studied properties of cross-linked potassium polyacrylate as cation exchanger in this thesis, the interaction with macro and micro nutrients (Chen *et al*., 2014) and the improvement of fertilizers use efficiency (Mao *et al*., 2011), should be considered as a possible mechanism of action in future studies. In the other hand, another possible and not properly explored mechanism of action might be the impact on beneficial soil microorganisms (Parvathy *et al*., 2014) which should be as well considered in future research with regards the application of superabsorbent polymers as soil amendments. Most probably a combination of the previously described effects together with other not yet explored might be the explanation to the results of this study demonstrating that cross-linked potassium polyacrylate might help crops to grow healthier and better overcome natural abiotic stress events under field conditions reducing the gap to their maximum yield potential.

CHAPTER V

GENERAL CONCLUSIONS

GENERAL CONCLUSIONS

Based on the presented hypothesis and objectives, the obtained experimental results and the specific conclusions from chapters II and III of this doctoral thesis, the following general conclusions can be made:

1. The intrinsic characteristics of cross-linked potassium polyacrylate (Luquasorb®1280R) associated to its water absorption ability and its outstanding cation exchange capacity, convert this polymer a priori into a highly appealing soil amendment for agricultural systems. When it is applied in soils with poor hydric properties at the right concentration, cross-linked potassium polyacrylate increases the water holding capacity and reduce water losses by evaporation enhancing plant available water.

2. The application of pressure, the presence of ions in the media and concentration of surface cross-linker have a remarkable influence on the swelling and drying properties of cross-linked potassium polyacrylate (Luquasorb®1280R) which as the same time influence the ability to exchange cations. Consequently these restricting parameters must be taken into account for future development of improved superabsorbent polymer for agricultural purposes.

3. Despite this concept was not deeply studied within this thesis, the ability of cross-linked potassium polyacrylate (Luquasorb®1280R) to interact with cationic forms of macro and micro-nutrients opens the potential application of these polymers in combination with fertilizers in order to improve plant nutrition efficiency. Furthermore the addition of different counter cations in the design of more advanced superabsorbent polymers for agricultural purposes must be considered.

4. The application of cross-linked potassium polyacrylate (Luquasorb®1280R) at economically feasible dose-rates (20-40 kg/ha) to field processing tomato varieties

(*Solanum lycopersicum* L.) supports crop establishment, enhance plant growth and increase marketable yield especially in light-sandy and medium-loamy soils. These remarkable benefits would heavily justify the use of cross-linked potassium polyacrylate (Luquasorb®1280R) as agricultural amendment from the economical point of view within the processing tomato agronomic practices in the Mediterranean area.

5. The mechanisms of activity of cross-linked potassium polyacrylate (Luquasorb®1280R) under field conditions goes certainly beyond purely water absorption. The localized humidity together with the ability to retain and release nutrients might potentially impact positively the soil microbiota. The interaction between water, nutrients and micro-organisms with the plant root system could support crops to better overcome adverse environmental conditions.

6. The studied characteristics and effects of cross-linked potassium polyacrylate (Luquasorb®1280R) as soil amendment could be of large socioeconomic importance in future implementation of sustainable agronomic practices with respect to the need of increasing yields within restricted agricultural lands.

FINAL REMARKS

Based on the findings and conclusions it would be of interest to further investigate the following areas to complement the results of this thesis:

- Understanding the degradation of the cross-linked potassium polyacrylate in soil.
- Study the effects on cation exchange capacity and nutrient dynamics on soils amended with cross-linked potassium polyacrylate.
- Understanding the interaction of cross-linked potassium polyacrylate with fertilizers and fertigation systems under field conditions.
- Study the effects on soil microbiology communities of soils amended with cross-linked potassium polyacrylate.

CONCLUSIONES GENERALES

De acuerdo con la hipótesis y objetivos planteados, con los resultados experimentales obtenidos y con las conclusiones específicas de los capítulos II y III de esta tesis doctoral, se pueden establecer las siguientes conclusiones generales:

1. Las propiedades intrínsecas del poliacrilato potásico entrecruzado (Luquasorb®1280R) asociadas a su capacidad de absorción y su extraordinaria capacidad de intercambio catiónico, hacen a priori de este polímero una atractiva enmienda agrícola. Cuando se aplica en la concentración apropiada a suelos con propiedades hídricas limitadas, el poliacrilato potásico entrecruzado aumenta la capacidad de retención de agua, reduce la pérdida por evaporación y mejora la disponibilidad de agua para las plantas.

2. La aplicación de presión, la presencia de iones en el medio y la concentración de entrecruzante superficial de las partículas influyen notablemente en las propiedades de hinchamiento y secado del poliacrilato potásico entrecruzado (Luquasorb®1280R), lo cual afecta al mismo tiempo a su capacidad de intercambiar cationes. Por consecuencia estos parámetros limitantes deben ser tenidos en cuenta a la hora de desarrollar futuros polímeros superabsorbentes con finalidad agrícola.

3. A pesar de que este concepto no ha sido estudiado en profundidad en esta tesis, la capacidad del poliacrilato potásico entrecruzado (Luquasorb®1280R) para interactuar con formas catiónicas de macro y micronutrientes abren un nuevo campo de aplicación de estos polímero en combinación con fertilizantes con el propósito de mejorar su eficacia. Además, debe tenerse en cuenta la posibilidad de incluir diferentes cationes en el futuro diseño de polímeros superabsorbentes para agricultura.

4. La utilización de poliacrilato potásico entrecruzado (Luquasorb®1280R) en dosis de aplicación económicamente viables, bajo condiciones de campo en variedades de tomate de industria (*Solanum lycopersicum* L.), mejora el establecimiento del cultivo,

favorece el crecimiento de las plantas y aumenta la cosecha comercial especialmente en suelos ligeros-arenosos e intermedios-francos. Estos beneficios justifican ampliamente el uso de poliacrilato potásico entrecruzado (Luquasorb®1280R) como enmienda agrícola desde el punto de vista económico y dentro de las prácticas agrícolas de la zona Mediterránea en tomate de industria.

5. Los mecanismos de acción del poliacrilato potásico entrecruzado (Luquasorb®1280R) aplicado bajo condiciones de campo, van claramente más allá de la mera capacidad de absorción de agua. La concentración de humedad localizada junto con la capacidad de retener y liberar nutrientes podría tener un impacto positivo en la microbiota del suelo. La interacción entre agua, nutrientes y micro-organismos con el sistema radicular de las plantas podría ayudar a los cultivos a resistir mejor condiciones medioambientales adversas.

6. Las características y efectos estudiados del poliacrilato potásico entrecruzado (Luquasorb®1280R) como enmienda de suelo podrían ser de enorme importancia socioeconómica en la futura implantación de prácticas sostenibles relacionadas con la necesidad de incrementar las cosechas dentro de zonas agrícolas limitadas.

COMENTARIOS FINALES

En base a los hallazgos y conclusiones de este trabajo, sería de interés el estudio de las siguientes áreas como complemento a los resultados de esta tesis doctoral:

- Entender la degradación de poliacrilato potásico entrecruzado en suelos.
- Estudiar los efectos en la capacidad de intercambio catiónico y la dinámica de nutrientes en suelos enmendados con poliacrilato potásico entrecruzado.
- Entender la interacción del poliacrilato potásico entrecruzado con fertilizantes y sistemas de fertirrigación bajo condiciones de campo.
- Estudiar los efectos en comunidades de microorganismos en suelos enmendados con poliacrilato potásico entrecruzado.

CHAPTER 6

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ANNEX I

Properties and analytics of materials, substrates and soils

Table AI.1 - Typical physicochemical properties of Luquasorb®1280R measured for hygiene purposes using the EDANA (International associations of the nonwovens and related industries) official analysis methods.

Property	®1280RS	®1280RM	®1280RL
Centrifuge water retention capacity (g/g) – NaCl 0.9%	29	32	28
pH (5g/l NaCl 0.9%)	5.5 – 6.5	5.5 – 6.5	5.5 – 6.5
Apparent specific gravity	approx. 0.6	approx. 0.6	approx. 0.6
Vortex test (sec) – swelling velocity	<17	<30	< 90
Residual Monomers (ppm)	<400	<400	< 400

**Data source: BASF Care Chemicals division.*

Table AI.2 – Chemical analysis of the silica sand from the company Sales del Centro S.L.

Compound	Silica sand (Sales del Centro S.L.)
Silica SiO_2 (%)	99.51
Aluminium oxide Al_2O_3 (%)	0.26
Iron oxide Fe_2O_3 (%)	0.05
Potassium oxide K_2O (%)	0.04
Calcium oxide CaO (%)	0.02
Titanium oxide TiO_2 (%)	0.02
Sodium oxide Na_2O (%)	0.01
Losses by calcination (%)	0.05

**Data source: Sales del Centro S.L.*

Table AI.3 – Comparative table of physicochemical properties of the sandy, loamy and clay soils from Utrera, El Coronil and Maribañez (Seville, Spain) used in some of the tests of chapter II.

Parameters	Soil 1 Utrera	Soil 2 Coronil	Soil 3 Maribañez
Physical properties			
Clay (%)	5	29	50
Silt (%)	10	14	16
Sand (%)	85	57	33
USDA texture classification	Loamy sand	Sandy clay loam	Clay
Chemical properties			
pH	7.15	8.31	8.22
EC – Electric conductivity (µS/cm)	177.1	190.4	450
$CaCO_3$ (%)	< 0.5	3.18	8.78
Organic matter (%)	0.78	1.78	1.4
Nitrogen (mg/kg)	415.2	1130.9	920.6
Available phosphorus (meq/100g)	237.14	46.28	38.7
Available calcium (meq/100g)	2.84	17.34	16.9
Available magnesium (meq/100g)	0.53	1.1	1.6
Available potassium (meq/100g)	0.49	1.58	0.2
Available sodium (meq/100g)	0.41	0.44	3.9

**Data source: Soil analyses database ARS Utrera, BASF*

Table AI.4 – Properties of the teabags material used in some of the experiments.

Specified Property	Units	Value
Basis weight	g/m^2	16.5
Dry tensile (machine direction MD)	N/m	630
Dry tensile (cross direction CD)	N/m	190
Wet tensile (cross direction CD)	N/m	70
Moisture	%	6
Delamination	mN	300

**Data source: PTG Unionpack Lohnabfüllung GmbH*

Table AI.5 – Solutions used for the measurement of SAP hygroscopicity.

Compound	Humidity obtained (%)
Calcium chloride $CaCl_2$ (saturated)	35
Ammonium nitrate NH_4NO_3 (saturated)	63
Potassium chloride KCl (saturated)	86
Distilled H_2O	100

Table AI.6 – Salts used for the evaluation of their effect on swelling capacity of KPA.

Compound	Cation	Ion
Sodium Chloride - NaCl	Na^+	Cl^-
Calcium Chloride - $CaCl_2$	Ca^{2+}	Cl^-
Iron Chloride 3 - $FeCl_3$	Fe^{3+}	Cl^-

Table AI.7 – Technical data of the soluble commercial fertilizers Hakaphos®Naranja and Hakaphos®Verde.

Compound	Hakaphos®Naranja	Hakaphos®Verde
Total Nitrogen (N)	15.0%	15.0%
Nitrate Nitrogen (NO_3-N)	10.2%	11.0%
Ammonium Nitrogen (NH_4-N)	4.8%	4.0%
Urea Nitrogen (NH_2-N)	-	-
Phosphorous (P_2O_5)	5.0%	10.0%
Potassium (K_2O)	30.0%	15.0%
Calcium (CaO)	-	-
Magnesium (MgO)	1.3%	2.0%
Sufur (SO_3)	9.0%	30.0%
Boron (B)	0.010%	0.010%
Copper (Cu)	0.020%	0.020%
Iron (Fe)	0.050%	0.050%
Manganese (Mn)	0.050%	0.050%
Molybdenum (Mo)	0.001%	0.001%
Zinc (Zn)	0.020%	0.020%
Color	Orange	Green
Density	1.1 g/L	-

**Data source: COMPO GmbH & Co. KG*

Table AI.8 – Salts used in the test for describing exchange kinetics of cross-linked potassium polyacrylate.

Compound	Grams of salt = 1.5 meq of cation.	Cation	Ion
Sodium Chloride – $NaCl$	0.0877	Na^+	Cl^-
Calcium Chloride – $CaCl_2$	0.0832	Ca^{2+}	Cl^-

Table AI.9 – Salts used in the test for evaluation cation selectivity of cross-linked potassium polyacrylate.

Compound	Grams of salt = 0.5 meq of cation.	Cation	Ion
Sodium Nitrate – $NaNO_3$		Na^+	NO_3^-
Calcium Nitrate – $Ca(NO_3)_2$		Ca^{2+}	NO_3^-
Zinc Sulphate – $ZnSO_4$		Zn^{2+}	SO_4^-
Copper Sulphate – $CuSO_4$		Cu^{2+}	SO_4^-
Magnesium Sulphate – $MgSO_4$		Mg^{2+}	SO_4^-
Manganese Chloride – $MnCl_2$		Mn^{2+}	Cl^-
Iron Chloride 3 – $FeCl_3$		Fe^{3+}	Cl^-

ANNEX II

Additional figures and tables to Chapter II

Figure AII.1 – Linear adjustment of drying isotherms for Luquasorb®1280RS.

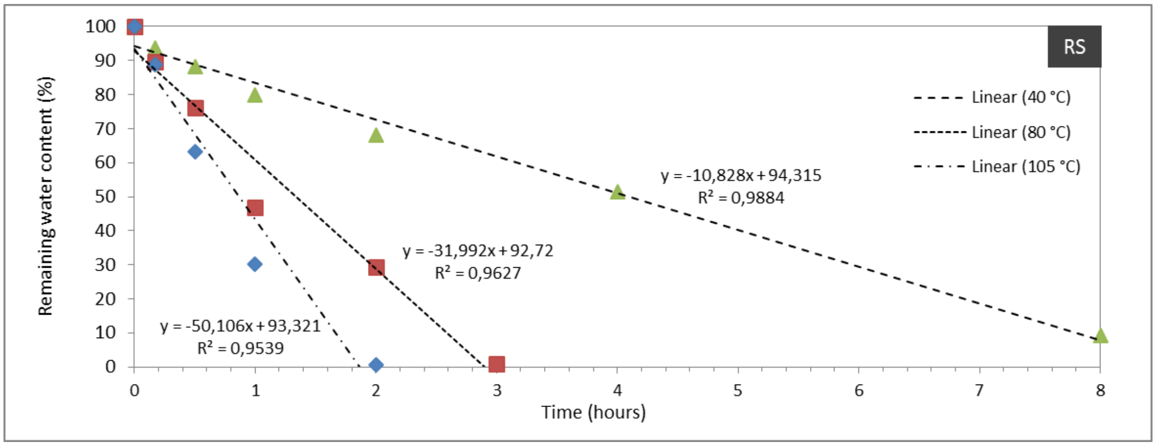


Figure AII.2 – Linear adjustment of drying isotherms for Luquasorb®1280RL.

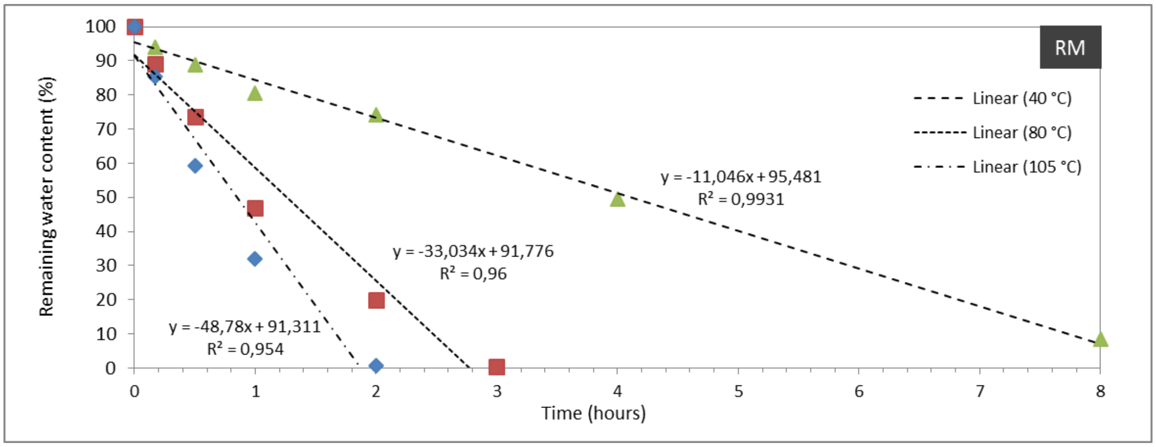


Figure AII.3 – Linear adjustment of drying isotherms for Luquasorb®1280RM.

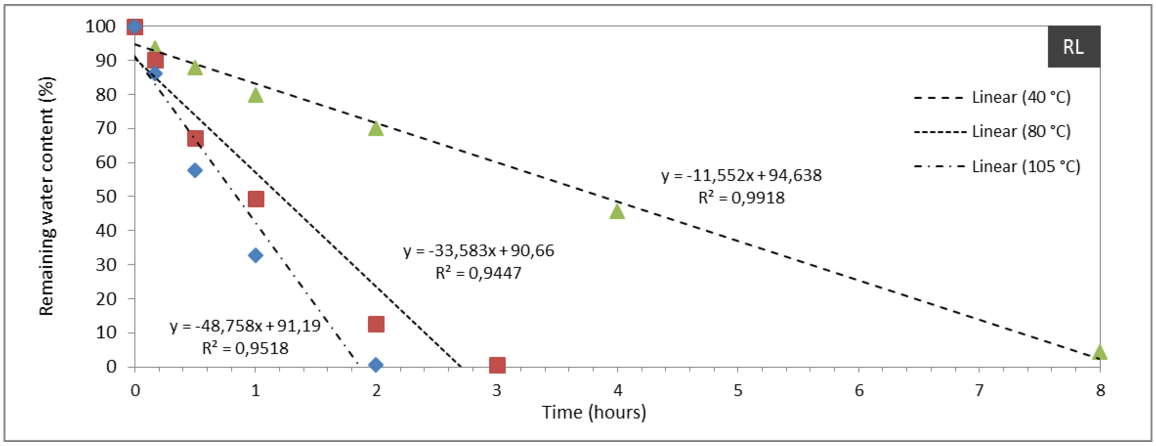


Figure AII.4 – Linear adjustment between oven and filtration methods used to measure FSC of Luquasorb®1280RS, ®1280RM and ®1280RL.

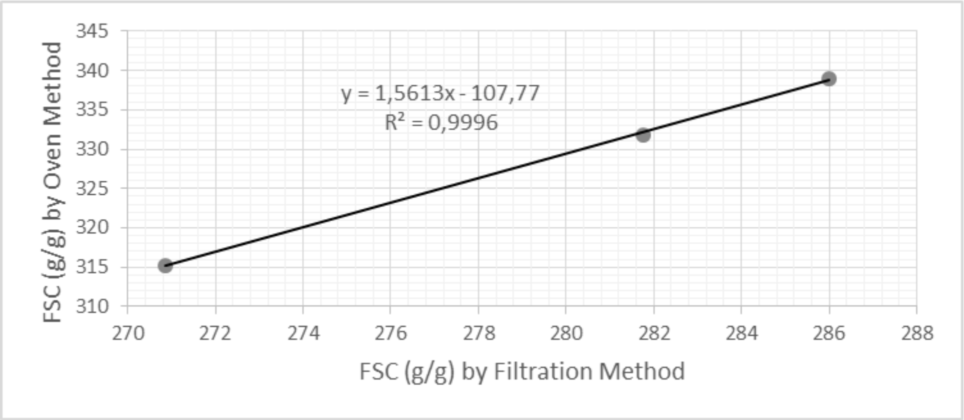


Table AII.1 – Results and statistical analysis on the Hygroscopicity of three granulometries of Luquasorb®1280R during 15 days under constant relative humidity of 35%.

Time (hours)	Luquasorb®1280RS		Luquasorb®1280RM		Luquasorb®1280RL	
	HW (g/g)	SD	HW (g/g)	SD	HW (g/g)	SD
0	0.00a	0.00	0.00a	0.00	0.00a	0.00
1	0.00a	0.02	0.00a	0.01	0.09a	0.08
2	0.04a	0.01	0.00a	0.02	0.02a	0.04
3	0.05a	0.01	0.00a	0.02	0.01a	0.05
4	0.05a	0.01	0.01a	0.03	0.03a	0.03
5	0.05a	0.01	0.06a	0.06	0.02a	0.03
6	0.06a	0.00	0.01a	0.02	0.03a	0.03
7	0.05a	0.01	0.01a	0.01	0.02a	0.03
24 (1 day)	0.06a	0.01	0.01a	0.01	0.03a	0.03
48 (2 days)	0.06a	0.01	0.02a	0.02	0.02a	0.04
120 (5 days)	0.06a	0.02	0.00a	0.04	0.05a	0.18
240 (10 days)	0.05a	0.00	0.00a	0.02	0.01a	0.03
360 (15 days)	0.06a	0.00	0.01a	0.02	0.02a	0.01

*Different letters indicate significant differences at $P \leq 0.05$ within each column by Tukey´s HSD test. *RH: relative humidity. *H.W.: hygroscopic water content expressed in grams per grams of dry product. *SD: standard deviation value.

Table AII.2 – Results and statistical analysis on the Hygroscopicity of three granulometries of Luquasorb®1280R during 15 days under constant relative humidity of 65%.

Time (hours)	Luquasorb®1280RS		Luquasorb®1280RM		Luquasorb®1280RL	
	HW (g/g)	SD	HW (g/g)	SD	HW (g/g)	SD
0	0.00e	0.00	0.00c	0.00	0.00e	0.00
1	0.15d	0.01	0.18ab	0.00	0.12d	0.01
2	0.16cd	0.00	0.19ab	0.01	0.19c	0.02
3	0.17abc	0.00	0.19a	0.01	0.21bc	0.01
4	0.18abc	0.01	0.20a	0.01	0.22bc	0.00
5	0.18a	0.01	0.19ab	0.00	0.27a	0.03
6	0.18a	0.00	0.19ab	0.01	0.24ab	0.03
7	0.18a	0.00	0.19a	0.02	0.23b	0.01
24 (1 day)	0.18a	0.00	0.20a	0.01	0.23b	0.01
48 (2 days)	0.18ab	0.01	0.20a	0.01	0.23b	0.01
120 (5 days)	0.16bcd	0.01	0.17b	0.02	0.21bc	0.00
240 (10 days)	0.17ab	0.01	0.19a	0.01	0.23b	0.01
360 (15 days)	0.16bcd	0.01	0.18ab	0.01	0.21bc	0.01

*Different letters indicate significant differences at $P \leq 0.05$ within each column by Tukey´s HSD test. *RH: relative humidity. *H.W.: hygroscopic water content expressed in grams per grams of dry product. *SD: standard deviation value.

Table AII.3 – Results and statistical analysis on the Hygroscopicity of three granulometries of Luquasorb®1280R during 15 days under constant relative humidity of 86%.

Time (hours)	Luquasorb®1280RS		Luquasorb®1280RM		Luquasorb®1280RL	
	HW (g/g)	SD	HW (g/g)	SD	HW (g/g)	SD
0	0.00f	0.00	0.00f	0.00	0.00h	0.00
1	0.24e	0.02	0.26e	0.01	0.17g	0.01
2	0.30d	0.02	0.33d	0.02	0.32f	0.02
3	0.36c	0.02	0.38c	0.02	0.37e	0.01
4	0.40bc	0.02	0.42bc	0.02	0.41d	0.01
5	0.41ab	0.01	0.43ab	0.02	0.46abc	0.01
6	0.41ab	0.02	0.43ab	0.02	0.43cd	0.00
7	0.42ab	0.01	0.42b	0.02	0.43bcd	0.02
24 (1 day)	0.45a	0.03	0.45ab	0.02	0.47a	0.01
48 (2 days)	0.46a	0.01	0.47a	0.01	0.48a	0.02
120 (5 days)	0.44a	0.02	0.45ab	0.02	0.47ab	0.01
240 (10 days)	0.43ab	0.01	0.44ab	0.02	0.46abc	0.02
360 (15 days)	0.44ab	0.02	0.45ab	0.02	0.46abc	0.01

*Different letters indicate significant differences at $P \leq 0.05$ within each column by Tukey´s HSD test. *RH: relative humidity. *H.W.: hygroscopic water content expressed in grams per grams of dry product. *SD: standard deviation value.

Table AII.4 – Results and statistical analysis on the Hygroscopicity of three granulometries of Luquasorb®1280R during 15 days under constant relative humidity of 100%.

Time (hours)	Luquasorb®1280RS		Luquasorb®1280RM		Luquasorb®1280RL	
	HW (g/g)	SD	HW (g/g)	SD	HW (g/g)	SD
0	0.00i	0.00	0.00i	0.00	0.00g	0.00
1	0.33h	0.04	0.35h	0.03	0.26fg	0.02
2	0.46gh	0.04	0.53gh	0.04	0.47ef	0.04
3	0.58fg	0.04	0.66fg	0.05	0.61de	0.03
4	0.69f	0.05	0.77ef	0.06	0.72de	0.04
5	0.76ef	0.05	0.85ef	0.05	0.92d	0.10
6	0.88e	0.12	0.90e	0.04	0.92d	0.16
7	0.87e	0.06	0.91e	0.05	0.83d	0.11
24 (1 day)	1.38d	0.07	1.56d	0.12	1.35c	0.11
48 (2 days)	1.85c	0.08	2.03c	0.11	2.01b	0.25
120 (5 days)	2.36b	0.12	2.63b	0.15	2.41a	0.27
240 (10 days)	2.62a	0.10	2.96a	0.09	2.58a	0.15
360 (15 days)	2.71a	0.08	3.06a	0.15	2.67a	0.19

*Different letters indicate significant differences at P $\leq$ 0.05 within each column by Tukey´s HSD test. *RH: relative humidity. *H.W.: hygroscopic water content expressed in grams per grams of dry product. *SD: standard deviation value.

Table AII.5 – Results and statistical analysis on the swelling capacity at different depth (absolute values).

Depth	Pressure/weight of wet soil (g)	Luquasorb®1280RS		Luquasorb®1280RM		Luquasorb®1280RL	
		Abs. Water (g/g)	SD	Abs. Water (g/g)	SD	Abs. Water (g/g)	SD
0 cm	0	255.16aB	3.59	285.99aA	0.92	288.96aA	12.83
1 cm	35	163.58bB	8.02	209.66bA	4.82	115.68bC	2.90
2.5 cm	85	90.00cB	7.49	132.56cA	1.18	50.94cC	2.88
5 cm	175	69.81dB	2.31	78.39dA	4.30	43.03dC	1.29
10 cm	350	48.57eB	2.07	62.92eA	1.51	28.80eC	1.12
20 cm	700	45.43eB	4.26	55.71fA	2.43	27.78eC	1.14
30 cm	1050	40.04eB	0.49	53.59fA	2.20	28.37eC	1.33

*Different letters indicate significant differences at P $\leq$ 0.05 within each column (small letters) and within each row (capital letters) by Tukey´s HSD test. *Abs. Water: grams of absorbed water per gram of product. *SD: standard deviation value.

Table AII.6 – Results and statistical analysis on the free swelling capacity (FSC) of Luquasorb®1280RM under different concentrations of salts and two commercial NPK soluble fertilizers.

Salinity (mg/l)	NaCl		$CaCl_2$		$FeCl_3$		Hakaphos®Green		Hakaphos®Orange	
	Rel. FSC (%)	SD	Rel. FSC (%)	SD	Rel. FSC (%)	SD	Rel. FSC (%)	SD	Rel. FSC (%)	SD
0	100aA	1.25	100aA	1.16	100aA	1.16	100aA	2.58	100aA	3.89
100	72.27bB	0.41	76.66bA	0.86	63.91bC	2.27	79.87bA	1.35	82.07bA	1.02
500	46.57cA	0.51	32.61cB	0.58	25.21cC	0.71	56.30cB	0.68	57.95cA	0.88
1000	35.33dA	0.13	0.98dC	0.08	4.29dB	0.14	44.86dA	0.88	44.22dA	0.62
1500	29.46eA	0.33	0.87dB	0.03	2.96dB	0.50	38.01eA	1.37	38.61eA	3.04
2000	25.55fA	0.25	0.73dC	0.11	2.52dB	0.04	32.19fA	0.34	32.99fA	0.78

*Different letters indicate significant differences at $P \leq 0.05$ within each column (small letters) and within each row (capital letters) by Tukey´s HSD test. *Rel. FSC: Relative free swelling capacity expressed in %. *SD: standard deviation. *Hakaphos®Green: 20-5-10+2MgO, *Hakaphos®Orange: 15-5-30+1.4MgO.

Figure AII.5 – Ionic strength of NaCl, CaCl2 and FeCl3 solutions at concentrations used for measuring the effect of dissolved salts on the swelling capacity of Luquasorb®1280RM.

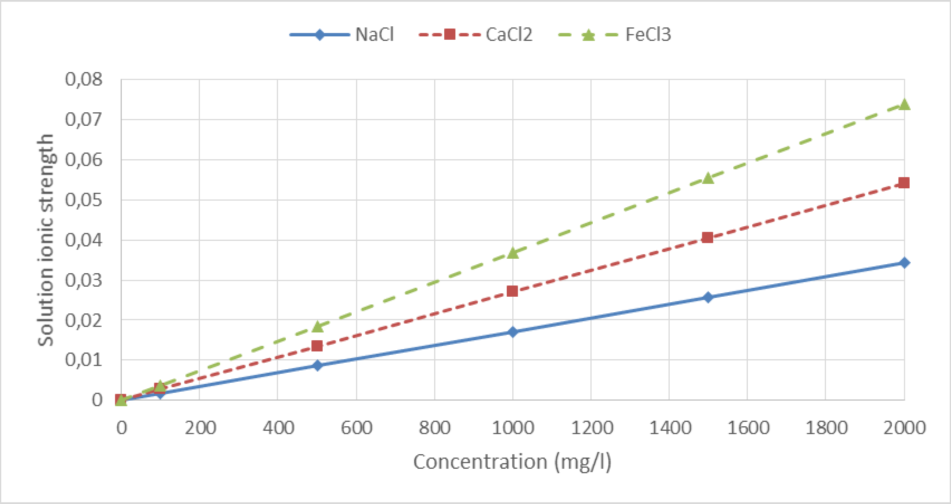


Figure AII.6 – Linear adjustment between soluble and chemically linked potassium fractions quantification measured in Luquasorb®1280R.

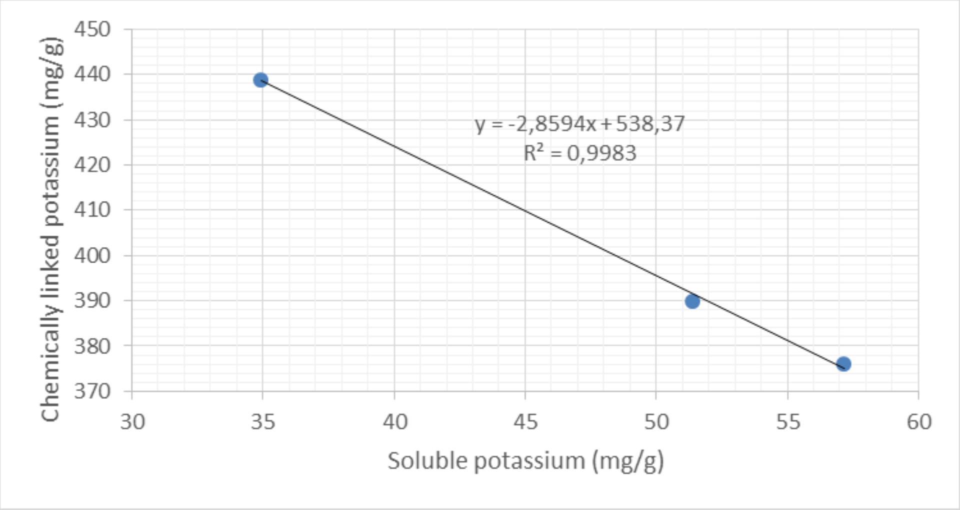


Table AII.7 – Results and statistical analysis on the potassium release kinetics of Luquasorb®1280RM by cationic exchange with 1.5 milliequivalents of sodium and calcium at two different concentrations.

Time (s)	15 meq Na^+ / l			7.5 meq Na^+ / l		
	Released K^+ (meq/100g)	SD	Velocity (meq/100g·s^{-1})	Released K^+ (meq/100g)	SD	Velocity (meq/100g·s^{-1})
5	1.00d	0,21	0,1997	0.80b	1,39	0,1604
10	1.60d	0,07	0,1595	1.33b	0,42	0,1334
30	1.30d	0,12	0,0434	2.00b	0,00	0,0000
60	0.87d	0,62	0,0145	2.00b	0,00	0,0000
300	3.16d	3,39	0,0105	0.14b	0,24	0,0005
600	20.76c	3,23	0,0231	0.93b	1,19	0,0015
1800	66.19b	1,79	0,0245	6.83ab	3,29	0,0038
3600	173.57a	38,6	0,0321	17.938a	7,29	0,0050

Time (s)	15 meq Ca^{2+} / l			7.5 meq Ca^{2+} / l		
	Released K^+ (meq/100g)	SD	Velocity (meq/100g·s^{-1})	Released K^+ (meq/100g)	SD	Velocity (meq/100g·s^{-1})
5	20.17d	0,21	4,0333	10.18b	2,71	2,0366
10	20.26d	0,50	2,0257	8.29b	0,46	0,8286
30	19.99d	0,07	0,6663	2.00b	0,94	0,2771
60	20.98d	1,26	0,3496	2.00b	3,07	0,1740
300	23.42d	1,98	0,0781	14.56b	6,04	0,0485
600	60.03c	36,6	0,1000	24.20b	14,4	0,0403
1800	187.52b	7,88	0,0695	22.80b	6,38	0,0127
3600	342.21a	24,0	0,0634	62.67a	11,2	0,0174

*Different letters indicate significant differences at $P \leq 0.05$ within each row and column by Tukey´s HSD test. *Released K^+: exchanged potassium expressed in milliequivalents per gram of product. *SD: standard deviation.

Table AII.8 – Results and statistical analysis for Luquasorb®1280RM on the released potassium by exchange with different cations and increasing concentration.

Cation concentration (meq)	Na^+		Mg^{2+}		Ca^{2+}		Mn^{2+}	
	Released K (meq/g)	SD	Released K (meq/g)	SD	Released K (meq/g)	SD	Released K (meq/g)	SD
0.0	0.60d	0.04	0.73f	0.03	0.69e	0.06	0.38e	0.06
2.5	1.17cd	0.23	1.34ef	0.15	1.85d	0.08	1.14d	0.09
5.0	1.58c	0.34	2.20de	0.57	2.80c	0.29	1.68d	0.29
10.0	1.85c	0.62	2.29de	0.88	5.00b	0.10	2.71c	0.54
20.0	1.99c	0.37	2.61d	0.26	6.13a	0.29	2.93c	0.41
40.0	2.94b	0.24	3.85c	0.55	6.23a	0.31	5.42a	0.56
80.0	4.07a	0.13	4.97b	0.51	6.18a	0.19	5.73a	0.12
160.0	4.11a	0.68	6.11a	0.20	6.29a	0.24	4.18b	0.24

Cation concentration (meq)	Zn^{2+}		Cu^{2+}		Fe^{3+}	
	Released K (meq/g)	SD	Released K (meq/g)	SD	Released K (meq/g)	SD
0.0	0.72f	0.04	0.76e	0.11	0.60f	0.12
2.5	1.66e	0.16	1.93d	0.08	1.56e	0.11
5.0	2.25d	0.06	2.82c	0.01	3.03d	0.04
10.0	3.41c	0.08	4.71b	0.12	4.76c	0.22
20.0	5.68b	0.17	5.94a	0.46	6.81a	0.18
40.0	6.66a	0.37	6.14a	0.20	6.55a	0.14
80.0	6.99a	0.40	6.13a	0.34	6.64a	0.13
160.0	6.77a	0.40	6.25a	0.05	5.25b	0.22

*Different letters indicate significant differences at $P \leq 0.05$ within each column by Tukey´s HSD test. *FSC: free swelling capacity expressed in grams of absorbed solution per gram of dry product. *SD: standard deviation. *Hakaphos®Green: 20-5-10+2MgO, *Hakaphos®Orange: 15-5-30+1.4MgO.

Table AII.9 – Results and statistical analysis for Luquasorb®1280RM on the release of previously exchanged cations by exchange with ammonium acetate 1N.

Cation (meq)	Released Na^+		Released Mg^{2+}		Released Ca^{2+}		Released Mn^{2+}	
	(meq/g)	SD	(meq/g)	SD	(meq/g)	SD	(meq/g)	SD
0.0	0.46e	0.04	0.04d	0.04	0.20f	0.00	0.00c	0.00
2.5	0.82d	0.04	0.44c	0.06	0.54e	0.01	0.07b	0.03
5.0	0.99cd	0.05	0.60c	0.02	0.92d	0.02	0.07b	0.04
10.0	1.29cd	0.25	0.70c	0.11	1.54c	0.09	0.15a	0.02
20.0	1.40c	0.17	1.14b	0.06	1.80b	0.17	0.20a	0.01
40.0	2.07b	0.27	1.30b	0.21	2.27a	0.20	0.21a	0.01
80.0	2.38ab	0.33	1.67a	0.37	2.31a	0.10	0.17a	0.06
160.0	2.70a	0.17	1.66a	0.31	2.30a	0.09	0.21a	0.01

Cation (meq)	Released Zn^{2+}		Released Cu^{2+}		Released Fe^{3+}	
	(meq/g)	SD	(meq/g)	SD	(meq/g)	SD
0.0	0.00d	0.00	0.00c	0.00	0.00a	0,00
2.5	0.05ac	0.00	0.00c	0.00	0.00a	0,00
5.0	0.04c	0.03	0.06bc	0.06	0.00a	0,00
10.0	0.07a	0.00	0.11ab	0.04	0.00a	0,00
20.0	0.07a	0.00	0.05bc	0.02	0.00a	0,00
40.0	0.07a	0.00	0.15a	0.06	0.00a	0,00
80.0	0.07a	0.00	0.19a	0.03	0.00a	0,00
160.0	0.07a	0.00	0.19a	0.02	0.00a	0,00

*Different letters indicate significant differences at $P \leq 0.05$ within each row by Tukey´s HSD test. *FSC: free swelling capacity expressed in grams of absorbed solution per gram of dry product. *SD: standard deviation. *Hakaphos®Green: 20-5-10+2MgO, *Hakaphos®Orange: 15-5-30+1.4MgO.

Table AII.10 – Results and statistical analysis on the water content (%) of volume of three soil samples (sandy, loamy and clay) and its mixture with 0.05, 0.1 and 0.2% of Luquasorb®1280RM.

Pressure (bar)	Soil 1 (Sandy) 0.00% SAP		Soil 1 (Sandy) 0.05% SAP		Soil 1 (Sandy) 0.1% SAP		Soil 1 (Sandy) 0.2% SAP	
	Water (%)	SD	Water (%)	SD	Water (%)	SD	Water (%)	SD
0	14.38c	0.15	16.85b	0.87	18.05b	1.08	20.18a	2.06
0.33 (pF 2.5)	**5.80b**	0.41	**6.08b**	0.47	**7.72a**	0.95	**7.54a**	0.17
1	4.54c	0.40	4.91c	0.34	5.40b	0.34	6.32a	0.16
2.5	3.24b	0.16	3.67b	0.21	5.09a	0.70	5.03a	0.11
5	2.91b	0.57	3.50ab	0.57	4.18a	0.98	4.40a	0.25
10	2.82a	0.06	3.10a	0.26	3.92a	1.04	3.81a	1.45
15 (pF 4.2)	**2.81ab**	0.05	**3.04ab**	0.15	**3.25a**	0.71	**2.43b**	0.31

Pressure (bar)	Soil 2 (Loamy) 0.00% SAP		Soil 2 (Loamy) 0.05% SAP		Soil 2 (Loamy) 0.1% SAP		Soil 2 (Loamy) 0.2% SAP	
	Water (%)	SD	Water (%)	SD	Water (%)	SD	Water (%)	SD
0	56.81b	4.22	57.88b	2.63	61.27b	2.75	66.67a	3.83
0.33 (pF 2.5)	**19.32d**	0.83	**20.96c**	0.34	**22.15b**	0.71	**23.15a**	0.86
1	16.09b	0.23	15.86b	0.24	17.76a	0.85	17.25a	0.41
2.5	13.18b	0.17	13.30b	0.18	13.74a	0.34	14.00a	0.40
5	12.28a	1.21	11.79a	0.23	11.86a	0.33	12.30a	0.36
10	9.93b	0.20	10.05b	0.40	11.37a	0.32	11.79a	0.75
15 (pF 4.2)	**8.99b**	0.84	**10.50a**	0.45	**10.76a**	0.36	**10.00a**	0.61

Pressure (bar)	Soil 3 (Clay) 0.00% SAP		Soil 3 (Clay) 0.05% SAP		Soil 3 (Clay) 0.1% SAP		Soil 3 (Clay) 0.2% SAP	
	Water (%)	SD	Water (%)	SD	Water (%)	SD	Water (%)	SD
0	56.37c	0.97	61.82b	3.26	60.61b	0.53	67.21a	4.03
0.33 (pF 2.5)	**32.86b**	2.42	**33.78b**	0.26	**36.14a**	0.65	**35.81a**	0.57
1	28.80b	0.47	29.48ab	0.46	29.77a	0.77	30.08a	0.53
2.5	25.69a	1.87	25.21a	1.86	25.30a	0.88	25.46a	0.41
5	24.39b	1.15	25.16ab	1.11	25.91a	0.45	25.27ab	0.56
10	23.88b	0.79	25.33ab	1.18	24.70ab	0.30	26.00a	1.92
15 (pF 4.2)	**21.78a**	1.92	**22.64a**	1.83	**24.06a**	0.93	**23.10a**	1.97

*Different letters indicate significant differences at $P \leq 0.05$ within each column by Tukey´s HSD test. *pF 2.5: field capacity. *pF 4.2: wilting point. *SD: standard deviation value.

ANNEX III

Additional figures and tables to Chapter III

Figure AIII.1 – General overview of the field experiment localizations.

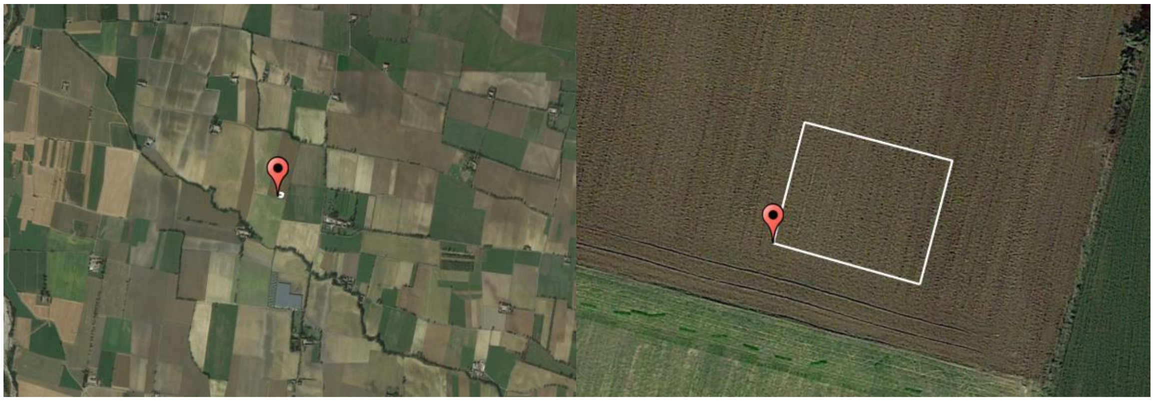
*****2011 sites (red markers) and 2012 sites (blue markers). **Picture source: Google Earth Pro. Picture date: 04.10.2013*

Figure AIII.2 – Aerial images of the field experimental sites from ~5 km (left) and ~150 m (right) high.

*****ES11-01. Jerez-Las Pachecas (Cádiz), SPAIN. **Picture source: Google Earth Pro. Picture date: 14.09.2012*

*ES11-02. Lebrija-BXII (Sevilla), SPAIN. **Picture source: Google Earth Pro. Picture date: 15.05.2015*

*ES11-03. Jerez-La Isleta (Sevilla), SPAIN. **Picture source: Google Earth Pro. Picture date: 14.09.2012*



*IT11-01. Pontecurone (Piedmont), ITALY. **Picture source: Google Earth Pro. Picture date: 24.10.2014*

*IT11-02. Borgo-Tressant-A (Puglia), ITALY. **Picture source: Google Earth Pro. Picture date: 30.08.2015*

*IT11-02. Borgo-Tressant-B (Puglia), ITALY. **Picture source: Google Earth Pro. Picture date: 30.08.2015*

ES12-01. Coria del Rio (Sevilla), SPAIN. **Picture source: Google Earth Pro. Picture date: 15.05.2015*

ES12-02. Jerez-Romanina (Cádiz), SPAIN. **Picture source: Google Earth Pro. Picture date: 15.10.2012*

ES12-02. Utrera (Sevilla), SPAIN. **Picture source: Google Earth Pro. Picture date: 05.09.2011*

IT12-01. Monticelli D'Ongina (Emilia-Romagna), ITALY. **Picture source: Google Earth Pro. Picture date: 12.03.2014*

IT12-02. Frugarolo (Piedmont), ITALY. **Picture source: Google Earth Pro. Picture date: 10.08.2013*

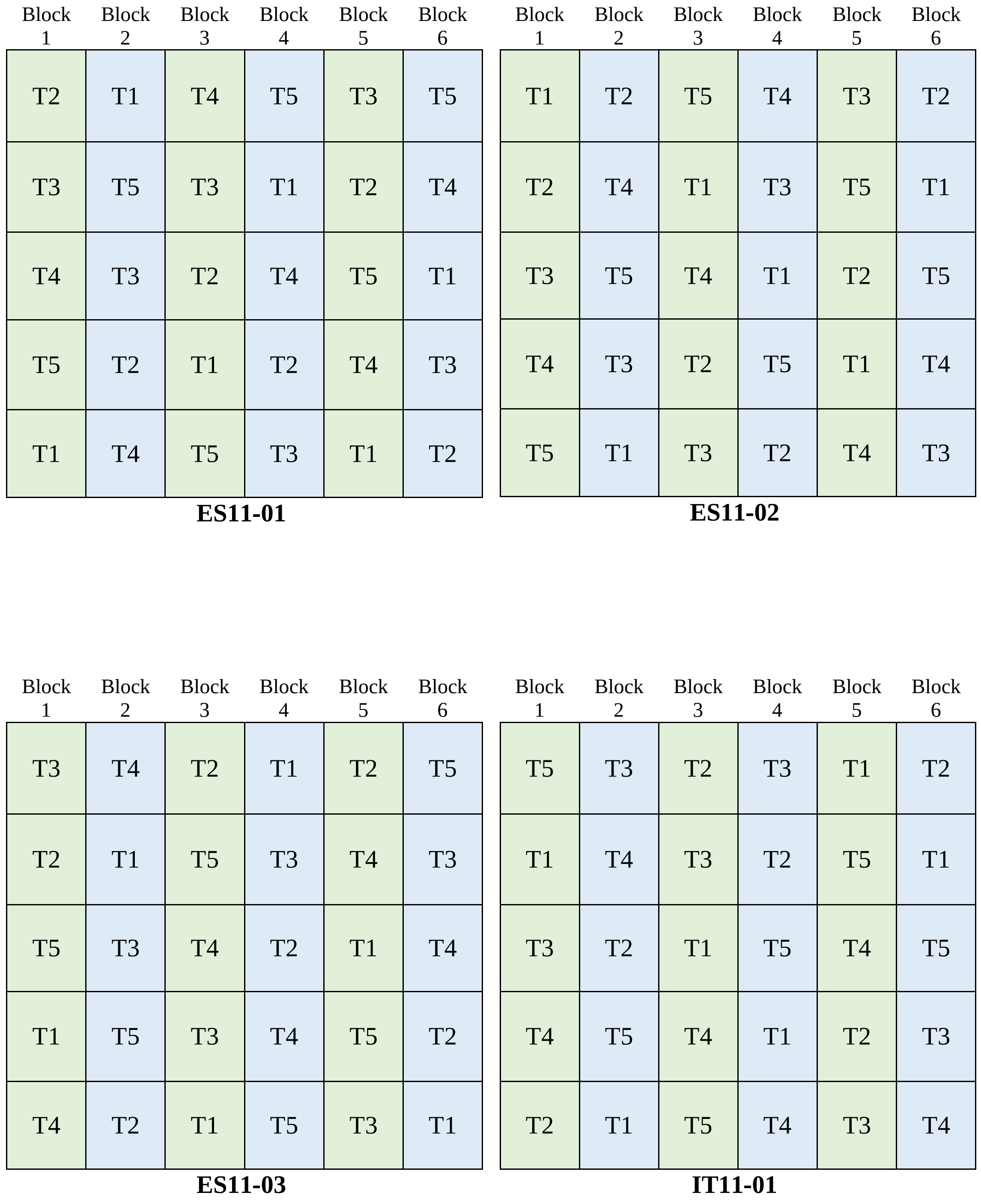
IT12-03. Ottavello-Rivergaro (Emilia-Romagna), ITALY. **Picture source: Google Earth Pro. Picture date: 29.08.2015*

Table AIII.1 – Weather data of the field experimental sites during the crop season.

Site-Ref.	Nearest Weather Station	Annual Rainfall (mm)	Air Temperature (°C)				RH (%)	Season Precipitation (mm)
			Max.	Min.	Dif.	Av.		
ES11-01 ES11-02 ES11-03	Jerez de la Frontera.	628	30.9	16.3	14.6	23.0	59.0	86
IT11-01	Milano-Linate	600	28.0	17.1	10.9	22.7	57.5	210
IT11-02 IT11-03	Bari-Palese	563	27.7	17.7	10.0	23.1	59.4	62
ES12-01	Seville	558	32.0	16.9	15.1	24.2	42.9	31
ES12-02	Jerez de la Frontera	620	30.1	14.8	15.3	22.1	54.6	75
ES12-03	Seville-San Pablo	552	34.8	19.1	15.7	26.7	41.0	37
IT12-01 IT12-03	Piacenza-S.Damiano	784	27.5	14.7	12.8	22.0	64.5	235
IT12-02	Milano-Linate	575	26.2	15.8	10.4	21.0	61.6	244

*Annual rainfall as the average of the last 10 years previous to the experiment. *RH = relative humidity.

Figure AIII.3 – Trial maps of the field experimental sites.



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T3	T5	T3	T1	T2	T4
T4	T3	T2	T4	T5	T1
T5	T2	T1	T2	T4	T3
T1	T4	T5	T3	T1	T2

ES11-01

Block 1	Block 2	Block 3	Block 4	Block 5	Block 6
T1	T2	T5	T4	T3	T2
T2	T4	T1	T3	T5	T1
T3	T5	T4	T1	T2	T5
T4	T3	T2	T5	T1	T4
T5	T1	T3	T2	T4	T3

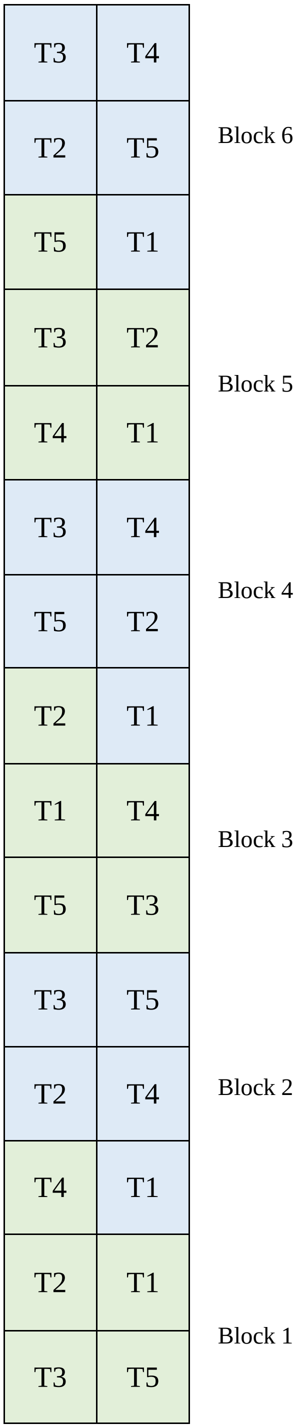
ES11-02

Block 1	Block 2	Block 3	Block 4	Block 5	Block 6
T3	T4	T2	T1	T2	T5
T2	T1	T5	T3	T4	T3
T5	T3	T4	T2	T1	T4
T1	T5	T3	T4	T5	T2
T4	T2	T1	T5	T3	T1

ES11-03

Block 1	Block 2	Block 3	Block 4	Block 5	Block 6
T5	T3	T2	T3	T1	T2
T1	T4	T3	T2	T5	T1
T3	T2	T1	T5	T4	T5
T4	T5	T4	T1	T2	T3
T2	T1	T5	T4	T3	T4

IT11-01



T3	T4	
T2	T5	Block 6
T5	T1	
T3	T2	Block 5
T4	T1	
T3	T4	
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T2	T1	
T1	T4	Block 3
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T3	T5	
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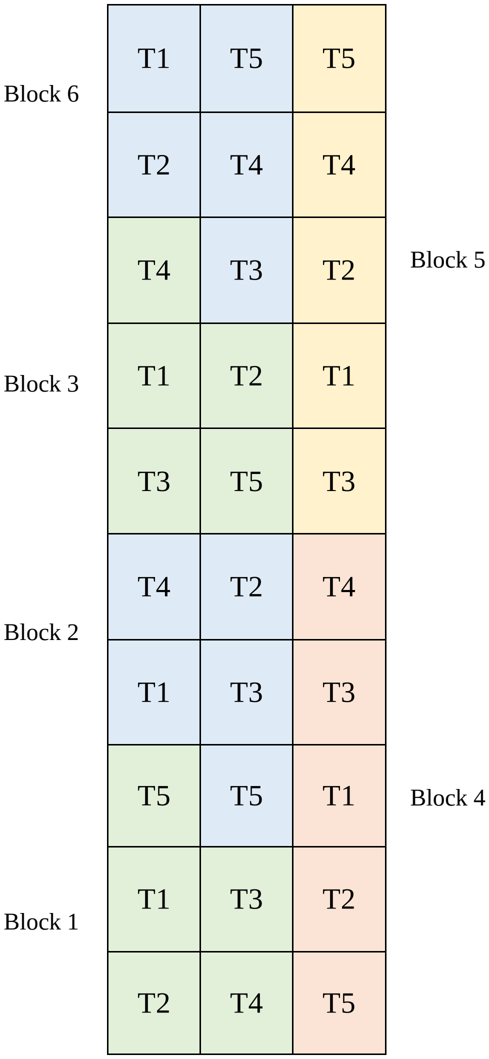
T2	T1	
T3	T5	Block 1

IT11-02



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	T2	T4	T4	
	T4	T3	T2	Block 5
Block 3	T1	T2	T1	
	T3	T5	T3	
Block 2	T4	T2	T4	
	T1	T3	T3	
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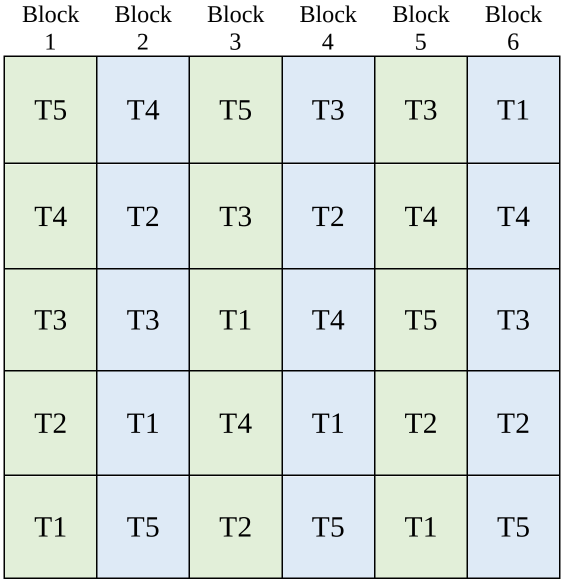
Block 1	T1	T3	T2	
	T2	T4	T5	

IT11-03



Block 1	Block 2	Block 3	Block 4	Block 5	Block 6
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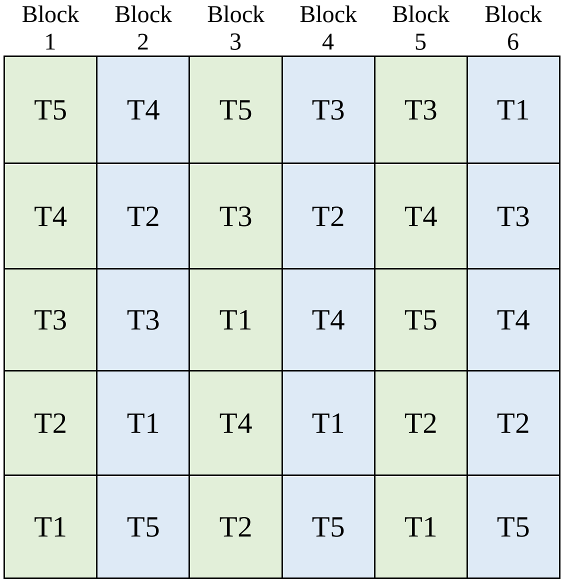
T4	T2	T3	T2	T4	T4
T3	T3	T1	T4	T5	T3
T2	T1	T4	T1	T2	T2
T1	T5	T2	T5	T1	T5

ES12-01



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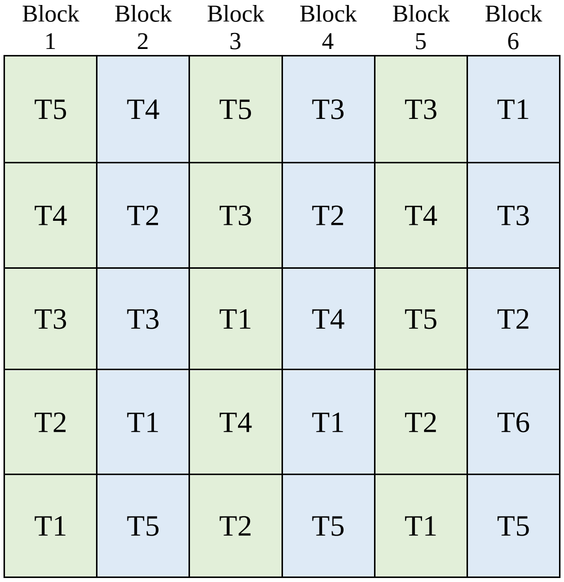
ES12-02



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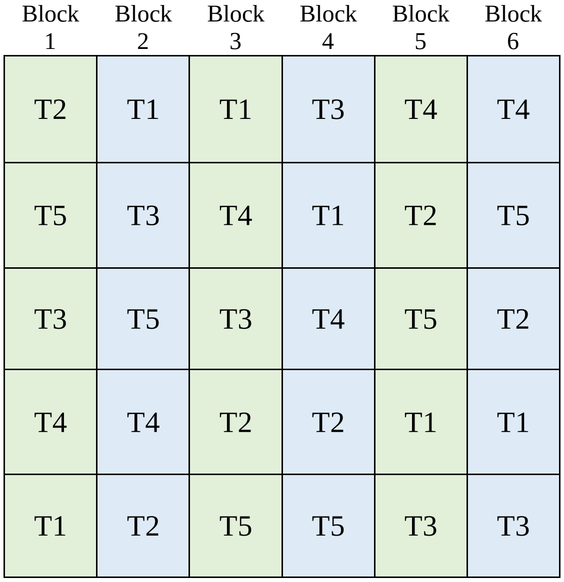
ES12-03



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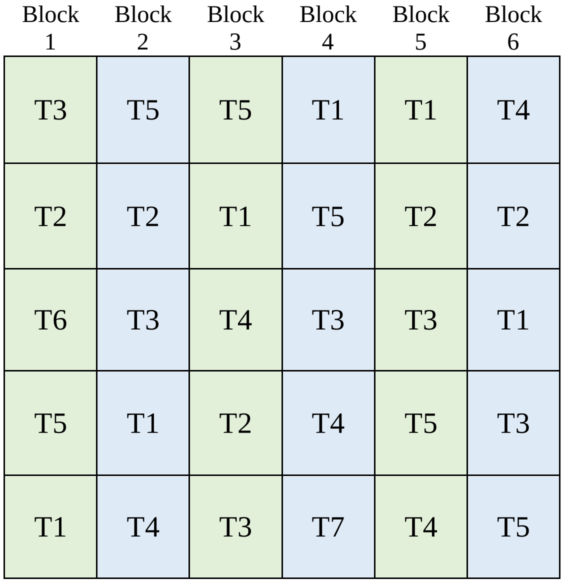
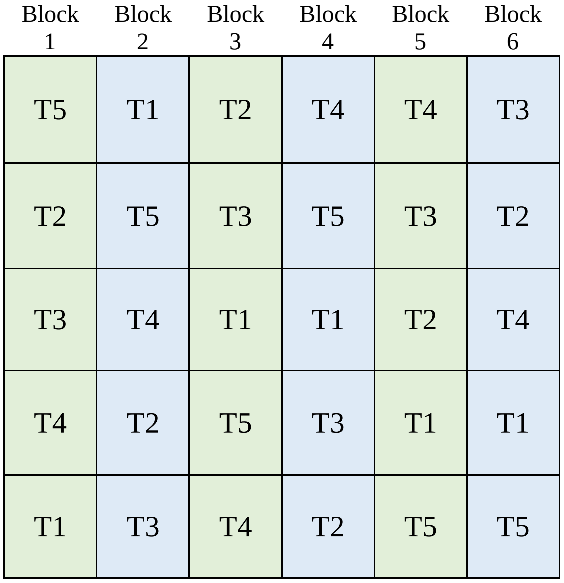
T4	T4	T2	T2	T1	T1
T1	T2	T5	T5	T3	T3

IT12-01



Block 1	Block 2	Block 3	Block 4	Block 5	Block 6
T3	T5	T5	T1	T1	T4
T2	T2	T1	T5	T2	T2
T6	T3	T4	T3	T3	T1
T5	T1	T2	T4	T5	T3
T1	T4	T3	T7	T4	T5

IT12-02



Block 1	Block 2	Block 3	Block 4	Block 5	Block 6
T5	T1	T2	T4	T4	T3
T2	T5	T3	T5	T3	T2
T3	T4	T1	T1	T2	T4
T4	T2	T5	T3	T1	T1
T1	T3	T4	T2	T5	T5

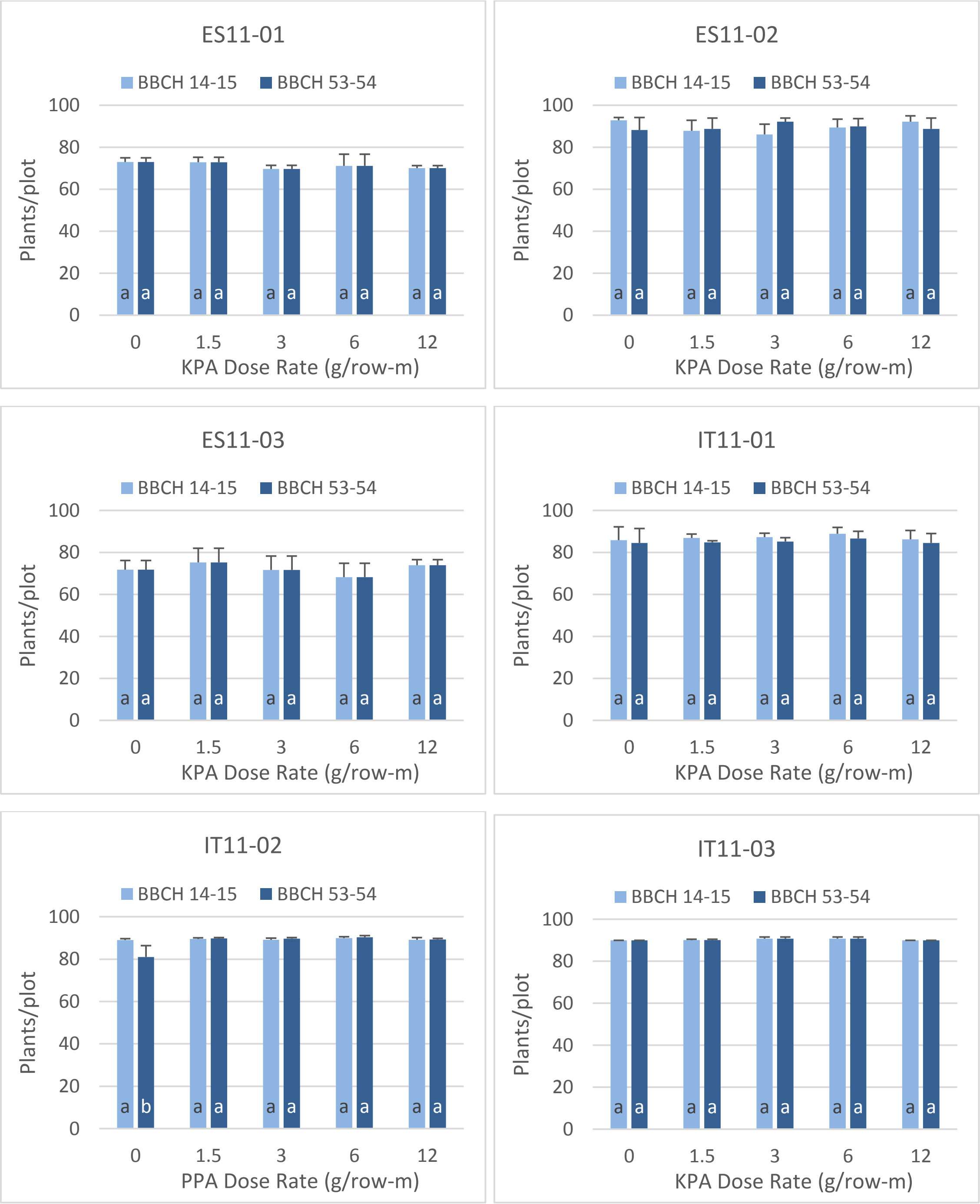
IT12-03

Table AIII.2 – Crop vigor (0-10) results for all field experimental sites.

Site-Ref.	0 g/row-m		1.5 g/row-m		3 g/row-m		6 g/row-m		12 g/row-m	
	BBCH 14-15	BBCH 53-54	BBCH 14-15	BBCH 53-54	BBCH 14-15	BBCH 53-54	BBCH 14-15	BBCH 53-54	BBCH 14-15	BBCH 53-54
ES11-01	5.0	4.8	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
ES11-02	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
ES11-03	4.8	4.7	5.0	5.0	5.0	5.5	5.0	5.0	5.0	5.7
IT11-01	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
IT11-02	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
IT11-03	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
ES12-01	5.0	5.0	5.7	5.8	5.2	5.7	5.5	6.0	5.5	6.0
ES12-02	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
ES12-03	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
IT12-01	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
IT12-02	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
IT12-03	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0

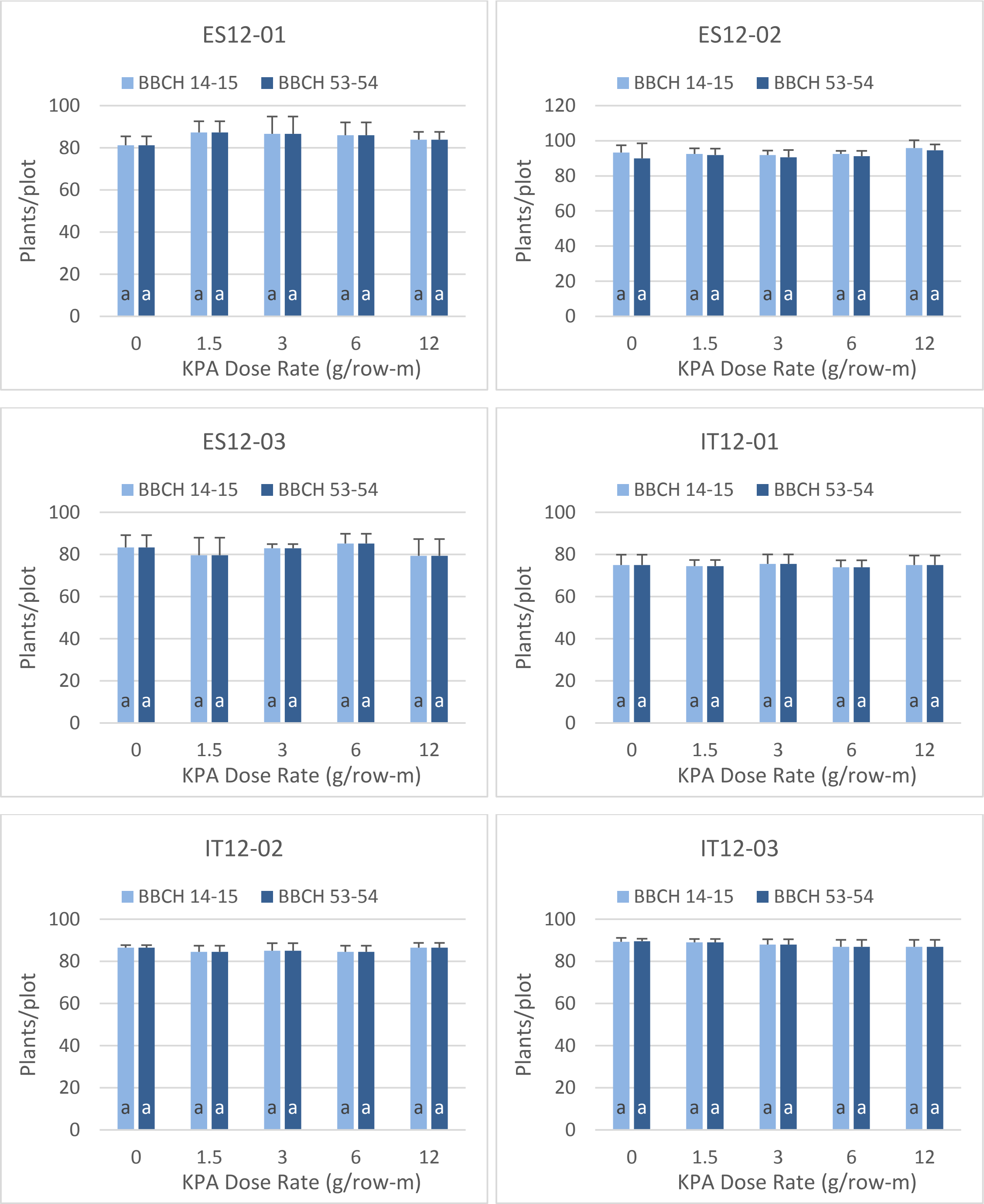
*SD = standard deviation. Different letters indicate significant differences at $P < 0.05$ between rows (small letters) and between columns (capital letters) by SNK-test.

Figure AIII.4 – Plant population at growth stage BBCH 14-15 and BBCH 53-54 in the 2011 experimental sites.



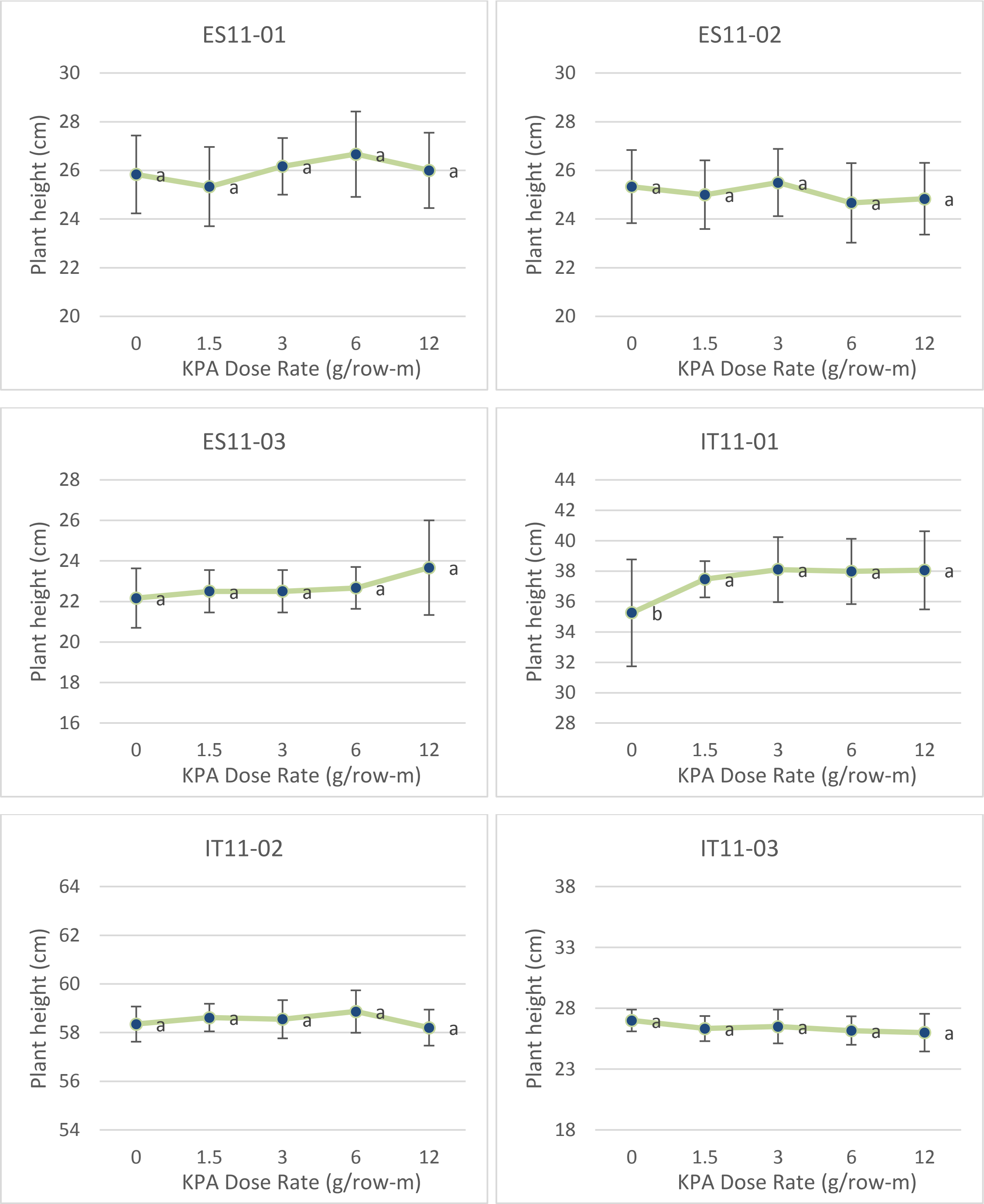
*Error bars represent standard deviation. Different letters indicate significant differences at $p \leq 0.05$ between bars of the same color by SNK-test.

Figure AIII.5 – Plant population at growth stage BBCH 14-15 and BBCH 53-54 in the 2012 experimental sites.



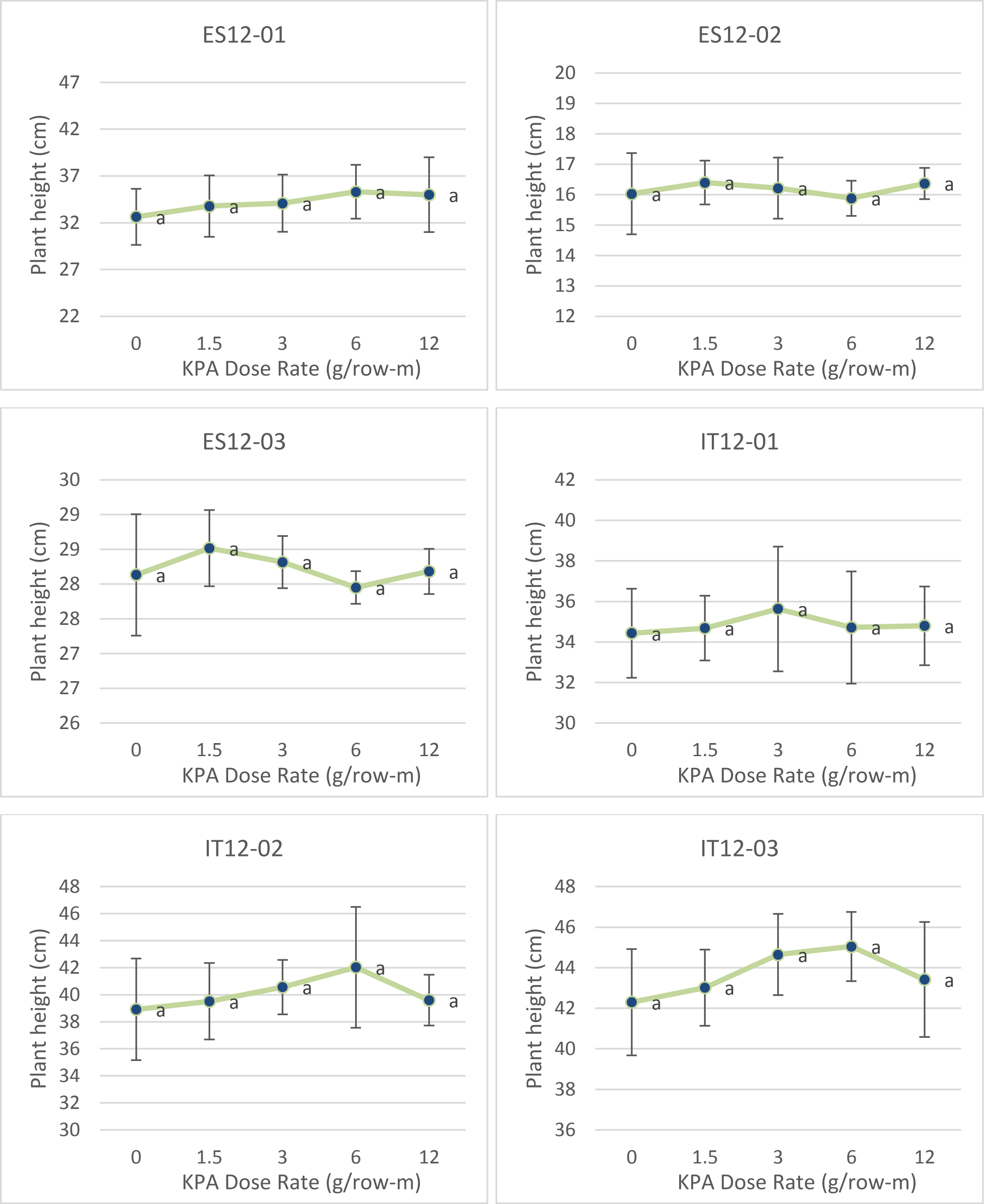
*Error bars represent standard deviation. Different letters indicate significant differences at $p \leq 0.05$ between bars of the same color by SNK-test.

Figure AIII.6 – Plant height measurements at growth stage BBCH 53-54 in the 2011 experimental sites.



*Error bars represent standard deviation. Different letters indicate significant differences between treatments at $p \leq 0.05$ by SNK-test.

Figure AIII.7 – Plant height measurements at growth stage BBCH 53-54 in the 2012 experimental sites.

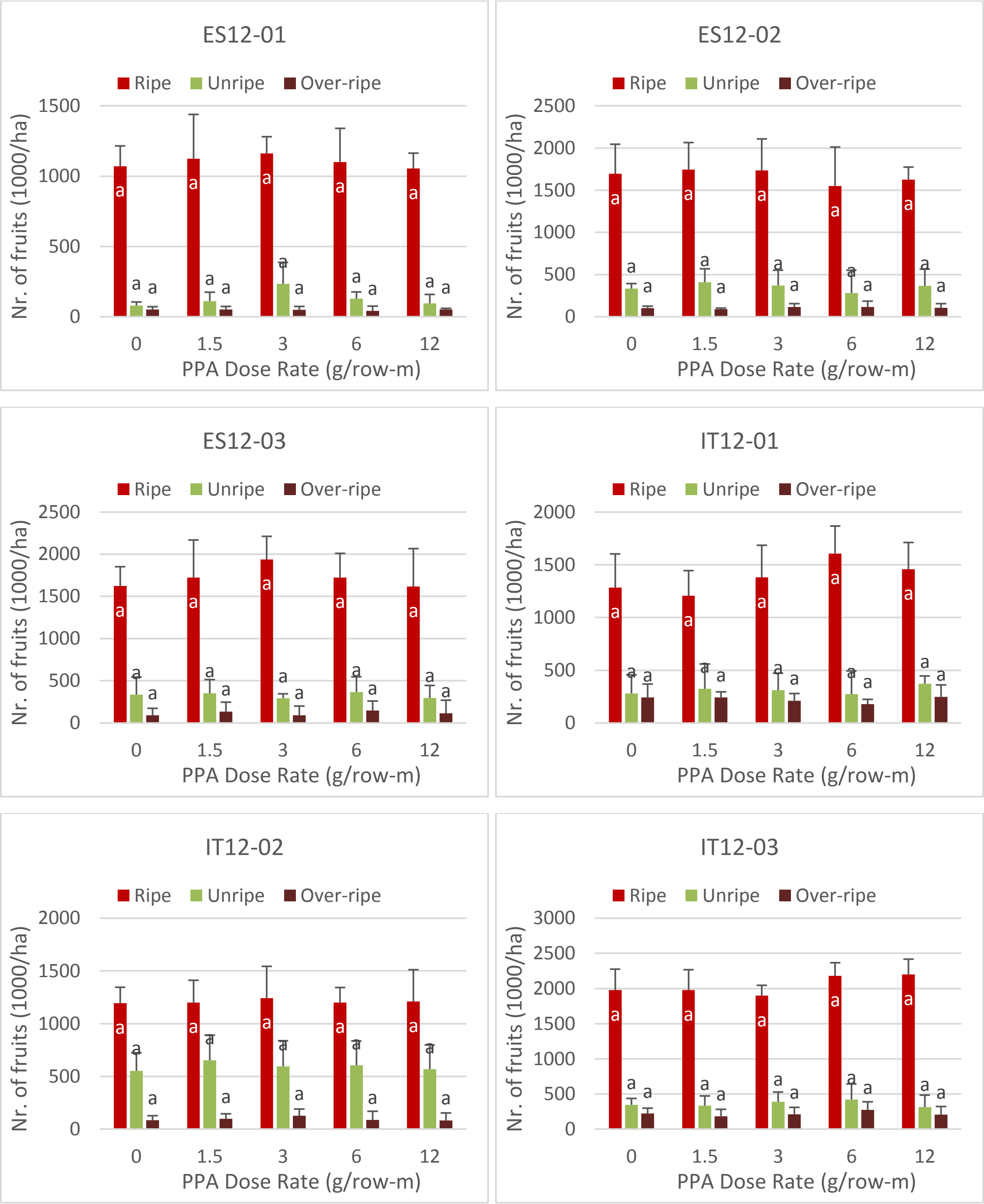


*Error bars represent standard deviation. Different letters indicate significant differences between treatments at $p \leq 0.05$ by SNK-test.

Figure AIII.8 – Number of harvested fruits (1000/ha) in the 2011 experimental sites.

*Error bars represent standard deviation. Different letters indicate significant differences between treatments within the same fruit class at $p \leq 0.05$ by SNK-test.

Figure AIII.9 – Number of harvested fruits (1000/ha) in the 2012 experimental sites.



*Error bars represent standard deviation. Different letters indicate significant differences between treatments within the same fruit class at $p \leq 0.05$ by SNK-test.